Gerald B. Fosdyke
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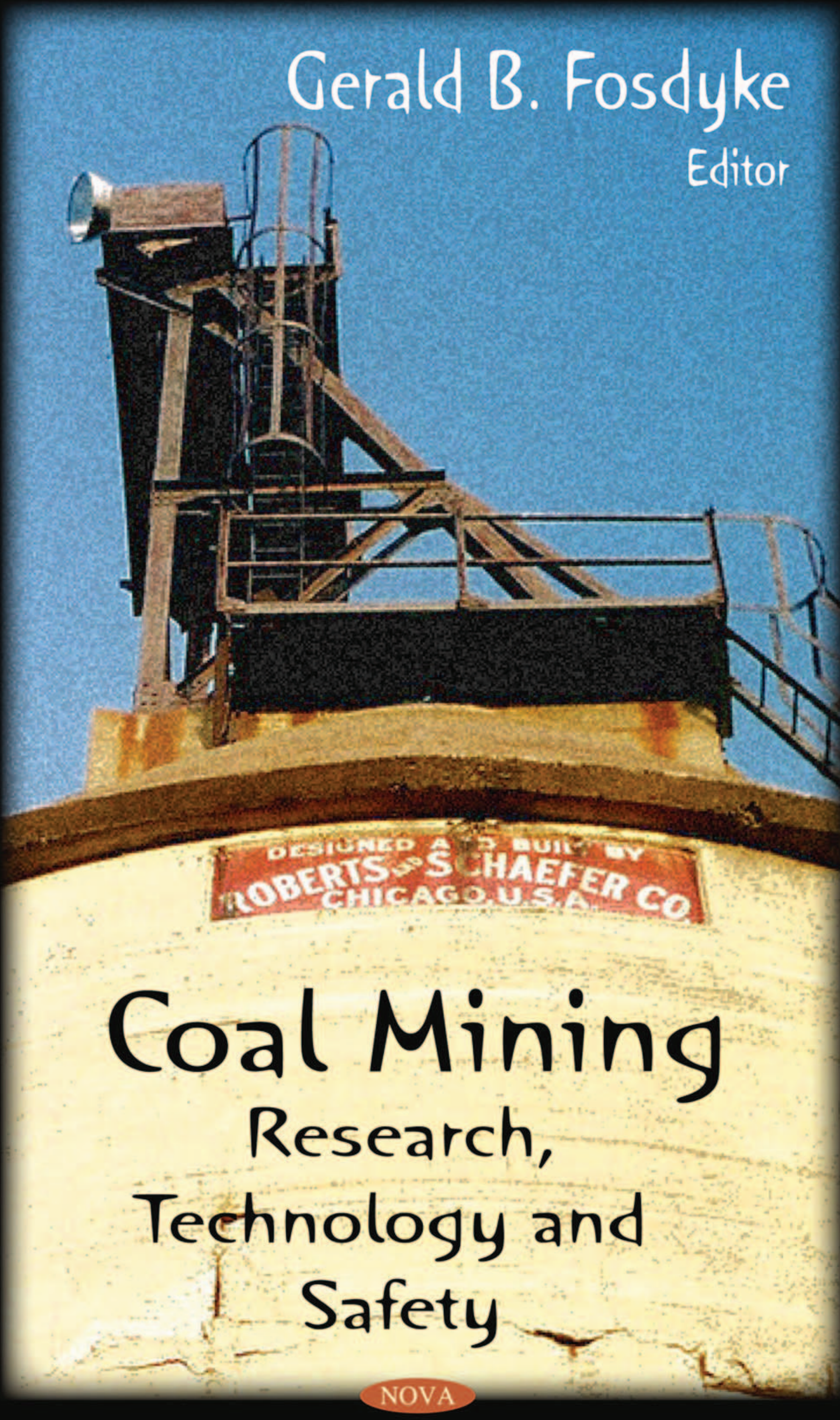

Coal Mining
Research, Technology and Safety

NOVA

COAL MINING: RESEARCH, TECHNOLOGY AND SAFETY

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Contents

PREFACE

Although it is a rock rather than a mineral (the building blocks of rocks), coal is often considered to be a mineral resource. Coal has been mined since ancient Roman times, but it has become a major energy source only since the Industrial Revolution. It currently provides 22 percent of the world's energy, and is used to generate approximately 40 percent of electricity worldwide. Coal generates more than half of all electricity in the United States. Coal is also an important ingredient in the creation of methanol which turns up in such items as plywood (binding resin) and plastic bottles (acetic acid). Reserves are widely distributed throughout the globe, although the United States, Russia, China, and India account for more than half of the world's recoverable coal reserves.This new book presents new research in the field.

Short Commentary 1 - Agronomic crops grown on the reclaimed metal-mined wastelands are a pathway for toxic pollutants entering the human food chain. Agricultural rehabilitation of mine spoils in China is pretty common and its effect has been largely overlooked. Extensive sampling of the edible crops and associated soils have been conducted for the three typical manganese mine wastelands (Bayi, Lipu and Pingle) in Guangxi, south China and heavy metal contamination of crops was assessed against China Food Safety Standards. Simple pollution index (Pi) assessment indicated no Zn (except tea) and Cu pollution among these crops, but heavy pollution of Pb, Cd and Cr was found. Composite pollution index (Nemerow index, P_N) showed 36 crops from 41 were heavily polluted with heavy metals. Peanut, soybean, Chinese chestnut, persimmon, cassava, mandarin and sugarcane were the most severely contaminated crops. Consumption of these crops may pose a health risk for humans. Crops tended to have a higher Cd accumulation (as indicated by Biological Accumulation Factor) in edible parts, thus Cd is the most important food safety threat. In terms of China Soil Quality Standard (class II), the minesoils contained much higher Cd and Cr levels, not suitable for agricultural plantation. Simple reclamation for crop plantation on minesoils is legally untenable and must be strictly controlled by the local governments. In addition, more diverse restoration goals with lower environmental risk should be encouraged for the mine wastelands in South China.

Short Commentary 2 - Rhenium is very rare element with Clarke value (average content in the Earth's crust) about 0.001 ppm (= 1 ppb). Geochemistry of Re in coal is poorly known up to today because of analytical problems. Special analytical methods are needed for reliable Re determination in coal. Some coals are known, with Re contents 2–3 orders-of-magnitude higher than Re Clarke value in the Earth's crust, in the range from 0.n ppm up to few ppm.

In Re-bearing coals, it is no doubt that Re_{org} form exists. Perhaps, Re is sorbed on coal organics by weak, ion-exchange bonds. This has accounted for the Re leachability from coals by surface and ground waters. Some analogues with Re state in black shales indicate that some part of Re may be present in bituminous components of coal (liptinite). The other authigenic Re form may be its sulfide, ReS_2. However, Re sites in coal (modes of occurrence) is now only hypothetic; microprobe study is needed for more knowledge.

There are at least three genetic types of Re-concentrations in coal: Uzbek, Spanish and Kazakh. In *Uzbek* type, Re is probably syngenetic. Its accumulation is due to enhanced Re contents in source rocks. Rhenium leached from terrigenic material may further be captured on reducing peatbog barrier – in organic or sulfide form. In *Spanish* type Re is also mostly syngenetic. Its accumulation is due to considerable contribution of the bituminous organics (like black shale) having extremely high affinity to Re. In *Kazakh* type Re is close associated with U and its companions, in the infiltration epigenetic deposits of the "*bed oxidation*" type. Re dissolved in oxidized waters as perrhenate ion ReO_4^-, may be captured in brown-coal beds on the reducing barrier, in organic or sulfide forms.

Recently Re-bearing fumaroles were described in the Kurily Islands. Therefore, some Re accumulations may occur in peatbogs of the volcanic areas, or in young lignites – in orogenic depressions with synchronous volcanism. Such Re accumulations may be associated with In, Ge, Mo, Bi and some other elements enriching the volcanic exhalations.

Because Re is very valuable metal, Re-bearing coals may serve as Re industrial resource. The most promising are epigenetic uranium-coal deposits. In addition, some intermountain trough brown-coal fields must be studied for Re, if these coals are associated with volcanics.

Rhenium is ultra-rare chemical element having the Clarke value (mean content in Earth's crust) no more than 0.001 ppm = 1 ppb. All the studies on Re in coal are connected with Russian geochemical school that is noted also in Swaine's [1990] outline.

Chapter 1 - Upper Silesia (Southern Poland) is a region rich in mineral deposits. Among them the most important are hard coal. Many years of intensive mining activity has had a strong impact on the environment of this region. Mining waters, which carry about 6,500 tonnes of Cl^- and 0.5 tonnes of SO_4^{2-} per day, discharge into rivers, mainly the Vistula River and the Odra River. The watercourses of these rivers contain high levels of chlorides, sulphates, phosphates, nitrates, heavy metals, and low values of pH or radioactive matter. Pollution of the water environment by the waters from mining activities is a problem not only in Poland, but worldwide.

The values of taxa richness, community diversity indices, biotic indices calculated for the benthic macroinvertebrates or calculated for macrophytes reflect a decrease in the quality of water in the streams subjected to the pollution from hard coal mines. The macroinvertebrate taxa in these streams that are more sensitive to this type pollution, e.g. Ephemeroptera, Plecoptera, Trichoptera, Mollusca including highly acid-sensitive species are replaced by ones that are more tolerant.

In regions with coal mining activity, including Upper Silesia (Southern Poland), the natural ecosystems have changed into anthropogenic ecosystems in which new species of the flora and fauna previously unknown in these areas have appeared including alien species, e.g. *Ferrissia wautieri*, *Physella acuta* and invasive species e.g. *Potamopyrgus antipodarum*.

The mining subsidence reservoirs, which are not so degraded and provide a habitat where many species of the flora and fauna including rare, vulnerable or legally protected species can live, e.g. *Anodonta cygnea, Hippeutis complanatus, Utricularia vulgaris, Nymphaea alba, Nuphar lutea* or *Batrachium trichophyllum* should be protected on ecological grounds.

Some of the coal mining area, which also encompasses mining subsidence reservoirs that are refuges for wildlife may constitute an ecologically important area in terms of conservation biodiversity.

Chapter 2 - Coal is a mass product and has been mined for centuries on a global scale. Due to coal mining, transport and incomplete coal combustion, unburnt coal particles can be dispersed into soils and sediments where they can present a source of polycyclic aromatic hydrocarbons (PAHs).

The chemical group of PAHs comprises of hundreds of single and mostly carcinogenic substances. Predominantly, they are formed by incomplete combustion of organic material (pyrogenic) or derive from petrogenic sources such as crude oil, refining products, oil shale or coal. In coals, they are formed during diagenesis and catagenesis of organic matter. Total native concentrations of PAHs with two to six condensed aromatic rings including alkylated derivatives can reach hundreds or exceptionally few thousands of mg/kg in hard coals. Once released into the environment, coal particles play a pivotal role, amongst char coal, coke and soot, by carrying the predominant part of the (mostly) anthropogenic PAHs present in the sediment-water system. It is known that hard coal acts as a sink and source for hydrophobic organic contaminants, which is explained by strong sorption affinity and high capacity, compared to other organic matter.

Various concepts to describe the sorption-desorption characteristics of hydrophobic pollutants in the presence of different geosorbents have been established and the understanding of the related processes has improved steadily during the last decades. Coal is a very heterogeneous material depending on rank and origin and general characterization is difficult. Nevertheless, generally speaking, coal, and particularly hard coal and anthracite show high sorption capacities (comparable to black carbon) and nonlinear sorption behaviour.

The heterogeneities of coals also hamper general characterization of “coal” for source apportionment. Usually, PAHs from coal are catergorized amongst others e.g. from oil as petrogenic PAHs. They can be characterized by substantial concentrations of alkylated naphthalenes, phenanthrenes and chrysenes, by a bell-shaped form of the parent and alkylated homologue series and by certain PAH-ratios based on thermodynmical stabilities of the single compounds. Various methods can be used to investigate the impact of coal-bound PAHs including coal petrography, PAH distribution patterns, PAH ratios, biomarkers, alkane distributions, principal component analyses, and others.

Until today, there is a lack of knowledge about native PAHs in coals, environmental forensic characterization of coals and the bioavailability of toxic compounds such as native PAHs or NSO-PAHs in coals of different rank and origin is limited, particularly with respect to mined coals from large coal basins worldwide.

Chapter 3 - One side effect of coal mining is the formation of acidic drainage waters, resulting from microbial oxidation of inorganic sulfur compounds, such as pyrite or elemental sulfur, to sulfuric acid. In the course of this process, the pH of the drainage waters can drop to values of about 1 to 2. Therefore, the responsible microorganisms are adapted to this special environment as they are truly acidophilic. The same bacteria and archaea are employed in operations for winning of metals from sulfidic ores and are called leaching prokaryotes. Their substrate, the reduced sulfur compounds, is naturally occurring in both hard coal and lignite. The bacterial oxidation process starts when the coal is exposed to air and water, e.g., due to mining and accompanying measures, such as lowering the groundwater level. The acidic water, generally called Acid Mine Drainage (AMD) and often laden with toxic amounts of heavy metals, tends to pollute groundwater, lakes and rivers. Mitigation of AMD processes focus on the inhibition of bioleaching activities. Hence, for evaluation of these remediation measures, reliable monitoring methods for assessing the prokaryotic activities at AMD sites are required. Therefore, the authors have developed a robust and rapid test system combining two sensitive analytical techniques: quantification of heat evolution by microcalorimetry and determination of all relevant inorganic sulfur species by chromatographic methods. The combined test has been applied to various coal mining sites. In this chapter, the results of two case studies, a hard coal and a lignite site in Germany, respectively, will be presented. Furthermore, additional microbiological methods will be discussed possibly helping to deal with the AMD phenomenon.

Chapter 4 **-** The role of plants in the formation of post-mining soil is generally accepted, but much less is known about the role of soil biota in this process. The aim of this study is to give an overview of the main factors that determine occurrence of soil biota in post-mining soils, and of the role of soil biota in soil forming process. Studies conducted on reclaimed and non-reclaimed sites in two post-mining areas in the Czech Republic and Germany are summarized and compared with other post mining sites in Europe. This study is focused on forest reclamation or naturally revegetated areas covered by woody species, as forest reclamation is the most common reclamation practice in both areas.

Major constraints that determine colonization of post-mining sites by soil fauna are migration distance, character of substrate, namely substrate toxicity and physical properties, and development of vegetation. Development of vegetation can affect soil biota by the quality of litter, and the spatial organization of vegetation is also very important for soil fauna. Besides immediate vegetative cover, long-term development of soil horizons are crucial. Besides vegetation, soil biota also contributes to the development of soil horizons. Soil microflora play a crucial role in litter decomposition and nutrient dynamics in post-mining sites. The soil fauna affect soil microstructure, carbon and nutrient storage, soil physical properties and plant growth in post-mining sites.

Chapter 5 **-** In the frame of mining activities, such as for brown and hard coal, huge volumes of highly mineralised water are pumped to the surface, which can contain significant amounts of radionuclides of both the natural 238U and 232Th decay series. This concerns especially the decay product radium due to mobilisation processes such as the alpha-recoil effect and leaching in the coal layers and surrounding rock formations.

Despite the fact that coal seams are made of organic components and therefore do act as a sink for uranium in dependence from geological settings such as ascending uranium bearing waters, the coal’s initial uranium and thorium content are usually low. However, under reducing milieus as they are established in coal seams 238U, its next progenies and 232Th are indeed strongly immobile, but by disintegrating into radium the first significantly soluble radionuclide is formed within each decay scheme. In order to design radium enrichment in circulating formation waters, only ordinary radionuclide concentrations in the source rocks are required. Once those saline pit waters acting as a radium carrier are brought to the surface, different types of contamination by natural radionuclides, which means radium and its progenies, can occur due to changes in physical and chemical conditions. On the mining sites radionuclides can be concentrated in scales being precipitated inside tubes or in sludges being generated in tailing ponds by suspension settling, but also sewers and rivers in public areas can be affected if the brines are discharged untreated. In that case especially sediments along those streams can get contaminated by radionuclides.

In addition, special attention must be also paid for radon occurring as an isotope within both the decay series, because under environmental conditions it is a volatile element and therefore enabled to exhale from solids.

Chapter 6 - Selenium is a chemical element that is found in coal in small amounts. The potential for environmental problems begins when coal-bearing strata are exposed to air and water during the mining process, and when coal is washed prior to transport and distribution. This can mobilize selenium and form contaminated leachate and liquid waste, which often becomes a source of pollution to nearby surface waters. Once in the aquatic environment, selenium can rapidly bioaccumulate in food chains and reach levels that are toxic to aquatic life. Because of bioaccumulation, a small amount of selenium in water can translate to a significant environmental hazard. Case examples show that selenium from coal mining can result in a variety of impacts to fish, ranging from subtle effects on growth to severe deformities and complete reproductive failure. However, despite this negative implication, coal mining can be compatible with environmental needs if adequate steps are taken to prevent or reduce hazard. For prospective mines, this involves conducting a detailed site assessment and then matching operational parameters with environmental requirements. For active or decommissioned mines it is necessary to formulate and implement appropriate waste management and site reclamation plans.

Chapter 7 - The World average F content in coals (coal Clarke of F) for the hard and brown coals are, respectively, 82±6 and 90±7 ppm. On an ash basis, these contents are greatly increased and are 580±20 and 630±50 ppm, respectively. As an average, F content in ash is 605 ppm (lower than the Clarke value for sedimentary rocks, 650 ppm). F is, on average, *not a coalphile element.*

Nevertheless, some coals are known to have a F content one order of magnitude more than the coal Clarke level. In general, these are either high-ash or high-phosphorus coals, with both the features often combined. This (and some others) features show some similarity between F and P geochemistry in coal. In particular, F, like P, seems to be depleted from the buried peat during diagenesis toward hosting rocks.

No less than three F-forms (modes of occurrence) may be present in coal: phosphatic (F_{phosph}), silicatic (mostly F_{clay}), and organic (F_{org}). It can be suggested that F_{clay} dominates in high-ash coals, F_{phosph} in high-P coals, and in ordinary coals with moderate ash yield and near-Clarke P and F contents, F_{org} may be dominant. There is no information concerning chemical species of the F_{org} form. However, by an analogy with P, it seems to exist as an F compound with Ca_{org}, not with organics itself.

It is yet not clear, if F is in authigenic CaF_2 and what could be a contribution of such a form to total F content. It seems not to be excluded that such form may have genetic relation with F_{org} (diagenetic or catagenetic transformation, $F_{org} \Rightarrow F_{min}$?).

There are no clear relationships concerning F enrichment in coals. Plausible hypothesis is that F might be syngenetically enriched in coals (a) in paralic (near-marine) coals, and (b) in coals formed with a volcanic activity background. On the other hand, some F anomalies (like that in some Alabama coals) may resulted from epigenetic hydrothermal F-input, during (or after) coal metamorphism.

Chapter 8 - Land use zoning is gaining increasing popularity in India, amongst environmentalists and planners alike, as an important instrument governing siting of industrial, commercial, residential and other uses of land. 'Environmentally compatible land use zoning' is gaining increasing acceptance as an essential tool for effecting environmentally sustainable development. Most of the environmental problems in mining/ industrial regions can, in one way or the other, be related to improper land use zoning. Through an implicit integration of environmental constraints into the basic planning procedure, the zoning system arrests an otherwise (business-as-usual scenario) spiralling environmental management cost. However, environmentally compatible micro level zoning system is yet to find its right place in Indian planning set-up.

Land use is expected to be altered significantly in power grade coal bearing regions in India that typically have a mix of large opencast mining projects, thermal power plants and other associated industries in coalfields. Power grade coalfields in the country are in river valleys that host rivers and large tract of forests and agricultural lands amid a majority of tribal population. A need to carry out a scientific inquest into zoning study in the power grade coalfields in the country can hardly be over emphasized. The chapter discusses a new micro level zoning method applied for a representative power grade coalfield in the country. The authors have attempted to devise a mechanism for optimizing spatial zoning as per need based zoning policy. The study area was divided into segments of land parcels for spatial analysis of each parcel. Behaviour of infrastructural, socio economic and environmental attributes was studied to identify the underlying economic forces and environmental need. Land use forms of segments or land parcels were logically integrated to evolve overall land use zoning.

Chapter 9 - The long-term exposure of coal miners to respirable dust containing crystalline silicon dioxide (silica; SiO_2) causes a chronic inflammatory process in the alveoli, interstitial lung tissue and bronchi, which ultimately result in coal workers' pneumoconiosis (CWP), progressive massive fibrosis of the lung (PMF), as well as chronic obstructive pulmonary disease (COPD) and emphysema. These health disorders show a close pathogenetic and pathophysiological association and should not be considered individual entities. Many coal miners subjected to long-term exposure demonstrate several of these pathological findings in parallel, although their absolute degree may differ for each individual. Some individuals are rather resistant and others show severe effects, presumably because of variations in genetically based susceptibility. The risk of respiratory impairment in coal miners increases with increasing dust exposure in a dose-dependent manner, regardless of radiologically demonstrated CWP/PMF or not. Thus, COPD and emphysema should be added to CWP and PMF as occupational diseases arising from long-term employment in coal mines, even in the absence of pneumoconiosis.

Chapter 10 - In the last 30 years in the Polish coal mines several serious disasters have occurred. In each of them up to 30 coal miners were killed. Altogether more than 150 people lost their life in coal mining disasters. Among those who experienced accidents in mines, many were injured and sustained damage to their health. As a consequence of disaster decline in mental health has been occurred too. One of the most specific disturbances in mental health in the aftermath of disaster is post-traumatic stress disorder. In the authors' empirical study 52 coal miners, who took part in mining disaster and were injured, were taken into investigation. All of the subjects were men 23-54 years old (M=37.40, SD=7.41), they lived in the Silesian region (the region in which coal mining industry is the most widespread in Poland) and they experienced coal mining accident up to 25 months before the study. Several questionnaires were administered to the participants. Post-traumatic stress disorder symptoms were assessed as well as the range of their determinants, including emotional reactivity understood as a temperamental trait and sense of coherence. The findings show essential decline in mental health in survivors of coal mining disaster: about one third of the sample under study might be diagnosed as suffering from PTSD. In comparison with the findings in flood disaster survivors, the level of PTSD symptoms were higher, especially in the short period after accident. The range of determinants of PTSD symptoms, including temperamental trait emotional reactivity, seems to be comparable to the outcomes in flood survivors. In discussion the consequences of coal mining accident for mental health have been taken under consideration.

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Short Commentary 1

HEAVY METAL CONTAMINATION OF AGRONOMIC CROPS GROWN ON THREE RECLAIMED MINE WASTELANDS IN SOUTH CHINA AND IMPLICATIONS FOR ECOLOGICAL RESTORATION

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ABSTRACT

Agronomic crops grown on the reclaimed metal-mined wastelands are a pathway for toxic pollutants entering the human food chain. Agricultural rehabilitation of mine spoils in China is pretty common and its effect has been largely overlooked. Extensive sampling of the edible crops and associated soils have been conducted for the three typical manganese mine wastelands (Bayi, Lipu and Pingle) in Guangxi, south China and heavy metal contamination of crops was assessed against China Food Safety Standards. Simple pollution index (Pi) assessment indicated no Zn (except tea) and Cu pollution among these crops, but heavy pollution of Pb, Cd and Cr was found. Composite pollution index (Nemerow index, P_N) showed 36 crops from 41 were heavily polluted with heavy metals. Peanut, soybean, Chinese chestnut, persimmon, cassava, mandarin and sugarcane were the most severely contaminated crops. Consumption of these crops may pose a health risk for humans. Crops tended to have a higher Cd accumulation (as indicated by Biological Accumulation Factor) in edible parts, thus Cd is the most important food safety threat. In terms of China Soil Quality Standard (class II), the minesoils contained much higher Cd and Cr levels, not suitable for agricultural plantation. Simple reclamation for crop plantation on minesoils is legally untenable and must be strictly controlled by the local governments. In addition, more diverse restoration goals with lower environmental risk should be encouraged for the mine wastelands in South China.

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Keywords: heavy metal contamination, agronomic crops, Mn mine wasteland, simple pollution index, composite pollution index, ecological restoration, Guangxi.

INTRODUCTION

Food safety is fundamental to human survival and health. Recently, adverse publicity about China's contaminated food exports (e.g., rejected shipments of vegetables, tea, dumplings, shrimp, and poultry) reflected a gap between international and China's food safety standards. Also, a series of food safety incidents in the domestic market (e.g., respiratory diseases, acute pesticide residual poisons, and sudan yellow dye) prompted the Chinese government to raise domestic food safety standards and implement inspection and testing systems for consumer products and agricultural commodities. Metallic elements, either essential or nonessential, are potentially harmful food safety threats because they are generally invisible, accumulative (slow), and irreversible in effect. Of these elements, the most important in terms of food-chain contamination are arsenic (As), cadmium (Cd), mercury (Hg), lead (Pb), and selenium (Se) (McLaughlin et al., 1999). Except for Se, these toxic metals enter soils through anthropogenic sources, such as wastewater irrigation, sludge application, chemical fertilizer usage, ore extraction and smelting, industrial wastes, and atmospheric deposition.

It is reported widely that about 1/5 of the cultivated land (20 Mha) in China were contaminated with heavy metals (Sun et al., 2005), among which Cd and Pb were the main contaminants. Heavy metal contamination of foods has attracted great concern in China, especially in the big cities. Assessment of heavy metal pollution of paddy fields, kale yard soils, or orchard soils had been conducted extensively in the outskirts of Beijing, Shanghai, Guangzhou, Tianjing, Hanzhou, Fuzhou, Shenyang, Zhenzhou, Xi'an, Chendu, Chongqing, and Nanning (Liu & Chen, 2004), many of which the pollution of crops also was evaluated. For instance, in the notorious Zhangshi Irrigation Area of north China, the mean Cd level in its unpolished rice reached 1.06 mg/kg while the maximum allowed level was only 0.2 mg/kg (Chan & Shi, 2001). In the Pearl River Delta region, the world's manufacturing base which provides over 80% of the vegetables for Hong Kong, 40% of the farmland and vegetable fields were contaminated with multiple metals, and nearly 1/3 of the main-consumed vegetables were contaminated by metals especially Cd and Pb (Huayi net news, March 6, 2007).

Although the heavy metal contamination of staple food and their associated agricultural lands was really alarming, pollution of the minelands largely has been overlooked in China because they are usually remote to the densely populated urban areas. Mining is the second principal source of heavy metal contamination in soil after sewage sludge (Singh et al., 2005). As a primary contributor to the rapid economic boost of China, mining industry generated vast areas of wastelands (about 3.2 Mha) and caused serious environmental pollution (Li, 2006). A conservative estimate of economic loss (direct and indirect) resulted from mining pollution is nearly 40 billion RMB *yuan* in China each year (Liu & Shu, 2003). In addition, problems existed for the restoration practices in China because many of these wastelands were reclaimed for planting agronomic crops because China's cultivated lands are in serious shortage. In fact, the input of toxic metals into food web generates another potentially more harmful problem than the wasteland itself.

China has the world's second largest Mn-ore reserve. Guangxi *Zhuang* Autonomous Region, adjoining Guangdong Province in the east and bordering Vietnam to the southwest, is one of the most well-developed karst areas on earth. Meanwhile, mining is a pillar industry in Guangxi with Mn and Sn mining ranking first in China. Currently, there are over 6800 mines in operation (96% of the mines were private or collective-owned), destroying a total area of about 600,000 ha (Li, 2005). Due to the extreme shortage of surface soil and economic backwardness, agricultural reclamation of mine wastelands is more common in Guangxi than in other parts of China. The major edible plants grown include Chinese chestnut, sugarcane, peanut, mandarin, orange, plum, peach, persimmon, Taiwan green Jujube, shaddock, medical herbs, tea trees, and other vegetables such as Chinese cabbage and Chinese radish. Worries arose because there were usually no protective treatments in place before planting and no monitoring of toxic metals was conducted or source of food was indicated before they entered the market. This study, based on the investigation on the three typical Mn mine wastelands in Guangxi, aims to assess the heavy metal contamination of grown crops against China Food Safety Standards, and furthermore, the restoration practice is discussed in hope to provide insight to the proper rehabilitation of metal-mined wastelands in South China.

MATERIALS AND METHODS

The Study Site

The three Mn mines (Bayi, Lipu and Pingle) in Guangxi all employed opencast mining which ore extraction began in the late 50s. Lipu and Pingle mines were both medium-sized, about 105-115 km southeast from Guilin, the world's famous karst scenic spot (Fig. 1). Bayi mine was once one of the three largest Mn mines in China, situated in the central Guangxi. Due to the ore depletion, large excavations have ceased for the three mines, but some private miners were digging for residuals at the margin. These areas belong to the middle subtropical monsoon climatic zone. The regional vegetation is the typical subtropical evergreen broadleaf forest. Landform of these mines is basically hilly land and zonal soil is loess.

Large reclamation efforts (reclamation area > 10 ha) were made for these mine wastelands: Huge lands were planted with sugarcane and tea trees in Bayi while Chinese chestnuts were planted in Lipu and peach trees in Pingle (Yang et al., 2007). Other agronomic plants (e.g. peanuts) were grown in smaller scale or even small patches (e.g. vegetables) for family consumption. In addition to the edible crops, other reclamations for nursery, pulpwood, charcoal and medical herbs existed while some wastelands just lay fallow. In terms of the overall vegetation coverage, Lipu (90%) is the highest, and Pingle (30%) the lowest with Bayi (75%) in-between.

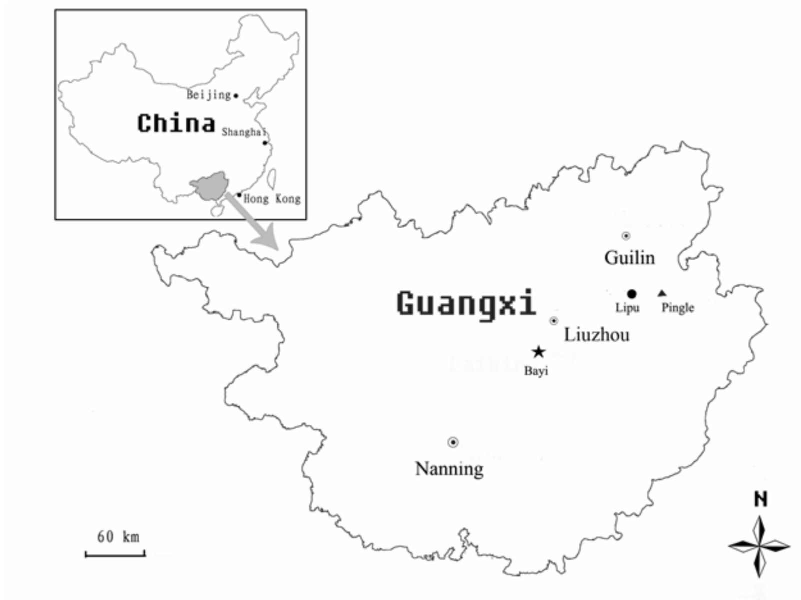

Figure 1. Map of Guangxi, showing locations of the three Mn mine wastelands: Bayi, Lipu, and Pingle

Sample Collection and Analysis

From November 2004 to October 2006, extensive ecological surveys and sampling have been carried out in the three mine wastelands respectively. The major edible crops were sampled at their appropriate seasons, each sample comprising 5-6 multipoint subsamples. Meanwhile, the associated top soils (0-20 cm) were collected for metal determination. Both plant and soil samples were taken in triplicates and sealed with polythene bags and transported into laboratory.

Plant samples were gently washed with tap water, and rinsed three times with deionized water. Samples were air-dried and weighed, first dried at 105℃ for 30 min, and then at 70℃ to constant weight. Dried plant materials were ground into fine powder. Soil samples were air-dried, homogenized and sieved through a 2-mm screen, then pulverized and passed through a 0.154-mm nylon sieve. Soil samples were digested with concentrated HCl + concentrated HNO_3 + HF + $HClO_4$ (10:5:5:3, v/v), and plant tissues digested with concentrated HNO_3 + $HClO_4$ (20:3-5, v/v). The total metal concentrations (Cd, Cr, Cu, Pb, Zn and Mn) in digest were determined with flame atomic absorption spectrophotometer. Quality assurance of metal determination was executed using rate of recovery of the added standard amount of metal into the digested solution, and the recovery rates for these measurements were within 89 - 106%. Statistical analyses were performed using SPSS 12 for Windows.

Pollution Assessment

Assessment Method

The simple pollution index (Pi) and composite pollution index (Nemerow index, P_N) were employed to assess the pollution degree of the edible crops. Pi considers single metal pollution separately whereas P_N, integrating the mean Pi with the extreme pollution scenario, is a comprehensive indication of pollution (Chen, 2006):

Pi = Ci / Si

where Ci represents the concentration of heavy metal *i* in plant tissue while Si indicates the relevant standard value for this metal (see the next); and

$$P_N = \sqrt{\frac{P_{i\,(ave)}^{2} + P_{i\,(max)}^{2}}{2}}$$

where $P_{i(ave)}$ is the average of Pi of metals, and $P_{i(max)}$ denotes the maximum value among Pi.

Assessment Criteria and Pollution Grading

The maximum allowable levels of contaminants in foods of China were used as the assessment criteria. Table 1 listed the maximum levels of Zn, Pb Cr, Cu and Cd in foods relevant to this study. There are no values stipulated for Mn, thus Pi and P_N for Mn were not calculated. Based on Pi and P_N values, heavy metal contamination were classified into different grades and the corresponding pollution levels were given in Table 2.

Table 1. Maximum allowable level of heavy metals in foods as assessment criteria

Food category	Allowable metal level ($mg \cdot kg^{-1}$ FW)				
	Zn	Pb	Cr	Cu	Cd
Beans	100	0.2	1.0	20	0.2 (soybean) 0.5 (peanut)
Potatoes & tubes	50	0.2	0.5	10	0.1
Fruits	5	0.1	0.5	10	0.05
Tea	100[a]	5	5[b]	60[c]	1[b]
Vegetables	20	0.3 (leaf) 0.1 (non-leaf)	0.5	10	0.1 (tuber) 0.2 (leaf) 0.05 (others)
Standards[d]	GB13106-1991	GB2762-2005	GB2762-2005	GB15199-1994	GB2762-2005

[a] Food categories were not exhaustive, and only relevant values related to this study were listed. For tea, only maximum Pb level was given. For Zn, the maximum level of foods was used in the assessment.

[b] For Cr and Cd levels in tea, the values are from the standard NY659-2003 issued by the Ministry of Agriculture, China.

[c] For Cu level in tea, the value is from the standard NY5017-2001 issued by the Ministry of Agriculture, China.

[d] These standards were issued by the Ministry of Health, China.

Table 2. Pollution index grading and corresponding pollution level of heavy metals

Grade	Simple pollution index (Pi)	Pollution level	Composite pollution index (P_N)	Pollution level
1	$P_i < 1$	Unpolluted	$P_N \le 0.7$	Unpolluted
2	$1 \le P_i < 2$	Slight	$0.7 < P_N \le 1$	Warning
3	$2 \le P_i < 3$	Medium	$1 < P_N \le 2$	Slight
4	$3 \le P_i$	Heavy	$2 < P_N \le 3$	Medium
5	-	-	$3 < P_N$	Heavy

Bioaccumulation Factor

The Bioaccumulation Factor (BAF) of a plant is the heavy metal concentration in plant tissue (dry weight) divided by the same metal concentration in soil (Li et al., 2007), and this expression is often used to evaluate the plant's uptake capacity of the metal from soil. Low accumulating crops (cultivars) of toxic metals are better choices for phytoremediation of metal-contaminated site.

RESULTS

Heavy Metals in Agronomic Crops

There were 9 crops from Bayi, 19 from Lipu and 13 from Pingle mine wastelands included in this study, and only the edible parts for human being were analyzed for heavy metals. The heavy metal contents in the edible parts of crops are presented in Table 3, and the summarized data in Table 4. If we consider each crop as an individual sample, the heavy metal levels in crops were generally in the order of Mn > Zn > Pb > Cr ~ Cu > Cd. There were great variations of metal content among different crops for the same metal and among different wastelands (Table 3). The highest values for Zn, Pb, Cr, Cu, Cd and Mn were in tea (Bayi), peanut (Pingle), tea (Bayi), tea (Bayi), peanut (Lipu) and tea (Bayi), respectively for each metal, and the lowest were in orange (Bayi), watermelon (Bayi), watermelon (Bayi), orange (Lipu), Nachi pear (Lipu) and Nachi pear (Lipu).

Overall, median values were all lower than the mean especially for Mn (Table 4) because median value eliminates the effect of extreme figures in a data set. Compared with the heavy metal levels of crops grown on the normal farmlands of China (Zhong et al., 2001), Zn and Cu levels of the crops on these minelands were well within the range, but Pb, Cd or Cr level, regardless of mean or median, was higher than the upper limit, indicating a potential multi-metal pollution.

Table 3. Heavy metal contents (mean ± SE, *n*=3) of agronomic crops on the three Mn mine wastelands in Guangxi

Crop	Scientific name	Edible part	Heavy metal content ($mg\cdot kg^{-1}$ FW)					
			Zn	Pb	Cr	Cu	Cd	Mn
Bayi mineland: 9 edible crops								
Peanut	*Arachis hypogaea*	earthnut	21.44±0.86	4.80±0.47	1.45±0.38	6.37±0.32	0.52±0.11	17.14±0.97
Soybean	*Glycine max*	seed	37.53±1.02	8.01±0.46	3.76±0.81	6.10±0.38	1.03±0.18	17.74±0.74
Sweet potato	*Ipomoea batatas*	tuber	3.12±0.69	3.24±0.09	2.41±0.55	1.81±0.13	0.39±0.06	11.41±3.25
Sweet potato	*Ipomoea batatas*	leaf	4.23±0.31	1.95±0.06	1.48±0.05	1.97±0.08	0.33±0.10	25.52±2.66
Cassava	*Manihot esculenta*	tuber	6.01±0.44	2.31±0.35	1.94±0.39	1.96±0.18	0.74±0.15	3.5±0.06
Orange	*Citrus sinensis*	fruit	1.03±0.08	0.66±0.09	0.27±0.12	0.39±0.03	0.18±0.02	0.78±0.24
Watermelon	*Citrullus lanatus*	fruit	1.24±0.13	0.32±0.02	0.11±0.01	0.16±0.01	0.06±0.01	1.55±0.03
Sugarcane	*Saccharum sinensis*	shoot	3.19±0.81	2.09±0.29	1.92±0.31	0.74±0.04	0.54±0.06	24.4±1.15
Tea	*Camellia sinensis*	leaf	96.02 ±21.39	13.01±0.54	9.28±1.69	9.71±0.16	0.76 ±0.13	1768.45±136.56
Lipu mineland: 19 edible crops								
Peanut	*Arachis hypogaea*	earthnut	20.46±1.52	5.73±1.36	3.09±0.35	3.84±0.03	2.76±0.06	23.62±1.08
Soybean	*Glycine max*	seed	20.46±0.51	8.96±2.00	2.34±0.19	6.24±0.18	2.30±0.09	30.14±1.71
Sweet potato	*Ipomoea batatas*	tuber	5.07±0.24	6.26±1.98	2.46±0.39	0.04±0.06	1.51±0.62	2.65±0.86
Sweet potato	*Ipomoea batatas*	leaf	2.93±0.07	1.04±0.12	1.07±0.18	0.76±0.01	0.08±0.00	8.83±0.06
Cassava	*Manihot esculenta*	tuber	7.41±0.47	7.33±1.75	2.32±0.22	2.39±0.07	1.79±0.11	1.49±0.09
Orange	*Citrus sinensis*	fruit	1.94±0.32	5.39±0.86	1.01±0.11	0.01±0.09	0.24±0.03	1.59±0.64
Sugarcane	*Saccharum sinensis*	shoot	3.65±0.21	7.34±1.87	2.09±0.09	2.22±0.06	1.80±0.09	12.18±0.09
Nachi pear	*Pyrus pyrifolia*	fruit	2.12±0.92	0.66±0.18	2.02±0.29	0.85±0.02	0.01±0.01	0.66±0.09
Persimmon	*Diospyros kaki*	fruit	2.99±0.18	5.88±1.25	2.47±0.53	0.18±0.04	0.72±0.04	7.58±0.51
Peach	*Amygdalus persica*	fruit	2.86±0.32	1.50±0.08	1.06±0.10	0.74±0.05	0.06±0.01	1.37±0.08
Chinese Chestnut	*Castanea mollissima*	nut	9.58±1.64	11.05±0.81	2.94±0.79	3.45±0.31	1.89±0.17	66.27±6.97
Shallot	*Allium fistulosum*	shoot + leaf	4.26±0.43	1.70±0.47	1.34±0.37	0.56±0.00	0.36±0.01	21.18±5.11

Table 3. Heavy metal contents (mean ± SE, *n*=3) of agronomic crops on the three Mn mine wastelands in Guangxi (Continued)

Crop	Scientific name	Edible part	Heavy metal content (mg·kg^{-1} FW)					
			Zn	Pb	Cr	Cu	Cd	Mn
Garlic	*Allium sativum*	shoot + leaf	4.50±0.78	2.29±0.71	1.19±0.04	0.78±0.04	0.64±0.04	19.72±2.10
Capsicum	*Capsicum annuum*	fruit	8.82±1.01	8.21±1.35	4.87±1.42	2.78±0.31	0.92±0.05	8.21±2.07
Eggplant	*Solanum melongena*	fruit	1.18±0.05	0.65±0.05	1.07±0.20	0.43±0.01	0.03±0.00	13.09±4.22
Chinese radish	*Raphanus sativus*	tuber	2.45±0.21	0.88±0.23	0.63±0.20	0.26±0.01	0.13±0.01	2.85±0.18
Cowpea	*Vinga unguiculata*	fruit	5.13±0.04	2.49±0.65	0.93±0.14	0.52±0.16	0.43±0.06	50.15±0.96
Endive	*Cichorium endivia*	leaf	5.20±0.24	0.83±0.11	0.75±0.09	0.42±0.02	0.12±0.00	6.37±0.24
Lettuce	*Lactuca sativa*	leaf	3.30±0.18	0.52±0.15	0.33±0.02	0.34±0.05	0.20±0.00	5.86±0.38
Pingle mineland: 13 edible crops								
Peanut	*Arachis hypogaea*	earthnut	15.39±0.26	16.16±2.83	6.62±0.73	2.74±0.11	0.74±0.04	9.64±0.09
Chinese Chestnut	*Castanea mollissima*	nut	9.17±1.50	3.50±0.35	3.43±0.32	5.30±0.25	0.98±0.05	69.82±2.02
Soybean	*Glycine max*	seed	18.13±0.08	4.23±0.62	5.47±0.58	5.21±0.29	0.04±0.02	29.62±0.67
Cowpea	*Vinga unguiculata*	fruit	6.85±0.19	1.02±0.06	2.32±0.17	0.70±0.01	0.06±0.00	60.1±1.73
Sweet potato	*Ipomoea batatas*	tuber	4.78±0.17	9.91±0.26	3.69±0.11	1.20±0.13	0.78±0.03	40.47±6.69
Cassava	*Manihot esculenta*	tuber	6.06±0.78	10.46±3.67	1.18±0.10	0.54±0.10	0.68±0.04	17.51±3.24
Mandarin	*Citrus reticulata*	fruit	1.49±0.05	5.90±0.40	2.23±0.04	0.34±0.05	0.48±0.05	5.02±0.33
Persimmon	*Diospyros kaki*	fruit	1.80±0.43	8.62±0.07	0.97±0.17	0.28±0.07	0.55±0.09	21.22±6.41
Peach	*Amygdalus persica*	fruit	1.56±0.11	0.66±0.09	0.96±0.14	0.32±0.01	0.01±0.00	1.29±0.03
Taro	*Colocasia esculenta*	tuber	19.28±2.99	6.76±1.61	3.78±0.00	1.16±0.22	0.73±0.04	160.79±4.10
Ginger	*Zingiber officinale*	tuber	4.69±0.12	2.93±0.27	1.51±0.11	0.58±0.04	0.32±0.02	334.09±41.68
Tomato	*Lycopersicon esculentum*	fruit	1.27±0.04	0.54±0.04	1.19±0.08	0.45±0.14	0.03±0.00	1.77±0.03
Capsicum	*Capsicum annuum*	fruit	3.25±0.16	3.11±0.27	1.60±0.23	1.28±0.08	0.38±0.05	16.83±2.43

Table 4. Summarized analyses of heavy metal concentrations in agronomic crops on the three mine wastelands in Guangxi

	Heavy metal concentration ($mg \cdot kg^{-1}$)					
	Zn	Pb	Cr	Cu	Cd	Mn
Bayi mineland						
Maximum	96.02	13.01	9.28	9.71	1.03	1768.45
Minimum	1.03	0.32	0.11	0.16	0.06	0.78
Mean	19.31	4.04	2.51	3.25	0.51	232.39
Median	4.23	2.31	1.92	1.96	0.52	17.44
Number of crops	9	9	9	9	9	9
Lipu mineland						
Maximum	20.46	11.05	4.87	6.24	2.76	66.27
Minimum	1.18	0.52	0.33	0.01	0.01	0.66
Mean	6.02	4.14	1.79	1.41	0.84	14.94
Median	4.26	2.49	1.34	0.74	0.43	8.21
Number of crops	19	19	19	19	19	19
Pingle mineland						
Maximum	19.28	16.16	6.62	5.3	0.98	334.09
Minimum	1.27	0.54	0.96	0.28	0.01	1.29
Mean	7.21	5.68	2.69	1.55	0.44	59.09
Median	4.78	4.23	2.23	0.7	0.48	21.22
Number of crops	13	13	13	13	13	13
Overall						
Maximum	96.02	16.16	9.28	9.71	2.76	1768.45
Minimum	1.03	0.32	0.11	0.01	0.01	0.66
Mean	9.31	4.61	2.23	1.86	0.64	72.78
Median	4.5	3.24	1.92	0.76	0.48	14.96
Number of crops	41	41	41	41	41	41
Range in crops of China ($mg \cdot kg^{-1}$)	2.547~26.33	0.01~3.265	0.069~0.651	0.384~5.86	0.012~0.319	-

Pollution Assessment of Agronomic Crops

The pollution indices (Pi and P_N) of the crops and the corresponding pollution levels are shown in Table 5. For the five toxic metals studied (Mn was not assessed since no criteria of food safety is available), basically no Zn (except tea) or Cu pollution existed in these crops. Almost all crops were polluted with Pb, Cd and Cr. The pollution patterns of heavy metals were consistent throughout the three wastelands.

From a comprehensive consideration of heavy metals, 36 crops (87.8%) of 41 were heavily polluted; only 3 (orange in Bayi, sweet potato leaf in Lipu and endive in Lipu) were polluted moderately, and 2 (watermelon in Bayi and lettuce in Lipu) were slightly polluted (Table 5). If $P_N > 9$ (three times the 'heavy' limit) was regarded as extremely heavy pollution, the percentage of this class represented 63.4% of the total edible crops. Consumption of these food crops may pose a great health risk for humans.

Table 5. Pollution assessment of the edible crops on the three mine wastelands in Guangxi

Crop	Pollution index of metals in crops by region					
	Pi (Zn)	Pi (Pb)	Pi (Cr)	Pi (Cu)	Pi (Cd)	P_N
Bayi						
Peanut	0.2 unpolluted[a]	24 heavy	1.5 slight	0.3 unpolluted	1 slight	17.4 heavy
Soybean	0.4 unpolluted	40.5 heavy	3.8 heavy	0.3 unpolluted	5.2 heavy	29.5 heavy
Sweet potato (tuber)	0.1 unpolluted	11.6 heavy	3.9 heavy	0.2 unpolluted	7.4 heavy	8.8 heavy
Sweet potato (leaf)	0.2 unpolluted	6.5 heavy	3 heavy	0.2 unpolluted	1.7 slight	4.9 heavy
Cassava	0.1 unpolluted	16.2 heavy	4.8 heavy	0.2 unpolluted	3.9 heavy	12.0 heavy
Orange	0.2 unpolluted	3.3 heavy	0.5 unpolluted	0 unpolluted	3.6 heavy	2.8 medium
Watermelon	0.2 unpolluted	1.6 slight	0.2 unpolluted	0 unpolluted	1.2 slight	1.2 slight
Sugarcane	0.6 unpolluted	20.9 heavy	3.8 heavy	0.1 unpolluted	10.8 heavy	15.6 heavy
Tea	4.8 heavy	2.6 medium	18.6 heavy	0.97 unpolluted	3.8 heavy	13.9 heavy
Lipu						
Peanut	0.2 unpolluted	28.7 heavy	3.1 heavy	0.2 unpolluted	5.5 heavy	21.0 heavy
Soybean	0.2 unpolluted	44.8 heavy	2.3 medium	0.3 unpolluted	11.5 heavy	32.8 heavy
Sweet potato (tuber)	0.1 unpolluted	31.3 heavy	4.9 heavy	0 unpolluted	15.1 heavy	23.3 heavy
Sweet potato (leaf)	0.1 unpolluted	3.5 heavy	2.1 medium	0.1 unpolluted	0.4 unpolluted	2.6 medium
Cassava	0.1 unpolluted	36.6 heavy	4.6 heavy	0.2 unpolluted	17.9 heavy	27.2 heavy
Orange	0.4 unpolluted	53.9 heavy	2 medium	0 unpolluted	4.8 heavy	39.1 heavy
Sugarcane	0.7 unpolluted	73.4 heavy	4.2 heavy	0.2 unpolluted	36 heavy	54.4 heavy
Nachi pear	0.4 unpolluted	6.6 heavy	4 heavy	0.1 unpolluted	0.2 unpolluted	4.9 heavy
Persimmon	0.6 unpolluted	58.8 heavy	4.9 heavy	0 unpolluted	14.4 heavy	43.0 heavy
Peach	0.6 unpolluted	15 heavy	2.1 medium	0.1 unpolluted	1.2 slight	10.9 heavy
Chinese Chestnut	1.9 slight	110.5 heavy	5.9 heavy	0.3 unpolluted	37.8 heavy	81.2 heavy
Shallot	0.2 unpolluted	5.7 heavy	2.7 medium	0.1 unpolluted	1.8 slight	4.3 heavy
Garlic	0.2 unpolluted	7.6 heavy	2.4 medium	0.1 unpolluted	3.2 heavy	5.7 heavy
Capsicum	0.4 unpolluted	82.1 heavy	9.7 heavy	0.3 unpolluted	18.4 heavy	60.1 heavy
Eggplant	0.1 unpolluted	6.5 heavy	2.1 medium	0 unpolluted	0.5 unpolluted	4.8 heavy
Chinese radish	0.1 unpolluted	8.8 heavy	1.3 slight	0 unpolluted	2.5 medium	6.5 heavy
Cowpea	0.3 unpolluted	24.9 heavy	1.9 slight	0.1 unpolluted	8.6 heavy	18.3 heavy
Endive	0.3 unpolluted	2.8 medium	1.5 slight	0 unpolluted	0.6 unpolluted	2.1 medium
Lettuce	0.2 unpolluted	1.7 slight	0.7 unpolluted	0 unpolluted	1 slight	1.3 slight

Table 5. Continued

Crop	Pollution index of metals in crops by region					
	Pi (Zn)	Pi (Pb)	Pi (Cr)	Pi (Cu)	Pi (Cd)	P_N
Pingle						
Peanut	0.2 unpolluted	80.8 heavy	6.6 heavy	0.1 unpolluted	1.5 slight	58.5 heavy
Chinese Chestnut	1.8 slight	35 heavy	6.9 heavy	0.5 unpolluted	19.6 heavy	26.3 heavy
Soybean	0.2 unpolluted	21.2 heavy	5.5 heavy	0.3 unpolluted	0.2 unpolluted	15.5 heavy
Cowpea	0.3 unpolluted	10.2 heavy	4.6 heavy	0.1 unpolluted	1.2 slight	7.6 heavy
Sweet potato (tuber)	0.1 unpolluted	49.5 heavy	7.4 heavy	0.1 unpolluted	7.8 heavy	36.2 heavy
Cassava	0.1 unpolluted	52.3 heavy	2.4 medium	0.1 unpolluted	6.8 heavy	38.0 heavy
Mandarin	0.3 unpolluted	59 heavy	4.5 heavy	0 unpolluted	9.6 heavy	43.0 heavy
Persimmon	0.4 unpolluted	86.2 heavy	1.9 slight	0 unpolluted	11 heavy	62.6 heavy
Peach	0.3 unpolluted	6.6 heavy	1.9 slight	0 unpolluted	0.3 unpolluted	4.8 heavy
Taro	0.4 unpolluted	33.8 heavy	7.6 heavy	0.1 unpolluted	7.3 heavy	24.9 heavy
Ginger	0.2 unpolluted	29.3 heavy	3 heavy	0.1 unpolluted	3.2 heavy	21.3 heavy
Tomato	0.1 unpolluted	5.4 heavy	2.4 medium	0 unpolluted	0.6 unpolluted	4.0 heavy
Capsicum	0.2 unpolluted	31.1 heavy	3.2 heavy	0.1 unpolluted	7.5 heavy	22.8 heavy

[a] Right to the pollution index is pollution level according to the Table 2.

Heavy Metals in Soils and Crop Accumulation

A total of 21 crop-associated top soil samples (0-20 cm) from Bayi, 34 samples from Lipu, and 34 from Pingle were gathered, and a detailed assessment is to be presented in another article. The average heavy metal concentrations in these minesoils are shown in Fig. 2. Soil pH ranged from 4.37 to 7.88 (averaged 6.21, 6.00, and 5.68 for Bayi, Lipu and Pingle, respectively), indicating an acid nature. Overall, Bayi minesoil had the highest Cd; Lipu had the highest Pb and Cr, and Pingle had the highest Zn, Mn and Cu (but no significant difference to the Cu level in Lipu). For Cd, with soil pollution warning threshold being 0.3 mg/kg according to the soil quality standard (GB15618-1995), these minesoils had substantially higher Cd levels (28 to about 94 times the warning value).

Table 6 presents the Bioaccumulation Factor (BAF) of the grown edible crops. None of the BAFs were beyond 1, and only six crops had BAFs for Cd larger than 0.5. Of the six metals studied, crops tended to have stronger Cd accumulation in edible parts; thus, Cd is the most important food safety threat. For other major contaminants, Pb and Cr, BAFs were largely below 0.1, and these may result from their relatively lower phyto-availability (2.03% for Pb, and 1.2% for Cr with 0.1M HCl extraction). Crops generally had very low Mn-accumulation ability (most BAFs were less than 0.05), but tea leaf in Bayi contained unusually high Mn contents, and this is in agreement with other results showing that tea tree is an Al and Mn accumulator.

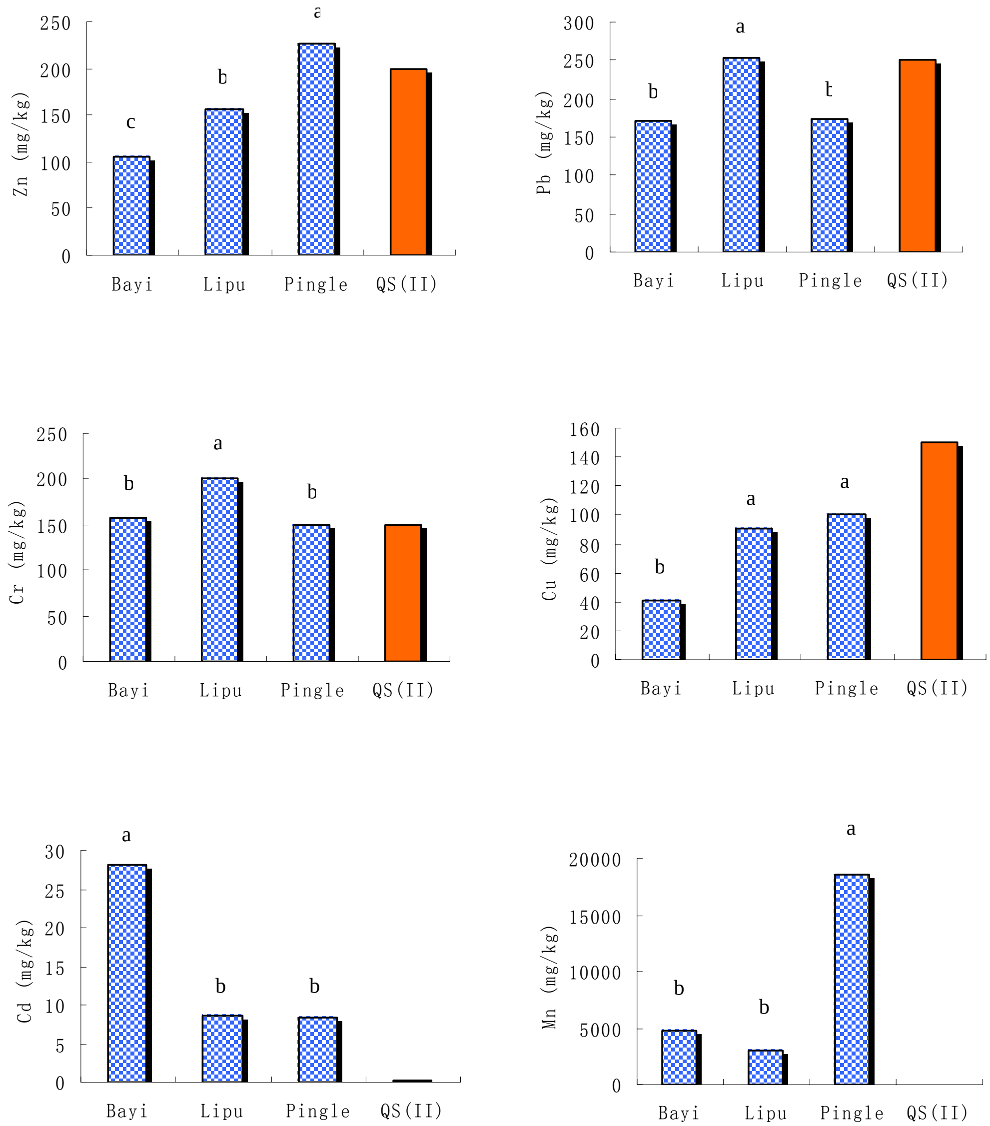

Figure 2. Heavy metal concentrations of soils from the three Mn mine wastelands. Different letters above bars indicate a significant difference ($P < 0.05$) using LSD test. QS(II) represents the soil quality standard value (GB15618-1995, Grade II for pH<6.5), indicating a pollution warning threshold. There was no standard value given for Mn.

DISCUSSION

Safety of Agronomic Crops Grown on the Reclaimed Mine Wastelands

Food safety problems in China can be traced largely to cultivated land. The substrate that crops grow is a fundamental warranty of agrarian product quality. Heavy metal contamination of staple foods has aroused a lot public concern not because of its actual harmful consequences (unlike pesticide residues) but because of the recent rejected exported food commodities and of publicity of heavy metal toxicities (Pb and Cd, in particular) by mass media. However, heavy metal pollution of mineland crops is far away to be addressed by the public as well as the local governments mainly because the pollution effect is usually slow and limited to regions. A recent study on a Dabaoshan mine area (a large multi-metal sulfide mine) of north Guangdong province revealed a horrible ‘cancer village’ – over 210 villagers of all ages died of cancer, 8.7 times of the national average (Chen, 2005), a tragic outburst of severe heavy metal contamination 30 years after the mining.

Table 6. Biological Accumulation Factors (BAFs) of grown crops on the three Mn mine wastelands in Guangxi

Crop	BAF of crops grown in mine wasteland regions					
	Zn	Pb	Cr	Cu	Cd	Mn
Bayi						
Peanut	0.330	0.046	0.015	0.250	0.030	0.006
Soybean	0.405	0.054	0.027	0.168	0.042	0.004
Sweet potato (tuber)	0.100	0.065	0.052	0.148	0.047	0.008
Sweet potato (leaf)	0.300	0.086	0.071	0.358	0.089	0.040
Cassava	0.143	0.034	0.031	0.119	0.066	0.002
Orange	0.096	0.038	0.017	0.093	0.062	0.002
Watermelon	0.347	0.055	0.021	0.117	0.065	0.010
Sugarcane	0.122	0.050	0.049	0.072	0.077	0.021
Tea	0.906	0.076	0.059	0.234	0.027	0.372
Lipu						
Peanut	0.230	0.040	0.027	0.074	0.567	0.014
Soybean	0.296	0.080	0.026	0.155	0.611	0.023
Sweet potato (tuber)	0.105	0.080	0.040	0.003	0.573	0.003
Sweet potato (leaf)	0.191	0.042	0.055	0.085	0.100	0.030
Cassava	0.146	0.089	0.036	0.081	0.643	0.002
Orange	0.079	0.135	0.032	0.012	0.176	0.003
Sugarcane	0.082	0.102	0.037	0.086	0.740	0.014
Nachi pear	0.114	0.022	0.085	0.079	0.015	0.002
Persimmon	0.080	0.098	0.052	0.008	0.354	0.011
Peach	0.126	0.041	0.036	0.056	0.049	0.003
Chinese Chestnut	0.106	0.076	0.025	0.066	0.383	0.038
Shallot	0.263	0.065	0.064	0.059	0.402	0.068
Garlic	0.212	0.066	0.044	0.063	0.548	0.048
Capsicum	0.218	0.125	0.094	0.118	0.418	0.011
Eggplant	0.109	0.037	0.077	0.069	0.042	0.063
Chinese radish	0.273	0.060	0.055	0.049	0.258	0.017
Cowpea	0.265	0.079	0.038	0.047	0.408	0.135
Endive	0.482	0.047	0.054	0.066	0.196	0.031

Table 6. Continued

Crop	BAF of crops grown in mine wasteland regions					
	Zn	Pb	Cr	Cu	Cd	Mn
Lettuce	0.348	0.034	0.027	0.061	0.379	0.032
Pingle						
Peanut	0.143	0.198	0.094	0.058	0.186	0.001
Chinese Chestnut	0.080	0.040	0.046	0.106	0.234	0.008
Soybean	0.195	0.060	0.090	0.128	0.013	0.004
Cowpea	0.195	0.038	0.101	0.046	0.046	0.021
Sweet potato (tuber)	0.065	0.178	0.077	0.037	0.288	0.007
Cassava	0.081	0.184	0.024	0.016	0.248	0.003
Mandarin	0.045	0.236	0.103	0.023	0.397	0.002
Persimmon	0.038	0.239	0.031	0.013	0.315	0.005
Peach	0.072	0.041	0.068	0.034	0.018	0.001
Taro	0.297	0.137	0.089	0.041	0.306	0.030
Ginger	0.246	0.202	0.120	0.069	0.454	0.215
Tomato	0.086	0.048	0.122	0.069	0.059	0.001
Capsicum	0.105	0.133	0.079	0.094	0.333	0.007
Overall Average	0.198	0.087	0.056	0.086	0.250	0.032

In comparison with the many studies of food contamination around urban areas (Bai, 2004; Chen et al., 2004; Fu & Li, 1999; Li et al., 2000; Liu & Chen, 2004), safety of mineland crops was rarely investigated (Garcia et al., 1974; Garcia et al., 1979; Zhu et al., 2007) worldwide although these plantation practices were fairly common in developing countries especially those facing population pressure. In a field experiment of crop plantation on copper mine tailings mixed with loess (soil to tailings, 2:1 w/w), Zhou et al. (2002) reported that the As, Cd, and Pb concentrations in corn, sorghum, peanut, and soybean were lower than the prescribed allowable limits and thus were considered that they were safe to eat. However, the conclusion is under question since other metals like Cr and Cu have exceeded the allowable standards, still posing health risk to consumers. In the corn grown on a Pb-Zn minesoil of Liaoning Province (North China), the Cd and Pb concentrations exceeded the standards by 1.5 and 2.0 times, respectively (Gu et al., 2005). Also in Baiyin Pb-Zn mine of northwest China, the Pb, Cd, Zn and Cu contents in forage grass and grain were greatly and significantly higher than those of uncontaminated sites, and grazing horses and sheep contained very high Pb and Cd levels in their blood, hair, liver, kidney, and skeleton, and showed obvious morbid symptoms in appearance (Liu, 2005).

In the present study, sugarcane (Bayi), tea (Bayi), Chinese chestnut (Lipu), and peach (Pingle) were all planted in large areas (>10 ha), and these products would enter human's food chain directly nearby and remotely through marketing and raw product processing. In terms of P_N, these four main crops were all severely contaminated, unacceptable as food according to the current food safety standards. Other crops were also heavily contaminated, but the health risk was mostly confined to the local inhabitants. Local governments should exercise monitoring programs of these crops and educate the mine-area residents to avoid the possible toxic effect in the long term.

Implications for Restoration of Mine Wastelands

The aim of restoration of mine wastelands is to remediate ecological destruction and reduce pollution dispersion. If rehabilitation of mine spoils causes another serious pollution to human being, the loss outweighs the gain. A general tendency of mineland rehabilitation in China is the utilitarian reclamation for agriculture. In fact, reclamation for planting crops is usually the last option of restoration in developed countries (Cook & Johnson, 2002) because it is very costly to meet the stringent soil requirement. The lax environmental controls and food safety enforcement in China as well as shortage of cultivable lands may account for this practice, and in Guangxi, this practice has been encouraged to some extent by the local government (Li, 2006; Li et al., 2007) due to severer lack of arable land. However, this restoration mode must be reconsidered carefully or modified.

First, China Environmental Quality Standard for Soils requires soils for agricultural crops meet Grade II criteria (see Fig. 2 for reference). Unfortunately almost all minesoils, especially of the metal-mined wasteland, can not satisfy the standard prior to remediation. Thus simple reclamation for crop growth is of high risk unless sufficient treatments, e.g., separation layer, cover of guest soil over 50-cm deep (Wong, 2003), or substantial substrate amendments (Li, 2006; Wong & Luo, 2003), are in place before planting. Even so, the yield of crops may reduce and quality be compromised. Another option is to choose low-accumulation cultivars of crops (Hu, 2004; Yao et al., 2006) or plant non-edible agronomic crops like ramee or use for pulpwood and charcoal wood.

Second, mono culture of crops is not good for restoration of pre-mining biodiversity. Biodiversity, vegetation structure, and ecological processes are the most important ecosystem attributes to evaluate restoration success (Ruiz-Jaen & Aide, 2005). In terms of these attributes, few of the China’s reclamation efforts for agricultural plantation can be deemed successful although some may help generate short-term income for local residents.

Finally, miners and restorers need to leap out of this utilitarianism-oriented reclamation. Restoration of minelands can have much more diverse functions, such as nursery, forestry, biodiversity conservation, recreation and tourism, providing habitat to wildlife, checking soil and wind erosion, or just beautifying the damaged landscape.

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Short Commentary 2

NOTE ON RHENIUM IN COAL

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ABSTRACT

Rhenium is very a rare element with Clarke value (average content in the Earth's crust) about 0.001 ppm (= 1 ppb). Geochemistry of Re in coal is poorly known up to today because of analytical problems. Special analytical methods are needed for reliable Re determination in coal. Some coals are known, with Re contents 2–3 orders-of-magnitude higher than Re Clarke value in the Earth's crust, in the range from 0.n ppm up to few ppm.

In Re-bearing coals, it is no doubt that Re_{org} form exists. Perhaps, Re is sorbed on coal organics by weak, ion-exchange bonds. This has accounted for the Re leachability from coals by surface and ground waters. Some analogues with Re state in black shales indicate that some part of Re may be present in bituminous components of coal (liptinite). The other authigenic Re form may be its sulfide, ReS_2. However, Re sites in coal (modes of occurrence) is now only hypothetic; microprobe study is needed for more knowledge.

There are at least three genetic types of Re-concentrations in coal: Uzbek, Spanish and Kazakh. In *Uzbek* type, Re is probably syngenetic. Its accumulation is due to enhanced Re contents in source rocks. Rhenium leached from terrigenic material may further be captured on reducing peatbog barrier – in organic or sulfide form. In *Spanish* type Re is also mostly syngenetic. Its accumulation is due to considerable contribution of the bituminous organics (like black shale) having extremely high affinity to Re. In *Kazakh* type Re is close associated with U and its companions, in the infiltration epigenetic deposits of the "*bed oxidation*" type. Re dissolved in oxidized waters as perrhenate ion ReO_4^-, may be captured in brown-coal beds on the reducing barrier, in organic or sulfide forms.

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Recently Re-bearing fumaroles were described in the Kurily Islands. Therefore, some Re accumulations may occur in peatbogs of the volcanic areas, or in young lignites – in orogenic depressions with synchronous volcanism. Such Re accumulations may be associated with In, Ge, Mo, Bi and some other elements enriching the volcanic exhalations.

Because Re is very valuable metal, Re-bearing coals may serve as Re industrial resource. The most promising are epigenetic uranium-coal deposits. In addition, some intermountain trough brown-coal fields must be studied for Re, if these coals are associated with volcanics.

Rhenium is ultra-rare chemical element having the Clarke value (mean content in Earth's crust) no more than 0.001 ppm = 1 ppb. All the studies on Re in coal are connected with Russian geochemical school that is noted also in Swaine's (1990) outline.

Keywords: Rhenium; Coal; Geochemistry; Coal combustion.

RHENIUM IN COALS OF THE FORMER USSR: UZBEKISTAN, RUSSIA AND UKRAINE

First note about Re contents in coals within the range of 0.084–0.328 ppm appeared in Russian literature in 1961 (Kuznetsova and Saukov, 1961). In sulfide-rich Jurassic dull lignites of Angren coalfield (Uzbekistan), Re content of 0.08 ppm was found, and in bright low-ash coals – as much as 0.29 ppm (Razenkova and Kuznetsova, 1963). Other samples of the same deposit showed 0.17 ppm (Baranov, 1966) and 0.2–0.4 ppm (Kler and Nenakhova, 1981, p. 49). Later, Baranov (1966) found 0.39 ppm Re in the Sakhalin Island coal, and Yurowsky (1968) published the data on Re content in Donets basin (Donbas) coals. In 18 samples representing high-volatile bituminous coals from 13 Donbas mines, Re contents were in the range from 0.2–0.8 ppm. In cleaned coal (with A^d, ash yield, of 8 %) from Privol'nyanskaya Yuzhnaya mine, Re content was as much as 4 ppm (Yurowsky, 1968).

There are some data indicated Re content in some Russian brown coals as much as 20 ppm (Ratynsky, Spirt, Krasnobaeva, 1980). Moreover, in so-called *infiltration uranium-coal deposits*, Re contents can (?) reach so extremely values as 200–400 ppm (Kler, 1987, p. 93)[1]. Some data also appeared about Re presence in coal sulfides and vitrains (Maksimova and Shmariovich, 1982; Ratynsky, Spirt, Krasnobaeva, 1980; Spirt, Ratynsky, Zharov, Zekel, 1984).

An Estimation of Coal Clarke Value of Re

Because of all analyses published represent only Re-bearing coals with enhanced Re-contents, it is impossible to evaluate Re coal Clarke value some correctly. Therefore, coal Clarke of Re can be calculated only conditionally true. For example, some "background" Re content in the former USSR coals was estimated by Kler (1987) as 0.06 ppm. He based from

[1] Some doubts are cast upon these data; anyhow, maximum Re content cited in (Maksimova and Shmariovich, 1982), is one order of magnitude lower – 52 ppm.

Re/Mo ratio, 1: 100, in sulfide deposits. However, Kler noted: *"this Re-content level is true if the Re/Mo ratio holds for low-Re coals"* (Kler, 1987, p. 94).

If such estimation is true, coal Clarke value for Re is one order of magnitude higher than Earth's crust Clarke value. If so, we must attest Re as *coalphile element* (about coalphile coefficients, or "coal affinity index", see, for example, Russian monograph (Yudovich and Ketris, 2002) or some papers in English, such as (Yudovich and Ketris, 2004)).

Rhenium average distribution trough coal density fractions (for former USSR coals) also support the coalphile nature of Re. The normalized Re contents in high-ash (>1.7 g/cm^3) and low-ash (<1.7 g/cm^3) fractions are in the range of 0.75–1.0 and 1.0–2.9 correspondingly; in ash of the low-ash fractions – from 1.8 up 6.6, and high-ash-fraction Re contribution was from 50 up 63 % from gross Re content in coal (Spirt et al., 1990, p. 189). Therefore, the highest Re concentration coefficient in ash is as high as 6.6.

In Jurassic Nazar-Ailok anthracites (Tadzhikistan), Re contents in low-ash (A^d = 3.2 %) and high-ash (A^d=17.9 %) coals are close, 2.1 and 3.3 ppm. This indicates that Re-forms (Re$_{min}$ and Re$_{org}$) are commensurable (Valiev, Gofen, Pachadzhanov, 1993).

In latest years some Re-analyses by INAA appeared; they show that coals have Re contents at least no less than hosting rocks. For example, four ash of north Ontario (Canada) Lower Cretaceous lignites show Re contents <1, <1, 3 and 5 ppb, that are higher that in hosting rocks (<1 ppb) (Kronberg et al., 1987).

SPANISH RE-BEARING "LIGNITES"

In 1960–1970, special study of Paleogene Spanish "lignites" were performed (Gracia, Martin, 1968; Martin, Garcia-Rosell, 1970, 1971; Martin, Gracia, 1970). In lignite-bearing sandstones of Granada (Arenas-del-Rey) and carbonates of Ebro depression, geochemistry of U and Re was studied.

In lignites from sandstones, where U and Re are syngenetic, average Re contents (ash basis, A^d = 45 %) is in the range of 0.24–2.28 ppm, up to 1.08 ppm. *In lignites from presumably carbonate strata,* Re content in ash reaches up to 9 ppm. More detailed study performed on the Tres Amigos mine (Martin, Gracia, 1970) showed that Re is concentrated near the lignite beds roofs, and laterally enriches some bed parts through of few meters long. For example, at average Re content in the Lower bed of 0.35 ppm, the content of 0.94 ppm was found near the roof, and 0.06 ppm – near the bed bottom. This may indicate epigenetic Re input into the lignite bed from the roof.

It must be noted that Spanish "lignites" probably have much bituminous (aquagenic) matter, and by this reason, may be close to the oil shales. This may be indicated by their association with carbonate rocks and very high ash yield in many beds, that is known as very characteristic for oil shales. If it is the case, the Re-enrichment becomes more understandable because Re is "an element No. 1" for oil shales; it is known to be sharp Re enrichments in oils and bitumen (Yudovich and Ketris, 1994, p. 170–176). These (preliminary) suggestions indicate that some Re-enrichments may be found in coals with sapropelic admixtures, and, may be also – in lipto-biolithic coal varieties (Yudovich, Ketris, Merts, 1985). It is of note, some extraordinaire Re content was found in one sample of vascular plant – 1500 ppm (?!) in ash (Shacklette, 1965).

RHENIUM IN INFILTRATION URANIUM-COAL DEPOSITS

In Mid Asian, besides Angren and Nazar-Ailok coals, Re is found in so called *infiltration uranium-coal deposits*, in association with U, Mo, Se, Ag, Zn, Ge, Co, Pb and some other elements (Maksimova and Shmariovich, 1982).

In one of such deposits[2], for which three drillholes sketchy[3] column are published, epigenetic "ore-controlling" zonality is clearly seen. It is most fully presented in the No. 1 drillhole, where it embraces entire coal bed with hosting rocks (Maksimova and Shmariovich, 1982, p. 73, Figure 2). There are three zones (from above) having some more small subzones:

1. Oxidation zone. It includes continental, strong limonitized sand-gravel layers, covered the coal bed with erosion contact. Contents of U and its companions are on the Clarke levels.

2. Transitional zone. It includes upper part of the coal bed, and in his pinching-out places – entire coal bed. Two subzones are distinguished: upper (I) with co-existed Fe-oxides and pyrite and lower (II) with sharp pyrite predominance. In upper subzone, U-ore mineralization is near absence, in lower – is weak U-ore mineralization

3. Reduced (ore-bearing) zone. It also includes subzones: upper (III) and lower (IV). In the uppermost part of III subzone, the richest U-ores are, in its lower part the ores are poor. The IV subzone is a primary aureole beneath ore body. The U contents are there no more than 0.00n %, and only sometimes its companions show geochemical anomalies.

Coal bed underlayed by the weathering crust of the basement rocks. In places where coal bed is pinching-out, the U-ore partly extends to also the weathering crust.

As is seen from the Table 1, maximum Re contents, reaching up to 52 ppm, are in the rich U-ore zone (subzone III).

Mode of Reoccurrence in Coal

Since pioneer studies by Kuznetsova and Saukov (1961) and Razenkova and Kuznetsova (1963), it became known that, in Angren mostly fusain brown coals, Re distribution strongly differs from Mo distribution, although both the elements were suggested earlier as full geochemical analogues. So, Re did not concentrated in sulfides (where Mo was enriched), and bonded with coal organics much weaker than Mo. Perhaps, this bond was ion-exchangeable, because of most Re (up to 62 % in bright, and up to 96 % – in dull coals) was leached by

[2] As one can think, it may be Low-Ili deposit in Kazakhstan, where U-ore is localized in upper part of 4-m-thick coal bed.

[3] Out of scale.

Table 1. Typization of the "F–Ash" Correlations for Central Appalachian Coals

Plot subtype	Description	Coal beds	Comment
Type I. F-contents (*ash basis*) of coals with the least ash yield are much more than of coals with the greatest ash yield[1]. F-contents (*coal basis)* do not correlate with an ash yield, or positively correlate. There are three subtypes:			
Subtype Ia	F-contents (*ash basis*) sharply monotone decrease along with ash yield increase; F-contents (*coal basis)* show no correlation with ash yield, or the correlation exists – linear or non-linear (with intermediate extremes)	Kentucky: Richardson and Peach Orchard.	No correlation "F–P" is observed
Subtype Ib	F-contents (*ash basis*) fast decrease along with ash yield increase from the beginning and further again increase but far not reaching the values of low-ash coals; F-contents (*coal basis)* show in general linear positive correlation (and rarer non-linear)	Tennessy: Big Mary; West Virginia: Beckley, Sewell (including Virginia); Kentucky: Fire Clay, Blue Gem, Jellico, Hazard.	More than 50 % beds show positive correlation "F–P"
Subtype Ic	F-contents (*ash basis*) show the same picture but ***with intermediate maximum*** *in rather ash-enriched coals*; F-contents (*coal basis)* show mostly non-linear positive correlation	Virginia: Upper Banner, Lowe; West Virginia: Stockton, Campbell Creek, Eagle, Winifrede, Bens Creek, Coalburg, Pocahontas-4 (including Virginia); Kentucky: Lily, Hazard-7, Unnamed, Alma (including West Virginia)	40 % beds show positive correlation "F–P"
Type II. F-contents (*ash basis*) of low-ash coals are some more (or even no more) than of high-ash coals but ***pass maxima*** on moderate- and/or high-ash coals. F-contents (*coal basis)* do not correlate with an ash yield, or positively non-linear correlate. There are five subtypes:			
Subtype IIa	F-contents (*ash basis*) weakly decrease along with ash yield increase and pass ***only one maximum*** on the middle-ash coals. F-contents (*coal basis)* show mostly non-linear positive correlation	Virginia: Lyons, Kennedy, Clintwood; West Virginia: Cedar Grove, Fire Creek; Kentucky: Hindman, Upper Elkhorn, Fire Clay Rider. 3.2 %.	Clintwood bed is included conditionally; it stands out by sharp F anomaly: 27500 ppm in ash (coal with an ash yield of 3.2 %). Only Fire Clay Rider bed shows positive correlation "F–P"

[1] These terms are only relative because, in general, rather low ash yield of the Appalachian coals. For example, "low-ash" means there up to 6 %, "moderate-ash" – 6–12 % and "high-ash" – more than 12 % ash yield.

Table 1. Typization of the "F–Ash" Correlations for Central Appalachian Coals (Continued)

Plot subtype	Description	Coal beds	Comment
Subtype IIb	F-contents (*ash basis*) weakly decrease along with ash yield increase and pass ***two maxima on the middle-and high-ash coals, and the first maximum is more high than the second.*** F-contents (*coal basis)* show no correlation or non-linear positive correlation.	Virginia: Dorchester; West Virginia: Peerless; Kentucky: Skyline, Manchester, Amburgy, Princess 3-9, Upper Peach Orchard.	Two beds from seven studied show positive correlation "F–P"
Subtype IIc	F-contents (*ash basis*) show similar picture but ***the second maximum is more high than the first.*** F-contents (*coal basis)* show no correlation or non-linear positive correlation	Virginia: Jewel; West Virginia: Blair, Pocahontas-3 (including Virginia)	Two beds from tree studied show positive correlation "F–P"
Subtype IId	F-contents (*ash basis*) weakly decrease along with ash yield increase and pass ***absolute minimum on the low-ash coals.*** F-contents (*coal basis)* show no correlation with an ash yield.	The only example: Little Ralegh bed, West Virginia	
Subtype IIe	F-contents (*ash basis*) weakly decrease along with ash yield increase and pass ***absolute minimum on the high-ash coals.*** F-contents (*coal basis)* show no correlation with an ash yield.	The only example: Splashdam bed, Virginia	
Type III: F-contents (*coal basis*) increase along with ash increase (that is normal); F-contents (*ash basis*) also increase (that is very unusual). There are two subtipes:			
Subtype IIIa	F-contents (*ash basis*) droningly increase	The only example: Pocahontas-6 bed, West Virginia	
Subtype IIIb	F-contents (*ash basis*) increase with intermediate maximum	The only example: Broas bed, Kentucky	

Re contents in the epigenetic zonality column, on Low-Ili (?) uranium-coal deposit.
Compiled from the data of *Maksimova and Shmariovich* (1982, p. 74).

water (Kuznetsova and Saukov, 1961 Razenkova and Kuznetsova, 1963). Experiments with ion-exchange resins showed that Re can partly bind with carboxyl and much weaker – with hydroxyl functionality. However, both the processes are much weaker appeared than for Mo (Kuznetsova and Saukov, 1961).

Further study on epigenetic uranium-coal deposits showed that coal serve as reducing barrier for perrhenate ion (ReO_4^-); Re is concentrated, probably, in sulfide form – in lower part of "transitional" zone, and in upper part of "reduced" (ore) zone. Assuming the Re concentration range in connate waters as $1.8 \cdot 10^{-8}$–$1.9 \cdot 10^{-6}$ g/L (10^{-10}–10^{-8} mol/kg H_2O), one can calculate Eh of Re-sulfide precipitation, in the redox equation "perrhenate – sulfide":

$$ReO_4^- (L) + 2S^o (S) + 8H^+ + 7e \rightarrow ReS_2 (S) + 4H_2O$$

The calculations result in:

Eh = (+167 – +150) mV for pH = 6,
Eh = (+32 – +15) mV for pH = 8

> " Therefore… a Re reduction up to sulfide form must appear… in general at low values of redox-potential… Calculated area for the Re precipitation from connate waters as ReS2 lies beneath equilibrium line between areas of Se (as Seo) and Mo (as MoS2) precipitations, localizing inside the wide U-precipitation band… The Re precipitation … may occur at Eh-values needed for U solid phase formation, and does not need so strong redox potential lowering as it occurs for Mo-mineralization formation… One can think that known in geology close association Re with Mo-sulfides is due to not the coincidence of the thermodynamic reduction conditions for both the elements but rather unlimited ReS2 and MoS2 isomorphism in ores" (Maksimova and Shmariovich, 1982, p. 77).

It is of note, however, some contradiction. If Re was precipitated in sulfide form, it would be concentrated in pyrites but this is not the case. Therefore, though above conclusive proofs, they do not give clear answer: how is Re mode of occurrence in U-ores? That is why, Maksimova and Shmariovich said ambivalent: *"The absence of direct Re-Mo correlation and Re-accumulations in Fe-disulfides may indicate either for either ReS_2, or Re bonding with organics* (Maksimova and Shmariovich, 1982, p. 78).

All the indirect data argued for the weak Re bonding with coal organics: Re permanently presents in mine waters; in circulating water of the coal-cleaning plants (Donbas, Ukraine); in connate waters of coal-bearing strata (Angren, Uzbekistan). For example, Re contents in the Donbas circulating waters reach up to 0.6 ppm, and Re was also found in water condensates by underground gasification of the Angren coals (Kler, 1987, p. 94).

BEHAVIOR OF RE IN COAL COMBUSTION

In Russian power plants, in mostly stoker combustion, Re output in gas phase from high-temperature furnace zone, with slag-removal coefficient 0.8 is 96–98 % (Shpirt et al., 1990, p. 193). Therefore, Re has extremely high volatility. This implays that, after its condensation from gas phase, it must enrich the fly ash, that is of industrial interest. According to Russian official norm (Valuable…, 1986, p. 14), minimal Re contents being of industrial interest, is 0.1 ppm (coal basis) and 0.5 ppm (ash basis). Therefore, some coals (and, very probable, their fly ashes) have Re contents that may be extracted by coal utilization.

DISCUSSION AND CONCLUSIONS

1. Geochemistry of Re in coal is poor known up to day because of analytical problems. Special analytical methods are needed for reliable Re determination in coal.

2. Some coals are known, with Re contents 2–3 orders-of-magnitude higher than Re Clarke value in the Earth's crust, in the range from 0.n ppm up to few ppm.

3. In the Re-bearing coals, it is no doubt that Re_{org} form exists. Perhaps, Re is sorbed on coal organics by weak, ion-exchange bonds. This is accounted for Re leachability from coals by surface and ground waters. Some analogues with Re state in black shales indicate that some part of Re may be present in bituminous components of coal (liptinite). The other authigenic Re form may be its sulfide, ReS_2. However, Re sites in coal (modes of occurrence) is now only hypothetic; microprobe study is needed for more knowledge.

4. There are at least three genetic types of Re-concentrations in coal: Uzbek, Spanish and Kazakh.

In Uzbek type (Angren Ge-bearing brown coal deposit), Re is probably syngenetic. Its accumulation is due to enhanced Re contents in source rocks. Rhenium leached from terrigenic material may further be captured on reducing peatbog barrier – in organic or sulfide form.

In Spanish type (Arenas del Rey and some others lignites) Re is also mostly syngenetic. Its accumulation is due to considerable contribution of the bituminous organics (like black shale) having extremely high affinity to Re.

In Kazakh type Re is close associated with U and its companions, in the infiltration epigenetic deposits of the "*bed oxidation*" type. Re dissolved in oxidized waters as perrhenate ion ReO_4^-, may be captured in brown-coal beds on the reduction barrier, in organic or sulfide forms.

5. Recently Re-bearing fumaroles were described in the Kurily Islands (Shaderman and Kremenetski, 2000). Therefore, some Re accumulations may occur in peatbogs of the volcanic areas, or in young lignites – in orogenic depressions with synchronous volcanism. Such Re accumulations may be associated with In, Ge, Mo, Bi and some other elements enriching the volcanic exhalations.

6. Because Re is very valuable metal, Re-bearing coals may serve as Re industrial resource. The most promising are epigenetic uranium-coal deposits. In addition, some intermountain trough brown-coal fields must be studied for Re, if these coals are associated with volcanics.

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Chapter 1

COAL MINING: RESEARCH, TECHNOLOGY AND SAFETY

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"The effects of coal mining on the freshwater environment: mining subsidence reservoirs, invertebrates, macrophytes and the physical and chemical parameters of surface waters"

Iga Lewin

ABSTRACT

Upper Silesia (Southern Poland) is a region rich in mineral deposits. Among them the most important is hard coal. Many years of intensive mining activity has had a strong impact on the environment of this region. Mining waters, which carry about 6,500 tonnes of Cl^- and 0.5 tonnes of SO_4^{2-} per day, discharge into rivers, mainly the Vistula River and the Odra River. The watercourses of these rivers contain high levels of chlorides, sulphates, phosphates, nitrates, heavy metals, and low values of pH or radioactive matter. Pollution of the water environment by the waters from mining activities is a problem not only in Poland, but worldwide.

The values of taxa richness, community diversity indices, biotic indices calculated for the benthic macroinvertebrates or calculated for macrophytes reflect a decrease in the quality of water in the streams subjected to the pollution from hard coal mines. The macroinvertebrate taxa in these streams that are more sensitive to this type pollution, e.g. Ephemeroptera, Plecoptera, Trichoptera, Mollusca including highly acid-sensitive species are replaced by ones that are more tolerant.

In regions with coal mining activity, including Upper Silesia (Southern Poland), the natural ecosystems have changed into anthropogenic ecosystems in which new species of

the flora and fauna previously unknown in these areas have appeared including alien species, e.g., *Ferrissia wautieri, Physella acuta* and invasive species e.g. *Potamopyrgus antipodarum*.

The mining subsidence reservoirs, which are not so degraded and provide a habitat where many species of the flora and fauna including rare, vulnerable or legally protected species can live, e.g. *Anodonta cygnea, Hippeutis complanatus, Utricularia vulgaris, Nymphaea alba, Nuphar lutea* or *Batrachium trichophyllum* should be protected on ecological grounds.

Some of the coal mining area, which also encompasses mining subsidence reservoirs that are refuges for wildlife may constitute an ecologically important area in terms of conservation biodiversity.

1. Coal Mining and Its Impact on the Environment (Upper Silesia, Southern Poland)

Upper Silesia (Southern Poland) is a region rich in mineral deposits. Among them the most important are hard coal (Carbon deposit), iron ore and lignite (Jurassic deposit) or zinc-lead ore (Triassic deposit) and rock minerals (Molenda, 2005). Many years of intensive mining activity has had a strong impact on the environment of this region. The natural ecosystems have changed into anthropogenic ecosystems in which new species of flora and fauna have appeared which were unknown in this area including many alien species.

Hard coal has been mined in 3 areas in Poland: (1) the Upper Silesian Coal Basin (USCB), (2) the Lower Silesian Coal Basin and (3) the Lublin Coal Basin.

The area of the Upper Silesian Coal Basin (USCB) comprises 7,500 km^2, 5,500 km^2 on the territory of Poland and 2,000 km^2 on the territory of the Czech Republic. The basement of productive rocks of the USCB consists of Precambrian, Cambrian, Devonian and Lower Carboniferous sequences. Production began in the USCB in the 18th century (Figure 1). In the Polish part of the USCB all coal mining is carried out underground (Różkowski, 2004).

Figure 1. Coal mine “Klimontów” in 1924, Upper Silesia (Southern Poland) (Photographer: not known).

The intensive, underground hard coal mining has led to changes in water circulation and has caused water shortages, contamination of both surface and ground waters, bounces, subsidences or earthquakes. For example, in February 2008, an earthquake of the magnitude 4.0 on the Richter scale rocked the Saarland (Germany). Subsidences, which are very common in Upper Silesia, cause damage to underground pipelines and above-ground structures, decrease the stability of slopes and escarpments and cause the dewatering of streams and groundwater supplies. Experience with longwall mining indicates that about 95% of the subsidence occurs during the first year after coal is extracted, particularly when the overburden depth is more than 300 m (Sidle et. al., 2000).

In Upper Silesia, the depth of mining works ranges from 300 m to 1,200 m.

Mine waters from Polish mines are pumped out in a total quantity of 692 m^3/minute. The pumped out mine waters are divided into 4 groups according to the content of the total dissolved solids, chlorides and sulphates concentration:

1. Fresh waters - total dissolved solids concentration below 1.0 g/dm^3, Cl^- and SO_4^{2-} concentration below 0.6 g/dm^3 (encompass 39% of the total amount of groundwater inflow).
2. Industrial waters - total dissolved solids concentration ranges from 1.0 g/dm^3 to 3.0 g/dm^3, Cl^- and SO_4^{2-} concentration ranges from 0.6 g/dm^3 to 1.8 g/dm^3 (encompass 25% of the total amount of groundwater inflow).
3. Saline waters - the total dissolved solids concentration ranges from 7.0 g/dm^3 to 70.0 g/dm^3, Cl^- and SO_4^{2-} concentration ranges from 1.8 g/dm^3 to 42.0 g/dm^3 (encompass 29% of the total amount of groundwater inflow).
4. Brines - total dissolved solids concentration above 70.0 g/dm^3, Cl^- and SO_4^{2-} concentration above 42.0 g/dm^3 (encompass 7% of the total amount of groundwater inflow) (Różkowski 2000; Różkowski 2004).

The majority of watercourses in Upper Silesia have a high level of chlorides, sulphates, phosphates, nitrates, heavy metals and radioactive matter. These water conditions are reflected in high values of conductivity, total dissolved solids and BOD_5 (Michalik-Kucharz, Strzelec, Serafiński, 2000).

Mining waters, which carry about 6,500 tonnes of Cl^- and 0.5 tonnes of SO_4^{2-} per day, discharge into rivers, mainly the Vistula River and the Odra River. An example of this type of watercourse is the Mleczna River, which carries municipal, industrial and mining waters from the “Murcki” coal mine in Czułów, near Katowice (see part 6.5.).

The catchments of the Vistula River and Odra River are strongly affected by naturally mineralised and polluted waters originating from the dewatering of coal mines. In the Upper Silesian Coal Basin mineralised waters of coal mines have showed high concentration of natural radioactive isotopes. The concentration of ^{226}Ra in waters discharged mainly into the Vistula River and the Odra River ranged from <0.1 to 28.1 kBq/m^3 (Ericsson, Hallmans, 1994; Helios Rybicka, 1996; Czaja, 1999).

The survey carried out by Pluta and Trembaczowski (2001) showed that in Poland, the major pollution of the Vistula River and the Odra River is caused by hard coal mines. The discharged water from some coal mines, which contains toxic elements such as barium and radium, flow into these rivers. In the “Silesia” coal mine, the waters flowing from the coal mine workings are mostly brines, in which the concentration of Cl^- amounted to 60 g/dm^3 and the concentrations of barium and radium (^{226}Ra) amounted to 260 mg/dm^3 and 45 Bq/dm^3, respectively.

These contaminated waters have been discharged from the “Silesia” coal mine into Rontok Pond, and then into a stream that flows into the Vistula River. The chemical parameters of water discharged from the “Silesia” coal mine into Rontok Pond and the stream is shown in Table 1.

Table 1. The chemical parameters of water discharged from the “Silesia” coal mine into Rontok Pond (Modified from Pluta, Trembaczowski, 2001).

Sampling site	Cl^- (mg/dm^3)	Ba^{2+} (mg/dm^3)	^{226}Ra (Bq/dm^3)
Inflow into pond	38,400	<10	0.8
Outflow from pond	35,950	60	4.5
Stream	35,520	60	4.5

The concentration of Ba^{2+} in the outflow from the pond and in the stream was higher compared to the inflow into the pond because the toxic elements from the pond sediment have dissolved. Rontok Pond is a reservoir which contains components that have been carried by coal mine waters for the last 20 years. Table 2 shows the chemical composition of Rontok Pond sediments.

Table 2. The chemical composition of Rontok Pond sediments (Modified from Pluta, Trembaczowski, 2001)

Parameter	Concentration
Ba (mg/g)	49.9
^{226}Ra (Bq/g)	100
Fe (mg/g)	57.8
Mn (mg/g)	0.41
Zn (mg/g)	0.21

Nowadays, this pond is no longer in use, but the bottom sediments with an enhanced activity concentration from radium isotopes still exist (Leopold, Michalik, Wiegand, 2007).

In Upper Silesia, the environmental impact of coal mining wastes is still very serious. The coal mine waste dumps are a long-term source of ground water contamination (Szczepańska, Twardowska, 1999). Production of 1 tonne of hard coal is accompanied by an additional 0.4 tonnes of wastes, of which 46% remains underground and 54% is dumped on the surface. The wastes are Carboniferous sediments mainly containing variable amounts of heavy metal sulphides. About 900 million m^3 of spoils were dumped during the years 1984-2000. The annual load of chlorides in these spoils is as high as 40,000 tonnes. Such a volume is sufficient to contaminate 133 million m^3 of water at concentrations exceeding the quality standards (Helios Rybicka, 1996). The waste rock has been reused including back-filling of mine-workings, reclamation of areas impacted by subsidence, river and ponds embankments

(Figure 2). Almost all production of coal-mining waste (50.2 million tonnes/year) is concentrated in the Upper Silesian Coal Basin, an area that comprises 1.7 % of Poland (Szczepańska, Twardowska, 1999).

Figure 2. Mining subsidence reservoir's embankments (waste rock) (Photographer: Iga Lewin).

Hard coal-mining waste dumps can be a long term source of ground water contamination including chloride salinity, sulphur content and acid generation potential (Szczepańska, Twardowska, 1999). For example, the major compounds which are realise from 18-year old waste that exceed maximum permissible concentration levels are total dissolved solids, sulphates, aluminium, zinc, manganese and iron. Iron abundantly precipitate as $Fe(OH)_3$ in oxide conditions.

Many hard coal mines in Europe have been or are going to be closed. For example, in Belgium, the last coal mine was closed in 1992. In the Czech Republic underground mining continues only in a small part of the USCB. In Saarland (Germany) where mining will be phased out by 2014, or 2018 at the latest, the hard coal production rate amounts to about 5,400,000 tonnes/year (Wolkersdorfer, Bowell, 2005a).

In Poland, after the political changes caused by the Solidarity movement (1989), unprofitable coal mines were closed (Wolkersdorfer, Bowell, 2005b) (Figure 3). In Upper Silesia, in the 1980s and 1990s hard coal was exploited in 72 coal mines. In Poland, at this moment, there are 32 operating hard coal mines, including "Bogdanka" which is located in the Lublin Coal Basin. In 2007, the annual exploitation of hard coal amounted to 87.2 million tonnes in Poland. For comparison, in 1988 the exploitation of hard coal amounted to about 192 million tonnes and drastically decreased to 96 million tonnes in 2002 (Gientka, 2003).

Figure 3. Coal mine “Sosnowiec” closed in 1997, Upper Silesia (Southern Poland) (Photographer: Iga Lewin).

2. Impact of Coal Mine Waters on the Freshwater Organisms

2.1. Diversity Indices and Water Quality Assessment

Macroinvertebrates have been widely used to evaluate the effects of anthropogenic stressors including coal mine effects, coal mine water discharge, acid mine drainage (AMD), heavy metals pollution at all levels of biological organization (from the molecular to the ecosystem) (Gerhardt, Janssens de Bisthoven, Soares, 2004; Batty, Atkin, Manning, 2005; Carter et al., 2006; Merricks et al., 2007; Porter, Nairn, 2008).

Multiple measures of community structure can be grouped into several categories, such as:

1. Taxa richness (family, generic or species level) of either the benthic community or of specific components, i.e. tolerant organisms such Chironomidae or intolerant ones such mayflies (Ephemeroptera), stoneflies (Plecoptera) and caddisflies (Trichoptera) to pollution (so-called EPT taxa).
2. Community diversity indices which summarize richness and evenness, e.g. the distribution of numbers of individuals among the species (e.g. the Shannon-Wiener index, the Simpson index, the Margalef index).
3. Functional feeding group ratios (e.g. percentage of the shredders, collectors, scrapers etc.; e.g. heavy metal uptake by algae would affect grazers).

4. Biotic indices, e.g. the Biological Monitoring Working Party (BMWP), the Hilsenhoff Biotic Index (HBI), the Belgian Biotic Index (BBI) (based on the macroinvertebrate taxa) or the Mean Trophic Rank (MTR) (based on the macrophyte taxa).

Taxa, such as Ephemeroptera, Plecoptera and Trichoptera are potentially sensitive to coal mine pollution in water environments. The EPT family richness and BMWP indices are successfully applied in the evaluation of water quality in coalfields (García-Criado et al., 1999; Jarvis, Younger, 2000). García-Criado et al., (1999) have found that both indices showed a negative correlation with sulphate concentrations in water and conductivity values ($P<0.01$).

2.2. Impact of Coal Mine Waters on Macroinvertebrates in Streams (Rivers)

Both underground and surface coal mining lead to the contamination of groundwater and surface waters. In the Appalachian regions of the USA, coal mining disturbances to headwater stream watersheds are common and are permitted under federal laws including the Surface Mining Control and Reclamation Act. Surface coal mining operations are connected with removing earth materials and replacing them in the mined cavities so as to restore the landscape after mining. The results of the survey on the effect of waters draining from hollow fills with settling ponds on macroinvertebrate communities within headwater streams originating directly from the fill drainages showed e.g. significant differences among the reference station and stations downstream of the settling ponds (Merricks et al., 2007). The value of the Hilsenhoff Biotic Index (HBI) amounted to 1.91 at the reference station, whereas mean values of the HBI ranged from 4.62 to 6.06 at stations downstream of the settling ponds. The HBI is an indicator of community tolerance of anoxia induced by organic loading. The lowest value of the HBI at the reference site suggests that sensitive taxa were present and dominant. The mean for Ephemeroptera amounted to 16.9 %, for Plecoptera it amounted to 52.8% and for shredders it amounted to 49.9% at the reference site, whereas at stations downstream of the settling ponds it ranged from 0 to 6.1, from 0.5 to 29.1 and from 0.3 to 17.1, respectively.

The effects of coal mine drainage on a lotic ecosystem was also carried out in northwest Colorado, USA (Chadwick, Canton, 1983). The results of the survey showed that the Shannon-Wiener index values for benthic macroinvertebrates decreased downstream of coal mine drainage from 3.84 to 3.22. The density of the major macroinvertebrate taxa showed a similar decreasing tendency. For example, the density of Gastropoda amounted to 71 individuals/m^2 upstream of mining activity and 43 individuals/m^2 downstream of coal mine drainage, the density of Hydracarina amounted to 35 individuals/m^2 and 2 individuals/m^2, and Plecoptera amounted to 278 and 101 individuals/m^2, respectively.

Much attention has been paid to coal mining disturbances to headwater stream watersheds in many parts of the world as well as to the treatment process of mining waters. For example, a survey was carried out on both the treated mine water stream and the raceway stream in West Virginia, USA (Buzby, Viadero, 2007), where the mine water was subjected to a treatment process e.g. by mechanical aeration and precipitation of the metal hydroxides: iron, aluminium and manganese hydroxides. The result showed that in the treated mine water stream the mean macroinvertebrate density amounted to 9,389 individuals/m^2. The filter feeders, mainly Symuliidae, Hydropsychidae, Ostracoda were the dominant group and comprised 2.4%-67.8% of the community. Collectors/gatherers, mainly Chironomidae and Oligochaeta, comprised 0.4%-96.1% of the community. The addition of aquaculture effluent to the treated mine water had an influence on colonization by additional taxa and on increasing leaf decomposition rates.

According to Bruns (2005), the mining effect was confirmed with dissolved iron and sulphate concentrations as well as levels of sedimentation and iron deposition explaining the variability across macroinvertebrate parameters (e.g. EPT richness, percent collector-gatherer, taxa richness).

Anthropopressure associated with past and ongoing coal mining activities has resulted in severe ecological degradation in water environments in the anthracite fields of northeastern Pennsylvania. It has been estimated that through 1944 about 3.5 billion tonnes of coal were mined over a 150-year period in the Eastern Anthracite Field which is situated on the North Branch of the Susquehanna River. The study was carried out in an area which encompasses 6,478 ha of abandoned coal mining lands (the Upper Susquehanna-Lackawanna American Heritage River). According to the mining impact degree, 3 types of sampling sites were chosen: watersheds with a significant mining impact, intermediate mining impact and reference sites where mining and urban development were minimal and land cover was mostly in the naturally forested state. The differences in the range of chemical parameters between sites with a significant mining impact and low mining impact is shown in Table 3.

Table 3. The chemical parameters of water and indices based on macroinvertebrate taxa at sites subjected to mining impact (Modified from Bruns, 2005).

Parameter	Sites with a minimal mining impact and minimal urban development	Sites with an intermediate mining impact and high urban development	Sites with a significant mining impact and high urban development
pH	6.0-7.3	6.4-8.2	3.4-7.7
Alkalinity (mg $CaCO_3/dm^3$)	10-40	59-99	0-178
Sulphates (mg/dm^3)	8-16	25-700	122-959
$N\text{-}NO_3$ (µg/dm^3)	193-532	136-490	100-331
Fe (mg/dm^3)	0.1	0.6-37.6	0.1-5.4
TDS (mg/dm^3)	50-300	290-1,400	470-1,760
Macroinvertebrate indicators			
Richness	8-13	1-6	2-8
EPT-R (richness)	3-7	0-2	0-2
EPT-A Abundance (numbers)	1-74	0-7	0-17
Diptera-R (richness)	1-3	1-2	13-32
Diptera-A Abundance (numbers)	1-3	1-29	11-114

Table 3. (Continued).

Parameter	Sites with a minimal mining impact and minimal urban development	Sites with an intermediate mining impact and high urban development	Sites with a significant mining impact and high urban development
Percent composition of macroinvertebrates			
Ephemeroptera	1-33	0	0
Plecoptera	6-44	0	0
Trichoptera	18-23	0-6	2-41
Chironomidae	18-27	20-84	18-99
Gastropoda	0	0-1	0
Gammaridae	0	0-1	0-1

According to Table 3, the concentrations of sulphates, the total dissolved solids and iron are high at sites with a intermediate and significant mining impact. Richness, EPT-R and EPT-A are high at sites with a minimal mining impact and minimal urban development. Ephemeroptera and Plecoptera are absent from the sites with a significant and intermediate mining impact and high urban development. Dissolved iron had a negative influence on EPT richness.

Some studies have evaluated the impact of coal ash on aquatic macroinvertebrates, for example in a river (South Carolina) by Cherry et al., (1979). The result showed that 15 of the 20 elements in water were highest in the ash-impacted stations. Chironomidae incorporated 12 elements, e.g., Al, Fe, Zn, Cu or Na in greater concentrations compared to Enallagma, crayfish or Libellula. Crayfish concentrated Br, Ca, Cd, Mn and Se to the greatest extent.

The macroinvertebrates most tolerant to coal ash stress were Odonata (Libellula sp. and Enallagma sp.), crayfish (Procambarus sp.), amphipods (Gammarus sp.), gastropods (Physa sp.) and midges (Chironomidae).

Most macroinvertebrates were absent or rare at the stations with coal ash impact. Physa sp., Procambarus sp. and Gammarus sp. were found at the stations where coal ash impact was reduced.

3. Acid-Mine Drainage and Metals in Relation to Freshwater Organisms

3.1. What Exactly is Acid Mine Drainage (AMD)?

One consequence of coal mining activity is acid-mine drainage (AMD), which has a significant impact on surface waters in many parts of the world. Acid mine drainage (AMD) occurs in mines in which the sulphur content ranges from 1% to 5% in the form of pyrite (FeS_2). AMD is a chemical phenomenon due to the sulphur oxidation of metal-sulphide minerals such as pyrite (FeS_2) by atmospheric oxygen.

Pyrites react with water and oxygen in the presence of thiobacillus bacteria to produce sulphuric acid and iron hydroxide or iron sulphates. The low values of pH results in the further dissolution of minerals and the release of metals. In underground coal mines groundwater infiltrates into the mine and comes into contact with pyretic coal and thus form acid mine drainage (Tiwary, 2001).

The reaction mechanism of acid generation is as follows:

$FeS_2 + 3.5\ O_2 + H_2O = Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$
$Fe^{2+} + 0.25\ O_2 + H^+ = Fe^{3+} + 0.5\ H_2O$
$Fe^{3+} + 3\ H_2O = Fe(OH)_3 + 3\ H^+$
$FeS_2 + 14\ Fe^{3+} + 8\ H_2O = 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+$

Mine waters discharged from both underground and opencast coal mines contain high levels of the total dissolved solids, chlorides, sulphates, nitrates, metals, a high value of the conductivity and hardness. The toxicity of heavy metals in inland water depends on their concentration, pH, water hardness and adsorbing or complexing agents.

Table 4. Mine water quality (the chemical parameters and their ranges, acidic and non-acidic mines) (Modified from Tiwary, 2001).

Parameter	Non acidic mines	Acidic mines
pH	6.5-9.2	1.5-6.7
TDS (mg/dm^3)	136.0-860.0	380.0-3,300.0
SO_4^{2-} (mg/dm^3)	10.2-401.0	400.0-1,948.9
Fe (mg/dm^3)	0.1-1.5	2.0-84.3

Coal mine waters may be acidic or neutral depending on the pyrite content in the coal as inorganic impurities. Table 4 shows the differences of the chemical parameters between coal mine waters of non-acidic and acidic mines.

Ferruginous mine waters are considered to be deleterious to surface water quality due to the smothering of benthic habitats by Fe precipitates. Iron precipitates if the total concentrations of Fe are in excess of 0.5 mg/dm^3. Both this smothering and the particulate Fe in the water column’s influence on decreasing light penetration to benthic primary producers and oxygen circulation in river (stream) sediments.

Oxidation of ferrous iron (Fe^{2+}) to the ferric form (Fe^{3+}) leads to the precipitation of a voluminous orange coating of ferric hydroxides (“ochre”) on a stream bed. A thick coating of ferric hydroxides on a stream bed causes the elimination of benthic algae and macroinvertebrates (Younger, Wolkersdorfer, 2004). Dissolved iron is not as ecotoxic compared to other metals associated with mine waters, e.g. cadmium, copper, nickel and zinc (Mayes et al., 2008).

3.2. Impact of AMD on Algae and Bryophytes

Algae and bryophytes, which are the major primary producers in streams and rivers, are affected by low pH and metal toxicity. An accumulation of metals in algae and bryophytes exposes fish and other consumers to concentrations of metals that are several orders of magnitude greater per unit weight than the water in which they live. In fish the toxicity and bioavailability of metals is decreased by complexation with organic ligands, i.e. dissolved organic carbon (DOC) or inorganic ligands such as SO_4 and F. Bryophytes may absorb some complexed forms from the water, thus the availability of metals may not be reduced by complexation with ligands. According to Engelman Jr and McDiffett, (1996), the accumulation of aluminium in bryophyte tissues depends on pH and is highest (26.14 mg/g) at the sampling site with an intermediate pH of 5.2. The concentration of iron in the tissues is highest at the most acidic sampling site (52.63 mg/g).

3.3. The Biological Consequences of Low Values of pH

A high pH level contributes to the release of phosphorus from oxidized sediments in shallow reservoirs that have an influence on eutrophication. A low pH level has an influence on the solubility of cyanide and heavy metals e.g. cadmium, lead, zinc and mercury. The mercury content in fish often increases with a decreasing pH level in water. Low pH causes less diversity of planktonic algae, zooplankton, insects, snails, mussels, crustaceans, fish and amphibians, an increase in the quantity of filamentous benthic algae due to the reduced feeding activity by macroinvertebrates and a decrease in the rate of decomposition of organic matter. A reduced decomposition rate of organic matter may be related to low densities of detritivorous invertebrates.

Gastropoda are among the most acid-sensitive groups of freshwater organisms. At a low pH value, calcium is not easily accessible to gastropods (Økland, 1983; Clarke, Scruton, 1997). With increasing calcium concentration, lower pH values may be tolerated by gastropods since calcium ameliorates acidic stress (Økland, 1990; Kalff, 2003). Above pH 7.0 an increase in the number of gastropod species and their densities was observed in southeastern Norway (Økland, 1990). The number of snail species increases with an increasing level of pH in waters. In Canada (Sudbury, Ontario) gastropods were not observed in water environments with pH<5.0 with some exceptions: e.g. Ferrissia sp. was found at pH 5.5, *Amnicola limosa* (Say, 1817), *Gyraulus deflectus* (Say, 1824) were observed at pH 5.5-6.0 and *Physella gyrina* (Say, 1821) at pH 5.8 (Bendell, McNicol, 1993). Gastropods are more sensitive to pH changes than fish.

The acidification process involves a loss of alkalinity prior to the pH decreasing. It is expected that the disappearance of gastropods could be a reliable early warning indicator of acidification (Økland, 1983).

According to Kalff (2003), a high H^+ concentration leads to the release of metals, including toxic metals, from the sediments directly into the overlying water. Aluminium solubility increases when the pH of sediments drops below 5.5. The loss of species richness (biodiversity) commences when acidic deposition causes the pH of water bodies to drop below pH 6.0. A Norwegian survey of 1,500 water environments showed that snails are highly sensitive to pH and some species disappear at pH below 6.0. When calcium concentration increases (or total salt concentration) species of crustaceans, molluscs and insects show an increased tolerance to low pH.

Jeffries and Mills (1990) showed that the isopod *Asellus aquaticus* (Linnaeus, 1758) is able to survive to pH 5.0. More sensitive to low pH, the amphipod *Gammarus pulex* (Linnaeus, 1758) is not able to survive below pH 5.5 and avoids waters with pH below 6.0.

Mayflies (Ephemeroptera) are vulnerable to species losses at pH below 6.5. Plankton shows the same decreases as the benthos with losses at pH 5.0-5.5.

A survey carried out under laboratory conditions by Felten et al. (2008) showed that exposure of *Gammarus pulex* to strongly acidic (pH 4.1, pH 5.1) and slightly acidic (pH 6.0) media induced an early significant decrease of osmolality and haemolymph Na^+ concentration. This failure in ionoregulation was accompanied by a significant mortality of *Gammarus pulex*.

The loss of fish populations is gradual because different species have different lower pH limits, but the decline is evident below pH 6.5. The low species richness observed in acidified waters is not simply due to low pH. It is often due to low pH and a high, toxic level of aluminum and other metals, or a high sulphur level in streams receiving hard coal or other mining effluents.

Increased concentrations of calcium reduce the toxic effect of heavy metals on both algae and fish. At low pH calcium modifies gill permeability to Na^+, Cl^- and H^+ ions in fish. In fish, e.g. salmonid eggs are vulnerable at pH below 5.0.

3.4. Impact of AMD on Streams, Sediments and Macroinvertebrates

In rivers and streams subjected to AMD stress typical physical and chemical parameters are observed: a lower value of pH, an increase of ion concentrations, mainly sulphates and iron concentration as a result of the pyrite oxidation through bacteria, and an elevated concentration of heavy metals including aluminium. Both a low value of pH and toxic concentrations of heavy metals eliminate macrophytes and animals, while the productivity, density and biomass of others are reduced.

The loss of species richness of macroinvertebrates in streams affected by pollution from hard coal mines has been observed by many authors (Scullion, Edwards, 1980; Winterbourn, McDiffett, Eppley, 2000; Cherry et al., 2001; Battaglia et al., 2005; Tripole et al., 2006). The macroinvertebrate taxa that are more sensitive to this type pollution are replaced by ones more tolerant.

The loss of species richness (biodiversity) has often been observed in streams subjected to AMD stress in many countries. For example, Petrin, Laudon and Malmqvist (2008) showed that in Swedish streams (24 stream sites), at circumneutral sites the mean pH ranged from 6.6-7.2, at naturally acidic sites the mean pH ranged from 4.3-5.7 and at anthropogenically acidified sites the mean pH ranged from 4.4-5.6. Total species richness was higher in circumneutral streams than in acidic streams. Total macroinvertebrate and Ephemeroptera species densities were higher in circumneutral streams than in acidic ones.

The loss of species richness (biodiversity) was also observed by Guerold et al., (2000) in 41 streams in France (the Vosges Mountains). In streams, characterized by low pH, low calcium and a high aluminium concentration, the taxa richness of macroinvertebrates decreased dramatically. Mollusca, Crustacea and Ephemeroptera totally disappeared from strongly acidified streams. The mean pH values ranged from 4.29 to 7.0, the mean aluminium concentration ranged from 22 $\mu g/dm^3$ to 1,063 $\mu g/dm^3$, and the mean calcium concentration ranged from 23 to 592 $\mu eq/dm^3$. *Ancylus fluviatilis* O. F. Müller, 1774, *Gammarus fossarum* Koch, 1835 and *Gammarus pulex*, highly acid-sensitive species were present only in well-buffered streams. The taxon richness of the taxonomic groups i.e. Ephemeroptera, Plecoptera, Trichoptera, Coleoptera and Diptera were significantly correlated with the chemical parameters of water: positively with pH values and calcium concentrations and negatively with total aluminium concentration (The Pearson Moment Correlation Coefficient). Below pH 6.3, Ephemeroptera species: e.g. *Rhitrogena semicolorata* (Curtis, 1834), *Epeorus sylvicola* (Pictet, 1865), *Habrophlebia lauta* Eaton, 1884 or *Baetis muticus* (Linnaeus, 1758) totally disappeared.

The results of a survey carried out in 3 streams in Australia (New South Wales) (Battaglia et al., 2005) showed differences in the physical and chemical parameters among reference streams (Megalong Creek, Jocks Creek) and an acid-mine impacted stream (Neubecks Creek). In the reference streams the conductivity was lower and the values of pH and alkalinity were greater compared to the acid-mine impacted stream (Table 5).

The mean taxa richness and mean density of macroinvertebrates was significantly lower in the acid-mine impacted stream compared to reference streams ($P < 0.05$). In the acid-mine impacted stream (Neubecks Creek) the number of taxa amounted to 4, with only 1 or 2 taxa in any sample. In comparison, in the Megalong Creek and Jocks Creek the number of taxa richness ranged from 32 to 39. Ephemeroptera, Plecoptera and Trichoptera were absent from Neubecks Creek, whereas Leptophlebiidae (mayfly), Gripopterygidae (stonefly) and Leptoceridae (caddisfly) were common in Megalong Creek and Jocks Creek. These differences could by explained by the physical and chemical parameters of the acid-mine impacted stream (low value pH and metal contamination: a high concentration of calcium, cadmium, potassium, magnesium, manganese, nickel, sulphur and zinc). The mean density of macroinvertebrates in Neubecks Creek amounted to less than 50 individuals/m^2, whereas it was above 200 individuals/m^2 and above 800 individuals/m^2 in Megalong Creek and Jocks Creek, respectively.

Table 5. The physical and chemical parameters of water in the reference streams (Megalong Creek, Jocks Creek) compared to acid-mine impacted stream (Neubecks Creek) (Modified from Battaglia et al., 2005)

Parameter	Reference streams		Acid-mine impacted stream
	Megalong Creek	Jocks Creek	Neubecks Creek
Conductivity µS/cm	132.0±5.0	17.0±3.0	787.0±1.0
pH	6.5±0.0	6.7±0.4	5.1±0.1
Alkalinity (mg $CaCO_3/dm^3$)	51.0±1.0	7.0±3.0	3.0±0.0
Dissolved oxygen (mg/dm^3)	4.9±0.1	5.9±0.7	6.7±0.1
Total N (mg/dm3)	0.45±0.1	0.17±0.0	0.21±0.0
Total P (µg/dm3)	24.0±3.0	13.0±6.2	8.7±4.6

In Northern England, a study carried out by Armitage (1980) showed the occurrence of only 4 taxa in a river site receiving drainage from an old coal mine (Dowgang Burn, the Nent system, the Northern Pennine): *Esolus parallelepipedus* Müller, 1806, Orthocladiinae, the tipulid Rhypholophus and Enchytraeidae. The pH value and concentration of Fe recorded at this sampling site amounted to 3.9 and 7.80 mg/dm^3, respectively. The heavy metal solubility decreased with an increasing pH. A high value of pH causes the rapid precipitation of discharged metals into sediments. The sediment-bound metals may be released by flushes of acid waters and thereby increase the toxicity of stream water downstream.

A similar result was obtained in the Ely Creek watershed in Lee County, VA, USA (Cherry et al., 2001). A survey on the effects of AMD on macroinvertebrates showed reduced diversity and abundance in impacted areas relative to unimpacted ones and the occurrence of tolerant taxa in the rivers instead of intolerant. At reference sites the value of pH ranged from 5.58 to 8.2 and was higher compared to sites affected by AMD (the lowest value of pH amounted to 2.73). The values of conductivity ranged from 40 to 440 μS/cm for reference sites and from 110 to 3,620 μS/cm for acid mine drainage-influenced sites. Table 6 shows differences in the elements of sediments between reference sites and acid mine drainage-influenced sites.

The reference sites also showed a relatively high richness and abundance of benthic macroinvertebrates (total abundance, total richness, Ephemeroptera abundance, value of EPT indices) compared to the acid mine drainage-influenced sites.

Table 6. Differences between the elements of sediments (mg x kg^{-1}, ranges) at reference sites and acid mine drainage sites (Modified from Cherry et al., 2001)

Elements	Reference sites	Acid mine drainage-influenced sites
Fe	1,124.3-6,956.0	3,137.9-18,392.3
Cr	0.611-3.097	1.143-7.223
Zn	9.240-20.427	3.308-29.710
Ba	6.41-16.37	5.39-35.50

The loss of species richness (biodiversity) was also observed in the 24 streams subjected to AMD stress caused by hard coal mines in New Zealand (North Westland, South Island) (Winterbourn, McDiffett, Eppley, 2000). The taxonomic richness of the macroinvertebrates was severely reduced at a low value of pH and a high concentration of heavy metals. Chironomidae (Diptera) are often the dominant taxa in such streams. In these streams (pH ranged from 2.6 to 6.2, the maximum concentration of total dissolved Al and Fe ranged up to 35.5 mg/dm^3 and 32.6 mg/dm^3, respectively) the benthic macroinvertebrate fauna was dominated by insects. The number of taxa and the number of EPT taxa increased with an increasing level of pH and a decreasing concentration of aluminium and iron. The mean concentration of aluminium and iron in the water of these streams, plant tissues and invertebrates is strictly dependent on pH value (Table 7).

Table 7. Mean concentration of Al and Fe in 24 streams (North Westland, South Island, New Zealand), water plants and invertebrates depending on pH values (significant differences were recorded only between pH ranges and Al, Fe content in water) (Modified from Winterbourn, McDiffett, Eppley, 2000).

Ranges of pH values	Al			Fe		
	Water (mg/dm^3)	Plants (mg/g)	Inverte-brates (mg/g)	Water (mg/dm^3)	Plants (mg/g)	Inverte-brates (mg/g)
2.6-3.7	11.4±11.6	1.7±1.3	1.2±0.8	8.0±0.0	7.7±7.1	2.9±2.0
4.1-4.0	0.6±0.5	2.0±0.7	1.1±1.0	1.2±0.7	7.3±4.6	3.3±2.8
5.7-6.2	0.1±0.1	3.5±1.9	0.8±0.5	0.6±0.4	13.7±10.8	2.5±2.4

According to Table 7, the concentration of aluminium and iron in water decreases when the pH value increases. The concentration of aluminium in invertebrates decreases when the pH value increases. The concentration of aluminium and iron in plant tissues increases when the pH value increase.

Some species are able to survive in streams affected by acid mine drainage. For example, a survey carried out on the influence of AMD on the ecology of the filter-feeding caddisfly *Neureclipsis bimaculata* (Linnaeus, 1761) (Trichoptera, Polycentropodidae) in a stream where the pH value ranged from 2.5 to 3.6 (Lower Lusatia, Germany) showed their abundance to be relatively high. The mean annual abundance of caddisflies amounted to 1,380 individuals/m^2 with a biomass of 1,010 mg/m^2 (Hünken, Mutz, 2007).

The results of the survey do not support the hypothesis that acid mine drainage influences the growth and development of *Neureclipsis bimaculata*. A sufficient supply of available food and an absence of concurrent species are the main reasons for this phenomenon.

3.5. Rivers Contaminated by Metals in Relation to Algae, Macrophytes and Macroinvertebrates

Open cast coal mine effluents also usually contain high concentrations of suspended solids, total dissolved solids, heavy metals, oil, grease, sulphate, nitrates and a high value of hardness. Among the heavy metals: copper, cadmium, chromium, nickel and zinc, the mean concentration of zinc may range up to 7.1±0.4 mg/dm^3 (Mishra et al., 2008).

Heavy metals may have an influence on algae due to a disturbance in their metabolism and biological function, the inhibition of photosynthesis, and a reduction of cytochrome. This type of water pollution accumulates in algae and in such a way enters the food chain and may pose a serious threat to animals and to human health through biomagnification (Zhou et al., 2008).

Aquatic macrophytes obtain elements from the sediments by root uptake or they may absorb them from the water column by foliar uptake. The concentrated elements in macrophyte tissues may be higher than in the water. A survey carried out in the Kozi Bród River (a tributary of the Biała Przemsza River, Upper Silesia, Southern Poland) which flows through a highly industrial coal mining region showed an elevated concentration of Zn, Cd, Co, Cr in the water. The macrophytes investigated, e.g. aquatic moss *Hygrohypnum ochraceum* (Turn.), *Berula erecta* (Huds.) Coville, *Callitriche verna* (L.) exhibited a strong positive correlation between the concentration of Cd, Mn and Zn in the water and in the plants. These species may be useful in monitoring pollution by these metals in a river. *Hydrohypnum ochraceum* seemed to be able to survive in water with a high concentration of metals (Samecka-Cymerman, Kempers, 2001). Metals generally enter plant tissues in ionic form and accumulate in cell walls. Aquatic invertebrates receive heavy metals from the water column through ingested material.

Macroinvertebrates and fish are among the most common aquatic organisms sampled in surveys on metal contamination streams and rivers (Fialkowski et al., 2003; Brumbaugh, Schmitt, May, 2005).

In metal contaminated rivers benthic macroinvertebrate communities are characterised by an absence of gammarid amphipods and a reduced number of species and larval individuals of the insect families Heptageniidae, Leuctridae, Hydropsychidae and Chironomidae.

Both zinc and lead may lead to a depauperate invertebrate fauna of insect larvae *Tanypus nebulosus* Meigen 1804 and *Simulium latipes* (Meigen 1804) and some flatworms and fish are absent from these streams. The death of specific organisms is not the only consequence of heavy metal pollution. There may be reduced growth rates in those that survive and an accumulation of the metals in their bodies by factors of many thousands over the concentrations found in the environment.

In the province of Dalarna, Central Sweden, metal-affected streams are characterised by reduced species diversity. At these sites, EPT (Ephemeroptera, Plecoptera, Trichoptera) taxa richness was low mainly because the mayflies richness was seriously reduced, while stoneflies were only marginally affected at sites with a zinc concentration amounting to 1,480 $\mu g/dm^3$ and a lead concentration amounting to 16.6 $\mu g/dm^3$ or cadmium amounting to 3.4 $\mu g/dm^3$ (Malmqvist, Hoffsten, 1999).

4. THE EPISODIC AND CHRONIC IMPACT OF COAL MINE WATER ON MACROINVERTEBRATES IN STREAMS

Both episodic and chronic coal mine drainage have decreased the quality of water and have had an adverse impact on macroinvertebrates. The metal concentrations in rivers (streams) and pH value fluctuate widely depending on the seasons and the mine water discharged into the rivers (streams). The nature of episodic pollutions in rivers (streams) depends on the sources of the acidity and metals and the hydrology of rivers (streams).

The impact of episodic coal mine drainage pollution on macroinvertebrates compared to chronic impact sites and reference sites was investigated in streams in Pennsylvania, USA (Northumberland County and Schuylkill County) (MacCausland, McTammany, 2007). It was hypothesized that chronic coal mine pollution has a more adverse impact on macroinvertebrates than episodic pollution. The results showed that the taxonomic richness varied greatly among the sites (reference, episodic, chronic sites) and the seasons. At reference sites taxa of all aquatic orders were observed including pollution-sensitive taxa, e.g. Ephemeroptera, Plecoptera and Trichoptera. At chronic polluted sites the chironomid and other dipteran larvae and Oligochaeta were mainly recorded with low densities. At one of the episodic polluted site the taxonomic richness was similar to chronic polluted sites except for the occurrence of the hydropsychid caddisfly Diplectrona. Plecoptera, Coleoptera and Ephemeroptera occurred at the second episodic polluted site. The density of macroinvertebrates ranged from 856 to 1,566 individuals/m^2 at the reference sites, from 40 to 82 individuals/m^2 at episodic polluted sites and from 37 to 41 individuals/m^2 at chronic polluted sites. Family richness was highest and amounted to 26-34 at the reference sites compared to the episodic and chronic polluted sites and amounted to 7-18 and 10-15, respectively. EPT richness ranged from 13 to 17 (reference sites), from 1 to 6 (episodic polluted sites) and 3 (chronic polluted sites). What is more, the dissolved metal concentrations were positively correlated with conductivity, whereas conductivity was negatively correlated with macroinvertebrate density and richness.

The values of conductivity increased with the metal concentration in streams at the chronic and episodic polluted sites. In this region, the relatively high values of conductivity of the stream sites compared to other sites might indicate the coal mine drainage may have impaired macroinvertebrates. The physical and chemical parameters of the water is shown in Table 8.

Table 8. The physical and chemical parameters of the water (reference sites, sites episodic and chronic polluted by coal mine waters) and their values (Modified from MacCausland, McTammany, 2007)

Parameter	Reference sites	Episodic polluted sites	Chronic polluted sites
pH	4.32-7.56	4.62-6.73	4.94-7.10
Conductivity μS/cm	21.8-152.6	154.7-548.0	226.8-404.7
Total Fe mg/dm^3	0.0-0.7	1.2-7.1	3.8-11.4
Total Al mg/dm^3	0.0-0.3	0.2-2.7	0.4-2.0
Total Mn mg/dm^3	0.0-0.1	0.9-2.3	1.3-2.2

According to Table 8, the conductivity values, iron, aluminium and manganese concentrations were higher at episodic and chronic polluted sites compared to reference sites.

5. The Mining Subsidence Reservoirs of Upper Silesia (Southern Poland)

5.1. The Origin of the Mining Subsidence Reservoirs

Coal mining influences the vertical movement of the geological beds above the working area. The character and strength of this movement depends on the thickness of the coal strata, the depth of its dipping and on hydrology. This results in the ground sinking above the coal mine depletion. After a certain period of time, subsidence hollows fill with surface and ground water (Rzętała, 1998). In this way, mining subsidence reservoirs are created and are eventually colonized by macrophytes, invertebrates, amphibians and waterfowl (Figures 4, 5).

Mining subsidence reservoirs are usually supplied by surface waters, deep waters and atmospheric precipitation (Dumnicka, Krodkiewska, 2003; Lewin, Smoliński, 2006).

The surface area of the reservoirs ranges from 100 m^2 to 25,000 m^2, the average depth ranges from 0.5 to 2.0 m and the maximum depth from 2-4 m (Jankowski, Molenda, 2007).

Figure 4. (See caption for Figure 5.)

Figure 5. An overview of mining subsidence reservoirs, Czułów, Upper Silesia (Photographer: Iga Lewin).

5.2. The Physical and Chemical Parameters of Waters

The physical and chemical parameters of the water reservoirs are differentiated: total hardness ranges from 38 mg $CaCO_3/dm^3$ to 1,429 mg $CaCO_3/dm^3$, pH values from 7.0 to 8.5, chlorides concentration ranges from 20 to 522 mg/dm^3, magnesium 9-270 mg/dm^3, calcium 25-162 mg/dm^3, nitrates 1.0-17.8 mg/dm^3, phosphates 0.04-2.74 mg/dm^3, iron 0.05-1.5 mg/dm^3 or sulphates 50-350 (Strzelec, 1999; Dumnicka, Krodkiewska, 2003; Strzelec, Serafiński, 2004; Lewin, Smoliński 2006) and conductivity from 290 μS/cm, up to as much as 5,980 μS/cm (the wildfowl reserve "Żabie Doły", see part 7, Lewin, unpublished data).

5.3. The Bottom Sediments

In the mining subsidence reservoirs in Czułów near Katowice (Upper Silesia), which originated from the operation of the "Murcki" coal mine in the 1970s, a qualititative analysis of mineralogy showed that quartz was the main component of the bottom sediments. Nimite, kaolinite, illite, albite and strontium oxide are present in smaller amounts. During reclamation, the waterbanks of these reservoirs were stabilized with waste rock and slag. The predominant mineralogical components of waste rock are silicates and aluminosilicates and clay minerals. Some of the bottom sediment of the reservoirs components are typical of waste rock, i.e. kaolinite, illite or chlorite (Szczepańska, Twardowska, 1999; Lewin, Smoliński, 2006).

5.4. The Reclamation of Mining Subsidence Reservoirs

The reservoirs have been reclaimed. The waterbanks have been partly concrete-lined and stabilized with waste rock and slag. They have ussualy been stocked with fish: *Tinca tinca* (L.), *Carassius auratus gibelio* (Bloch), *Carassius auratus* (L.), *Anguilla anguilla* (L.), *Cyprinus carpio* (L.), *Esox lucius* (L.), *Perca fluviatilis* (L.), *Rutilus rutilus* (L.) and *Scardinus erytrophthalmus* (L.). The macrophytes have been partially removed and the reservoirs' output has been regulated as part of the reservoir management process. The reservoirs are used by anglers and hunters (wild ducks occurrence) (Lewin, Smoliński, 2006) (Figure 6).

5.5. The Mining Subsidence Reservoirs as Refuges for the Lives of Multiple Organisms

In Upper Silesia there is a lack of natural water bodies, only reservoirs of an anthropogenic origin are common. The reservoirs constitute refuges for many species of fauna and flora (Figure 7).

Figure 6. Mining subsidence reservoirs: reclamation- waterbanks concrete-lined and stabilized with waste rock and slag, Czułów, Upper Silesia (Photographer: Iga Lewin).

Figure 7. Mining subsidence reservoirs may constitute refuges for many species of fauna and flora (Photographer: Iga Lewin).

5.5.1. Rotifera

The number of Rotifera taxa is differentiated in the mining subsidence reservoirs of Upper Silesia and ranges from 12 to 19. Only in one of this type of reservoir (Bojszowy-Jedlina) was the number of taxa very high and amounted to 71 (Bielańska-Grajner, Niesler, 2002). Among these 3 species: *Brachionus forficula* Wierzejski, 1891, *Cephalodella misgurnus* Wulfert, 1937 and *Gastropus minor* Weber, 1898 are rare. One new species for Upper Silesia, e.g. *Erignatha clastopis* (Gosse, 1886) was also found in that reservoir. The mean density of rotifers ranged up to 3,502 individuals/m^2. For comparison, a reservoir of coal mine water with an area of 3.5 ha was investigated in terms of the occurrence of Rotifera in the Lublin Coal Basin, Eastern Poland in the 1980s (Radwan, Paleolog, 1983). The mine waters were pumped out from depths of 900 m into this reservoir. The chloride concentration in the reservoir ranged from 676.8 mg Cl^-/dm^3 to 683.1 mg Cl^-/dm^3. The sulphate concentration was low and amounted to up to 20 mg SO_4^{2-}/dm^3. The result showed a positive correlation between temperature, dissolved oxygen in the water and rotifer abundance similar to that in natural lakes. Only nine rotifer species were recorded in the reservoir: *Asplanchna* *brightwelli* Gosse, 1850, *Brachionus angularis* Gosse, 1851, *Brachionus calyciflorus* (Pallas, 1766), *Brachionus rubens* (Ehrenberg, 1838), *Keratella quadrata* (O. F. Müller, 1786), *Lecane closterocera* (Schmarda, 1853), *Lecane luna* (O. F. Müller, 1776), *Polyarthra vulgaris* Carlin, 1943 and *Rhinoglena frontalis* (Ehrenberg, 1853). The highest rotifer density was recorded at low sulphate and calacium concentrations in the reservoir**.**

5.5.2. Oligochaeta

In the mining subsidence reservoirs of Upper Silesia 19 Oligochaeta species occur (11 Naididae and 8 Tubificidae), e.g. *Dero digitata* (O. F. Müller, 1773), *Limnodrilus claparedeanus* Ratzel, 1868, *Aulodrilus pluriseta* (Piguet, 1906) or *Nais pardalis* Piguet, 1906. Among them, *Potamothrix bavaricus* (Oeschmann, 1913) is a rare species in the Polish fauna. The mean density of Oligochaeta in this type of reservoir ranges from 4,600 to 6,600 individuals/m^2. Oligochaetes are a taxon tolerant of coal mine pollution (García-Criado, Fernandez-Alaez, Fernandes-Alaez, 2002; Krodkiewska 2006).

Potamothrix bavaricus occurred in 10 mining subsidence reservoirs in which the mean value of conductivity ranged from 313.6 μS/cm to 1,813.8 μS/cm, chlorides concentration from 39.6 mg/dm^3 to 501.3 mg/dm^3 and hardness from 114 mg $CaCO_3$/dm^3 to 609 mg $CaCO_3$/dm^3. The mean density of *Potamothrix bavaricus* ranged from 21.4 to 228.6 individuals/m^2 (Krodkiewska, 2007). *Potamothrix bavaricus* is a Palearctic species of Ponto-Caspian origin that is also distributed in North and South America, in the Near East, Australia and New Zealand both in lentic and lotic sites (Pinder, Brinkhurst, 2000). In the mining subsidence reservoirs *Limnodrilus hoffmeisteri* Claparéde, 1862 and *Tubifex tubifex* (O. F. Müller, 1774) occurred very abundantly.

5.5.3. Hirudinea

In the mining subsidence reservoirs of Upper Silesia 9 leech species occur, whereas in sand pits there were 12 species and in gravel pits 11. The low number of species in the mining subsidence reservoirs may be explained by the specific physical and chemical parameters of the water in these habitats. For example, the concentration of chlorides, sulphates and hardness are relatively high: they amount to from 28.0 to 566.0 mg Cl/dm^3, from 35.0 to 783.0 mg SO_4^{2-}/dm^3 and from 204.0 to 801.9 mg $CaCO_3$/dm^3, respectively (Krodkiewska, 2003). In these reservoirs *Glossiphonia complanata* (Linnaeus, 1758), *Helobdella stagnalis* (Linnaeus, 1758) and *Erpobdella octoculata* (Linnaeus, 1758) occur very frequently, whereas e.g. *Hemiclepsis marginata* (O. F. Müller, 1774), *Erpobdella testacea* (Savigny, 1820), *Erpobdella monostriata* (Lindenfeld et Pietruszyński, 1890), *Haemopis sanguisuga* (Linnaeus, 1758) or *Theromyzon tessulatum* (O. F. Müller, 1774) are rare (Krodkiewska, 2003).

5.5.4. Mollusca

The number of species and the density of molluscs in the mining subsidence reservoirs are differentiated. For example, in the complex of reservoirs in Czułów (7 reservoirs), the mollusc communities are considerably diverse. In total, 19 mollusc species were recorded (Table 9) and in one of the reservoirs 15 species occurred. An opposite result was obtained by Strzelec (1993); Strzelec and Serafiński (2004). Data of their survey showed that the mining subsidence reservoirs of Upper Silesia are poor in terms of the numbers and densities of mollusc species. They found only single specimens of *Gyraulus crista* (Linnaeus, 1758), *Viviparus contectus* (Millet, 1813), *Acrloxus lacustris* (Linnaeus, 1758) or *Segmentina nitida* (O. F. Müller, 1774).

Among 31 gastropod taxa of Upper Silesia, the mean number of species observed by Michalik-Kucharz (2008) in the mining subsidence reservoirs amounted to 5.28±2.3.

According to Table 9, from 1993-2007, 23 species were observed. In the reservoirs, the number of species increased from 7 to 19. In the years 1993-1996 the Shannon-Wiener index values calculated for mollusc communities in the reservoirs shows an increasing tendency. The index values decreased from 3.22 in 2002 to 0.69 in 2007 (the result of the abundance of *Potamopyrgus antipodarum* (J. E. Gray, 1843) in the mollusc communities).

The basement complex and bottom sediments influence the mollusc communities in the mining subsidence reservoirs. For example, in Czułów, 19 mollusc species occur on the bottom which mainly consist of quartz, clay mineral and feldspar, whereas 9 gastropod species occur on the dolomite bottom and 18 gastropod species occur on shell limestone bottoms (Strzelec, 1999).

The occurrence of some mollusc species has been recorded in mining subsidence reservoirs here for the first time, e.g. *Bithynia tentaculata* (Linnaeus, 1758), *Radix auricularia* (Linnaeus, 1758), *Stagnicola palustris* (O. F. Müller, 1774), *Hippeutis complanatus* (Linnaeus, 1758), *Ferrissia wautieri* (Mirolli, 1960), *Anodonta antina* (Linnaeus, 1758), *Musculium lacustre* (O. F. Müller, 1774), *Pisidium casertanum* (Poli, 1791) by Lewin and Smoliński (2006) and *Anodonta cygnea* (Linnaeus, 1758) by Górniak (2006).

In the mining subsidence reservoirs in Czułów, a few rare species have also been found including *Acroloxus lacustris, Viviparus contectus, Physella acuta* (Draparnaud, 1805), *Hippeutis complanatus* and *Anodonta anatina* (Lewin, Smoliński, 2006).

According to the Red List of Upper Silesia Freshwater Molluscs, *Bithynia tentaculata, Hippeutis complanatus, Ferrissia wautieri, Musculium lacustre* and *Pisidium casertnum*, which were found in the reservoirs in Czułów (Table 9), have become a vulnerable species (VU) in this region (Serafiński, Michalik-Kucharz, Strzelec, 2001).

The occurrence of the Swan mussel (*Anodonta cygnea*), which is legally protected in Poland (Dziennik Ustaw, 2004), was recorded for the first time in the mining subsidence reservoir which is located in an industrial town (Zabrze near Katowice) (Górniak, 2006). The density of the Swan mussel in this reservoir ranged from 4 to 15 individuals/m^2. According to the Polish Red List of Species, the Swan mussel (*Anodonta cygnea*) has become an endangered species (EN). *Anodonta cygnea*, a Palearctic species, is becoming increasingly more rare. This species occurs mainly in the oxbow lakes, lakes and dam reservoirs. A decline in its population has been observed since the 1950s: the habitat degradation, destruction of small shallow reservoirs and water pollution maybe caused by (Głowaciński, Nowacki, 2004).

The alien gastropod species: *Physella acuta, Ferrissia wautieri* and *Potamopyrgus antipodarum* have been observed in the mining subsidence reservoirs of Upper Silesia.

The occurrence of *Ferrissia wautieri* was recorded in the reservoirs in Czułów in the years 2002-2003 (Table 9) and later in the other 5 mining subsidence reservoirs in Upper Silesia (Strzelec, 2005a). Only the ancyloid forms were found, indicating that the total dissolved oxygen does not decrease drastically in these reservoirs. The first time the occurrence of the septal form was observed in the mining subsidence reservoir was in 2008 in Zabrze near Katowice by Spyra (2008). Calais and Roger first found this species in France in

1944 (Mirolli, 1960). To date, this species is considered as a North American species *Ferrissia fragilis* (Tryon, 1863) (Walther et al., 2006; Walther, 2007).

Table 9. The values of the domination (D%) and the Shannon-Wiener (H') indices of the mollusc communities in the mining subsidence reservoirs in Czułów (Upper Silesia) (Lewin, Smoliński, 2006; Lewin, in. prep.)

Species	Years of the survey											
	1993	1995	1996	1997	2000	2001	2002	2003	2004	2005	2006	2007
Viviparus contectus (Millet, 1813)			6.6	0.4	0.8	2.9	2.4	3.4	5.5	0.6	0.8	0.3
Bithynia tentaculata (Linnaeus, 1758)					7.2	2.2	3.1	3.5	9.2	3.9	3.3	7.0
Potamopyrus antipodarum (J. E. Gray, 1843)				83.0	51.8	66.4	38.4	40.5	43.5	81.4	85.1	89.9
Acroloxus lacustris (Linnaeus, 1758)	36.4	31.6	1.9	0.1	7.6	0.7		1.5	1.6	0.3	2.0	0.3
Stagnicola palustris (O. F. Müller, 1774)			3.8	0.4								
Stagnicola corvus (Gmelin, 1791)			1.9	0.5								
Radix auricularia (Linnaeus, 1758)					4.0		1.8	0.4	1.0	0.1	0.4	0.1
Radix balthica (Linnaeus, 1758)	24.5	24.7	22.6	1.6	4.8	1.9	4.3	3.2	12.6	1.0	0.6	0.2
Lymnaea stagnalis (Linnaeus, 1758)	13.2	14.6	1.9	0.9	1.6	3.6	7.9	16.2	4.4	0.5	0.7	0.3
Physella acuta (Draparnaud, 1805)			9.4	2.4			1.8	0.3		0.5	0.8	0.3
Aplexa hypnorum (Linnaeus, 1758)									0.4	0.2	0.3	0.1
Planorbarius corneus (Linnaeus, 1758)	6.6	3.8	16.0	0.7	9.7	6.0	6.7	13.2	3.4	0.4	1.4	0.4
Ferrissia wautieri (Mirolli, 1960)							1.8	0.3				
Anisus spirorbis (Linnaeus, 1758)			3.8	2.3		0.5						
Bathyomphalus contortus (Linnaeus, 1758)				0.1					0.3		0.2	0.1
Gyraulus albus (O. F. Müller, 1774)	6.0	7.0	3.8	1.2	8.8	2.2	6.7	3.2	2.4	0.3	0.4	0.2
Gyraulus crista (Linnaeus, 1758)	1.3	6.3		0.2	1.6		3.7	1.8	7.8	4.2	0.5	0.2
Hippeutis complanatus (Linnaeus, 1758)			15.1	5.3	2.0	4.1	6.7	2.4	2.3	2.0	0.9	0.1
Segmentina nitida (O. F. Müller, 1774)	12.0	12.0	13.2	1.0		3.4	9.2	3.7	4.1	3.3	0.6	0.1
Anodonta anatina (Linnaeus, 1758)									0.6	0.2	0.3	0.1
Sphaerium corneum (Linnaeus, 1758)											0.8	0.2
Musculium lacustre (O. F. Müller, 1774)						4.8	3.1	2.1	0.4	0.2	0.5	0.1
Pisidium casertanum (Poli, 1791)						1.2	2.4	4.3	0.7	0.9	0.6	0.2
Σ of species	7	7	12	15	11	13	15	16	17	17	19	19
Σ of specimens	151	158	106	1,726	249	414	164	677	708	3,188	2,465	7,078
Value of the H'	2.36	2.49	3.22	1.18	2.44	2.03	3.22	2.89	2.88	1.80	1.16	0.69

Among the alien species recorded in these reservoirs, the New Zealand mud snail *Potamopyrgus antipodarum* is an invasive species. The New Zealand mud snail has successfully colonized freshwater and brackish habitats not only in almost all of Europe, but also in Australia, Japan and North America (Ponder, 1988; Mitsuaki, Ryoji, 2004; Richards, Shinn, 2004; Sousa, Antunes, Guilhermino, 2007; Čejka, Dvořák, Košel, 2008).

Parthenogenesis (Wallace, 1992) and euryhalinic may be major factors that contribute to the rapid rate of the New Zealand mud snail's spread throughout Europe and America. *Potamopyrgus antipodarum* is able to tolerate salinity even up to 30‰ (Costil, Dussart, Daguzan, 2001; Paavola, Olenin, Leppäkoski, 2005). The New Zealand mud snail can be transferred by birds, fish, fish stocking and angling boats, ships (attached to their hulls) and insects as well as by the Lymnaeid snail (*Potamopyrgus antipodarum* is able to go through the digestive system and remain alive).

To date, *Potamopyrgus antipodarum* has inhabited different types of water environments in Upper Silesia: rivers, streams and anthropogenic reservoirs including the mining subsidence reservoirs (Strzelec, Krodkiewska, 1994; Strzelec, Serafiński, 1996; Strzelec, 2005b).

In the mining subsidence reservoirs in Czułów, from 1997 to the present, a great invasion of the New Zealand mud snails has been observed (Lewin, Smoliński, 2006; Lewin, in prep.). In these mining subsidence reservoirs the density of *Potamopyrgus antipodarum* ranges from 85 to 7,800 individuals/m^2, whereas in the other mining subsidence reservoirs of this region the density ranges from 33 to 999 individuals/m^2 (Strzelec, 1993). For comparison, in other countries, the density of *Potamopyrus antipodarum* is differentiated and ranges from a few individuals/m^2 in Lake Erie, USA (Levri, Kelly, Love, 2007), 300,000 individuals/m^2 in the rivers and estuaries of the western part of the USA (Richards, Shinn, 2004) and in the Greater Yellowstone Ecosystem (Kerans et al., 2005), 500,000 individuals/m^2 in the Great Yellowstone Area to more than 700,000 individuals/m^2 in the Upper Ownes River Watershed (Noda, 2007).

Many of the mining subsidence reservoirs of Upper Silesia and their waterbanks also provide habitats for freshwater sponges, macrophytes (see part 7), many species of wildlife, birds of prey, amphibians and reptiles. Amphibians and reptiles are legally protected in Poland (Dziennik Ustaw, 2004). Some of the mining subsidence reservoirs of Upper Silesia, which are not so degraded and provide a refuge for wildlife, should be protected on ecological grounds.

6. The Effect of Coal Mining on Macrophytes

6.1. Ecological Classification of Macrophytes

The term hydrophytes refers to vascular aquatic plants, while the term aquatic macrophytes is widely used and refers to the macroscopic forms of aquatic vegetation and encompasses macroalgae (e.g. alga Cladophora), a few species of mosses, e.g. the willow moss *Fontinalis antipyretica* L. and ferns, e.g. *Salvinia natans* (L) Allioni, *Salvinia molesta* Mitchell, *Marsilea quadrifolia* L. adapted to the freshwater environments, and vascular plant angiosperms (Wetzel, 1983; Kalff, 2003). Macrophytes encompass:

1. Emergent macrophytes (helophytes): e.g. reed sweet grass *Glyceria maxima* (Hartm.) Holmb.
2. Floating-leaved macrophytes (nymphaeids): these attach to submersed sediments at water depths from 0.5 to 3.0 m, e.g. the white water lilies *Nymphaea alba* L., *Potamogeton natans* L.
3. Submerged rooted, e.g. Canadian pond weed *Elodea canadensis* Michx., *Myriophyllum spicatum* L.
4. Free-floating macrophytes (pleuston) e.g. water hyacinth *Eichhornia crassipes* (Mart.) Solms, *Hydrocharis morsus-ranae* L., *Lemna minor* L.
5. Submerged nonrooted (elodeids), e.g. hornwort *Ceratophyllum demersum* L.

6.2. Coal Mine Heaps, Coal Mine Sedimentation Pools and Mining Subsidence Reservoirs as Habitats for Macrophytes (Upper Silesia, Southern Poland)

Coal mine sedimentation pools are the places in which underground water containing coal dust and significant amounts of mineral components are deposited. After sedimentation, water is pumped into rivers, and the surface of coal mine sedimentation pools starts to gradually dry up. After that, plants begin to colonize these areas. A study of primary succession that was carried out on 137 sites showed a wide variety of 67 plant communities recorded at or near coal mine sedimentation pools. The two pioneer communities were *Diplotaxis muralis* (L.) DC. and *Chenopodium botrys* L. Indigenous and alien flora at or near coal mine sedimentation pools amounted to 428 species, among them 53 invasive species, which had been growing on coal dust (Woźniak, 2001a; Woźniak, 2003). In the coal mine sedimentation pools and the mining subsidence reservoirs of Upper Silesia, many rare and legally protected macrophytes occur (Table 10).

Coal mine heaps and coal mine sedimentation pools provide very poor habitats in terms of their mineral substratum which is poor in nutrients. At these types of habitats, in total 71 grass species are recorded (Rostański, Woźniak, 2007).

In the mining subsidence reservoirs which have different water sources a total of 21 species of macrophytes occur (Czułów near Katowice, Upper Silesia). The mining subsidence reservoirs that receive waters from the mine dewatering system and from a settling pond support more macrophyte species compared to the mining subsidence reservoirs with non-flowing water (Table 11) (Lewin, Smoliński, 2006; Lewin in prep.). In the mining subsidence reservoirs of this area rare, e.g. the spiny naiad *Najas marina* All. and legally protected macrophytes, e.g. the white water lilies *Nymphaea alba* and the common bladderwort *Utricularia vulgaris* L. have been observed.

The spiny naiad (*Najas marina*), a submerged annual macrophyte that also occurs in the USA, in New York and Pennsylvania, is endangered.

Utricularia vulgaris, the common bladderwort, which characterizes a very interesting ecology, is a carnivorous plant that preys on a wide range of aquatic invertebrates, especially zooplankton. *Utricularia vulgaris* captures prey with underwater trap-bladders. The common bladderwort preys on a wide variety of organisms, that originate from the Aufwuchs of the plants: e.g. cyclopoid copepods, cladocerans, ostracods, rotifers, insect larvae living in the

Aufwuchs and small autotrophic organisms. *Utricularia vulgaris* captures prey non-randomly. For example, the cyclopoid copepods are selected more frequently than *Polyphemus pediculus* (Linnaeus, 1761) (Harms, Johansson, 2000).

Table 10. Occurrence of rare and legally protected macrophytes at or near coal mine sedimentation pools and mining subsidence reservoirs of Upper Silesia (Modified from Woźniak, Kompała 2000; Woźniak, 2001b).

Species	Coal mine sedimentation pools		Mining subsidence reservoirs	
	Rare	Legally protected	Rare	Legally protected
Atriplex prostrata Boucher ex DC. ssp. prostrata	X			
Batrachium circinatum (Sibth.) Fr.	X			
Batrachium trichophyllum (Chaix) Bosch		X		
Bulboschoenus maritimus (L.) Palla	X		X	
Butomus umbellatus L.	X			
Centaurium erythraea Rafn ssp.erythraea		X		
Comarum palustre L.			X	
Chamaenerion palustre Scop.	X			
Chenopodium botrys L.	X			
Datura stramonium L.	X			
Diplotaxis muralis (L.) DC.	X			
Epipactis atrorubens (Hoffm.) Besser		X		
Epilobium palustre L.	X			
Equisetum hyemale L.	X			
Equisetum variegatum Schleich.		X		
Eriophorum latifolium Hoppe	X			
Frangula alnus Mill.		X		
Geranium phaeum L.	X			
Hottonia palustris L.			X	
Juncus bulbosus L.	X			
Juncus ranarius J. O. E. Perrier & Songeon	X			
Lemna gibba L.			X	
Myricaria germanica (L.) Desv.	X			
Nymphaea alba L.				X
Nuphar lutea (L.) Sibth. & Sm.				X
Parnassia palustris L.	X			
Plantago intermedia Gilib.	X			
Ranunculus sceleratus L.	X			
Sparganium minimum Wallr.			X	
Schoenoplectus tabernaeomontani (C. C. Gmel.)	X			
Spergularia salina J. Presl & C. Presl	X			

Species	Coal mine sedimentation pools		Mining subsidence reservoirs	
	Rare	Legally protected	Rare	Legally protected
Tofieldia calyculata (L.) Wahlenb.				X
Triglochin palustre L.	X		X	
Utricularia minor L.				X
Utricularia vulgaris L.				X
Viburnum opulus L.		X		

Table 11. Macrophyte occurrence in the mining subsidence reservoirs in Czułów (Upper Silesia) (After Lewin, Smoliński, 2006; Lewin in prep.)

Species	Reservoirs with flowing water (receiving waters from the mine dewatering system and from a settling pond)	Rreservoirs with non-flowing water
Acorus calamus L.	X	
Alisma plantago-aquatica L.	X	X
Callitriche copocarpa Sendtn.	X	
Ceratophyllum demersum L.	X	X
Eleocharis palustris (L.) Roem. & Sm.	X	
Elodea canadensis Michx.	X	X
Glyceria maxima (Hartm.) Holmb.	X	X
Iris pseudacorus L.	X	
Lemna minor L.	X	X
Lemna trisulca L.	X	
Myriophyllum spicatum L.	X	
Najas marina All.		X
Nuphar lutea (L.) Sibth. & Sm.	X	X
Nymphaea alba L.	X	X
Potamogeton crispus L.	X	X
Riccia fluitans L.	X	
Rumex hydrolapathum Huds.	X	X
Scirpus sylvaticus L.	X	
Sparganium erectum L. em. Rchb.	X	
Typha latifolia L.	X	X
Utricularia vulgaris L.	X	X
Σ of species	20	12

Also observed in mining subsidence reservoirs of Upper Silesia were: *Hydrocharis morsus-ranae* L., *Myriophyllum verticillatum* L., *Phragmites australis* (Cav.) Trin ex Steud., *Polygonum amphibium* L., *Potamogeton natans* L., *Potamogeton pectinatus* L., *Sagittaria sagittifolia* L. and *Sparganium erectum* L. em. Rchb. s.s. (Strzelec 1993; Bielańska-Grajner, Niesler, 2002; Krodkiewska, 2003; Strzelec, Serafiński, 2004).

6.3. Macrophytes Subjected to the Coal Mine Waters

Macrophytes, subjected to coal mine waters accumulate heavy metals in the tissue, e.g. *Eichhornia crassipes*, *Lemna minor* and *Spirodela polyrhiza* (L.) Schleid. Among them *Eichhornia crassipes* accumulates the highest amount of heavy metals compared to *Lemna minor* and *Spirodela polyrhiza*. *Eichhornia crassipes* is a fast-growing species with characteristic a fibrous root system and broad leaves. The roots of these macrophyte species accumulate more heavy metals and nutrients than their leaves. Table 12 shows the heavy metal concentrations in the macrophyte tissues (Mishra et al., 2008).

Table 12. The mean values of the heavy metal concentrations in the leaves and roots of macrophytes subjected to coal mine waters (Modified from Mishra et al., 2008)

	Eichhornia crassipes	*Lemna minor*	*Spirodela polyrhiza*
Roots Before being subjected to mine waters	Fe 0.19±0.01 Zn 0.45±0.01 Ni 0.15±0.003	Fe 0.09±0.01 Zn 0.11±0.001 Ni 0.074±0.002	Fe 0.037±0.001 Zn 0.09±0.001 Ni 0.033±0.001
Roots Subjected to mine waters	Fe 0.72±0.07 Zn 0.68±0.02 Ni 0.38±0.01	Fe 0.64±0.02 Zn 0.36±0.02 Ni 0.23±0.01	Fe 0.35±0.01 Zn 0.26±0.01 Ni 0.14±0.01
Leaves Before being subjected to mine waters	Fe 0.09±0.01 Zn 0.20±0.01 Ni 0.07±0.01	Fe 0.04±0.006 Zn 0.09±0.01 Ni 0.062±0.01	Fe 0.05±0.003 Zn 0.09±0.002 Ni 0.042±0.001
Leaves Subjected to mine waters	Fe 0.57±0.02 Zn 0.27±0.01 Ni 0.16±0.01	Fe 0.60±0.01 Zn 0.26±0.01 Ni 0.17±0.01	Fe 0.35±0.01 Zn 0.13±0.01 Ni 0.09±0.02

6.4. Macrophytes in the Coal Mine Water Treatment System

Helophytes could be successfully applied in wetland treatment systems to remove contaminating discharges from coal mines, but their growth may be reduced by the metal concentrations in coal mine waters. Besides, the mine water treatment wetlands, in some cases, may constitute habitats for some macroinvertebrates.

The result of a survey carried out by Batty and Younger, (2004) in the Shilbottle Colliery, Northumberland, United Kingdom, showed the differences in growth of *Phragmites australis* both in the wetlands contaminated by coal mine waters and in uncontaminated wetlands. Concentrations of Fe, Mn, Al, Ni, Ca or sulphates of surface waters were all significantly higher in the wetlands contaminated by coal mine waters compared to the uncontaminated wetlands. In the surface waters in contaminated wetlands the concentration of Fe ranged up to

450 mg/dm^3, Ni ranged up to 2.8 mg/dm^3 and Ca up to 480 mg/dm^3. The value of pH of surface waters in contaminated wetlands was low and ranged from 2.0 to 6.3. Growth of *Phragmites australis* is significantly reduced by metal toxicity in wetlands highly contaminated by coal mine waters (Table 13).

Shoot heights were significantly different in two wetlands with lower values than the contaminated wetland, whereas shoot density was not. The production of seeds was inhibited by the high metal concentrations in coal mine water. The root concentration of Fe was higher in *Phragmites australis* from the contaminated wetlands compared to the uncontaminated wetlands and amounted to 124,368 mg/kg dry weight, whereas the shoot concentration of Fe amounted to 8445 mg/kg dry weight.

Table 13. The differences in shoot height, shoot density and number of seeds of *Phragmites australis* growing in uncontaminated and contaminated wetlands (Modified from Batty, Younger, 2004)

	Shoot height (cm)	Shoot density (no/m^2)	No of seed heads/m^2
Uncontaminated wetlands	124-251	103-170	2-16
Contaminated wetlands	94-179	87-1,350	1-8

Helophytes, e.g. *Typha latifolia* L. and *Phragmites australis* are successfully applied in wetland treatment systems to remove contaminating discharges from coal mines. The removal of iron and manganese from coal mine waters is successfully achieved by connection of the oxidation ponds and wetlands with these helophytes i.e. at Whittle Colliery, UK. The concentration of iron decreased from an average influent level of 32 mg/dm^3 to 0.5 mg/dm^3 (Batty, Hooley, Younger, 2008).

Table 14. The list of macroinvertebrate taxa from two mine water treatment wetlands (Modified from Batty, Atkin, Manning, 2005)

Taxa	The Whittle treatment system	The Quaking Houses treatment system
Agabus spp.	X	X
Argyroneta aquatica (Clerck, 1757)		X
Baetis spp.	X	
Chironomus plumosus	X	X
Coenagrionidae	X	
Culex sp.	X	X
Dixa sp.	X	X
Helobdella stagnalis (Linnaeus, 1758)	X	
Herpetocypris spp.	X	X
Hydrobiidae	X	
Libellulidae	X	

Table 14. (Continued)

Taxa	The Whittle treatment system	The Quaking Houses treatment system
Lymnaea stagnalis (Linnaeus, 1758)	X	X
Notonecta glauca Linnaeus, 1758	X	
Theodoxus fluviatilis (Linnaeus, 1758)		X
Viviparus viviparus (Linnaeus, 1758)	X	

A survey carried out in the two mine water treatment wetlands in the north of England (The Quaking Houses wetland and the Whittle wetland) showed that this type of water environment can provide suitable habitats for some macroinvertebrates (Batty, Atkin, Manning, 2005). The Quaking Houses wetland contains four macrophyte species, i.e. *Phragmites australis, Typha latifolia*, *Juncus effusus* L. and *Iris pseudacorus* L., whereas the Whittle wetland contains two: *Phragmites australis* and *Typha latifolia*. The Quaking Houses wetland was constructed for treating net-acidic mine water with elevated concentrations of iron, aluminium, manganese and sulphates (the mean value of sulphate concentration ranged from 2,564 mg/dm^3 to 2,576 mg/dm^3), whereas the Whittle wetland was constructed for treating net-alkaline mine water. Both wetlands, which are additionally characterized by a high value of conductivity (mean value ranged from 5,142 µS/cm to 6,550 µS/cm) provide suitable habitats for the macroinvertebrate taxa shown in Table 14.

6.5. Macrophytes in the Assessment of Water Quality in Rivers Impacted by Coal Mine Waters

According to the Water Framework Directive (Directive 2000/60/EC), macrophytes are considered to be indicators of water pollution at the same level as benthic macroinvertebrates, fish or phytoplankton. In Europe, The Mean Trophic Rank indexation method (MTR) based on the macrophyte survey is widely used in the assessment of water quality in rivers (streams**)** (Baattrup-Pedersen et al., 2006; Feiler, Krebs, Heininger, 2006; Hering, et al., 2006). The same methods was applied e.g. in the Mleczna River (Czułów, Upper Silesia, Southern Poland) in the assessment of the water quality of coal mine water pollution (Szoszkiewicz et al., 2006). The Mleczna River receives coal mining water which flows from the mine dewatering system through a settling pond and then through mining subsidence reservoirs. (Figure 8). At this sampling site the conductivity ranged up to 2,850 µS/cm, chlorides concentration up to 570 mg/dm^3, nitrates up to 76.20 mg/dm^3, and the hardness ranged up to 400 mg $CaCO_3$/dm^3. The value of MTR, which amounted to 22.3, indicated a bad ecological status. Only 8 macrophyte taxa occur in the Mleczna River: Cladophora sp., *Glyceria maxima*, *Lemna minor*, *Potamogeton pectinatus*, *Sparganium erectum*, *Spirodela polyrhiza*, *Polygonum lapathifolium* L. and *Urtica dioica* L. The MTR value of 22.3 is relatively low compared to other rivers of Upper Silesia where the MTR values range from 26.2 (the Rawa River, which receives both industrial and sewage pollutions) to 60.8 (the Dobka River, a stream of good quality water in the Beskid Śląski Mountains).

Figure 8. The Mleczna River receives coal mining water which flows from the mine dewatering system through a settling pond and then through the mining subsidence reservoirs (Photographer: Iga Lewin).

7. Coal Mining Areas as Refuges for Wildlife

In Upper Silesia (Poland), some areas after coal mine exploitation ended and their reclamation was cmpleted have been designated as the nature reserves (sanctuaries), the nature-landscape complex or ecological grounds due to their distinctive environmental features. The above- mentioned areas constitute a refuge for wildlife, especially for protected and rare fauna and flora species.

The wildfowl reserve “Żabie Doły” (“Frog Pits”) is one example of this type of legally protected area (Nita, Myga-Piątek, 2006). The area of “Żabie Doły” was designated as a wildfowl reserve in 2002. The surface area of this reserve amounts to 217.66 ha and comprises mining subsidence reservoirs, coal mine heaps and coal mine sedimentation pools (Piontek, 2001; Molenda, 2005). In “Żabie Doły”, which is located between two towns - Bytom and Chorzów, 129 species of wildfowl have been recorded including 76 nesting species, e.g. the Common Coot *Fulica atra* Linnaeus, 1758, the Great Crested Grebe *Podiceps cristatus* (Linnaeus, 1758), the Little Crake *Porzana parva* (Scopoli, 1769) and Sand Martin *Riparia riparia* (Linnaeus, 1758). Among them the Common Snipe *Gallinago gallinago* (Linnaeus, 1758), the Common Moorhen *Gallinula chloropus* (Linnaeus, 1758), the Arctic Loon *Gavia arctica* (Linnaeus, 1758), the Horned Grebe *Podiceps auritus* (Linnaeus, 1758), the White-winged Scoter *Melanitta fusca* Linnaeus, (1758), the Red-necked the Phalarope *Phalaropus lobiatus* (Linnaeus, 1758), the Bluethroat *Luscinia svecica* (Linnaeus, 1758) and the Bearded Parrotbill *Panurus biarmicus* (Linnaeus, 1758) are rare species.

According to the the Polish Red Data Book of Animals, the following species are vulnerable species: the Great Bittern *Botaurus stellaris* (Linnaeus, 1758), the Little Bittern *Ixobrychus minutus* (Linnaeus, 1766), the Northern Pintail *Anas acuta* Linnaeus, 1758, the Black-crowned Night Heron *Nycticorax nycticorax* (Linnaeus, 1758) and the Ruff *Philomachus pugnax* (Linnaeus, 1758).

An addition, 250 vascular plant species have been recorded in "Żabie Doły" including legally protected species, e.g. the sea buckthorn *Hippophaë rhamnoides* L. and the German Greenweed *Genista germanica* L.

The area of "Żabie Doły" also supports 9 amphibian species, e.g., the common toad *Bufo bufo*, the European green toad *Bufo viridis*, Laurenti, 1768, a tree frog *Hyla arborea* Linnaeus, 1758, *Bombina bombina* Linnaeus, 1761, *Rana esculenta* Linnaeus, 1758, the pool frog *Rana lessonae* Camerano, 1882, as well as reptiles and mammals: the European Hedgehog *Erinaceus europaeus* Linnaues, 1758, the European mole *Talpa europaea* Linnaeus, 1758, the common shrew *Sorex araneus* Linnaeus, 1758, the stone marten *Martes foina* Erxleben, 1777 and the European polecat *Mustela putorius*, Linnaeus, 1758.

The wildfowl reserve "Żabie Doły" is an area of interest not only to ornithologists but also for hydrobiologists. In these mining subsidence reservoirs 14 species of Oligochaeta occur including 1 that is rare in Polish fauna species i.e. *Potamothrix bavaricus* (Dumnicka, Krodkiewska, 2003). An addition, from 1991 to date *Potamopyrgus antipodarum*, an invasive gastropod species was recorded in reservoirs as well (Strzelec, 1992).

The coal mine areas of the Upper Angara Region is an example of a refuge for 88 bird species including 63 nesting species and 8 migrating species (Salovarov, Kuznetsova, 2006). In the mining subsidence reservoirs of this area, 22 bird species which comprise 25% of the total species have been recorded. The area of the mining subsidence reservoirs is differentiated. The following species occur in the mining subsidence of the larger area: the Great-crested Grebe *Podiceps cristatus* (Linnaeus, 1758), the Mallard *Anas platyrhynchos* Linnaeus, 1758, the Garganey *Anas querquedula* Linnaeus, 1758, the Wigeon *Anas penelope* Linnaeus, 1758, the Marsh Sandpiper *Tringa stagnatilis* (Bechstein, 1803), the Common Heron *Ardea cinerea* Linnaeus, 1758, the Smew *Mergellus albellus* (Linnaeus, 1758), the Demoiselle Crane *Anthropoides virgo* (Linnaeus, 1758) and the Dunlin *Calidris alpina* (Linnaeus, 1758).

In the small mining subsidence reservoirs the Common Sandpiper *Actitis hypoleucos* (Linnaeus, 1758), the Ruddy Shelduck *Tadorna ferruginea* (Pallas, 1764) and the Little Ringed Plover *Charadrius dubius* Scopoli, 1786 have been observed.

Several abandoned mine sites have been designated as Sites of Special Scientific Interest, for example in the United Kingdom. In these areas many species of metallophytes and lichen flora occur (Batty, 2005).

The above examples provide evidence of the importance of the coal mining areas that also encompass mining subsidence reservoirs as refuges for wildlife including many rare, threatened and protected species.

8. Conclusion

Anthropopressure, which is associated with past and ongoing coal mining activities, has undoubtedly resulted in severe ecological degradation and a decrease in the quality of freshwater that have had an adverse impact on flora and fauna. Intensive, underground hard coal mining has led to changes in water circulation and has caused water shortages, bounces, subsidence or earthquakes, as well as pollution in both surface and ground waters. The catchments of rivers near coal mining activity regions in many countries are strongly affected by naturally mineralised and polluted waters that originate from the dewatering of coalmines. The watercourses of these rivers contain high levels of chlorides, sulphates, phosphates, nitrates, heavy metals, and low values of pH or radioactive matter, as is the case in of the rivers in Upper Silesia (Poland). These water conditions are reflected in high values of conductivity, total dissolved solids and BOD_5. Pollution of the water environment by the waters from mining activities is a problem not only in Poland, but worldwide. The loss of species richness of the flora and fauna in the rivers (streams) caused by pollution from hard coal mines, including streams subjected to acid mine drainage (AMD) stress, has been observed by many authors in many countries.

The values of taxa richness, community diversity indices, biotic indices, e.g. the Biological Monitoring Working Party (BMWP), the Hilsenhoff Biotic Index (HBI) calculated for the benthic macroinvertebrates or the Mean Trophic Rank (MTR) calculated for macrophytes reflect a decrease in the quality of water in the streams subjected to the pollution from hard coal mines. The macroinvertebrate taxa in these streams that are more sensitive to this type pollution, e.g. Ephemeroptera, Plecoptera, Trichoptera, Mollusca including highly acid-sensitive species (e.g. *Ancylus fluviatilis*, *Gammarus fossarum* and *Gammarus pulex*), are replaced by ones that are more tolerant (Chironomidae and other dipteran larvae or Oligochaeta).

In regions with coal mining activity, including Upper Silesia, the natural ecosystems have changed into anthropogenic ecosystems in which new species of the flora and fauna previously unknown in these areas have appeared including alien species, e.g., *Ferrissia wautieri*, *Physella acuta* and invasive species, e.g., the New Zealand mud snail (*Potamopyrgus antipodarum*). In addition, in some cases, mine water treatment wetlands provide suitable habitats for macroinvertebrates.

In Upper Silesia (Southern Poland) many rare (listed in the Polish Red Book of Species) and legally protected species occur, whose habitats are mainly connected with coal mine heaps, coal mine sedimentation pools and mining subsidence reservoirs, e.g., the Swan mussels *Anodonta cygnea*, macrophytes: *Utricularа minor*, *Utricularia vulgaris, Nymphaea alba*, *Nuphar lutea*, *Batrachium trichophyllum* or *Centaurium erythraea*. The occurrence of 9 mollusc species has been recorded in some mining subsidence reservoirs here for the first time. The mining subsidence reservoirs, which are not so degraded and provide a habitat where many species of the flora and fauna including rare, vulnerable or legally protected species can live should be protected on ecological grounds.

Some of the coal mining area, which also encompasses mining subsidence reservoirs that are refuges for wildlife (including, e.g., the wildfowl reserve “Żabie Doły” or the coal mine areas of the Upper Angara Region), may constitute an ecologically important area in terms of conservation biodiversity.

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Chapter 2

ENVIRONMENTAL IMPACT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN COAL PARTICLES ON SEDIMENT QUALITY

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ABSTRACT

Coal is a mass product and has been mined for centuries on a global scale. Due to coal mining, transport and incomplete coal combustion, unburnt coal particles can be dispersed into soils and sediments where they can present a source of polycyclic aromatic hydrocarbons (PAHs).

The chemical group of PAHs comprises of hundreds of single and mostly carcinogenic substances. Predominantly, they are formed by incomplete combustion of organic material (pyrogenic) or derive from petrogenic sources such as crude oil, refining products, oil shale or coal. In coals, they are formed during diagenesis and catagenesis of organic matter. Total native concentrations of PAHs with two to six condensed aromatic rings including alkylated derivatives can reach hundreds or exceptionally few thousands of mg/kg in hard coals. Once released into the environment, coal particles play a pivotal role, amongst char coal, coke and soot, by carrying the predominant part of the (mostly) anthropogenic PAHs present in the sediment-water system. It is known that hard coal acts as a sink and source for hydrophobic organic contaminants, which is explained by strong sorption affinity and high capacity, compared to other organic matter.

Various concepts to describe the sorption-desorption characteristics of hydrophobic pollutants in the presence of different geosorbents have been established and the understanding of the related processes has improved steadily during the last decades. Coal is a very heterogeneous material depending on rank and origin and general characterization is difficult. Nevertheless, generally speaking, coal, and particularly hard coal and anthracite show high sorption capacities (comparable to black carbon) and nonlinear sorption behaviour.

The heterogeneities of coals also hamper general characterization of "coal" for source apportionment. Usually, PAHs from coal are catergorized amongst others, e. g., from oil as petrogenic PAHs. They can be characterized by substantial concentrations of alkylated naphthalenes, phenanthrenes and chrysenes, by a bell-shaped form of the parent and alkylated homologue series and by certain PAH-ratios based on thermodynmical stabilities of the single compounds. Various methods can be used to investigate the impact of coal-bound PAHs including coal petrography, PAH distribution patterns, PAH ratios, biomarkers, alkane distributions, principal component analyses, and others.

Until today, there is a lack of knowledge about native PAHs in coals, environmental forensic characterization of coals and the bioavailability of toxic compounds such as native PAHs or NSO-PAHs in coals of different rank and origin is limited, particularly with respect to mined coals from large coal basins worldwide.

1. Introduction

While we appreciate the importance of coal as an energy source, we must recognize the environmental impact of associated unintended emissions of coal particles into soils and sediments. Hard coal is a mass product and has been mined on a global scale for centuries. Worldwide hard coal production has increased from less than 1 billon tons in 1900 to 4.96 billion tons in 2005 (Thielmann et al., 2007). Due to mining, coal transportation and incomplete coal combustion, unburnt coal and coal-derived particles can be dispersed into soils and sediments (Schejbal-Chwastek & Marszalek, 1999; Johnson & Bustin, 2006). Once unburnt coal particles are released into the environment, they play a pivotal role amongst char coal, coke and soot by carrying the predominant part of the recalcitrant hydrophobic organic compound (HOC) load, such as polycyclic aromatic hydrocarbons (PAHs) present in the sediment-water system. It is known that they act as a sink for hydrophobic contaminants which is explained by strong sorption with high capacity compared to other organic matter (Kleineidam et al., 2002; Wang et al., 2007; Yang et al., 2007 & 2008a & b).

Doubtlessly, most PAHs in soils and sediments originate from incomplete combustion of organic matter resulting in their ubiquitous presence. On a more local scale, they may originate from e. g. oil spills, contaminated industrial sites or used motor oil (Masclet et al., 2000; Boehm et al., 1998; Stout & Wasielewski, 2004). Nonetheless, native PAH concentrations in coals reach up to hundreds or a few thousands of mg/kg formed during the coalification process (Achten et al. 2007; Achten & Hofmann, 2008, Radke et al., 1990; Willsch & Radke, 1995; Van Kooten et al., 2002; Pies et al., 2007; Ahrens & Morrisey, 2005; Hofmann et al., 2007). Thus, coal does not only behave as a sink for PAHs in sediments, but can also be a significant source.

If PAH-rich coals enter the environment, e. g. in soils and sediments, the numerous specific single compound PAHs mostly exhibit complex patterns because they often derive from various sources and source apportionment of the PAHs is necessary. Due to increasing environmental awareness, contaminated sites often are required to be remediated. However, responsibilties and liabilities need to be found and environmental forensic methods are used to ascertain the polluter who will finally have to pay the remediation costs. Due to the toxicity of the PAHs and for an approppriate risk management but also for forensic reasons, it is crucial to identify the PAH emission sources.

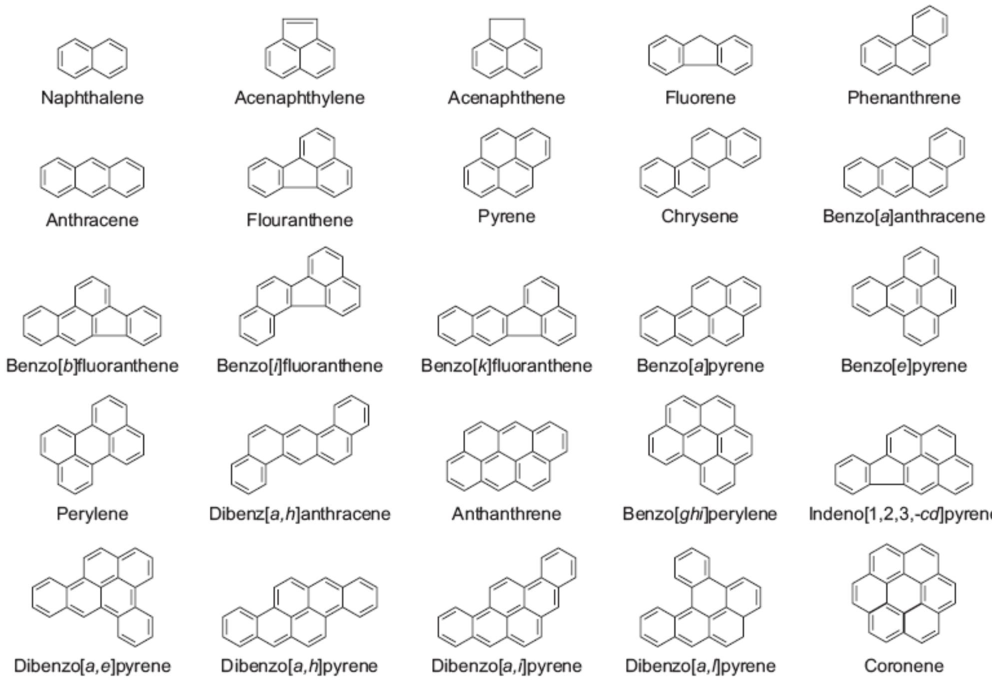

Figure 1. Parent compounds of polycyclic aromatic hydrocarbons (PAHs) including 16 EPA-PAHs. Alkylated derivatives of the different parent PAHs such as naphthalene, phenanthrene or chrysene are common in coals.

2. Polycyclic Aromatic Hydrocarbons (PAHs) in the Environment

2.1. PAH Characteristics, Properties and Toxicity

The chemical group of PAHs (Figure 1) comprises of hundreds of mostly carcinogenic substances. Many of them are ubiquitous in the environment and commonly detected using the recommended 16 selected compounds ranging from two to six aromatic condensed rings by the U. S. Environmental Protection Agency (EPA-PAHs). Due to the broad range of compounds, the behaviour of single PAHs varies widely from low to high molecular compounds. In short, PAHs up to three aromatic rings are commonly detected in surface and groundwater, the occurrence of higher molecular compounds is restricted by their low water solubility (Figure 2) and they are present in soils, sediments and other solids in the environment. Low molecular weight PAHs and specifically naphthalene easily evaporations under room temperature conditions. Based on water solubility, low molecular PAHs can be biodegraded more easily compared to higher molecular compounds which are generally characterized by higher toxicities. Aromatic compounds such as benzo[a]pyrene, dibenzo[a,l]pyrene and related isomers as well as 7,12-dimethylbenz[a]anthracene show significant carcinogenic and mutagenic activity (Bervall & Westerholm, 2006; IARC, 2006; WHO, 2000), and the latter two have only recently been included in environmental studies (Alexander & Alexander, 2000; Johnsen et al., 2006). Dibenzo[a,l]pyrene has been shown as the most carcinogenic organic substance ever tested and was given an equivalent factor of 100 compared to the most carcinogenic compound benzo[a]pyrene of the 16 EPA-PAHs (Deutsche Forschungsgemeinschaft, 2004). For many compounds, the toxic potential of individual PAHs is known but risks from PAH mixtures in the environment are mostly difficult to assess. Several studies could show synergistic as well as antagonistic interactions between low and high molecular PAHs (Hylland, 2006). Other researches demonstrated additive effects of parent PAH mixtures without alkylated substances. Therefore, the influence of alkylated PAHs could not be evaluated (Hermann, 1981; White, 2001). In contrast, Haugen and Peak (1983) reported an inhibition of mutagenic effects between PAHs which resulted in a lower toxicity. In hard coals, additional compounds to the EPA-PAHs such as alkylated naphthalenes, phenanthrenes and chrysenes play an important role.

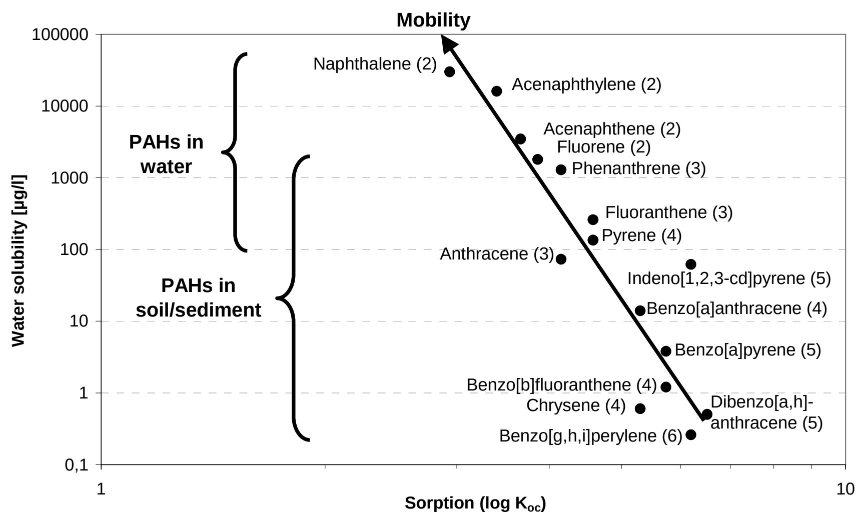

Figure 2. Water solubility with respect to sorption of PAHs to organic carbon (OC) expressed by the water-OC distribution coefficient indicating environmental behavior of PAHs in water-soil and sediment systems; numbers in brackets refer to amount of aromatic rings in the molecule

2.2. PAH Sources

Doubtlessly, most PAHs in the environment are of pyrogenic origin and derived from incomplete combustion of organic matter resulting in their ubiquitous presence (Lima et al., 2005). Additionally, on a more local scale, PAHs can originate from oil spills (Short et al., 2007), used motor oil (Stout et al, 2002a) or contaminated industrial sites such as manufactured gas plant sites (coal tar, coke) (Stout & Wasielewski, 2004), sites of wood treatment with creosote (Murphy & Brown, 2005), aluminium production (Booth & Gribben,

2005) or steel-making (Almaula, 2005). The occurrence of geogenically or anthropogenically (during refinement) produced petrogenic PAHs has been described in crude oil/petroleum, naphtha, fuels, diesel, bunker C (marine) fuels and lubricating oil (Stout et al. 2002a; Lima et al., 2005; Boehm et al., 2001; Wang & Fingas, 2006; Short et al., 2007). PAHs of biogenic origin such as retene, triaromatic triterpenoids/steroids or partially perylene are known but play a subordinate role in environmental investigations. Due to improved industrial and traffic emission standards, the impact of environmental PAH emissions from residential heating on the total PAH emissions is increasing in some countries and is the dominant emission source (70 %) in e.g. Austria.

PAHs in the environment exhibit highly complex patterns of individual compound concentrations and can often not easily be backtracked to a specific source but it can rather only be distinguished between pyrogenic and petrogenic origin. This is due to various influencing formation parameters such as nature of starting material, formation temperature and pressure, oxygen-supply, rearrangements and cleavages of the compounds and other controlling factors. Various attempts have been made to forensically characterize different emission sources, however, international literature about PAHs in coals formed during the coalification process is scarce.

2.3. PAHs in Coals

Unburnt hard coals (bituminous coals) are characterized by native PAH concentrations formed during diagenesis or catagenesis up to hundreds or exceptionally few thousands of mg/kg (Willsch & Radke, 1995; Püttmann & Schaefer, 1990; Radke et al., 1990 Kruge, 2000; Zhao et al., 2000; Van Kooten et al., 2002). The concentrations amongst the different coals vary significantly and it is indicated that maximum concentrations may occur within coal maturity in the range of the oil generation window at about 0.6 – 1.0 % vitrinite reflectance. However, this is not clear, because also high PAH concentrations occur at other ranks. Currently, PAHs in international hard coals are being studied also with respect to rank and origin (Achten et al., 2007; Achten & Hofmann, 2008). At low coal rank, such as brown coal, lignite or subbituminous coal, significantly lower concentrations of PAHs were detected (Chaffee & Johns, 1982; Bechtel et al., 2005; Püttmann, 1988). PAHs such as naphthalene, phenanthrene, anthracene, pyrene, chrysene, benzo[a]anthracene, perylene, benzo[a]pyrene, benzo[e]pyrene, benzo[b]chrysene, dibenzo[a,i]pyrene, dibenzo[a,h]pyrene and coronene were identified in Victorian brown coals from Australia (Kashimura et al., 2004). Radke et al., (1990) detected 243 mg/kg of total PAHs and 14 mg/kg of EPA-PAHs in subbituminous coal from the Wealden Basin, Germany. Regarding the opportunity of high PAH concentrations present in coals, this is surprising because much effort has been made in characterizing the various environmental PAH sources. With respect to the fact that coal is a mass product and has been mined on a global scale for centuries, coals as PAH sources in the environment cannot per se be regarded as negligible.

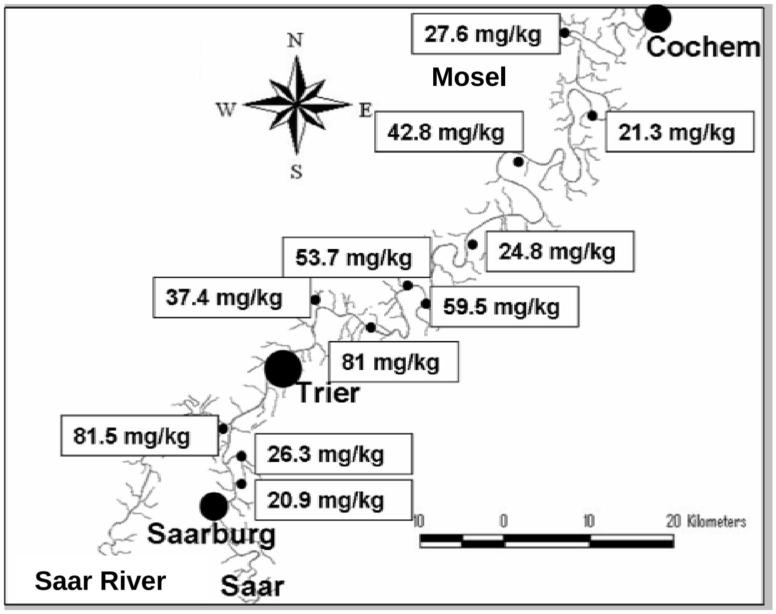

Figure 3. Sampling sites and maximum PAH concentrations (sum of EPA-PAHs, 1- and 2- methylated naphthalenes and perylene) in Saar and Mosel River floodplain soils, Germany, with permission from (Pies et al., 2007). The flow direction is from SW to NE and the Saar mining area is near Saarburg. Coal transportation by ships occurred from the mining area via the Saar River, towards NE into the Mosel River and further into the Rhine River.

3. Coals and PAH-Rich Coals in Sediments

In regions where coal is mined within large coal basins, enormous amounts of unburnt coal particles were and are emitted into the atmosphere, surface water, soils and sediments (Schejbal-Chwastek & Marszalek, 1999; Wagner, 2007; Johnson & Bustin 2006). Contemporary witnesses describe present coal dust in air and water often as “grey air”, “grey laundry on the clothesline” or “black river water”. On many industrial sites, coals are stored as stockpiles for the production of coke, gas or steam. The piles are subject to erosion by wind and water resulting in the distribution of black particles into the adjacent surrounding areas. Manufactured gas plant sites are known as sources for coal and coal derived particles such as coal dust and coke (Saber et al., 2006; Stout and Wasielewski, 2004). Additionally, spills during coal loading and transport or accidents by ships into freshwater or marine systems lead to a spreading of predominantly fine-grained particles into the surrounding soil, sediment and water. (Johnson & Bustin, 2006; Pies et al., 2007 & 2008; Chapman et al., 1996; Hofmann et al., 2007). In some areas, coal particles erode into aquatic systems from natural sedimentary rock outcroppings of coal seams (Stout et al., 2002b; Short et al., 1999). Due to the lower density of the carbonaceous fraction compared to the mineral fraction in soils and sediments, the black particles are preferentially transported and can accumulate in remote areas such as floodplain soils as reported by Pies et al. (2007 & 2008) and Yang et al., (2007 & 2008a & b). The authors investigated bank soil samples from the Saar and Mosel River which showed elevated PAH concentrations up to 80 mg/kg EPA-PAHs (Figure 3). The results showed, that predominantly former coal mining activities in the Saarland, Germany, upstream of the sampling sites are responsible for the PAH contamination in the downstream river sediments and floodplain soils. These studies confirmed, for the first time, that coal mining had resulted in a serious problem of an extensive PAH contamination in river floodplain soils. Until today, unburnt hard and brown coals have rarely been in focus as PAH sources in environmental research focussed on soils and sediments (Barrick et al., 1984; Stout et al., 2002b, Stout & Mattingly, 2008).

4. Identification of Geosorbents

Natural sediment and soil is not uniform, but consists of heterogeneous geosorbents which have different origin, formation, and physicochemical properties. These heterogeneous geosorbents exhibit widely different amounts and distribution patterns of PAHs. Organic carbon (OC) is thought to be the dominant geosorbent for PAHs if present in concentrations above about 0.1 % of natural soil and sediment organic matter (Johnson et al., 2001). Compared to OC, minerals in soils and sediments play a subordinate role, particularly at low total aqueous concentrations of the sorbate, which may result from the relative inaccessibility of surfaces to PAHs in aqueous solution due to the competitive sorption of water on the hydrophilic surfaces (Huang and Weber 1998). Humic substances, geopolymers (kerogens, coals) and black carbon (BC) from combustion and pyrolysis show different sorption-desorption characteristics and are the three main OC geosorbents in soils and sediments (Allen-King et al., 2002). In addition, “soft carbon” and “hard carbon” were defined by Weber (Weber et al., 1992) with respect to their physical and chemical characteristics. “Soft carbon”, such as geologically younger humic type organic matter (OM) can be hypothesized as amorphous and swollen soil organic matter (SOM), analogous to a rubbery polymer showing low sorption enthalpies, linear sorption behavior, noncompetitive exchange, rapid kinetics, and no sorption-desorption hysteresis. On the other hand, “hard carbon” is characterized by high sorption enthalpies, nonlinear sorption behavior, competitive exchange, slow kinetics, and possible sorption-desorption hysteresis. It can be envisioned as condensed and relatively rigid organic matrix, analogous to a glassy polymer such as kerogens and coals (Weber & Huang, 1996; Huang et al., 1997; Ran et al., 2004).

At present, no single method is able to quantify the entire continuum of carbonaceous geosorbents. Most importantly, many methods may artificially include non-pyrogenic carbon in their isolates and/or loss of hydrophobic soot-BC during solution handling (Middelburg et al., 1999; Elmquist et al., 2004). Chemothermal oxidation at 375°C in air (CTO-375 method) has often been used for the quantification of BC (Gustafsson et al., 2001). However, limitations of this method include (1) that it may remove also some less condensed pyrogenic constituents formed at lower combustion temperatures and (2) that particles with a high relative content of nitrogen may char to artificially form BC during combustion (Cornelissen et al., 2004; Elmquist et al., 2006).

A variety of methods such as elemental analysis and 13C-NMR are widely used to characterize organic geosorbents (Fernandes and Brooks 2003; Simpson and Hatcher 2004). However, such methods only provide general information about elemental or functional groups, and not about the heterogeneous constituents or the character of the organic matter. In contrast, organic petrography using optical microscopy enables the observation, identification, classification and quantification of heterogeneous OM in natural soil and sediment (Kleineidam et al., 1999; Ghosh et al., 2000; Rockne et al., 2002). With the application of organic petrography, Ligouis et al. (2005) distinguished three major groups of organic matter: (1) Recent OM that consists of woody phytoclasts, humic gels, suberinized tissues, fungal phytoclasts, pollen, spores and recent charcoal. This organic matter is for example typical of soils and of recent sediments in lakes and rivers. (2) Fossil OM that consists primarily of pollen, spores, algae, amorphous OM, xylite, coal, vitrite and fossil charcoal. Coal in this group corresponds to eroded and re-sedimented coal particles which can occur in clastic sediments. (3) Airborne OM is composed of particles of raw brown and hard coal, charcoal, brown- and hard-coal coke, char (including soot) and asphalt.

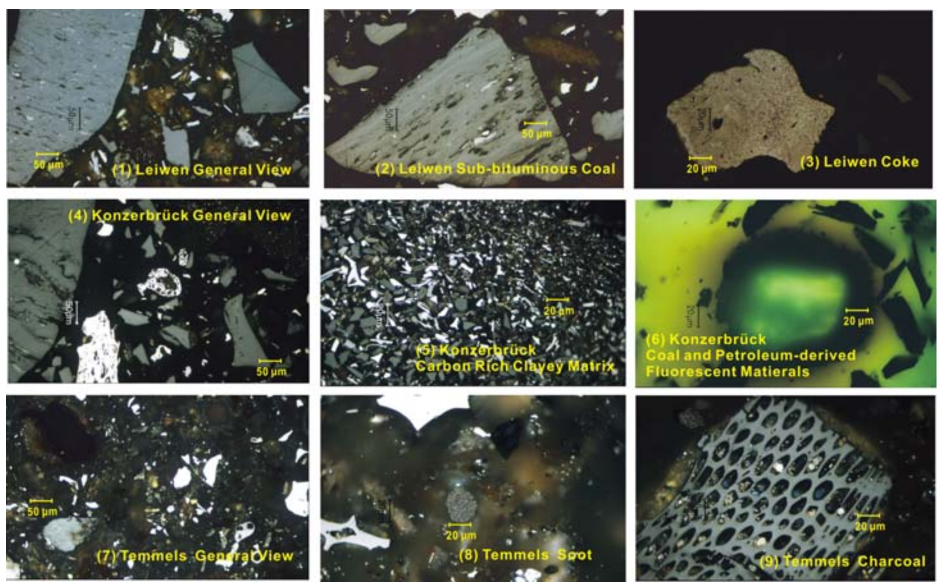

Figure 4. Photomicrographs showing different carbonaceous particles identified by organic petrography techniques in the light fractions (<2 g/cm^3) of soil samples collected from Mosel River floodplain soils, Germany: (1) and (2) coal (grey particles) and isotropic coke (white particles); (3) anisotropic coke (coke matrix with fused and unfused inclusions); (4) coal (grey particles) and char (white spheroidal particles with vesicles, center); (5) numerous small coal and coke particles embedded in a dark clayey matrix; (6) coal tar pitch particle producing greenish fluorescent hydrocarbons during UV-light excitation, note the high yellowish fluorescence of the embedding resin surrounding the pitch particle (resin acts as a chemical extractor); (7) dark asphalt or weathered coal tar particle (top left corner), coal (grey particle, bottom left), coke (white particles); (8) subrounded soot particle with grainy texture (centre), (9) well-preserved large particle of low reflecting charcoal. (1, 2, 4, 5, 7, 8, 9) white reflected light, oil immersion; (3) reflected plane-polarized light, oil immersion; (6) UV fluorescence mode, oil immersion. With permission from (Yang et al., 2008a).

Organic petrography was successfully applied to the light fractions (<2 g/cm^3) of Saar and Mosel River floodplain soils showing that at the heavily Saar coal impacted sites 75 - 90 % of the total PAHs mass was associated with mainly coal particles although the light fraction made up only 5 – 20 % of the total soil mass (Yang et al., 2008b). At these sites, about 45 – 75 % of hard coal (Saar coal) particles were identified in the light fractions. The soils near the Mosel River upstream of the confluence of the Mosel and Saar River (not along the Saar coal transportation route) revealed only about 15 % Saar coal particles in the light fraction. Here, more PAHs were associated with the heavy fraction (>2 g/cm³) and PAH patterns differed from the other sites indicating mineral oil contamination. Figure 4 shows an example of OMs with the application of organic petrography identification in river floodplain soils impacted by former coal mining activities.

In these samples, the optical properties of the coal particles are typical of particles from the industrial activity related to coal mining. Particles from coal industry and mining are larger, show little or no alteration, are not corroded and possess angular outlines in comparison to coal particles derived from ancient sediments which are generally very small (smaller than 30 µm), corroded and exhibit an oxidation rim at their periphery. Coal particles counted as vitrite are highly fragmented bituminous coal particles (fine coal dust) that contain only the maceral vitrinite (monomaceral particle in contrast to coal containing vitrinite, liptinite and inertinite, occurring as trimaceral particles). Fluvial and atmospheric emissions of coal dust and particles are clearly related to the former intensive coal mining production and treatment of coal.

5. Sorption and Desorption

5.1. Sorption

In soils and sediments, sorption includes adsorption and absorption. Adsorption describes a process in which the solute accumulation is generally restricted to a surface or interface (e. g. solid/liquid, solid/gas, liquid/gas). In contrast, absorption describes a process in which the solute penetrates the sorbent – similar to the solution in a solvent (Grathwohl, 1997). Due to the heterogeneous nature of soils and sediments, both processes may take place simultaneously, and cannot be separated from each other experimentally. Desorption is a process involving interphase mass transfer of e. g. PAHs from a solid phase of soils and sediments to a liquid phase of water. Sorption-desorption of soil and sediment bound PAHs is an important process because it controls fate and ecotoxicological risk of these contaminants in the aquatic environment.

Many studies demonstrated that sorptive distribution coefficients of HOCs between soils or sediments and aqueous solutions are proportional to both the content of OC and the hydrophobicity of the solutes (Chiou et al., 1979). This sorption interaction between sorbents and HOCs, such as PAHs, has been found to be characterized by low sorption energies (i. e. low exothermic enthalpies) and to be likely dominated by nonspecific and weak intermolecular interactions (van-der-Waals forces) including dipole-dipole, dipole-induced dipole and instantaneous dipole-induced dipole interactions (Grathwohl, 1997). Furthermore, recent studies have shown that the amounts and binding of PAHs to heterogeneous geosorbents in soils and sediments vary widely (Cornelissen et al., 2000; Ghosh et al., 2000). A simple and widely adopted model to describe the partitioning of a substance between the aqueous and the OC phase makes use of the partitioning coefficient (K_p):

$$C_s = K_p C_w = f_{oc} K_{oc} C_w \tag{1}$$

where C_s and C_w are the equilibrium solid phase and aqueous phase solute concentrations, respectively, and f_{oc} is the fraction of OC. If normalized to OC, this distribution coefficient (K_{oc}) for water is often constant for a wide variety of geosorbents and under various aqueous phase solute concentration conditions. K_{oc} can be estimated from the solubility (S) and octanol-water partitioning coefficient (K_{ow}) of the target compound (Chiou et al., 1979; Karickhoff, 1980; Schwarzenbach et al., 1993). For many compounds of low solubility, the K_{ow} seems more reliable or more frequently available than S, therefore the linear free energy relationships between K_{ow} and K_{oc} for HOCs are often used, such as

$$\log K_{oc} = 0.99 \log K_{ow} - 0.35 \quad \text{(Seth et al, 1999)} \tag{2}$$

The empirical Freundlich model is widely used to describe nonlinear sorption:

$$C_s = K_{Fr} C_w^n \tag{3}$$

where K_{Fr} (e. g. mg kg^{-1}/ (mg $L^{-1})^{1/n}$) and n [-] are the Freundlich sorption coefficients and the Freundlich exponent, respectively. Due to the heterogeneity of geosorbents in sediments, also a composite distributed reactivity model (DRM) is used to quantify the sorption data (Weber, 1992). The logic underlying the DRM is that sediments can be treated as the combination of active organic and inorganic components with respect to sorption equilibria. Each component has its own sorption energy and sorptive property, and exhibits either a nonlinear or a linear sorption behavior. The overall sorption isotherm can be described in the form of:

$$C_s = X_L K_{p,L} C_w + \sum_{i=1}^{m} X_{NL}^{i} K_{Fr}^{i} C_w^{n_i} \tag{4}$$

where X_L and X_{NL} are the mass fractions of the solid phase exhibiting linear and nonlinear sorption behavior, respectively. m is the number of discrete reactive sorption domains. Accardi-Dey & Gschwend (2003) successfully applied a BC-inclusive Freundlich sorption model in a sorption experiment of pyrene in the presence of environmental BC by the following term:

$$C_s = f_{OC} K_{OC} C_w + f_{BC} K_{BC} C_w^n \tag{5}$$

where f_{BC} and K_{BC} are the sediment mass fraction of BC, and the Freundlich BC-water distribution ratio, respectively. For all heterogeneous geosorbents in sediments that show non-linear sorption behavior, the combined Freundlich model should be appropriate:

$$C_s = \sum_{i=1}^{m} K_{Fr} C_w^{ni} \tag{6}$$

The Polanyi-Manes model is postulated to follow a pore-filling mechanism, which was first applied by Xia & Ball (1999), and later applied by other research groups (Kleineidam et al., 2002; Ran et al., 2004) to describe sorption of several HOCs by selected natural soils and sediments. The Polanyi adsorption model originally was set up for the quantification of the adsorption of gas molecules to energetically heterogeneous solids, and was extended to a wide range of vapor and liquid phase systems by Manes and his co-workers. The Polanyi theory considers that, for a molecule located within the attractive force field of a micro-porous solid, it exists an adsorption potential (ε) which is defined as the energy level required removing the molecule from the location to a point outside the attractive force field of the solid surface. For adsorption of partially miscible solutes from aqueous solution, the effective adsorption potential (ε_{sw}, cal/mol) can be defined as:

$$\varepsilon_{sw} = RT\ln(S_w/C_{eq}) \tag{7}$$

where S_w is the water solubility and C_{eq} the aqueous solute equilibrium concentration.

Dubinin suggested a plot of adsorbate volume against adsorption potential density (adsorption potential divided by sorbate molar volume). Following, Crittenden et al. (1999), suggested the following empirically derived relation between adsorbed volume and adsorption potential (ε):

$$\log(Cs) = \log(V_0) + a(\varepsilon_{sw}/V_s)^b \tag{8}$$

where V_O is the adsorption volume capacity at saturation per unit mass of sorbents (cm^3/kg), V_S is the molar volume of the solute (cm^3/mol) and the exponent b is often set to an integer. For b = 2, the Dubinin Radushkevich equation is obtained, which corresponds to a log-normal distribution of the sorption energies (Condon, 2000). Exponents of b larger than 2 are commonly found in some activated carbons showing a Weibull pore size distribution (Roque-Malherbe, 2000).

Hence, for heterogeneous geosorbents, the combined adsorption-partitioning model is described by a Polanyi-Manes type of modeling approach:

$$C_s = V_0 \times 10^{a(\varepsilon_{sw}/V_s)^b} \times \rho + f_{oc}K_pC_w \tag{9}$$

where a can be calculated as $-\frac{1}{2.3}(\frac{V_s}{E})^b$.

Kleineidam et al. (2002) used this combined model in the form of:

$$C_s = V_0 \times \exp[\frac{-RT(-\ln(\frac{C_w}{S}))}{E}] \times \rho + f_{oc}K_pC_w \tag{10}$$

In a recent study, sorption experiments have been performed with coal impacted soil samples. The light fraction (ρ <2 g/cm^3) showed high sorption capacity comparable to low rank coals (Yang et al., 2008c) which was about a factor of 100 higher than that of the heavy, predominantly mineral fraction of the soil. Sorption was strongly non-linear and the combined partitioning and pore filling model fitted better than the Freundlich sorption model (Figure 5).

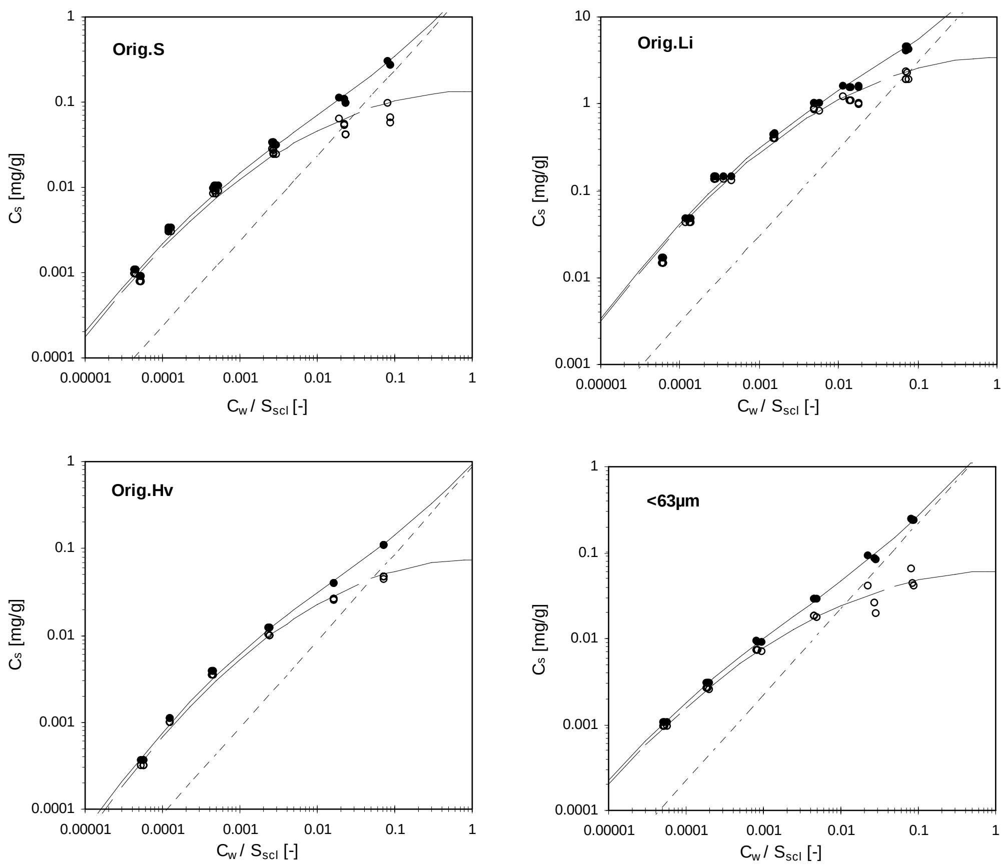

Figure 5. Combined pore-filling and partitioning sorption isotherm for phenanthrene (eq 10). Solid line: combined isotherm; dashed line: pore-filling part; dotted line: partitioning part. The partitioning part was predicted on the basis of the empirical relationship in eq 2.; open symbols indicate calculated data for the pore filling part. Orig.S: original soil sample; Orig.Li: light fraction (ρ <2 g/cm^3); Orig.Hv: heavy fraction (ρ <2 g/cm^3); <63 μm: <63 μm fraction. With permission from (Yang et al., 2008c).

5.2. Sorption-Desorption Hysteresis

Hysteresis describes the irreversible sorption during sorption-desorption of PAHs to soils and sediments and has gained more and more attention because it is important for the fate and remediation of contaminants. Recently, studies have shown that the sorption-desorption hysteresis, that is, K_d values measured from desorption process under equilibria (Huang & Weber, 1997; Kan et al., 1998; Ran et al., 2003) or under “aging” conditions (Alexander,

2000) were higher or much higher than those from the sorption process. For the convenience of comparing sorption and desorption, a residual-concentration-specific relative sorption-desorption hysteresis index (HI) was defined by Huang et al., (1998):

$$\mathrm{HI} = \left. \frac{q_e^d - q_e^s}{q_e^s} \right|_{T,C_e} \tag{11}$$

where q_e^s and q_e^d are solid-phase solute concentrations for the single-cycle sorption and desorption experiments, respectively, and the subscripts T and C_e specify constant conditions of temperature and residual solution phase concentration, respectively. For example, these indices are higher for geologically older shale and kerogen materials compared to younger humus-rich materials in soils and sediments (Huang et al., 1997).

The mechanism of the sorption-desorption hysteresis is not yet clear. Reasonable hypotheses were considered, such as entrapment of sorbed molecules into meso- and microporous structures with inorganic components of soil aggregates (Farrell & Reinhard, 1994) and irreversible sequestration of PAHs to certain components of soil aggregates, for example, the sorbent reconfiguration leading to physical entrapment of sorbates (Lu & Pignatello, 2002; Braida et al., 2003; Sander et al., 2005). However, artifacts during the experiments can occur and cause “pseudo-hysteresis”. They can result from the kinetics of the sorption-desorption process and a nonattainment of the equilibrium state, from the losses of the solute to reactor components and from the “solid effect” of dissolved macromolecular and colloidal organic matter (Young & Weber, 1995; Huang et al., 1998; Sander et al., 2005). Sabbah et al. (2005) showed that time is an important factor and they simulated sorption-desorption at a variety of time scales and concluded from the results that the sorption-desorption rates were controlled by sorption-retarded diffusion. They showed that even 50 days were far too short for the equilibration of phenanthrene and that sorption-desorption hysteresis vanished after 1,000 days pre-equilibration. Wang et al. (2007) developed a new sorption-desorption experimental protocol where the sorption-desorption process is driven by temperature changes to avoid artifacts instead of using the classic decant-refill method. In their sorption-desorption study, no significant hysteresis occured for the sorption-desorption of phenanthrene from peat, lignite and high-volatile bituminous coal.

5.3. Slow and Very Slow Desorption

Recently, several desorption kinetic studies showed a two-stage desorption: a rapid stage of a “labile” sorbed fraction (hours) followed by a slow desorption (days to months) of a nonlabile fraction. In addition, a very slow desorption stage (years) after the slow one was also observed (Cornelissen et al., 1998, 1999 & 2000) further supporting the hypothesis that bioavailability is limited by mass transfer kinetics. They also showed in their studies that it was only the rapidly desorbing fraction which was removed by biodegradation. The slow and very slow desorption of compounds from natural sorbents cause great attention, because they could be an obstacle in remediation, and are challenging concepts of cleanup standards and risk assessments (Luthy et al., 1997). However, desorption of PAHs from natural soils and sediments result from many interacting factors which are still not clear. Different techniques and methods have been applied to study the desorption of PAHs from soils and sediments, including long-term batch experiments (Kleineidam et al., 2004), column leaching experiments, desorption experiments with the use of sorbents, such as Tenax beads or XAD-4 (Carrol et al., 1994) as “infinitive sink” for desorbed solutes to mimic and measure the kinetics of the PAH desorption (Cornelissen et al., 1997, 1998 & 2001; Ten Hulscher et al., 2003). Recently, other techniques have emerged, such as using microprobe laser desorption laser-ionization mass spectroscopy (μL^2MS) (Ahn et al., 2005), semipermeable membrane devices (SPMD) and temperature-programmed desorption (TPD). Supercritical fluid extraction (SFE) was used to show that PAHs bound to the majority of carbonaceous geosorbents were observed to desorb over a time scale of decades to centuries (Jonker et al., 2005; Yang et al., 2008d).

The processes underlying the formation of resistant desorption are not well understood. Retarded diffusion is usually suggested to explain the slow desorption. This retarded diffusion either occurs through the organic matter matrix or entrapment, or through and along the walls of intraparticle micropores (Pignatello & Xing, 1996). Diffusion is an activated process and therefore it is positively temperature-dependent in an Arrhenius-like way. Aqueous desorption kinetic tests and TPD were used to evaluate phenanthrene diffusivities and desorption activation energies. It was indicated that the fraction of phenanthrene mass not diffusing from soils was located within micropores and narrow width mesopores (Abu & Smith, 2006). Cornelissen et al. (1998) used Tenax bead extraction and concluded that the observations for XAD-8 materials (in which slow desorption is assumed to be caused by slow diffusion along hydrophobic pore walls) were most similar to the ones for the sediment, indicating that diffusion through pores in the organic matter or pores coated with organic material play roles in slow desorption. Furthermore, desorption experiments of PAHs were predicted with the retarded intraparticle pore diffusion model. Extremely slow desorption kinetics are thought to occur due to the relatively long diffusion distances to the sorption sites inside the grains of soil samples, such as the carbonaceous microparticles (Ahn et al., 2005) and the sorption related retardation of solute diffusion in the water-filled pores (Kleineidam et al., 2004). However, it was suggested that intra-OM diffusion is not the mechanism of slow or very slow desorption due to the narrow range between the slow and very slow desorption rate constant. On the basis of this mechanism, it would be expected that an increasing OC content would lead to longer diffusion path lengths and, consequently, to smaller rate constants. In addition, it was suggested by Cornelissen et al. (2000) that desorption is fast from linearly sorbing organic matter, whereas, it is slow and very slow from nonlinearly sorbing sites.

6. SOURCE APPORTIONMENT

Due to the complex nature of the occurrence of PAHs in the environment, several attempts have been made to identify the different emission sources. Oil spills, such as the *Exxon Valdez* oil spill in 1989, are of great concern. In spite of the fast removal of almost all spilled crude oil in Prince William Sound, Alaska, there was concern that oil residues have been transported offshore. Therefore, petroleum chemical fingerprinting techniques were applied including analyses of stable carbon-isotopes, terpane biomarkers and PAHs (parent and alkylated) (Boehm et al., 1997). In the same region, outcropping coal deposits are known and Short et al. (1999) identified local coal as a more plausible source of backround hydrocarbons compared to oil seeps. They used total PAH concentrations and patterns, and calculation of triaromatic steranes to methylchrysenes ratios. Van Kooten et al. (2002) noted that these coals may only be a possible source in the area due to more complex PAH distributions. Additionally, this region is at present and was in the past strongly influenced by human activities such as active settlements, fish hatcheries, campsites and abandoned settlements, canneries, sawmills and mining camps. These activities caused inputs of mainly pyrogenic PAHs (Page et al., 1999) and a great variety of these compounds are present in the region which hampers source identification of the PAHs.

Besides the aforementioned forensic methodes, other identification methods exist. Apart from PAHs, other hydrocarbons may be included to further indicate a specific emission source. For example, biomarkers, such as isoalkanes, isoprenoids, steranes and terpanes were used for fingerprinting of crude oil, weathered crude oil, fuels and coal (Barrick et al., 1984; Kaplan et al., 1997 & 2001; Wang & Fingas, 2003). Barrick et al. (1984) detected pimarane-type C19 and C20 diterpanes typical for coal whereas triterpenes were of minor significance.

Comparing the distribution of n-alkanes with odd and even carbon numbers is helpful to detect oil, coal and fuel sources such as hydraulic or lubricating oils, diesel or gasoline. Therefore, the carbon preference index (CPI) is used, providing information about biogenic/terrestrial and petroleum inputs as well as pristane/phytane ratios and the n-alkane pattern (Radke, et al., 1980; Colombo et al., 1989; Stout et al., 2001 & 2002; Tolosa et al., 2004; Wu et al., 2007; Yunker and Macdonald, 2003).

Weathering and a mixture of different contaminations hamper exact source identifications. Diffuse sources of contaminants (in the background) are difficult to characterize (Pies et al., 2008; Stout et al., 2001). Pies et al., (2008) concluded in their study that in complex mixtures, the analysis of parent PAHs is beneficial for the identification of pyrogenic sources and the analysis of alkylated PAHs is essential to identify petrogenic sources. The study clearly shows the importance of analysing a broad spectrum of PAHs in complex mixtures. As a consequence of their study, they suggest a concept for source identification of particularly coal-impacted river bank soils which includes collection of site history information, coal petrography investigations, analyses of parent and alkylated PAHs, calculation of PAH ratios, n-alkane analyses, use of C1-C4 homologue series, if data are available, and the use of PCA if chemical characteristics are of interest. In the following the investigation of PAH distribution patterns, PAH ratios and PCA as significant source identification methods are described more in detail.

6.1. PAH Distribution Patterns

PAH distribution patterns consider the relative concentration of each single PAH. Low molecular weight PAHs with two to four fused aromatic rings as well as their alkylated homologues are major constituents of petroleum and coals (Fernandes et al., 1997; Stout et al., 2002a & b), and alkylated PAHs are more abundant than their parent homologues (Sporstöl et al., 1983; Stout et al., 2002a & b). Furthermore, homologues with two to three alkyl carbons are usually more abundant than homologues with more or less numbers of alkyl moieties, and thus the distribution of alkyl PAHs shows a bell shaped characteristic with respect to the degree of alkylation. Pies et al., (2008) determined PAH distribution patterns of individual coals and could confirm the bell shaped PAH distribution in the coal. The soil containing petrogenic PAHs which predominantly derive from particulate coal also shows this distribution of the lower molecular PAHs. However, these soils also show pyrogenic inputs (Figure 6). For the coal-rich soil, coal and a coexisting pyrogenic source were detected in the soil.

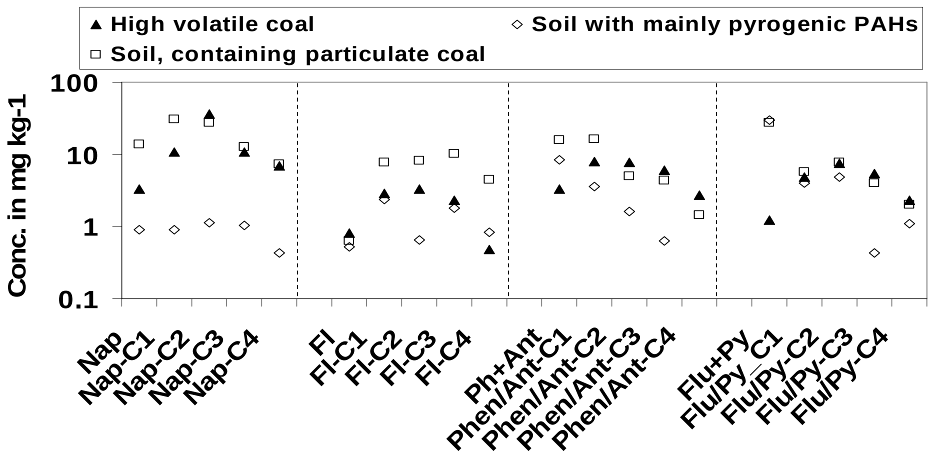

Figure 6. PAH alkyl homologue profiles of a high volatile bituminous coal, a soil containing mainly pyrogenic PAHs and a soil containing a mixture of petrogenic (predominantly particulate coal) and pyrogenic PAHs (Pies et al., 2008), modified

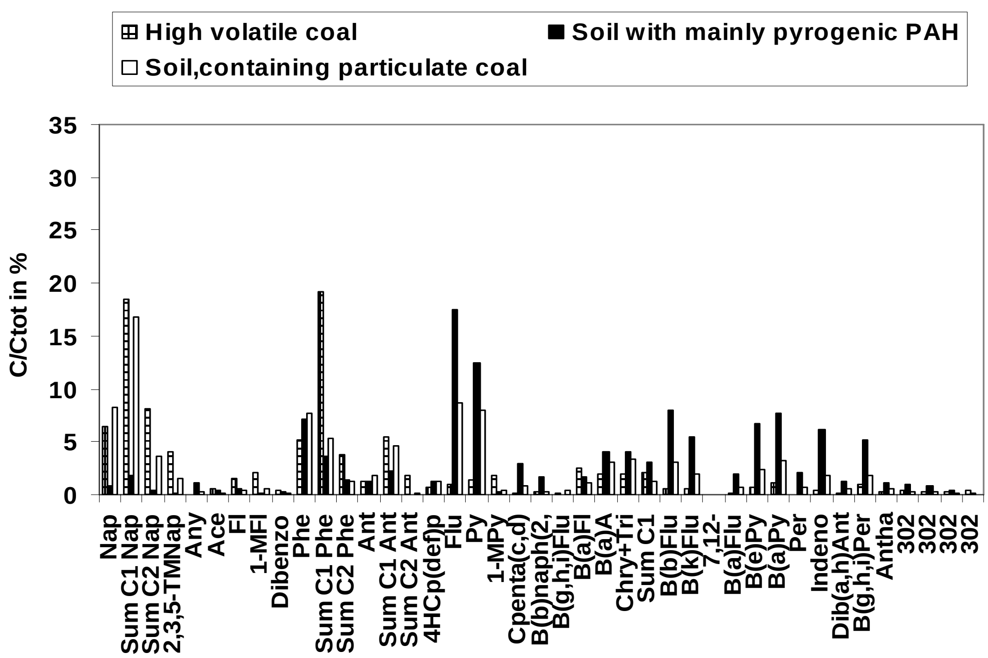

Figure 7. PAH distribution patterns of a high volatile bituminous coal, a soil with mainly pyrogenic PAHs and a soil containing particulate coal (Pies et al., 2008), modified

In general, high molecular weight PAHs with four to six rings are generated mainly by incomplete combustion of organic matter (e. g. fluoranthene, pyrene, benzo[ghi]perylene) (Fernandes et al., 1997). Pyrogenic sources are characterized by dominanting unsubstituted, parent PAHs or by a homologue series with only one or two alkyl substitutes and higher alkylated homologues are missing (Sporstöl et al., 1983; Stout et al., 2002 b).

The coexistance of coal (petrogenic PAHs) and pyrogenic PAHs in one of the investigated soils was confirmed by increased alkylated naphthalene and phenanthrene concentrations which are characteristic of some coals (Willsch & Radke, 1995). On the other hand, soil with predominantly pyrogenic PAHs showed increased characteristic four to six ring parent PAHs (Figure 7).

6.2. PAH Ratios

The use of single PAH compound ratios bases on the different thermodynamical stabilities of different single compounds. For distinguishing between petrogenic and pyrogenic sources PAH ratios of phenanthrene/anthracene or fluoranthene/pyrene are used (Yunker et al. 2002). For example, a phenanthrene/anthracene ratio >10 is indicative for a petrogenic source whereas <10 for a pyrogenic source and a fluoranthene/pyrene ratio >1 is indicative for a pyrogenic source whereas <1 for a petrogenic source.

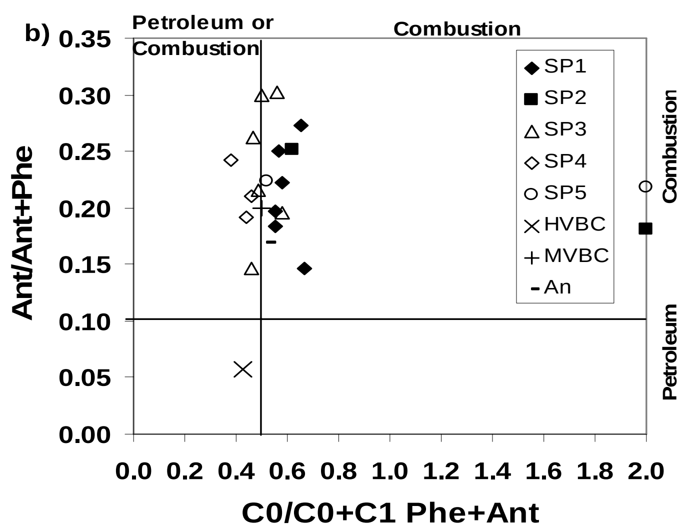

Figure 8. Cross plot C0/(C0+C1) of phenanthrene/[phenanthrene+(C1 phenanthrene+anthracene)] ratios versus Ant/(Ant+Phe) ratio (Yunker et al. 2002) for SP1 to SP5 and coals. With permission from (Pies et al., 2008).

The degree of alkylation can also be used for source apportionment. PAHs formed under low temperature conditions exhibit a great amount of alkylated derivates. The degree of alkylation decreases with increasing temperature (Lima et al., 2005). Hence, ratios of substituted and unsubstituted PAHs are crucial for source identification. Yunker et al. (2002) described a variety of ratios which can be indicative of individual sources. However, in a cross plot of anthracene/(anthracene+phenanthrene) to the $C_0/(C_0+C_1)$ phenanthrene and anthracene ratio, various investigated coal samples from the Saar and Ruhr mining region, Germany, plot not only in the petrogenic but also in the pyrogenic section (Figure 8) (Pies et al., 2008). PAH ratios from coals are ambiguous and allow a number of possible interpretations. Therefore, the determination of only PAH ratios are not an unambiguous method to detect coal particles in environmental samples.

6.3. Principal Component Analysis (PCA)

Exploratory statistical methods in the form of PCA are also often applied in attempts to identify contaminant sources (Burns et al., 1997; Ko et al., 2007, Kruge, 2000). Using this method, high information density is reduced to its most important or "principal" components. Additionally, the method permits the visualization of results, thus showing the general difference between samples. A factor score plot of the first and second principal components derived from 45 PAHs at 5 sampling sites at the Mosel River site is shown in Figure 9 (Pies et al., 2008). The plot clearly shows a correlation between sampling sites SP1 and SP2, which are mainly impacted by pyrogenic PAHs and a correlation between sampling sites SP3, SP4 and SP5 which are rich in coal particles (petrogenic signature). The use of PCA for data analysis can provide a better understanding of the differences between samples and therefore the contamination sources.

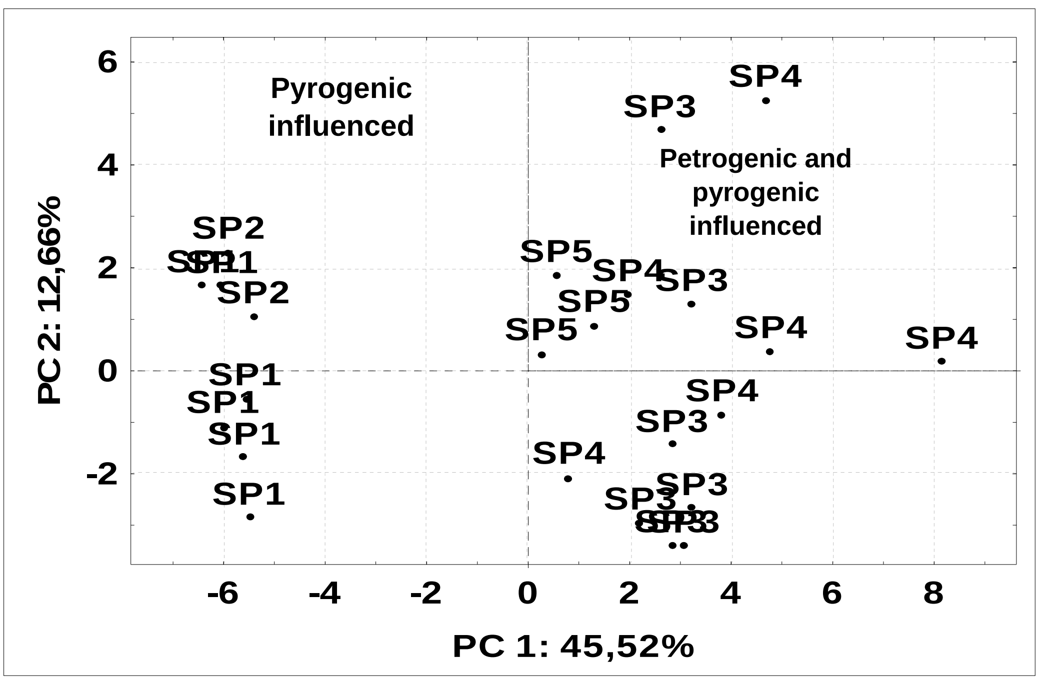

Figure 9. Principal component analysis visualizing samples plotting in the pyrogenic section and in the petrogenic and pyrogenic section due to PAH distributions. With permission from (Pies et al., 2008).

7. Conclusions

From an environmental perspective, notwithstanding the limited knowledge which has been gained until today about native PAHs in coals, it cannot be doubted that unburnt coal particles from mining activity can be abundantly present in adjacent soils and sediments. Due to their low density of coal particles, they are preferentially transported over large distances by air and water, and finally sedimented in remote areas. Native PAH concentrations including many compounds with significant carcinogenic and mutagenic activity have been detected in hard coals up to hundreds of mg/kg and exceptionally up to few thousands of mg/kg. The composition and rank of different coals vary widely. Due to high sorption capacities of coals (which are in a similar range as black carbon) compared to other geosorbents, emitted unburnt coal particles can act as source and sink of PAHs simultaneously.

For the evaluation of the environmental impact, key factors are the nature and amount of the freely water dissolved PAH concentrations from the different coals. Moreover, bioavailability from other pathways such as PAH mobilization from the coal during uptake by exposed organisms which is highly depending on the “extracting” digestive gut fluids needs to be known to estimate direct human uptake of PAHs from coals. As a result, if the pollutants are not or not significantly desorbed from the coal into water or into an organism, they cannot evoke (full) toxic effects and are subsequently released by the organism. Thus, even if PAHs are present in coal-rich sediments, they may not affect organisms. Hard coal, alike black carbon, acts as a very strong sorbent and these effects should be taken into account in future sediment and soil quality criteria.

Until today, there is a lack of knowledge about native PAHs in coals, environmental forensic characterization of coals and the bioavailability of toxic compounds such as native PAHs or NSO-PAH in coals of different rank and origin is limited, particularly with respect to mined coals from large coal basins worldwide.

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Chapter 3

MONITORING ACTIVITIES OF LEACHING MICROORGANISMS AT COAL MINING SITES

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ABSTRACT

One side effect of coal mining is the formation of acidic drainage waters, resulting from microbial oxidation of inorganic sulfur compounds, such as pyrite or elemental sulfur, to sulfuric acid. In the course of this process, the pH of the drainage waters can drop to values of about 1 to 2. Therefore, the responsible microorganisms are adapted to this special environment as they are truly acidophilic. The same bacteria and archaea are employed in operations for winning of metals from sulfidic ores and are called leaching prokaryotes. Their substrate, the reduced sulfur compounds, is naturally occurring in both hard coal and lignite. The bacterial oxidation process starts when the coal is exposed to air and water, e.g., due to mining and accompanying measures, such as lowering the groundwater level. The acidic water, generally called Acid Mine Drainage (AMD) and often laden with toxic amounts of heavy metals, tends to pollute groundwater, lakes and rivers. Mitigation of AMD processes focus on the inhibition of bioleaching activities. Hence, for evaluation of these remediation measures, reliable monitoring methods for assessing the prokaryotic activities at AMD sites are required. Therefore, we have developed a robust and rapid test system combining two sensitive analytical techniques: quantification of heat evolution by microcalorimetry and determination of all relevant inorganic sulfur species by chromatographic methods. The combined test has been applied to various coal mining sites. In this chapter, the results of two case studies, a hard coal and a lignite site in Germany, respectively, will be presented. Furthermore, additional microbiological methods will be discussed possibly helping to deal with the AMD phenomenon.

INTRODUCTION

Coal deposits and adjoining strata normally contain significant amounts of metal sulfides, dominantly pyrite or marcasite (both FeS_2, but with different crystal structures). In the course of coal mining, air and water gain access to the seams containing the metal sulfides. The latter are oxidized to sulfuric acid, resulting in acidic heavy metal-contaminated drainage waters, which have pH values of 1 to 3 and which are attributed to as Acid Mine Drainage (AMD) or Acid Rock Drainage (ARD). This phenomenon is an inseparable part of coal mining since historical times, and both underground and surface mining operations are equally affected (Dugan 1975; Evangelou 1995; Lowell 1983; Nordstrom 2000). In addition, AMD can be observed at natural sites where coal and its associated metal sulfides are exposed to the surface and thus weathering can occur. In mining operations, AMD formation is not restricted to the exposed coal seam but will also occur in the waste heaps containing low-grade coal, overburden, shale and other materials. This is due to the fact that all these materials can contain pyrite or other metal sulfides, which are readily oxidized when exposed to air and water. Consequently, also abandoned mining sites are affected, as long as oxidizable metal sulfides are present.

For a long time, AMD formation was attributed simply to abiotic oxidation processes. However, in 1919, Powell and Parr already suggested a bacterially catalyzed pyrite oxidation (Powell and Parr 1919). Not earlier than 1947, Colmer and Hinkle implicated in their pioneering work the coal mining-associated AMD with the activity of a bacterium which oxidizes Fe(II) to Fe(III) ions at acidic pH (Colmer and Hinkle 1947). In further studies, the biology and ecology of this new bacterial species was elucidated and its role in AMD formation confirmed (Leathen et al. 1953; Silverman et al. 1961; Temple and Colmer 1951; Temple and Delchamps 1953). Due to its special capacities of oxidizing both inorganic sulfur compounds and Fe(II) ions, this microorganism was originally described as *Thiobacillus ferrooxidans* (Colmer and Hinkle 1947). Recently, it was renamed as *Acidithiobacillus ferrooxidans* (Kelly and Wood 2000). Today, we know much more about the microorganisms thriving at AMD sites. It has clearly been shown that *At. ferrooxidans* and many other acidophilic species play a crucial role in AMD formation. These microorganisms are called leaching prokaryotes (bacteria plus archaea), as they can be employed for metal extraction from sulfidic ores (Bosecker 1997; Rawlings 2002; Schippers 2007).

AMD may give rise to several problems. The acidic solution usually contains a high concentration of Fe(III) ions having corrosive effects on mining equipment, i.e. any metallic object employed for water pumping etc. More serious, the environment, i.e. the soil, surface water and groundwater, can be significantly and for a long-term polluted by heavy metals and acidification. In the past, this unpleasant side effect of mining has been widely neglected or even tolerated. Consequently, worldwide large areas became unsuitable for many years with respect to agricultural, urban or recreational use. Growing ecological awareness and legislation, however, force mining companies and state agencies into alliances in order to fight effectively against AMD or at least to reduce its impact on the environment. However, we still have not developed any well-working short-term solution for the AMD problem (Evangelou 1995). It is possible, on the one hand, to treat the drainage water by routing it through constructed wetlands (Brenner 2001; Kalin et al. 2006). In this approach, the leaching products, Fe(III) ions, other heavy metals and sulfate, are reduced by activity of sulfate-reducing and other anaerobic prokaryotes and precipitate as metal sulfides in the sediments of the wetlands. On the other hand, AMD can be directly treated at its source. A standard method for the abatement of AMD is the addition of neutralizing chemicals such as limestone to the waste materials brought to the surface in the course of coal mining (Backes et al. 1993; Evangelou 1995). This treatment is quite costly as the waste has to be thoroughly mixed with the buffering reagent and neutralization has to be quantitative, i.e. acid production potential must be completely balanced by buffering capacity. In addition, physical barriers, such as plastic or clay liners, are constructed for preventing transfer of water and oxygen. An alternative could be the encapsulation of the pyrite by phosphate coatings (Evangelou 1995). Other proposals focus on the inhibition of the involved prokaryotes, e.g. by chemicals such as benzoate or dodecyl (lauryl) sulfate (Dugan 1975; Dugan and Apel 1983; Onysko et al. 1984; Sand et al. 2007; Schippers et al. 1998).

In all cases of mitigation activities, it should be kept in mind that the activity of leaching prokaryotes plays the central role in AMD formation. Consequently, improved AMD countermeasures can only be developed, if the biological basis of its formation is thoroughly known. Hence, an understanding of the microbiology and the mechanisms underlying metal sulfide bio-oxidation are prerequisites for a successful AMD remediation project. In addition, a suitable monitoring should accompany the process which enables a reliable quantification of the remaining leaching activities. In the following, we will therefore give a short overview on the relevant microbial flora and sulfur chemistry. Then, two methods for monitoring AMD activity, microcalorimetry and sulfur compound analysis, are described which have been combined and tested at two German AMD field sites. Finally, we will discuss additional monitoring methods which focus on the analysis of the relevant microbial community rather than on the AMD-forming activity, such as Fluorescence In Situ Hybridization (FISH) and other techniques.

MICROBIOLOGY OF METAL SULFIDE LEACHING

The biology of microorganisms involved in the leaching of metal sulfides becomes more and more complex. Since the discovery of *At. ferrooxidans* in 1947, many new species have been described and known species were reclassified (Baker and Banfield 2003; Hallberg and Johnson 2001; Karavaiko et al. 2006; Rawlings 2002; Schippers 2007). Due to the important role of Fe(III) ions in the (bio)leaching mechanism (see next section), the oxidation of metal sulfides can mainly be attributed to the activity of acidophilic Fe(II)-oxidizing prokaryotes. Hence, the latter group of microorganisms represents, in a strict sense, the leaching prokaryotes. However, other bacteria and archaea thrive in AMD habitats and are also involved in metal sulfide dissolution by oxidizing intermediate sulfur compounds, or they live on organic substances excreted by the chemolithoautotrophic species. In addition, a large diversity of eukaryotic microorganisms is found at AMD sites or acidic hydrothermal sulfur springs, such as fungi, algae and protozoa (Amaral Zettler et al. 2002; Baker et al. 2004; Brown and Wolfe 2006; Robbins et al. 2000).

Generally, AMD-producing microorganisms are extremely acidophilic prokaryotes (meaning organisms thriving at pH values below 3). They can be found in all major phylogenetic lineages of prokaryotes. According to their temperature optimum, three groups can be distinguished, mesophiles (up to 30 to 40 °C), moderate thermophiles (40 to 55 °C) and extreme thermophiles (55 to 80 °C, or even higher). Among the genus *Acidithiobacillus* (formerly *Thiobacillus*, Kelly and Wood 2000) are the first isolates of extremely acidophilic sulfur- and/or Fe(II)-oxidizing bacteria, the mesophilic *At. thiooxidans* (Waksman and Joffe 1922) and *At. ferrooxidans* (Colmer and Hinkle 1947). Together with the moderately thermophilic sulfur-oxidizing *At. caldus*, these bacteria belong to the Gram-negative γ-*Proteobacteria*. Other leaching proteobacteria are species of the genus *Acidiphilium*, such as *Ap. acidophilum* (Hiraishi et al. 1998), whereas members of the genus *Leptospirillum* belong to a different bacterial division (Hippe 2000; Coram and Rawlings 2002). Gram-positive leaching bacteria are moderately thermophilic members of the genera *Acidimicrobium*, *Ferromicrobium*, and *Sulfobacillus* (Schippers 2007). Leaching archaea have been known for many years and most belong to the *Sulfolobales*, a group of extremely thermophilic, sulfur and Fe(II) ion oxidizers, including genera such as *Sulfolobus*, *Acidianus*, *Metallosphaera*, and *Sulfurisphaera* (Schippers 2007). Recently, also mesoacidophilic Fe(II)-oxidizing archaea have been discovered. These belong to the *Thermoplasmales*, and several species, such as *Ferroplasma acidiphilum* (Golyshina et al. 2000) and *Fp. acidarmanus* (Edwards et al. 2000), have been described.

The physiological potential varies significantly among the different groups of leaching prokaryotes. *At. ferrooxidans*, for instance, is endowed with a remarkably broad metabolic capacity. This species lives on the aerobic oxidation of Fe(II) ions, reduced inorganic sulfur compounds, molecular hydrogen and formic acid. Anaerobic growth is possible by oxidation of sulfur compounds or hydrogen coupled with Fe(III) ion reduction (Pronk et al. 1992; Das et al. 1992; Ohmura et al. 2002). In addition, it has recently been demonstrated that *At. ferrooxidans* like *Acidianus* spp. reduces elemental sulfur in the course of anaerobic hydrogen oxidation (Ohmura et al. 2002). In other leaching prokaryotes, however, the substrate spectrum can be quite limited. In particular, *Leptospirillum ferrooxidans* and *Ls. ferriphilum* can only grow by aerobic oxidation of Fe(II) ions. With respect to carbon metabolism, *Acidithiobacillus* spp. and *Leptospirillum* spp. are strictly autotrophs, i.e., they are unable to assimilate significant amounts of carbon from organic sources but only able to fix carbon from CO_2. In contrast, *Ap. acidophilum* and *Acidimicrobium ferrooxidans* can grow autotrophically on sulfur compounds and Fe(II) ions, heterotrophically on organic compounds, and mixotrophically using all these substrates (Clark and Norris 1996; Hiraishi et al. 1998). An obligate mixotrophic Fe(II)-oxidizing bacterium is *Ferromicrobium acidophilus* (Johnson and Roberto 1997). Also some *Sulfobacillus* spp. show poor chemolithoautotrophic growth, as do many thermophilic *Sulfolobales* (Karavaiko et al. 2006). Surprisingly, several heterotrophic *Acidiphilium* spp. and *Acidisphaera rubrifaciens* can synthesize pigments which might confer the ability for photosynthesis and/or for protection from UV radiation (Hiraishi and Shimada 2001; Hiraishi et al. 1998). This capability might help to survive in the oligotrophic mining biotopes when exposed to sunlight.

In summary, the biology of leaching prokaryotes is characterized by an impressive diversity. This has direct consequences for AMD mitigation and treatment. Frequently used AMD countermeasures are flooding and organic covers, creating an anoxic environment in coal waste heaps. In this case, the fact that many leaching prokaryotes are facultative anaerobes and, thus, involved in the complete aerobic and anaerobic parts of the sulfur and iron cycles could be of great importance. Thus far, anaerobic oxidation of pyrite and other metal sulfides at low pH values has not been demonstrated. However, the above-mentioned anaerobic physiology of leaching prokaryotes and their presence in anoxic biotopes support the hypothesis of an anaerobic leaching process. The existence of *Acidithiobacillus*-like species, for example, has been demonstrated in an anoxic reactor designed for cleaning contaminated groundwater and lignite (Alfreider et al. 2002). Hence, one has to be careful when applying countermeasures like constructing an anaerobic environment since this does not necessarily mean that leaching of metal sulfides is completely stopped. In all these cases, a long-term monitoring of leaching activity is recommendable.

SULFUR CHEMISTRY AND HEAT PRODUCTION

At low pH values, leaching of metal sulfides is based on two mechanisms, attack by protons (protolysis) and electron extraction by Fe(III) ions (oxidation) (Schippers and Sand 1999; Sand et. al. 2001; Schippers 2004). Metal sulfides with valence bands which are derived only from orbitals of the metal atoms cannot be attacked by protons (acid-insoluble metal sulfides). In contrast, metal sulfides with valence bands derived from both the metal and the sulfide atom orbitals are more or less soluble in acids (acid-soluble metal sulfides).

Oxidation of Pyrite

Pyrite belongs to the class of acid-insoluble metal sulfides. Consequently, it can only be attacked by an electron-extracting reaction with Fe(III) ions. Hence, Fe(III) ions and the re-oxidation of the produced Fe(II) ions are absolutely required for the leaching of pyrite. Due to the low rate of abiotic Fe(II) oxidation under acidic conditions significant leaching is only observed when acidophilic Fe(II)-oxidizing bacteria, such as *At. ferrooxidans* and *Ls. ferrooxidans*, are present. The chemical bonds between sulfur atom and metal atom do not break until a total of 6 electrons have been transferred to Fe(III) ions (Schippers et al. 1996). The first sulfur compound that is released from the pyrite crystal is thiosulfate (eq. 1).

$$FeS_2 \rightarrow S_2O_3^{2-} \rightarrow S_4O_6^{2-}, S_nO_6^{2-} \rightarrow (S_8) + SO_4^{2-} \qquad (1)$$

Accordingly, this oxidation route is called “thiosulfate pathway” (Schippers et al. 1996). Then, thiosulfate is mainly oxidized via tetrathionate and other polythionates finally to sulfate. In the absence of biological sulfur compound oxidation, also significant amounts of elemental sulfur (10 to 20 %) are produced (Rohwerder et al. 1998; Schippers et al. 1999). In leaching biotopes, normally both biological sulfur compound and Fe(II) oxidation occur. Consequently, the intermediate sulfur species (eq. 1) are completely oxidized to sulfate plus protons. On the other hand, accumulation of polythionates or elemental sulfur might indicate abiotic oxidation of pyrite.

Oxidation of Other Metal Sulfides

Acid-soluble metal sulfides, such as sphalerite (ZnS) and galena (PbS) or arsenopyrite (FeAsS), are dissolved by a combined attack by Fe(III) ions and protons. In theory, after binding of two protons, hydrogen sulfide (H_2S) could be liberated from the metal sulfide. However, in the presence of Fe(III) ions, the sulfur moiety will be oxidized concomitantly with the proton attack. Hence, the first free sulfur compound most likely is a sulfide cation (H_2S^+), which can spontaneously dimerize to a free disulfide (H_2S_2) and is further oxidized via higher polysulfides and polysulfide radicals to elemental sulfur (eq. 2). Consequently, this leaching route was named “polysulfide pathway” (Schippers and Sand 1999).

$$ZnS \rightarrow H_2S,\ H_2S^+ \rightarrow H_2S_n \rightarrow S_8 + (SO_4^{2-}) \qquad (2)$$

In the absence of sulfur compound-oxidizing prokaryotes, more than 90 % of the sulfide moiety of a metal sulfide is transformed to elemental sulfur (Schippers and Sand 1999). Minor products formed are thiosulfate, polythionates, and sulfate (Schippers and Sand 1999). Due to the fact that the oxidizing action of Fe(III) ions is not an absolute requirement for the polysulfide pathway, acid-soluble metal sulfides may also be dissolved solely by the activity of sulfur compound-oxidizing prokaryotes. In the absence of Fe(III) ions, these microorganisms oxidize free sulfide (H_2S), resulting from the proton attack on the metal sulfide, via elemental sulfur to sulfuric acid.

Heat Evolution during Metal Sulfide Oxidation

Oxidation of pyrite and other metal sulfides is highly exothermic (eq. 3) and, hence, could result in a significant heating of the leaching environment. Consequently, measuring the heat output of a sample could be an appropriate method for determining activity of leaching prokaryotes. In a coal waste heap or other leaching sites where thermal insulation occurs, self-heating could raise the temperature up to 60 °C or higher. Then, thermophilic bacteria and archaea thrive and will continue pyrite oxidation. Besides these chemolithotrophic Fe(II) and sulfur oxidizers, also thermophilic heterotrophs have been found in coal refuse piles (Darland et al. 1970). In the worst case, spontaneous ignition of the coal becomes possible.

$$FeS_2 + 3.75\ O_2 + 0.5\ H_2O \rightarrow 2\ SO_4^{2-} + Fe^{3+} + H^+ \quad (\Delta H^0 = -1546\ \text{kJ/mol}) \qquad (3)$$

Generally, enthalpy changes for the oxidation of different metal sulfides do not vary significantly. The average value per sulfur moiety is about -800 kJ/mol. Hence, even if the exact composition of the metal sulfide species in a coal heap or other leaching site is not known, turnover rates of metal sulfide oxidation can easily be calculated on the basis of the enthalpy changes. The latter can be precisely measured by calorimetry.

COMBINED TEST FOR AMD ACTIVITY MONITORING

On the basis of the known sulfur chemistry and heat evolution during metal sulfide oxidation, a test system was developed which combines analytical methods measuring these two indicators of AMD-producing activity. This test has not only been used for analyzing coal spoil samples but was also applied for monitoring leaching activity and sulfur compound speciation in samples from other AMD sites, such as abandoned open pit mines, waste heaps or tailings of metal mining operations (Elberling et al. 2000; Herbert and Schippers 2008; Sand et al. 1993, 2004, 2007; Schippers et al. 1995, 2000, 2001).

Microcalorimetry

Calorimetry is a method for determining the heat output of a sample. Depending on the measuring conditions, this is either the change of enthalpy (ΔH; at constant pressure) or the change of internal energy (ΔU; at constant volume). In the case of pyrite oxidation, the latter can be easily calculated from the former according to eq. 4, where Δν is the oxygen consumption and R and T, respectively, the gas constant and the thermodynamic temperature (in Kelvin).

$$\Delta U = \Delta H - \Delta \nu RT \tag{4}$$

Modern micro- and nanocalorimeters have detection limits below 1 µW. In 1980, the first reports on use of calorimetry for studying leaching activities were published (Goodman and Ralph 1980; Soljanto and Tuovinen 1980). In the meantime, detailed calorimetric investigations on leaching bacteria have been added (Schröter and Sand 1993) and reaction energy values for biological pyrite oxidation (Rohwerder et al. 1997, 1998) as well as its temperature dependence (Rohwerder et al. 1999) have been determined.

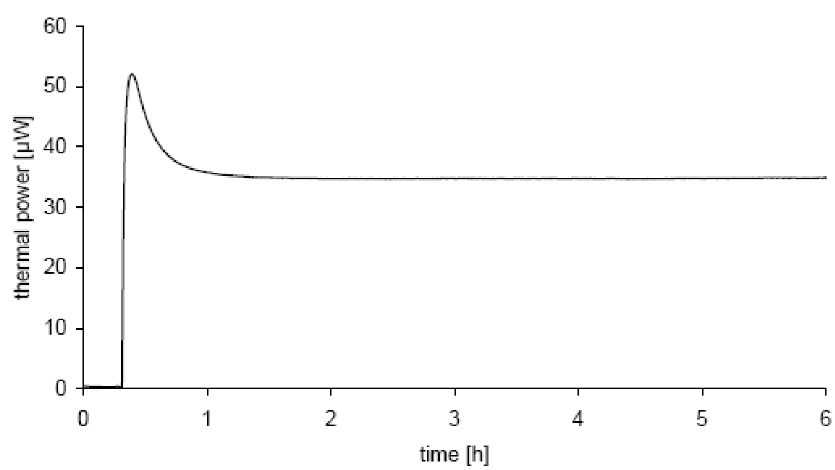

Figure 1. A typical thermogram recorded by a microcalorimeter (Thermal Activity Monitor, Thermometric AB, Sweden). The signal reaches a plateau phase within 60 min. This value represents the heat output of the sample and is directly correlated to the leaching activity.

In this study, a microcalorimeter was used for heat conduction measurements under quasi-isothermal conditions. Heat evolution of samples was measured using sealed glass ampoules with a volume of 4 mL. Sample material was filled in glass ampoules (1 to 2 g wet weight per ampoule), and calorimetrically measured as previously described (Rohwerder et al. 1997, 1998). Because of the restricted oxygen concentration in the sealed ampoules, the measuring time of the experiments was limited. However, at moderate activity (less than 100 μW) it was found that, once the heat output had entered the plateau phase, the calorimetric signal was constant for several hours (Figure 1). On the basis of the enthalpy change during metal sulfide oxidation, e.g. pyrite oxidation according to eq. 3, leaching rates can be directly calculated from the calorimetric signal, as the recorded thermal power value represents already a rate, i.e. heat output per time period (1 W = 1 J/s). A comparison between abiotic and biological activities is possible by measuring both the total heat evolution and the activity after complete inhibition of the microbial flora. The latter can be achieved by several methods, e.g., by heat treatment and addition of azide or other toxic chemicals.

Sulfur Compound Analysis

For analyzing inorganic sulfur species, several chromatographic systems were used. Elemental sulfur, thiosulfate and polythionates were analyzed by reversed-phase and ion pair chromatography employing UV detection with an HPLC system (Kontron/BIO-TEK Instruments) as previously described (Rohwerder and Sand 2003; Schippers et al. 1996). Sulfite, thiosulfate and sulfate were quantified by ion exchange chromatography and conductivity detection (Rohwerder and Sand 2003, 2008). A Dionex DX 500 system was applied. For elemental sulfur quantification, samples were extracted with ethanol and/or n-octane (in case of high concentrations). The water-soluble sulfur compounds were extracted with deionized water or phosphate buffer (in case of acidic samples).

WASTE MATERIAL FROM HARD COAL MINING IN THE SAARLAND, GERMANY

Hard coal in the Saarland is deep mined (from about 800 m depth). It belongs to the coal deposit Saarland-Lothringen. Coal and overburden contain usually about 1 % pyritic sulfur. From 1997 to 1999, several sampling campaigns were performed for monitoring the bioleaching activities in a coal waste heap (in cooperation with the local mining company and the Technical University Clausthal, Germany). This heap is a refuse pile of a mine which was already closed in the late 1960s. During operation of the underground mine, residues from coal processing and overburden material were transported via conveyor belts to the top of the pile. Due to this disposal technique a cone-shaped heap formed, characterized by a very steep slope. In the last decades, several attempts of rehabilitation failed. Obviously, the shape of the pile is unfavorable for plant growth. In addition, pyrite concentration in the deposited coal refuse was above the average value. Due to a local variation in the coal deposit the overburden contained about 2.5 to 3 % pyritic sulfur. In combination with an insufficient buffering capacity of the waste material, its weathering resulted in an acidic environment at the surface of the heap. Even after 40 years, drainage water of the pile could be characterized as typical AMD, having a pH of about 3 and containing high concentrations of sulfate, Fe(III) species, aluminum and other metals.

Samples from the surface of the refuse pile (up to 50 to 100 cm depth) generally showed low calorimetric activity (data not shown). This material was fully oxidized and acidic (pH values about 3). In addition, it contained high concentrations of precipitated sulfate and Fe(III) species. In line with these findings, reduced sulfur compounds were absent or only detected at very low concentration. Due to erosion from the top and slope, this layer of weathered overburden could be as massive as 200 cm at the bottom of the waste heap. Further down, however, partially weathered and completely unoxidized material was found. The latter exhibits properties very similar to the original coal waste deposited 30 to 40 years ago.

In the following, a section taken at the bottom of the pile is described in more detail (Figure 2). At the surface and up to a depth of about 80 to 90 cm, only completely oxidized material was found, characterized by a quite low pH of 3, high content of Fe(III) ions and high redox potentials, indicated by relatively low Fe(II) ion concentrations (Figure 2A). In the following 20 to 40 cm, pH values dropped slightly and a maximum in extractable Fe(III) was observed, which was also reflected by a distinct yellow-colored band in the section. Finally, in a depth of 120 to 130 cm, the properties of the waste material changed dramatically. In contrast to the other two layers, samples from this depth and below exhibited nearly neutral pH values, low Fe(III) concentrations and low redox potentials. In addition, this layer showed the grey or even black color of the original coal waste.

Although three layers could be easily distinguished by color, pH and Fe concentrations, AMD-forming activities cannot be deduced from these analyses. Therefore, additional tests were made (Figure 2B to 2D). Calorimetric analysis clearly showed that the first layer was characterized by very low abiotic as well as biological activities. Starting from about 90 cm up to 130 cm, total heat production of the samples was significantly higher, exhibiting a quite high variation from 5 up to 70 µW/g (Figure 2B). More important, only in this part of the section calorimetric values could be mainly attributed to biological activities. In the third layer, significant total activities of about 10 to 15 µW/g were measured. However, biological activities were not observed in samples from this layer. In combination with the sulfur compound analysis (Figure 2C and 2D), these results can easily be interpreted. (1) Samples from the top layer did not exhibit any relevant AMD-forming activity. (2) The two major sulfur products of pyrite oxidation under acidic conditions, elemental sulfur and sulfate, were only detectable at high concentration in the second layer, indicating high leaching rates. Obviously, metal sulfide oxidation was dominated by activities of acidophilic leaching microorganisms, as pH values were about 2 and the biological activity was 60 to 95 % of the total heat evolution. (3) A merely abiotic pyrite oxidation could be observed in the bottom layer which consisted of unoxidized waste material. Besides the calorimetric values, this interpretation is mostly supported by the detection of polythionates, as tetra- and pentathionate are typical indicators for an abiotic pyrite oxidation under neutral conditions. In the presence of sulfur compound-oxidizing bacteria and/or low pH, these instable sulfur species would be rapidly degraded and, hence, not detectable. The abiotic pyrite oxidation in the bottom layer, however, is obviously not occurring in situ and was only initiated when the material was exposed to air during sampling and measuring procedures in the lab. As indicated by the relatively high Fe(II) concentration (Figure 2A), oxygen could not reach this depth and was already consumed in the middle layer.

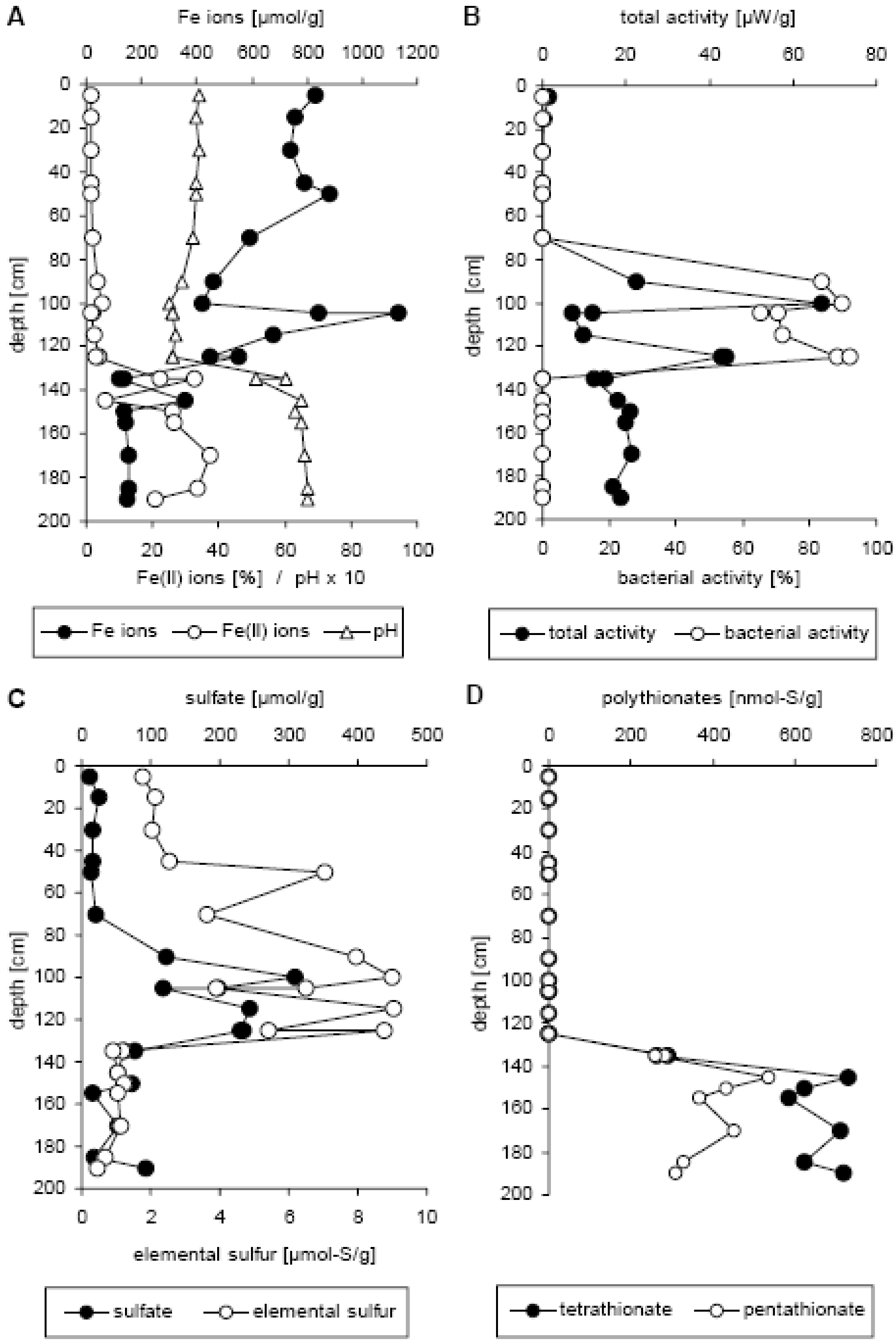

Figure 2. Microbial activity and other parameters in a section from the bottom of a 40-year-old coal refuse pile (Saarland, Germany). A: pH values and extractable Fe(III) and Fe(II) ions; Fe(II) concentration is given as percent of total iron. B: microcalorimetric activities (measured at 30 °C); biological activity is given as percent of total activity. C: concentrations of extractable sulfate and elemental sulfur. D: Concentrations of tetra- and pentathionate. Concentrations of reduced sulfur compounds (S_8, $S_4O_6^{2-}$, $S_5O_6^{2-}$) are given as µmol-S or nmol-S, considering the number of sulfur atoms in these compounds. All values are referred to 1 g dry weight of sample.

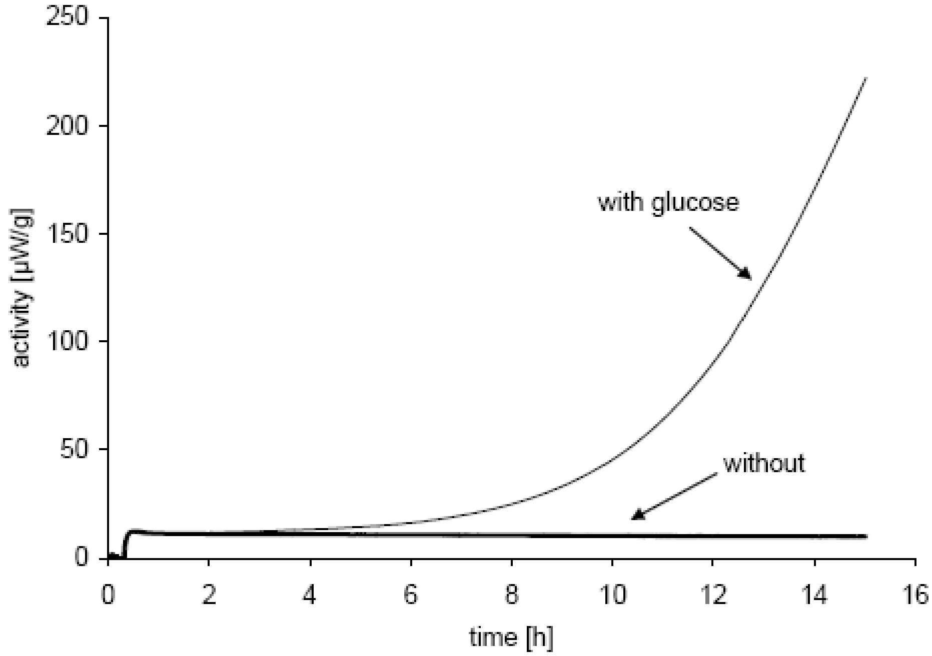

Figure 3. Calorimetric activity of a sample taken at the surface of a waste heap where coal refuse had been mixed with organic material. Samples were incubated at 30 °C with and without addition of glucose.

In summary, in the case of the 40-year-old refuse pile, AMD-forming activities could be localized at high resolution and quantified by simply applying microcalorimetry. The additional analyses, i.e. measuring of pH, iron ions and sulfur compounds of the samples, are necessary for relating the calorimetric activity to AMD formation. In other cases, additional tests may be needed for an unambiguous classification of the calorimetric values, as the heat output could also be related to other exothermic processes. In rehabilitation projects, heaps are often covered with layers containing organic materials, resulting in a heat production due to the degradation of these compounds but not due to the oxidation of pyrite. However, microcalorimetry can also be used in this case by extending the basically unspecific method. This is shown in Figure 3. The heat evolution of a sample taken at the surface of a waste heap where coal refuse had been mixed with organic material was measured over a 15-hour time period. The untreated sample exhibited an initial activity of 12 µW/g slightly decreasing to about 10 µW/g at the end of the experiment. In contrast, when an organic substrate, glucose, had been added to the sample, the calorimetric signal significantly increased and reached 230 µW/g after 15 hours of incubation. Obviously, this sample was dominated by an active heterotrophic microbial flora, as the added glucose was rapidly degraded. In the same way, the chemolithotrophic potential of a sample can be tested by adding suitable inorganic substrates, such as elemental sulfur, polythionates or Fe(II) ions.

Table 1. Microbial activity and other parameters of samples from dumps containing refuse from strip mining of two lignite seams (Lower Saxony, Germany)

No.	Age	pH	Microcalorimetry		Sulfur compounds [nmol-S/g]		
			total [µW/g]	biol. [%]	$S_4O_6^{2-}$	$S_5O_6^{2-}$	S_8
	upper seam						
1	d	4.2	11	47	3.0	7.5	480
2	d	5.7	8.8	41	2.9	0.7	130
3	w-m	5.7	6.4	10	n.d.	n.d.	110
	lower seam						
4	d	6.5	1.3	68	n.d.	n.d.	48
5	d	6.3	10	20	n.d.	n.d.	24
6	y	5.8	3.4	46	n.d.	n.d.	84
7	d	5.7	**128**	42	9.0	12	2300
8	y	5.6	2.5	60	n.d.	n.d.	530
9	w-m	4.9	**50**	23	0.8	0.8	1600
10	d	4.7	**61**	34	25.5	39	2200
11	d	4.4	**48**	24	13	23	2000
12	w-m	3.8	**27**	26	9.0	12	5200
13	y	3.1	**107**	47	n.d.	n.d.	5100
14	y	3.0	5.9	71	n.d.	n.d.	9200
15	y	2.7	1.0	79	n.d.	n.d.	140
16	y	2.5	**24**	44	n.d.	n.d.	3600
17	y	2.4	**118**	75	23	n.d.	6400
18	y	2.2	**22**	73	n.d.	n.d.	6800

Age: d, deposited within the last 7 days; w-m, deposited within weeks to several months; y, deposited 1 year ago or older. Microcalorimetry: biological (biol.) activity is given as percent of total activity (both measured at 30 °C). Sulfur compounds: amounts are given as nmol-S, considering the number of sulfur atoms in these compounds (S8, S4O62-, S5O62). All values are referred to 1 g dry weight of sample; n.d., not detectable.

WASTE MATERIAL FROM LIGNITE MINING IN LOWER SAXONY, GERMANY

Lignite at the sampling site in Lower Saxony is strip mined. It belongs to the lignite area Helmstedt. There are two seams with different sulfur content. Lignite from the upper seam contained about 1 to 2.5 % pyritic sulfur whereas its concentration in the lower seam is even higher and amounts to values of about 2 to 3.5 %. The metal sulfide FeS_2 is finely dispersed within the lignite and could be pyrite as well as marcasite. In 1998, sampling campaigns were performed for monitoring the bioleaching activities in several dumps and surface waters (in cooperation with the local mining company and the Technical University Clausthal, Germany). In contrast to the sampling of the refuse pile in the Saarland, mining was still in operation when samples were taken from the dumps.

Overburden material of different age and originating from both seams was investigated (Table 1, samples 1 to 18). Generally, weathering of the material was very rapid. Surface waters resulted from a 1-week-old precipitation event exhibited pH values of 2 to 3 and contained high concentrations of Fe(III) ions and sulfate (data not shown). This rapid acidification was also observed in the dumps. Samples consisting of material deposited only a few days ago already showed pH values as low as 4.2 (Table 1, sample 1). In line with this finding, microcalorimetric activities were high in many samples, exceeding 100 µW/g in 3 out of the 18 samples. However, the activities could not be completely attributed to bioleaching processes as the biological contribution only ranged from 10 to 75 % of total heat output.

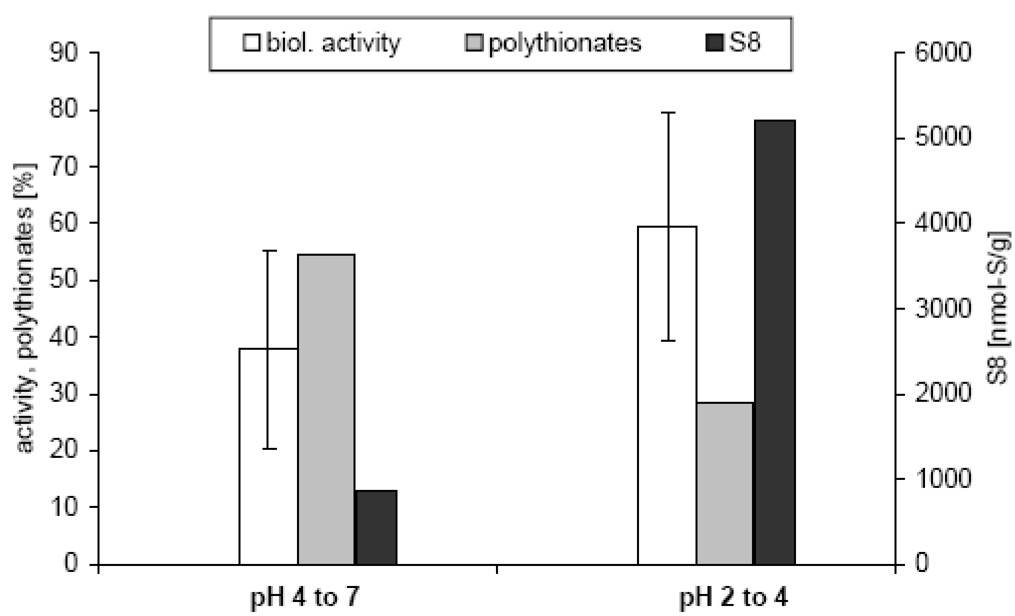

Figure 4. The 18 samples of dumps containing refuse from strip mining of two lignite seams (Lower Saxony, Germany; see Table 1) have been classified in two groups according to their pH. Average values of biological activity (percent of total calorimetric activity) and elemental sulfur concentration have been calculated. In addition, the relative frequency of polythionate detection is given.

Different age and origin of the samples are reflected by a great variation in pH, activity and concentration of reduced sulfur species. Samples from the upper seam exhibited relatively low activities of about 10 µW/g, dominated by abiotic processes (biology contributed less than 50 % to total activity). However, this low heat production can be clearly related to metal sulfide oxidation, as polythionates were detected in at least 2 of the 3 samples. Samples from the lower seam were very inhomogeneous. In 9 out of 15 samples, heat output exceeded 20 µW/g (given in boldface in Table 1). Very similar to the samples from the upper seam, in most of these cases polythionates were detected. In contrast, the other 6 samples from the lower seam exhibited activities of 10 µW/g or less and neither tetrathionate nor pentathionate were detectable, indicating insignificant leaching activities.

Despite the inhomogeneity of the 18 samples, they can be classified in two groups depending on their pH (Figure 4). The majority of the samples (11) are characterized by a moderately acidophilic environment (pH 4 to 7). Here, average biological activity (less than 40 %) and the average concentration of elemental sulfur (less than 1000 nmol-S/g) were low. However, polythionates were detected in 55 % of the samples. In conclusion, most of the heat evolution can be related to metal sulfide oxidation which is dominated by abiotic processes. On the other hand, 7 samples exhibited pH values below 4 (pH 2 to 4). This group shows relatively high biological activities (an average of 59 %), high amounts of elemental sulfur (an average of 5200 nmol-S/g) and polythionates were only present in less than 30 % of the samples. In conclusion, heat evolution in the second group can be mainly attributed to bioleaching processes.

Comparison of Calorimetry with Other Monitoring Methods

In the two case studies, microcalorimetry was successfully used for the monitoring of AMD-forming activity in samples from coal mining sites. As the measured heat output is basically an unspecific signal, additional analytical methods such as quantification of extractable Fe ions and sulfur compounds were applied. Thus, samples exhibiting metal sulfide oxidation could be identified and activities could be quantified. Applying these methods, all the necessary analyses can be done within a few hours at high throughput and at reasonable costs.

Besides microcalorimetry, several other methods for the monitoring of AMD-forming activity have been proposed. A quite labor-intensive approach is the quantification of the relevant Fe(II)- and sulfur compound-oxidizing microorganisms. For doing this, the Most Probable Number technique (MPN) is applied where dilution series of selective growth media in test tubes or microtiter plates are inoculated with the sample material. Although the quantification by MPN is associated with a high error, this technique gives quite reliable results. However, due to the slow growth of the relevant prokaryotes, an incubation time of 4 to 6 weeks is needed. In comparison with calorimetry, AMD-forming activity is not quantified by MPN but only sites exhibiting bioleaching activity can be identified. In contrast, activity of leaching prokaryotes can be quantified by using radioactive labeling. In a study investigating autotrophic Fe(II)-oxidizing bacteria from coal refuse, CO_2 fixation rates were determined by monitoring the incorporation of added $^{14}CO_2$ (Belly and Brock 1974). In addition, sulfur oxidation could be quantified by addition of ^{35}S-labeled elemental sulfur.

Although this method does not directly give the in situ occurring pyrite oxidation rates, leaching activities might be estimated on the basis of the obtained data. However, for measuring incorporation and oxidation rates, quite long incubation periods of several hours are required. In addition, working with radioactive isotopes needs special lab equipment. On the other hand, stable isotope analysis is becoming a frequently used technique for investigating biogeochemical processes. In the case of pyrite oxidation, fractionation between the stable isotopes of S, Fe and O in educts and products can provide valuable information about the S and Fe cycles at AMD sites (Dold and Spangenberg 2005; Herbert and Schippers 2008; Taylor and Wheeler 1984). However, these analyses will give only an overview on the ongoing processes but the obtained data cannot be used for calculating oxidation rates. Most similar to calorimetry is the measurement of oxygen consumption rates. According to eq. 3, pyrite oxidation is directly correlated to both heat evolution and oxygen consumption. Depending on the instrument used, microcalorimetry normally exhibits higher accuracy and lower detection limits. In addition, oxidation rates are obtained in a shorter time period than by monitoring changes in oxygen concentration, as the calorimetric signal (thermal power) already represents an activity value. Besides these advantages, the most important pro might be the potential of calorimetry for monitoring anaerobic processes. In deeper layers, metal sulfide oxidation could be uncoupled from oxygen consumption but could run by reduction of Fe(III) species. In contrast to oxygen measurements, this latter process can be quantified by calorimetry as precisely as the aerobic reactions. In conclusion, a combination of microcalorimetry with sulfur compound analysis is a suitable tool for monitoring AMD-generating activities at high spatial resolution.

ANALYSIS OF MICROBIAL COMMUNITIES AT AMD SITES BY MOLECULAR TOOLS

In addition to activity measurement, microbial community analysis is of great value for understanding the AMD-generating processes. Today, it is possible to study the biological diversity at AMD sites or other ecosystems by so-called molecular tools. This way, identity and distribution of leaching prokaryotes in samples from coal mining or other AMD sites can be determined in a short time (González-Toril et al. 2006; Schippers 2007).

Usually, for quantifying microbial cell numbers, the DNA in the samples is stained with nucleic acid-binding fluorescence dyes, such as 4’,6-diamino-2-phenylindol (DAPI), acridine orange and SybrGreen, and cell counting is done under a fluorescence microscope. Thus, total counts of DNA-containing structures, i.e. the microbial cells, are obtained, however, irrespective of their physiological state and phylogenetic affiliation. Hence, information on the viability and the identity of the species in a sample is not provided. For the identification and quantification of known and unknown microorganisms, molecular techniques based on the extraction of the DNA from a culture or sample are used. In the case of prokaryotes (bacteria plus archaea), the 16S ribosomal RNA (16S rRNA) gene is targeted. The extracted DNA is amplified by the Polymerase Chain Reaction (PCR) and the amplified PCR products can be cloned. Finally, the 16S rRNA genes of the clones in the clone library can be sequenced and similarities of the sequences and thereby phylogenetic affiliation to other microorganisms can be calculated and shown in phylogenetic trees. In the last years, the 16S rRNA approach has often been chosen for analyzing microbial communities in natural acidic environments and bioleaching operations (Bruneel et al. 2005; Goebel and Strackebrandt 1994; González-Toril et al. 2005). Instead of making clone libraries, the PCR product (amplified 16 S rRNA gene fragments) can be separated by Denaturing Gradient Gel Electrophoresis (DGGE). By this method, different base-pair sequences with the same length can be separated and cut out of the gel to address the phylogenetic affiliation of the microorganisms.

A further nucleic acid-based molecular monitoring technique is the Fluorescence In Situ Hybridization (FISH) whose target is also the ribosomal RNA (rRNA) (Bond and Banfield 2001; González-Toril et al. 2006; Pernthaler et al. 2001). In the following, the FISH technique for the identification of acidophilic coal mining microorganisms is briefly introduced. The protocols for the hybridization in acidic conditions are standard methods with only a few modifications (González-Toril et al. 2006; Mahmound et al. 2005; Nicomrat et al. 2006). For a successful identification of organisms by FISH, particularly the fixation of the sample is of importance. Samples can be fixed and analyzed on different materials, such as filters, glass slides or also attached to pyrite coupons. The carrier material is chosen dependent on the sample. After coating, the respective material with the sample is fixed with formaldehyde (4 %) at 4°C for 30 min. Then, several washing steps, two times with acidic water and two times with a phosphate buffer are accomplished. Two different procedures are described to improve the fixation of cells by coating (González-Toril et al. 2006). One possibility is the use of poly-L-lysine to cover the glass slides; the other one is to cover the sample with agarose (0.2 %) on the respective carrier material. The last step of the fixation is the immersion of the sample in ethanol in increasing concentrations (50 %, 75 % and 100 %).

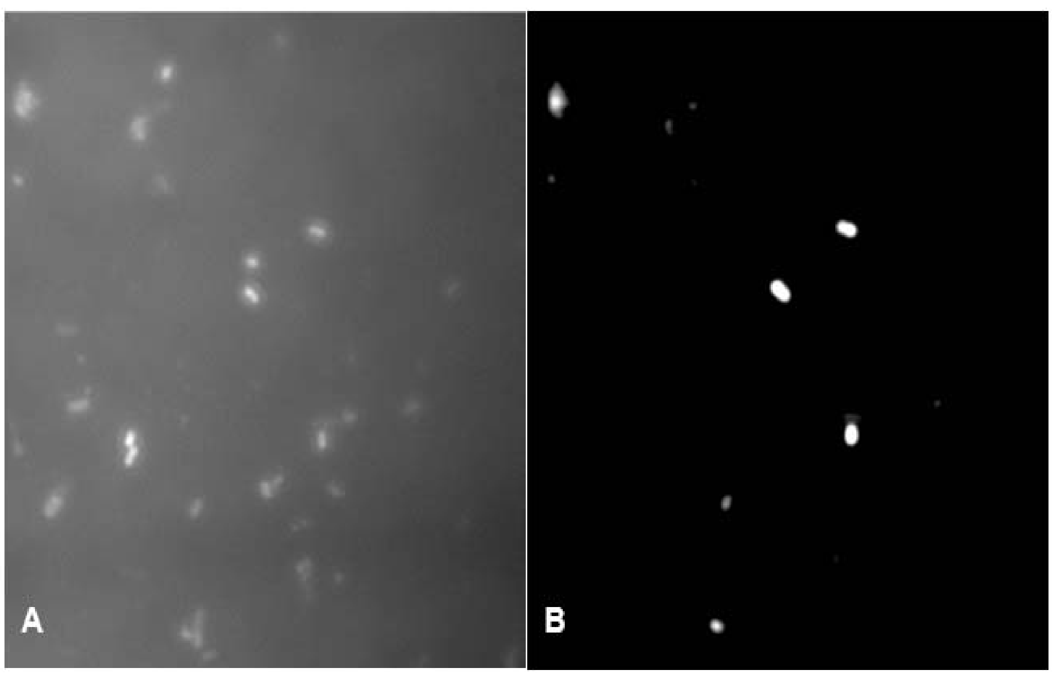

Figure 5. Epifluorescence microscopic images of a mixed culture of At. ferrooxidans and Ap. cryptum attached to pyrite. A: DNA of all cells is labeled by DAPI. B: The same sample location as in A. Only cells of At. ferrooxidans are visible due to labeling by a specific FISH probe.

At this point of the protocol, the sample can be stored at -20 °C prior to hybridization with the probe or directly hybridized by different protocols which are depending on the type of sample and its environmental origin. Most of the used protocols for acidophilic mining microorganisms are based on Amann's protocols (Amann 1995). In general, a hybridization buffer is prepared. Depending on the probe, the formamide concentration can vary. The assortment of the FISH probes is based on the 18 (± 3) mer oligonucleotides complementary to specific zones of the 16S rRNA genes of the target organism (Amann 1995). The latter both are added to the sample and the hybridization takes place in a saturated hybridization chamber in a hybridization oven. After hybridization, the sample is washed in a preheated washing buffer and incubated for approximately 20 min at 48 °C. After a washing step with ultra clean water to remove salts, the sample is dried. In addition to the FISH procedure, samples can be stained with contrast fluorochrome. Therefore, put DAPI with a final concentration of 1 µg mL^{-1} over the sample and incubate for 1 minute. The stained sample is briefly washed with ethanol 80 % and air dried. To view the microorganism, an epifluorescence microscope equipped with suitable filters for the probe fluorochrome and DAPI is used (Figure 5).

CONCLUSIONS

A suitable monitoring of the oxidation of pyrite and other metal sulfides should accompany AMD rehabilitation projects. Thereby, a reliable quantification of the remaining leaching activities should be possible. This monitoring at coal mining and other AMD sites can easily be done by applying a combination of microcalorimetry with sulfur compound analysis. In this way, leaching activities can be precisely quantified at high spatial resolution. In addition, this short-term and high throughput test allows a differentiation between abiotic and biological oxidation rates. In comparison to calorimetry, among alternative monitoring methods, only the measuring of oxygen consumption rates could give similar results. However, besides several technical disadvantages, the latter methods does not allow a determination of relevant anaerobic processes, which can be measured by calorimetry as precisely as the aerobic ones. AMD sites are inhabited by a large diversity of microoganisms which are all directly or indirectly contributing to leaching activities. Consequently, beyond the quantification of leaching rates, analysis of the microbial community by molecular tools is recommended for an understanding of the underlying mechanisms. In the future, identification of the dominant species in an AMD biotope might even help to develop selective inhibitors.

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Chapter 4

SOIL BIOTA DEVELOPMENT IN AREAS AFFECTED BY OPEN COAST COAL MINING IN EUROPE AND ITS ROLE IN SOIL FORMATION

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ABSTRACT

The role of plants in the formation of post-mining soil is generally accepted, but much less is known about the role of soil biota in this process. The aim of this study is to give an overview of the main factors that determine occurrence of soil biota in post-mining soils, and of the role of soil biota in soil forming process. Studies conducted on reclaimed and non-reclaimed sites in two post-mining areas in the Czech Republic and Germany are summarized and compared with other post mining sites in Europe. This study is focused on forest reclamation or naturally revegetated areas covered by woody species, as forest reclamation is the most common reclamation practice in both areas.

Major constraints that determine colonization of post-mining sites by soil fauna are migration distance, character of substrate, namely substrate toxicity and physical properties, and development of vegetation. Development of vegetation can affect soil biota by the quality of litter, and the spatial organization of vegetation is also very important for soil fauna. Besides immediate vegetative cover, long-term development of soil horizons are crucial. Besides vegetation, soil biota also contributes to the development of soil horizons. Soil microflora play a crucial role in litter decomposition and nutrient dynamics in post-mining sites. The soil fauna affect soil microstructure, carbon and nutrient storage, soil physical properties and plant growth in post-mining sites.

INTRODUCTION

Open-cast coal mining causes massive disturbance of ecosystems. Large areas are either excavated, or buried under the heaps where spoil material overlying the coal layer is deposited. The heaps may reach thousands of hectares in area and elevations of more than 100m above the original terrain (Frouz et al., 2007). Materials overlying the coal layer often have adverse physical and chemical conditions, and a lack of recent organic matter (Sourkova et al., 2005a). Reconstruction of soil, soil biota and soil biological functions are important in the restoration of functional ecosystems in the post-mining landscape (Bradshaw, 1993). Despite extensive disturbance, there are natural processes that may lead to the gradual build up of an ecosystem in these heavily disturbed areas. These processes are usually slow and sometimes have a low degree of predictability (Bradshaw, 1993, 1997). On the other hand, they may result in the production of ecologically valuable ecosystems, well adapted to local conditions, and often for lower cost that man made reclamation (Bradshaw, 1993, 1997). In fact, most processes employed during reclamation enhance natural succession processes. Thus better understanding of these natural processes can be important in improvements of reclamation practice.

Interactions between biota and the abiotic environment during succession have been emphasized many times (Clements, 1936, Odum, 1969, and Glenn and Lewinn et al., 1992). However the majority of empirical succession studies deal with plants only, while studies covering the interactions between other trophic levels during succession are less frequent (Gibson and Brown 1991). It is generally accepted that vegetation changes during succession are crucial for the successional development of other organisms, including soil biota (Dunger, 1968, 1991, Frouz, 1997, Kaufamann, 2001, Pižl, 2001). Plants form the bottom of the food web and also play a principal role in the formation of the physical structure of the habitat. However, other trophic levels may also affect plant succession; many examples are available of the effects of herbivores (Bach, 1994, Brown and Gange 1989, Fagan and Bishop 2000). So far, less attention has been paid to the effects of soil biota on plant communities (De Deyn et al., 2003, Thompson et al., 1993). Soil biota may affect successional changes of vegetation by below-ground herbivory (Brown and Gange, 1989), by effects on nutrient availability (Alphei et al., 1996, Harinikumar and Bagyaraj, 1994, Lopez et al., 2003) and by affecting soil formation and the modification of soil as a habitat for plants (Thompson et al., 1993). Engineering effects of plants in soil formation has received considerable attention; however, little attention was paid to the function of individual groups of soil biota in soil formation, particularly in sites that develop under spontaneous succession. Soil microflora plays a crucial role in decomposition of plant litter which enters into soil, and in this way affects nutrient dynamics of the soil (Anderson and Ineson, 1984, Lavelle et al., 1997). Soil fauna, on the other hand, contributes only a little to plant litter mineralization. However, soil fauna can alter soil conditions by the formation of soil structure, distribution of organic matter, etc., which may indirectly affect many soil processes including decomposition rate (Lavalle et al., 1997, Ponge, 2003). The short term effect of soil fauna may be observable mainly in microscale. However soil fauna often contributes to the formation of persistent structure which may accumulate in soil over time, and eventually alter conditions in whole soil profile (Lavelle et al., 1997). Most studies focused on these interactions were conducted under laboratory conditions (Thomson et al., 1993), while field studies are rare (De Deyn et al., 2003, Frouz et al., 2008).

Soil harbors tremendous biodiversity (Lavelle et al., 1997) with large bioindication potential. This is true also in mining sites, where development of soil biota can be a sensitive indicator of reclamation success and ecosystem recovery (Dunger, 1968, 1991).

The aims of this review are: to summarize long-term research about soil biota development and function in the soil forming process on reclaimed and non-reclaimed post-mining sites in two contrasting post mining areas (Sokolov coal mining region in the Czech Republic and in Cottbus mining area in Germany), to compare these results with other coal mining areas in Europe, to elucidate the main factors that determine soil biota development in post-mining sites, to explore the interactions between soil biota, soil development and plant succession, and to discuss their potential relationships.

This review will focus on the situation where soil is developing in situ, without topsoil application.

STUDY SITES AND METHOD

In this review we summarized extensive research of soil biota done in two contrasting post mining areas: Sokolov area in the northwest part of the Czech Republic and the Cottbus area in the eastern part of Germany. Colliery spoil heaps studied in open-cast coal mining near Sokolov are mainly heaps consisting of material excavated from the pit and dumped outside the pit on the surrounding terrain. Morphologically they represent artificial hills, typically with an area of several hundreds of hectares and elevation more than 100m above surrounding terrain. Their altitude is 500-600 m a.s.l. Spoil substrates in this area are highly variable e.g. pH (H_2O) is ranging from 2.1 to 8.5 (Frouz et al., 2005). However, alkaline tertiary clays called the Cypris formation prevail. They consist of a mixture of kaolonite, illite, quartz and limestone (Kříbek et al., 1998, Rojík, 2004), are alkaline (pH 8) which gradually decreases with development of vegetation (Šourková et al., 2005a), and are rich in basic nutrients (Šourková et al., 2005a). The mean annual precipitation of the area is 650 mm and the mean annual temperature is 6.8°C, for more details see Frouz et al. (2001ab). Two chronosequences were established in this area: the first covers alder plantations (mixture of *Alnus glutinosa* and *Alnus incana*) ranging in age from 5 to 45 years, the second includes unreclaimed sites ranging in age from 0 to 45 years. Alder forest unaffected by mining, but located in the vicinity was used as a reference site. In Sokolov, area vegetation development is rather fast, tree plantations close their canopy in 15-20 years after planting (Šourková et al., 2005a). On non-reclaimed plots, pioneer herbs and grasses were dominated by *Tusilago farfara* and *Calamagrostie epigeios* (Frouz et al., 2008a) and initial development of herb layer was slower than in other post-mining sites in Czech (Prach, 1987). However, 15-20 years old sites are typically covered by willow shrubs (*Salix caprea*), and 25-30 year old unreclaimed sites are usually covered by young forest dominated by *Populus tremula* and *Betula pendula* (Frouz et al., 2001b, Frouz et al., 2008) (Figure. 1).

Heaps near Cottbus are mostly internal heaps dumped inside the mining pit. Prevailing spoil materials are tertiary marine and lacustrine sands. These sands often contain some proportion of lignite and pyrite, which make their pH acidic (5.7), in some cases with high salinity. Sites are usually ameliorated by alkaline fly-ash from a power plant, or with lime. The mean annual temperature is 8.5°C and annual precipitation is 625mm. In Cottbus the chronosequence on pine (*Pinus silvestris*) plantations ranging in age from 8 to 40 years was studied, and an approximately 50-year-old pine forest, unaffected by mining and in vicinity of mines, was used as reference site.

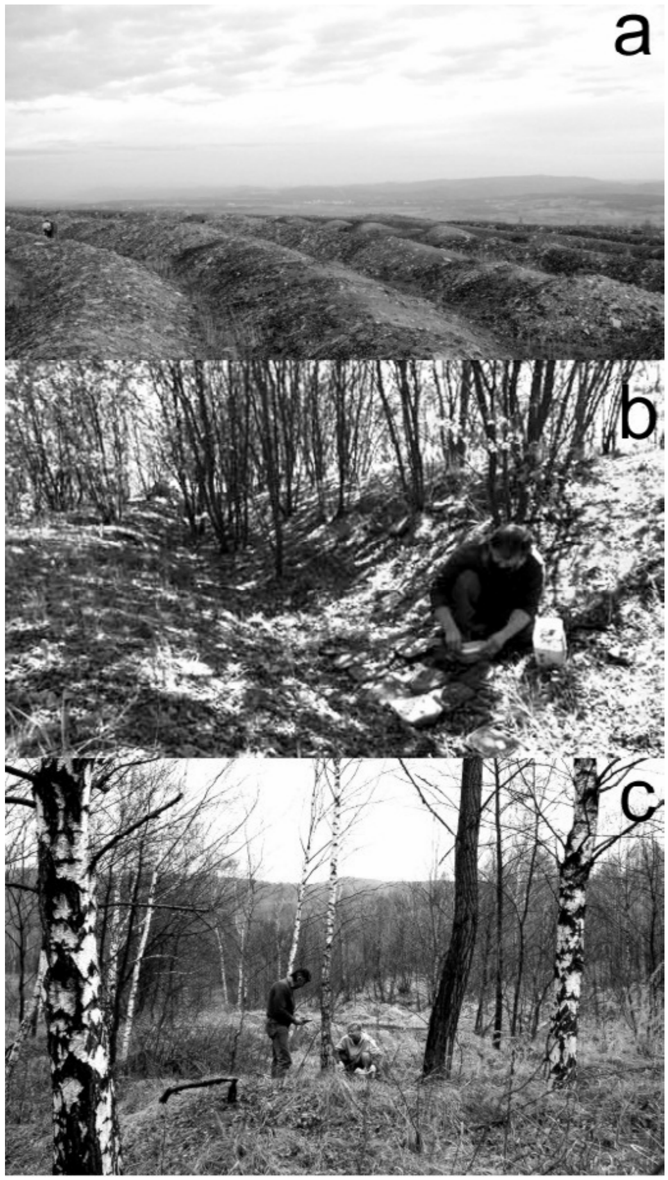

Figure 1. Natural revegetation on unreclaimed post-mining sites near Sokolov; 10 year old site (a), 20 year old site (b) and 40 year old site (c).

Most of the data presented in this review refers to already published results, so that reader can find more detailed information in individual papers. However an outline of methods used is summarized below so one can get the impression how the data were obtained without reviewing numerous literature sources, and also learn how a few unpublished results, included in this paper, were obtained. To study soil biota composition, soil sampling was performed typically twice a year; in spring and autumn. As the young soils of post-mining sites are shallow, sampling covered the top 5 cm of soil, unless stated mentioned otherwise. Composite samples representing about 0.5 kg of soil per site were collected to study soil microflora. Bacterial numbers were established as direct counts using DAPI staining and epifluorescent microscopy (Bloem, 1995). Microbial respiration was measured as CO_2 production by trapping CO_2 with NaOH in an airtight vial (for one week in 20 ^oC) and consequent titration of NaOH by HCl after BaCl addition. Microbial biomass was quantified by the chloroform fumigation-extraction method (Jenkinson and Powlson, 1976).

To study soil microfauna and mesofauna, typically composite samples were taken in each plot, each consisting of five particular samples (area of each 10 cm^2). Two sets of samples were collected, one for the extraction of microfauna and enchytraeids, and the second for the rest of the mesofauna. Samples of the first set were homogenized, 1 g of the mixed soil was diluted and used for the direct count of testate amoebae (protozoans). A further 10 g of the soil was exposed on modified Baermann funnels to isolate metazoan microfauna (nematodes, rotifers, tardigrades) and enchytraeids.

The Tullgren apparatus was used for the extraction of other mesofauna groups. To study soil macrofauna, five samples of 125 cm^2 each or three samples each with an area of 625 cm^2 were taken in each plot. Macrofauna was extracted by the Tullgren apparatus.

To study colonization of heaps by soil fauna, two parallel transects of pitfall traps were established in Velka podkrusnohorska heap, the largest heap of Sokolov coal mining area (Frouz, 1999a). The first transect was located in woody vegetation, the second in open habitats without vegetation, or with low vegetation only.

Thin sections were used to evaluate the role of soil fauna in the soil forming process (Kooistra, 1991). Soil monoliths taken from a depth of 0-10 cm for thin soil sectioning were air-dried, saturated with epoxide resin and, after hardening, two vertical thin soil sections were prepared (Rusek, 1978) covering an area of 5x5 cm and depths of 0-5 and 5-10 cm.

Microcosms simulating the topsoil layer were used to estimate effect of soil biota, namely soil macrofauna on soil mixing and litter decomposition (Frouz, 2002, 2008 Frouz et al. 2006). The microcosms consisted of plastic boxes covered with dense net (0.2 mm) on the top and bottom surfaces. In macrofauna accessible treatments, six horizontal openings were located on each longer lateral side; no such openings were in the non-accessible treatments. Each box contained mineral layer and litter layers. A net, pervious for all size group of soil macrofauna separated both layers and serves only as a marker of original border between the litter and the mineral layer. The microcosms were exposed in the field for one or three years. They were partially buried in the fermentation and the humus layers of soil in such a way that about half of the large openings on the sides of macrofauna accessible treatment were buried and half emerged above the surface. The litter and the mineral layers were separated after exposure using the net placed between the layers in the beginning of experiment was used as an arbitrary border, dried, and C and N content was established. The total amount of C (or N) in individual layers was calculated as the dry weight of the layer times the C (or N) content. The amount of C removed from the litter layer was calculated as the amount of C added in the litter layer in the begining of the experiment subtracted from the amount of C in the litter layer at the end of the experiment. The amount of C accumulated in the mineral layer was calculated as the amount of C in the mineral layer at the end of the experiment minus the amount of C in the mineral layer at the start of the experiment. Overall, the loss of C (carbon mineralization) from the system was calculated as the difference between C removal from the litter layer and C accumulation in the mineral layer.

SOIL BIOTA ESTABLISHMENT IN POST-MINING SITES, CONSTRAINTS, AND COLONIZATION

Colonization of sites by soil biota is limited by site conditions in situ, and by factors that affect migration into the post-mining site. Among in situ conditions that affect the site colonization by soil biota are substrate toxicity and adverse physical conditions (Bradshaw, 1993, 1997), vegetation development, and the development of soil which is another important factor that determine migration and establishment of soil biota in post mining sites.

Toxicity of spoil materials for soil biota was seldom studied. Some work has been done in applying hydrobiological tests in post mining-sites (Galli et al., 1994). Frouz et al. (2005) to compare more than 60 various post-mining substrates from post-mining sites in Czech republic and Germany, using modification of the enchytraeid reproduction test (Röempke et al, 1998, ISO 16387, 2003). This test was originally developed to test toxicity of various chemicals; the principle of the test is the cultivation of potworm (*Enchytraeus albidus* or *Enchytraeius crypricus*) in standard conditions on soil treated with various chemicals. Here we cultivated potworm in various post-mining substrates and compared population growth with growth on meadow soil from undisturbed habitat. Mining substrates display large variability in toxicity for potworm. All tested quaternary material such as quaternary sand supported the same population growth of potworms as control soil (Frouz et al., 2005). Also the most common substrates in Sokolov post mining area, alkaline tertiary clays, were not limiting for *E. crypticus* population growth (Frouz et al., 2005). On the contrary, lignite- and pyrite-rich tertiary sand, frequent in Cottbus area in eastern Germany, slows down population growth of E. *crypticus* in laboratory tests, and may be responsible for slower colonization of these sites under field conditions (Dageförde et al., 2000, Frouz et al., 2001). Toxicity of spoil substrates can be attributed to multiple factors (Frouz et al., 2005). Spoil substrates that come from close proximity to the coal layer, with high conductivity, or with low pH and high polyphenol content are toxic for soil biota (Frouz et al., 2005). All sites with a pH below 3 show acute toxicity for potworms, sites with pH below 4 show often some reduction of population growth. Most sites with pH above 5 did not show substantial reduction of potworm growth (Figure 2). Toxicity caused by low pH connected with high pyrite content can be very severe, for example a comparison of substrate toxicity in a chronosequence of pyrite- and coal-rich clays in Sokolov shows, even after 50 years from heaping, the same toxicity as freshly damped substrate (Frouz et al., 2003). However even spots with neutral or alkaline pH but with high salt accumulation (Figure. 2) were toxic (Frouz et al., 2005). Other studies report toxicity of metals such as Se, As, Cd, Cu, Zn (Jener and Jansenmommen, 1993, Scharrnasarkar and Vance, 1997, Sample and Suter, 2002) in post-mining sites. In conclusion, to estimate toxicity of a post-mining site for soil biota it can be recommended either conduct a biological test, such as enchytraeid reproduction test, or measure pH, conductivity and content of metals that are likely to occur in given mining area.

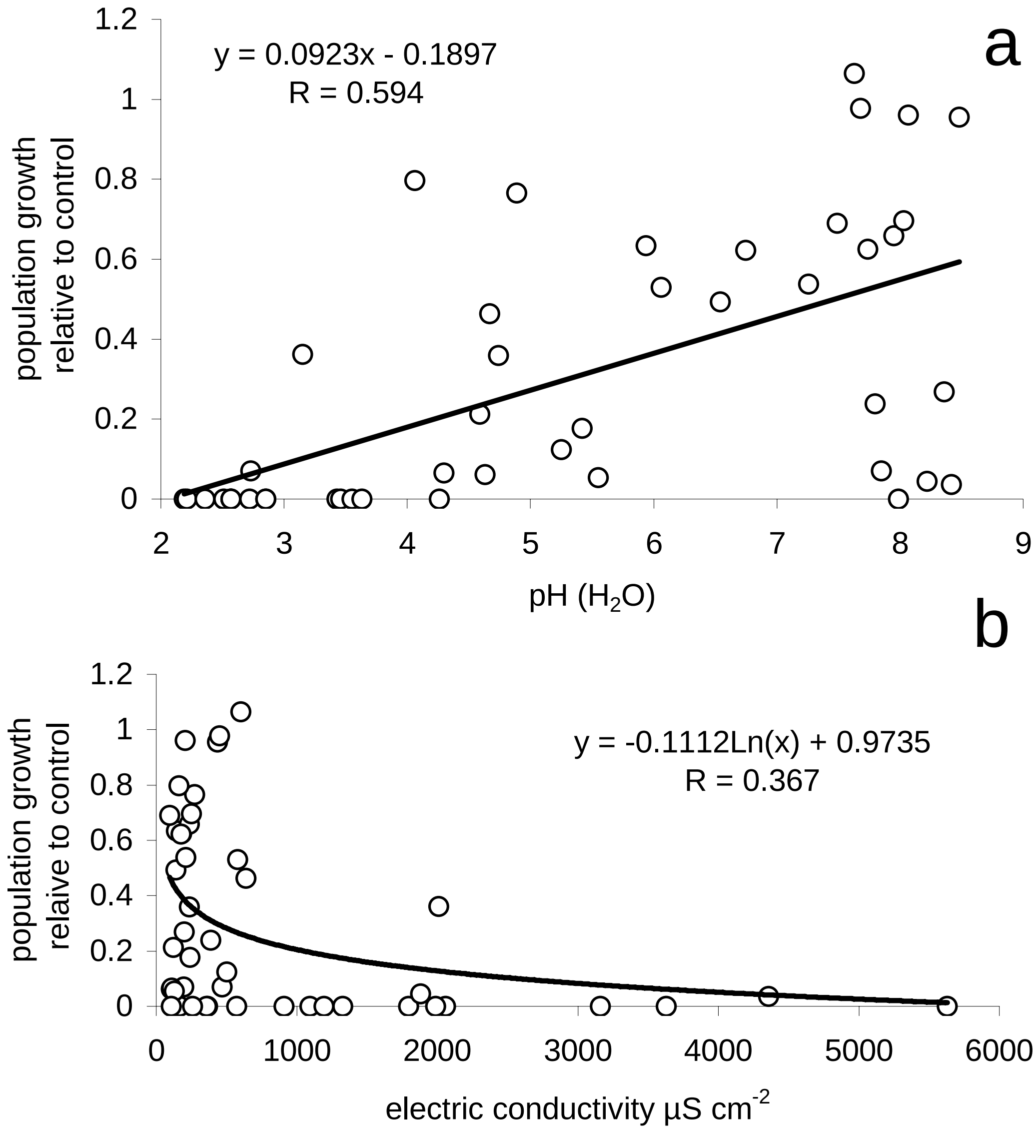

Figure 2. Relative population growth (growth in post mining substrate/growth in control meadow soil) of *Enchytraeus crypticus* in relation to substrate pH and conductivity both measured in water solution (1:5 sample: water ratio, Frouz et al. (2005)).

In addition to substrate toxicity, adverse physical conditions may slow down soil biota development. Besides salinity mentioned above, extreme texture (Bradford et al., 1993, 1997) and hydrophobicity (Gerke et al. 2001) can cause problems in post-mining sites.

Migration is another factor that affects colonization of post mining sites by soil biota. We have only a little data about migration of microflora on the heap, but we expect most of it is airborne. However, we have also found some viable microflora in aseptically sampled deep subsurface layers (c. 200m deep) of tertiary clays in mining pits of the Sokolov coal-mining district (Elhottová et al., 2006). Deep subsurface microflora occurs in many geological situations (Pedersen 1993) but its role on microbial colonization of heaps is not clear.

Dunger et al., 2001 and Wanner and Dunger 2002, show by study of post-mining sites near Görlitz in eastern Germany, that protists, soil microarthropods and spiders are mostly passively airborne, while larger invertebrates fly or crawl from the surrounding landscape. Distance from surrounding landscape can by important, particularly for colonization of crawlers. For example, Frouz (1999a) showed that the proportion of wingless Diptera significantly decreased from the surrounding landscape towards the heap center, where fliers prevail (Figure 3). However, even between flying insects, significant interspecific differences can be found. For example, winged females of the ant *Lasius niger* can be found even on the top of the heap, while females of *Lasius flavus* cannot be found even few meters from closest nest (Holec and Frouz, 2005). Trapping of soil invertebrates on a gradient from the surrounding landscape to heap center show that in addition to distance, habitat connectivity is also important (Frouz, 1999a). Here it should be considered that the same vegetation may be corridor for one species, but a barrier for others (Frouz, 1999a, Frouz and Olejníček, 1999, Frouz an Paoletti, 2000). In particular, tall vegetation can serve as an important corridor for most of epigeic invertebrates, on the other hand, it can reduce migration of flying and airborne species (Frouz 1999a, Frouz and Olejníček, 1999, Frouz an Paoletti, 2000). For example, winged females of the ant *L. niger* were found in pitfall traps located with low vegetation from bottom to the top of the heap. In tall woody vegetation, they were found only in the very bottom of the heap (Figure 3), this indicates that woody vegetation may represent a barrier for their migration (Holec and Frouz, 2005). Some species also require a specific combination of habitat, as they use different habitat for different purpose. For example, Holec et al. (2006) showed in post-mining sites near Sokolov that the ant *Lasius niger* prefers patches with open vegetation or bare soil for building their nests, however pitfall trapping in the nest surrounding shows that areas with dense vegetation are preferred for foraging (Figure 3).

Transport of soils from the surrounding landscape to the heap can substantially speed up colonization. For example, in the Sokolov coal mining area, unreclaimed sites are colonized by earthworms after 20 years of succession (Frouz et al 2001b, 2002) however reclaimed sites were colonized by worms almost instantly after tree planting (Pižl, 1999, 2001). It is expected that worms were brought to reclaimed sites by soil attached to plant seedlings. Marashi and Scullion (2003) show that in disturbed soil, earthworms can reach population densities common in undisturbed meadow just three years after inoculation of these plots by worms. All this supports the idea that migration is an important barrier for worm establishment in post-mining sites, which can be overcome by worm inoculation. Earthworms can be inoculated by catching them in surrounding landscape and introducing in holes made in target sites, this approach is very useful in experimental application (Marashi and Scullion, 2003). In reclamation practice, transferring blocks of soil bearing earthworms may be more practical. Educated practitioners can easily perform this operation with little or no knowledge about worm biology and soil also provide shelter for introduced population of worms. Experiments done in Sokolov area show that a strip of topsoil from seminatural meadow, unaffected by mining, c. 18 m^2 in area and 0.3m thick can maintain a sustainable population of earthworms for many years even if introduced on a bare, non vegetated heap (Frouz, 1995).

In Sokolov coal mining district agriculture soil is removed before mining, stored on temprarly on piles and then used for reclamation purposes. This can improve soil conditions and can serve as an important source of soil biota. On the other hand, storing soil on the piles reduces biological quality of the soil. These piles are typically several m high and detailed study of depth distribution of soil biota shows that most of biological activity is concentrated in top 10-20 cm (Frouz, 1999b). Similar adverse effects of soil storage have been found also in other post-mining areas (Scullion et al., 1988). So wherever it is possible, bringing fresh topsoil may have a stronger inoculation effect than bringing soil stored for some time in piles.

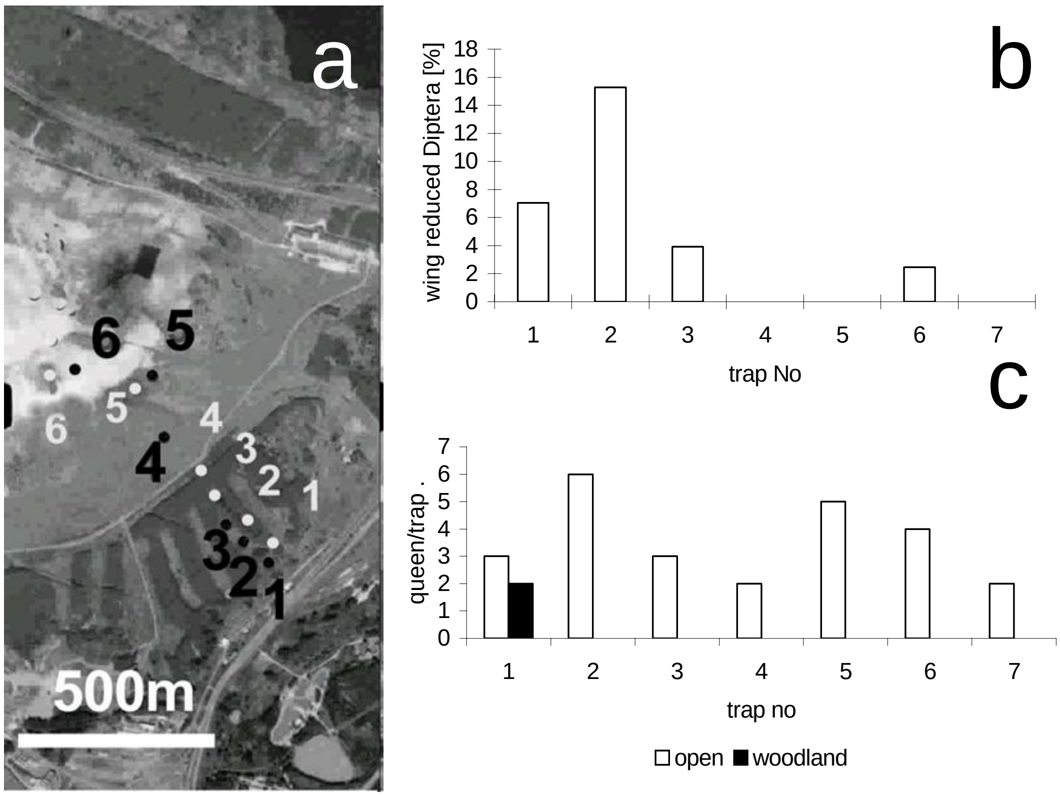

Figure 3. Aerial photo of transects of the pitfall trap from bottom to the top of the heap(a), trap number increases from bottom to the top, traps in woodland patches are black, traps in open patches white. Proportion of Diptera with reduced wings from total catch (b) and number of queens of ant *Lasius niger* found in individual traps (b), based on Frouz (1999) and Holec and Frouz (2005) data. Proportion of Diptera with reduced wings is significantly higher in traps located in bottom of the transect (1-3) that in the top ones (4-6) ($\chi 2$ test $p<0.05$), number of *L. niger* queens in open vegetation is significantly higher that in woodland (t test $p<0.05$).

So in conclusion, connectivity with the surrounding landscape is important here for colonization by soil fauna, and fast revegetation of marginal areas as soon material placement is complete can be very beneficial. However, one should keep in mind that many organisms come by air and hence keeping some open area without vegetation or creating a mosaic of tall and low vegetation can promote migration of these air borne organisms. Transport of soil from surrounding landscape either purposely, or with plant material, can substantially speed up colonization namely for slow migrants such as earthworms.

Soil animals that colonize post-mining sites are mostly ubiquitous eurivalent species common in the surrounding landscape (Pižl, 1999; Pižl, 2001; Holec and Frouz 2005). However, in many cases some rare species missing in surrounding landscape were found on the heaps of Sokolov area, and for some of them, post-mining areas are the only known locality of the species in the country. In some cases species new to science were found in heaps (Ježek, 1996,1999, Ježek and Barták, 2000, Holec and Frouz 2005). Similarly, Broring et al (2005) and Broring and Weigleb (2005) showed that Cottbus post mining sites harbor a large proportion of the invertebrates species known within Germany, and a particularly large number of rare and endangered species. These species typically inhabit some non-forest habitats such as mountains, or are species characteristically found in steppes, saline habitats, small wetlands (Ježek, 1996, 1999, Ježek and Barták, 2000, Holec and Frouz 2005). A similar phenomenon was earlier recorded in plants; several studies reviewed by Prach et al., (2001) show that post-mining sites, particularly their non-reclaimed parts, harbor rare and endangered plant species. The European landscape has been extensively used for centuries, and in particular, non forest habitat suffers from large anthropogenic pressures that include tillage, eutrophication either due to high load of fertilizers or wastes, changes in vegetation composition, cultivation of monocultures or low diversity plant cover, etc. Post-mining sites, on the other hand, are often nutrient poor, and offer a wide variety of habitats (Prach et al., 2001), including some habitats rare in the surrounding landscape, such as saline wetlands. All these factors may enhance occurrence of some rare species. Another factor that may increase species diversity in unreclaimed sites is that these sites are usually not leveled, and original surface heterogeneity formed by heaping remains. This surface heterogeneity resulted in heterogeneity of environmental conditions, e.g. occurrence of wetter and drier places in close proximity. This may allow co-occurrence of different communities on the same place (Topp et al., 2001, Frouz et al., 2008) or occurrence of species that require variable habitats for various activities as shown earlier on example of *L. niger* ants.

Soil Biota Development in Post-Mining Sites with Various Vegetation Cover

When comparing soil development in different post-mining sites we have to consider that sites with different vegetative cover may aim toward different target communities of soil biota. (Dunger and Voigtlander, 2005). In particular, strong differences can be found between deciduous and coniferous forests (Figure 4). This can be illustrated by the comparison of soil biota development in a pine plantation near Cottbus and an alder plantation near Sokolov (Frouz et al., 2001a).

Comparison of soil microflora activity reveals a much higher microbial respiration and rate of cellulose decomposition in alder sites near Sokolov in comparison with pine plantation near Cottbus, and microbial biomass in the alder plantation was higher than in the pine plantation, particularly when patches without understory were considered (Šourková et al., 2005b). Looking across the whole chronosequence, bacteria seem to be more abundant in the alder plantation near Sokolov, while fungi were abundant in the pine plantation near Cottbus (Frouz et al., 2001a).

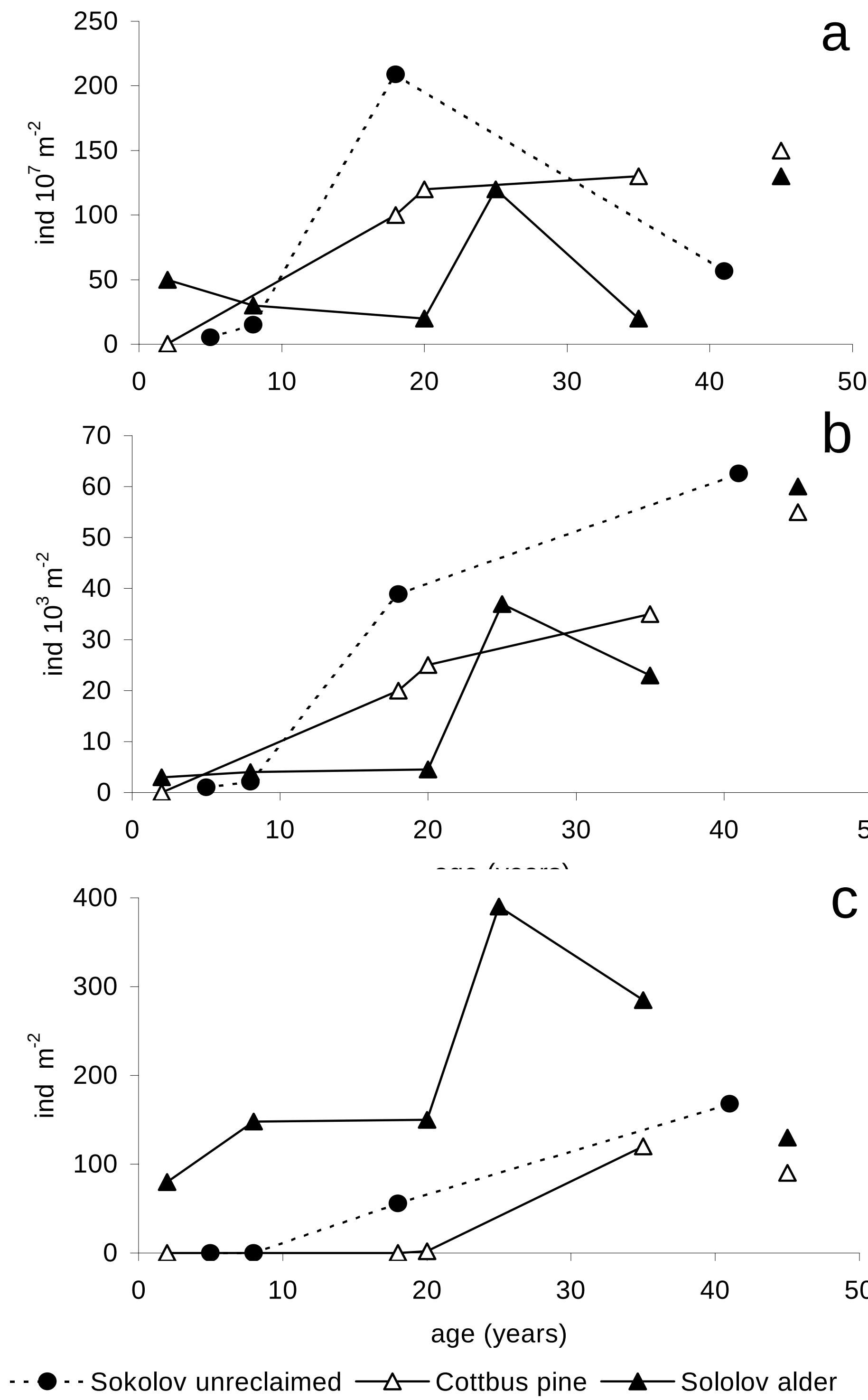

Figure 4. Changes in abundance of testacea amoebae (a), oribatid mites (b) and earthworms (c) in chronosequences of unreclaimed sites near Sokolov, pine plantations near Cottbus and alder plantation near Sokolov; based on Frouz et al. 2001 and 2008.

In the Cottbus area the abundance of all groups of soil fauna, with the exception of nematodes, gradually increased with successional age. A more variable pattern of successional changes was observed in the Sokolov area where, with the exception of nematodes, fauna abundance increased in young plots and peaked in the 20-30 year plot (Frouz et al., 2001a). After this, peak abundance either decreased (Oribatid mites earthworms, terrestrial isopodes) or followed some depression (collembolans, testacea amoebe, enchytraeids), or the rate of increase became much less (diptera).

The pattern of community changes along the successional gradient varied among both investigated groups of fauna, and between chronosequences. In the Cottbus chronosequence, quite often (in testacea amoebae, springtails, diptera and earthworms) no apparent change of dominance was observed with increasing plot age (Frouz et al., 2001a). In the Sokolov chronosequence, this happened only in Testacea amoebae, which were dominated by small, ubiquitous species such as *Trinema lineare* or *Coriotrion dubium* in both chronosequences. In the Cottbus chronosequence Collembola were dominated by the ubiquitous *Isotoma notabilis*, and microsaprophagous Chironomidae and Cecidomyiidae dominated among diptera (Frouz et al., 2001a). In this chronosequence only one ubiquitous epigeic species, *Dendrobaena octaedra*, represented earthworms (Frouz et al., 2001a, Pižl 2001). In other groups, eurivalent species were replaced by more eurivalent ones with increasing successional age. In Cottbus, bacteriaophagous and mycophagous species dominated the Nematoda community in pioneer plots, and later on all ecological groups increased in their proportion with an increase in mycophagous species in latter succession stages that seems to correspond with mycorrhizal development. On the contrary, in the Sokolov, the proportion of bacteriophagous species increased in older plots (Frouz et al., 2001a, Háněl, 2001, 2002, 2003). In potworms, replacement of Eurivalent *Enchytraeus* by more specialized *Fridericia* was observed in both chronosequences (Frouz et al., 2001a). In Sokolov, *D. octaedra* and *Lumbricus rubellus* were the most common species of earthworms in younger plots. The abundance of endogeic species *Aporrectodea caliginosa*, *Apporectodea rosea* and *Octolasium lacteum* increased in older plots (Frouz et al., 2001a, Pižl 2001). Ubiquitous *Tectocephalus sarecensis* and *Oppiella nova* dominated in the pioneer plots in both chronosequences, and were gradually replaced by ecologically more demanding species with increasing successional age (Frouz et al., 2001a). *Isotoma notabilis* dominated springtails in pioneer plots near Sokolov, while in older plots species of genera *Folsomia* and *Hypogastrura* were abundant (Frouz et al., 2001a). Among dipteran larvae, phytophagous Tipulidae dominated younger sites while saprophagous Tipulidae, Bibionidae and Limoniidae dominated older sites. In conclusion, groups that accelerate litter breakdown and soil mixing, such as terrestrial isopods, millipedes, large saprophagous diptera larvae and endogeig earthworms, were abundant in the alder plantation near Sokolov while some micro and mesofauna groups such as testacea amoebae, oribatid mites and potworms were abundant in the pine plantation near Cottbus (Frouz et al., 2001a). Similar differences were also observed when soil fauna were compared between deciduous and coniferous forests in other coal mining areas of Germany (Dunger, 1968; Dunger, 1991, Dunger et al., 2001, Topp et al., 1991).

A detailed comparison of reclaimed and non-reclaimed sites covered by alder plantations and natural revegetation was conducted in the Sokolov area. No apparent differences in microbial parameters were found between reclaimed and unreclaimed sites (Frouz and Nováková 2005; Šourková et al., 2005b). Reclaimed sites harbor higher densities of soil macrofauna, especially earthworms, which were significantly more abundant in reclaimed sites than in non-reclaimed ones, this is particularly true for endogeic species that occur only in the oldest unreclaimed sites (Frouz et al., 2001b, 2002, 2008). In Diptera, groups that play an important role in litter fragmentation dominate on reclaimed sites, whereas microsaprophagous groups dominate spontaneous sites (Frouz et al., 2001b, 2002, 2008). On the contrary, spontaneous sites harbor significantly higher densities of soil micro- and mesofauna such as testate amoebae and oribatid mites, namely in middle stages of succession (Frouz et al., 2004) (Figure 4). In older sites, earthworms also start to colonize spontaneously; in 40 years sites even endogenous species are present (Frouz et al., 2001b; Frouz et al.,2002; Frouz et al., 2004).

In conclusion, differences between reclaimed and unreclaimed sites seem to be driven by several factors, the first of these being litter quality. Similar to the above-mentioned comparison of pine and alder plantations, sites that are supplied with poorly-decomposable litter support more micro- and mesofauna than sites supplied with easily decomposable litter rich in nitrogen, which supports more saprophagous macrofauna. However, differences between unreclaimed and reclaimed sites seem to be affected also by colonisation rate, particularly in earthworms. They colonize spontaneous sites after 20 - 25 year of succession (Frouz et al., 2008), while in the reclaimed alder plantation they appear immediately after tree planting (Pižl, 1999, 2001) (Figure 4).

THE EFFECT OF SOIL BIOTA ON SOIL FORMATION NUTRIENT TURNOVER AND PLANT GROWTH.

As already mentioned, macrofauna is more abundant in the alder plantation on Sokolov than in plots near Cottbus reclaimed with pine, or unreclaimed sites in Sokolov. This is reflected in soil micromorphology and development of the topsoil layer. In the alder plantation of Sololov, the effect of fauna on litter breakdown was observed even in young sites (Frouz et al., 2001a and 2007b). In about 20-year-old plantations there is almost no leaf litter that could be seen on thin soil sections, and all the litter was transferred into fecal pellets of soil macrofauna, namely millipedes and Diptera larvae (Frouz et al., 2001a and 2007b). These fecal pellets are at the same time incorporated into casts of earthworm, namely *Lumbricus rubellus*, which dominate these intermediate sites (Pižl 1999, Frouz et al., 2001a and 2007b). In older alder plantation, with an age of around 40 years, almost all topsoil is formed by earthworm casts; fecal pellets of macroartropods are absent and litter fragments are dominated by less decomposable material such as small branches, etc. The absence of fecal pellets of millipedes and Diptera larvae is not due to a reduction of these groups, they are in fact more abundant in latter stages of succession than in intermediate ones, so the absence of their fecal pellets in soil profile is likely to correspond with more intensive incorporation of these structures in earthworm casts (Frouz et al. 2007b).

On the contrary, in the pine plantation near Cottbus there was no apparent activity of macrofauna in the topsoil. In young sites there were only pine needles lying on the soil surface. In older sites, we observed excrements of collembola oribatid mites and potworms in the soil profile. In 30 to 40 year old sites the layer of needles gradually increased, and excrements of mesofauna were moved down with percolating water together with fragments of needles. Excrements of mesofauna together with pine needle fragments formed a continuous layer on the interface between needles and mineral sand. This layer became more compacted with depth, most likely due to the action of water, and was penetrated by roots and fungal hyphae that bind individual particles together (Frouz et al., 2001a). In contrast to the alder plantation in Sokolov, no mixing of organic material into mineral layer was observed. We can conclude that whereas in alder plantations the soil grows down from the original surface by gradual incorporation of organic material in successively deeper layers, in the pine plantation the soil is built upwards by the gradual accumulation of fine organic particles on the original surface of mineral soil. The difference between the pine and alder plantations is in agreement with general concept of humus formation (Ponge, 2003). According to this concept, topsoil of coniferous forests that produce slowly decomposable litter is formed by a so-called moor type of humus, which is created mainly by the action of fungi and soil mesofauna. In deciduous forests the role of soil macrofauna is important, which leads to the formation of a moder type of humus, while in chernozem steppes and some southern deciduous forests most of the litter is processed with anetic earthworms which lead to formation of a mull type of humus. In Sokolov alder plantations, the topsoil of intermediate stages can be categorized as moder, while in older successional areas as moder with some shift to mull (Frouz et al. 2001ab).

There are also micromorphologically observable differences in the behavior of mineral parts between sands of Cottbus area and clays near Sokolov. While in Cottbus pine needles were found lying on the soil surface without any incorporation into mineral sand, in Sokolov some incorporation of litter fragments into mineral soil was observed even without the action of macrofauna, namely in young sites. This is due to the fact that clays display much larger changes in volume as a result of moisture and temperature changes than do sands. Shrinking during desiccation may form cracks into which fine particles of litter can be washed by percolating water after rain, and consequent swelling of clay will bind them into the clay matrix. Freezing and thawing can have a similar effect (Frouz et al., 2001a).

Development of topsoil micromorphology in unreclaimed sites near Sokolov, overgrown by natural revegetation, is even more complex. In initial stages of succession, one can observe only mineral spoil and few fragments of litter laying on the surface. In intermediate stages of succession a dense layer of leaf litter develops. In this layer we observed excrements of millipede, potworms and some Diptera larvae. In contrast to reclaimed alder plantations, there are much fewer of them and they are mostly located in the litter being more abundant in the bottom part of the litter layer, apparently washed there by percolating water (Frouz et al., 2007b). Only very little mixing was observed between organic and mineral layers and this mixing, if it occurs, seems to be caused mainly by mechanical washing of macroaorthropod fecal pellets into deeper soil layers. In older unreclaimed sites, from 30 to 40 years old, the earthworms colonize the sites which result in removal of this organic layer from the soil surface and its incorporation into the mineral layer in the form of earthworm casts. Thus in unreclaimed spontaneously revegetated soils near Sololov, the topsoil firstly grows upwards and moor type of humus develops. Later on, after earthworms colonize the sites, litter and fermentation layers were mixed into soil profile, soils start to grow downwards, and topsoil can be characterized as a moder-mull type of humus (Frouz et al., 2007a). A similar pattern was observed by Rusek (1978) during spontaneous primary succession, and by Dunger (1991) who observed first formation of a mood moodier type of humus then later, after earthworm colonization, a shift to moder mull-like type of humus. Described changes in micromorphology certainly affect development of soil layers (Frouz et al., 2001a, 2004). In the pine plantation near Cottbus, litter and fermentation layer thickness gradually increases with plot age (Frouz et al., 2001) (Figure 5). In the alder plantation near Sokolov, organic mineral A layer began to develop in young sites and their thickness increased with plot age (Fig 5) (Frouz et al., 2001b; 2002, 2004, 2007b). The difference in soil formation between the alder plantation and non-reclaimed plots near Sokolov was the most pronounced in intermediate stages of succession, where litter accumulates on the soil surface and a massive Oe layer develops in non reclaimed sites (Figure 5). In older plots, this difference was decreased as a consequence of earthworm colonization of non-reclaimed sites and consequent massive mixing of soil and A layer formation (Frouz et al., 2002, 2006, 2007a,b). This shift of dead organic matter from aboveground (litter) to belowground pool is characteristic for more advanced successional stages (Schafer et al., 1979).

The importance of soil macrofauna, particularly earthworms, for soil organic matter mixing was indicated in other studies as well (Lavelle and Martin, 1992; Hendriksen, 1997; Frouz, 2002, Frouz et al., 2007a). To measure this macrofaunal activity more precisely, we developed specialized enclosures that contain litter and mineral layer (Figure 6). The top litter layer can be used to estimate how much C is lost from the litter layer, in a manner similarl to classical litterbag studies. In litterbag experiments, the term "decomposition" is frequently used for any matter loss of litter in the enclosure. This matter loss may be caused by various processes resulting in different final stages of organic carbon, such as mineralization resulting in volatile CO_2, leaching of water soluble substances from the system, or fragmentation of litter and its deposition in the soil in the form of excrements of soil fauna. On the other hand, in the macrofauna accessible treatments, the important part of matter loss can be attributed to soil fauna consumption. Soil fauna have low assimilation efficiency so an important part of this C is released in form of excrement which may be deposited outside the litter bag and accumulated in the mineral soil layer. Thus matter loss measured in macrofauna accessible litterbags measure both mineralization and soil mixing. Similar conclusions were made by Wachendorf et al. (1997) using a comparison of total mass loss and mass loss caused by microbial and animal respiration in litterbags. Including the mineral layer in the enclosures allows us to estimate both processes: mineralization, and mixing of organic material into the mineral layer. In treatments inaccessible for macrofauna, the C loss from litter layer was not accompanied by C accumulation in mineral layer, and thus the majority of litter weight loss leaves the system in the form of CO_2, or by leaching. On the contrary, in treatments accessible to soil saprophagous macrofauna, most of the C that was lost from litter layer was actually accumulated in mineral layer, and consequently macrofauna caused no enhancement of C mineralization, but support C storage in mineral layer (Figure 6). This was true when saprofaugous macrofauna was present on the site. When saprophagous macrofauna was rare and the majority of macrofauna on the site was actually predators such as centipedes or carabid beetles, then macrofauna access can have no effect. It can even decrease C loss from litter treatment because access of predaceous macrofauna reduces the occurrence of soil mesofauna such as springtails or potworms. So when we compared reclaimed and non-reclaimed sites we saw that the amount of litter which is mineralized and lost from the system is similar in both reclaimed and spontaneous sites (Frouz 2002; Frouz et al., 2006). Removal of litter from the soil surface and soil mixing, however, differ substantially between sites. In spontaneous sites the majority of litter remains on the soil surface, but in the reclaimed sites the majority of litter was removed from litter layer and mixed into mineral layer (Frouz 2002; Frouz et al., 2006).

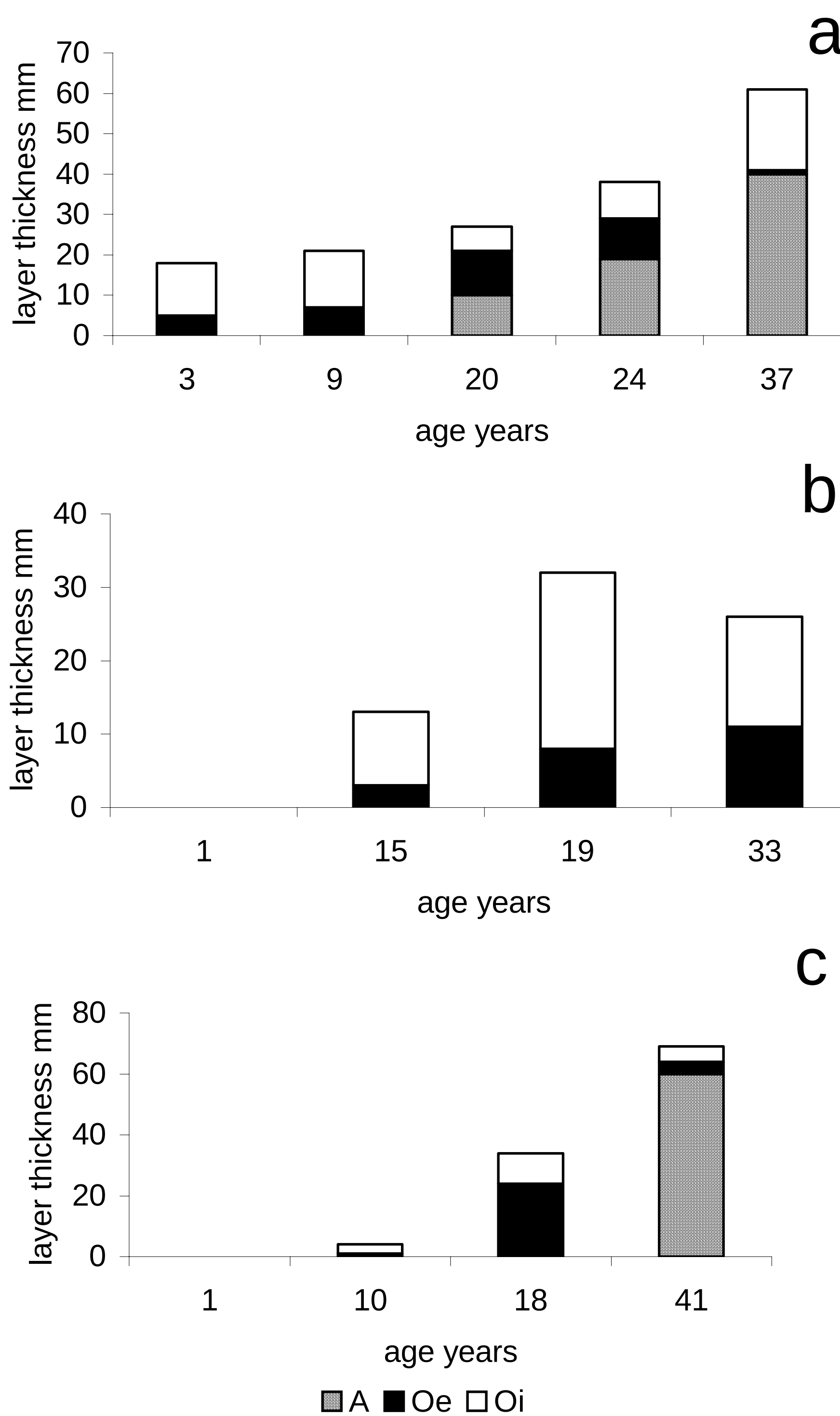

Figure 5. Changes in thickness of litter (Oi), fermentation layer (Oe) and organomineral humus horizon (A) in chronosequences of alder plantation near Sokolov (a), pine plantations near Cottbus (b) and unreclaimed sites near Sokolov (c); based on Frouz et al. 2001 and 2008.

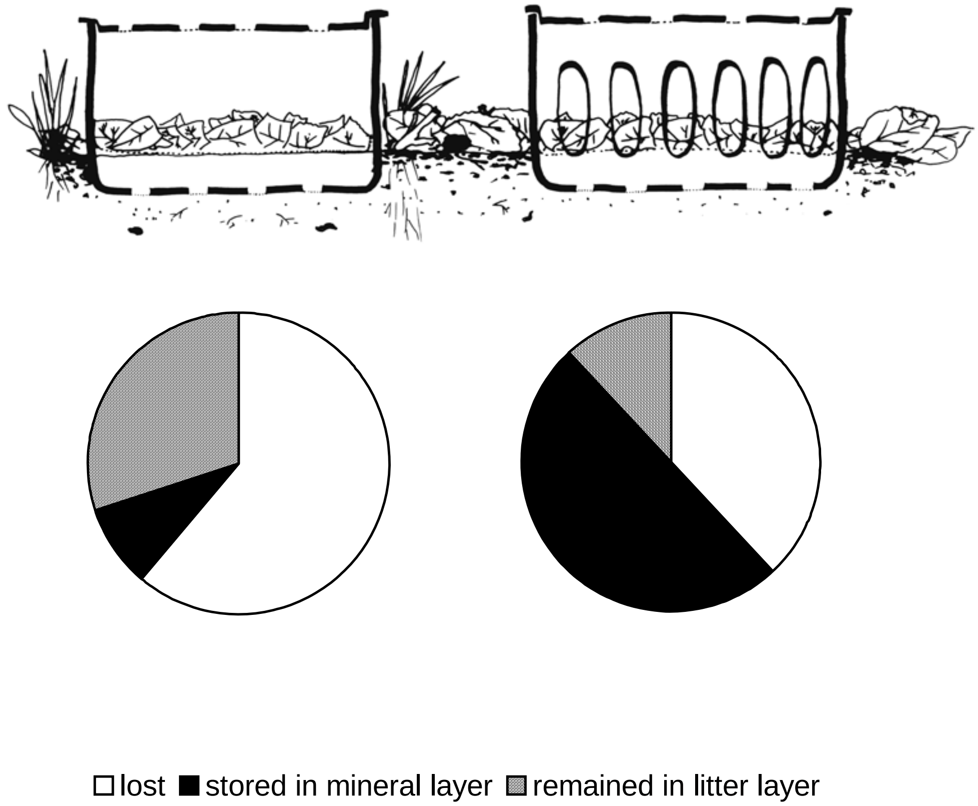

Figure 6. Distribution of carbon from litter added in to the enclosures between carbon lost from the enclosure (mineralized or leached), carbon retained in the mineral layer and carbon that is incorporated into the mineral layer. Enclosures were either non accessible (left) or accessible for soil macrofana and exposed in 38 year old alder plantation near Sokolov for one year, according Frouz (2002).

In reclaimed sites more C is stored in mineral soil due to activity of soil fauna. Macrofauna, namely earthworms, are more common on these sites due to above-mentioned non-target inoculation of reclaimed sites by fauna through the transport of soil with seedlings or machinery (Frouz et al., 2001a). However, soil macrofauna is sensitive to the amount and quality of litter (Lavelle et al., 1997). Higher densities of soil macrofauna in reclaimed sites probably correspond with a better quality of litter (lower C/N ratio – Šourková et al., 2005a). To differentiate the effects of litter quality and faunal set, field and laboratory experiments were conducted. In field experiments litter boxes were used that were similar to those described above, either accessible or non-accessible to soil fauna. In these two types of enclosures both types of litter, alder litter from the reclaimed site and willow dominated litter from unreclaimed sites were used. As expected, macrofaunal access enhanced C storage in the mineral layer of reclaimed sites, but had little or no effect on non reclaimed sites which were not yet colonized by earthworms (Frouz, 2008).

Organic matter mixed with mineral soil may plays an important role in the alteration of soil physical and chemical properties such as the increase of water holding or sorption capacity (Allison, 1973; Frouz et al., 2007a). For example, water holding capacity, water field capacity, and wilting point increased when the post-mining substrate was subjected to earthworm mediated soil mixing (Frouz et al., 2007a). More importantly, earthworm activity also increased the amount of plant-available water, calculated as the difference between water field capacity and wilting point (Frouz et al., 2007a). However not only earthworms, but also other macrofauna can have such a positive effect, for example, conversion of litter to fecal pellets of St Marks fly (*Bibio marci*) larvae have similar positive effect on retention of plant available water (Kuráž and Frouz, 2008). This is consistent with other studies in Europe showing that earthworm colonization may improve physical conditions of post-mining sites (Marashi and Scullion, 2003). This is mainly due to increasing aggregate stability (Malik and Sculion 1998, Scullion and Malik, 2000, Marashi and Scullion, 2003).

Earthworm colonization also affects other soil biota. Baldrian et al. (2008), who studied composition of microbial phospholipid fatty acids and the content of ergosterol in unreclaimed sites near Sokolov, observed a shift from a microbial community with a higher proportion of fungi to a bacteria-dominated community after earthworm colonization. Massive mixing of litter into the mineral layer and consequent reduction of the fermentation layer in reclaimed plots seems to be the reason for lower abundance of soil meso- and microfauna in reclaimed vs. spontaneous sites (Frouz et al., 2001b, 2002 and 2008). Similarly, Dunger (1968, 1991) and Frouz et al. (2001a) observed a decrease in mesofauna and microfauna in latter stages of succession in deciduous forests on post-mining heaps. In later successional stages described in these studies, earthworms become more abundant and also some shift from moder-like to mull-like form of humus was observed. These changes also closely correspond with changes in herbaceous vegetation (Frouz et al. 2008). A detailed survey of vegetation development on post-mining sites near Sokolov reveal two major clusters of vegetation. The first one was dominated by ruderal plants and was typical of young successional stages. In the second cluster, forest and meadow specialists are more common and this cluster was typical of later successiona; stages. Using discriminant analysis and backward selection, the only factor that explains the difference between clusters is presence or absence of the Organic mineral A horizon (Frouz et al., 2008). As was already mentioned, micromorphological studies done on the same plots show that the A horizon is formed mainly by earthworm casts (Frouz et al 2007b, 2008). Changes in vegetation also correspond with colonization of these sites by earthworms, which take part in soil mixing (Frouz et al., 2008). This led to hypothesis that colonization of post mining sites by worms changes soil site conditions and enables establishment of more demanding plant species. Certainly previous development of pioneer vegetation that produces plant litter on which earthworms can feed is an essential precondition for earthworm colonization. The hypothesis, that earthworm colonization supports development of later successional plant species, is also supported by some preliminary field and laboratory experiments that show faster growth of later successional plant species in presence of earthworms (Roubíčková et al., 2008). The colonization of post-mining sites has very dramatic effects on ecosystem development, as has been seen after the introduction of exotic worms to some forests in Northern America (Bohlen et al., 2004). However, here it happens in range of their natural occurence.

CONCLUSION

Before applying the results of this study, one should be aware that this research was achieved in only two post-mining areas in Europe, and reasonable caution should be taken before results are applied in other parts of the world.

Results show that substrate toxicity, adverse physical condition, vegetative development and migration constraints are the major environmental barrier for development of soil biota in post-mining sites. Site toxicity may have multiple origins, often correlated with low pH, high salinity and high metal content. Because of the multiple origin of toxicity in the post-mining substrates, wider use of biological tests for the determination of post-mining site toxicity are highly recommended.

Connectivity with the surrounding landscape and maintenance of site heterogeneity on the landscape, as well as on the local scale, may facilitate colonization of post mining sites by soil fauna. When the spoil is not toxic and physical conditions are not extreme then vegetative development, namely woody species, is a major driver that determines development of soil biota. Coniferous forests typically develop a soil community dominated by fungi and soil mesofauna, while a bacteria and macrofauna-dominated community is more likely to develop under deciduous forests, namely when the litter has low C/N value. Reclaimed sites often yield development of a diverse community, however its development is somewhat slower than development of reclaimed sites????. In suitable conditions, leaving some area to natural recolonisation may enhance diversity of future post-mining sites.

In post-mining sites reclaimed by conifers with a low presence of soil macrofauna, soil growth is often upwards and is characterized by formation of moor-type of humus with no or limited mixing of organic and mineral horizons. On the contrary, in deciduous forests, namely those with low C/N ratio, soil growth downward and moder- or moder-mull type of humus develops with apparent formation of an A horizon and mixing of organic and mineral layers. Comparison of spontaneous sites colonized and uncolonised by earthworms, and enclosure experiments clearly show that this soil mixing is mainly done by earthworms and other soil macrofauna. This mixing affects occurence of other soil biota, soil microbial chemical and physical properties including retention capacity, aggregate stability, etc. These effects on soil development can also indirectly affect plant growth.

Recent studies show that soil biota, namely soil fauna, development is an important factor that may affect reclamation success and require further attention in research and practical applications.

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Chapter 5

CONTAMINATIONS BY NATURAL RADIONUCLIDES AS A RESULT OF COAL MINING ACTIVITIES

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ABSTRACT

In the frame of mining activities, such as for brown and hard coal, huge volumes of highly mineralised water are pumped to the surface, which can contain significant amounts of radionuclides of both the natural 238U and 232Th decay series. This concerns especially the decay product radium due to mobilisation processes such as the alpha-recoil effect and leaching in the coal layers and surrounding rock formations.

Despite the fact that coal seams are made of organic components and therefore do act as a sink for uranium in dependence from geological settings such as ascending uranium bearing waters, the coal's initial uranium and thorium content are usually low. However, under reducing milieus as they are established in coal seams 238U, its next progenies and 232Th are indeed strongly immobile, but by disintegrating into radium the first significantly soluble radionuclide is formed within each decay scheme. In order to design radium enrichment in circulating formation waters, only ordinary radionuclide concentrations in the source rocks are required. Once those saline pit waters acting as a radium carrier are brought to the surface, different types of contamination by natural radionuclides, which means radium and its progenies, can occur due to changes in physical and chemical conditions. On the mining sites radionuclides can be concentrated in scales being precipitated inside tubes or in sludges being generated in tailing ponds by suspension settling, but also sewers and rivers in public areas can be affected if the brines are discharged untreated. In that case especially sediments along those streams can get contaminated by radionuclides.

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In addition, special attention must be also paid for radon occurring as an isotope within both the decay series, because under environmental conditions it is a volatile element and therefore enabled to exhale from solids.

INTRODUCTION

In general, mining activities for all kinds of resources are usually connected with the force to deal with formation water. In some cases such as the oil and gas exploitation that water can be pumped back into the reservoir immediately (in that special case also with the positive aspect of enhancing the reservoir pressure), but if there is a need to send miners into the pit, it is inevitable to develop a treatment scheme for the pit water to be brought on the surface. The pumping activity comes along with changes in physical and chemical conditions due to decreasing temperature and pressure and/or available oxygen (or other chemical reagents), which then react with the substances transported in the water. As a result, sediments are settling on the bottom of installations or precipitations occur. These phenomenons are very well known for hazardeous ingredients such as heavy metals, which moreover can be concentrated in the settled suspensions, but also naturally radioactive elements can be affected by those processes. In frame of coal mining special attention must be paid for radium, because that is the natural radionuclide being mainly transported with the pit water to the surface and there, it can be concentrated as scale in tubes or in sediments of tailing ponds, sewers and rivers. Since radium is part of the ^{238}U decay series also progenies are produced, from which the volatile ^{222}Rn and the long-living ^{210}Pb with a half-life of more than 22a must be emphasised.

The knowledge about the phenomenon of enhanced natural radionuclide concentrations as an accompaniment of non-uranium mining traces back to the early beginning of the 20th century when Elster & Geitel (1904) discovered an enrichment of radioactive substances in thermal brines, which were raised to the surface as an unwanted by-product in frame of oil- and gas exploitation. It was the same year when radon was found in petroleum by Himstedt. Nevertheless, no profound investigations were undertaken until the early seventies. In 1975, Gesell measured elevated ambient gamma dose rates on the installation surfaces of a gas processing plant, which he attributed to radon progenies, and identified ^{210}Pb on the internal surface of processing equipment as a significant potential exposure hazard in frame of maintenance operations as well. In 1965 enhanced gamma radiation was discovered in Polish hard coal mines by Saldan, but regular surveys have not been started before the seventies by Tomza & Lebecka (1981), who determined radium as the main radiation cause due to the pumping of radium-bearing waters from the underground to the surface. In 1982 also Gans et al. reported the occurrence of high radium concentrations in waste waters from hard coal mining in the German Ruhr-basin. Since then, especially in Germany and Poland a lot of investigations have been carried out to understand and estimate the radium's hazard potential as a result of coal mining activities (e.g. Lebecka et al., 1994, Feige & Wiegand, 1999, Chalupnik et al., 2001, Schmidt & Wiegand, 2003, Leopold et al., 2007).

NATURAL RADIOACTIVITY

The chemical behaviour of an element is determined by its electronic configuration (Riedel, 1994). In contrast, the phenomenon of radioactivity just depends on the composition of the element’s nucleus, which means the balance of neutrons in comparison with the amount of positrons. The nucleus of a radioactive element is unstable in its energy condition and therefore characterised by spontaneously decaying resulting in emitting ionising radiation, which can change the physical or chemical structure of other atoms of matter it passes through. This radiation consists of either alpha or beta particles and is commonly accompanied by simultaneous gamma radiation (Stroppe, 1994). Alpha particles are positive charged helium nuclei and are easily absorbed by a few centimetres of air and are not able to penetrate a sheet of paper or the human skin. Nevertheless, in case of incorporation alpha particles are the most destructive kind of radiation. Beta particles are occurring if there is an oversized amount of neutrons in comparison with the amount of protons and do consist of fast, negatively charged electrons, so another positron is created in the nucleus. Beta particles can affect in metre-scale in air; in case of soft tissue they reach a few millimetres up to centimetre. Gamma radiation is a type of high energy electromagnetic wave and therefore consists of photons, whose energy in each special case depends on the kind of nucleus decaying, the kind of conversion happening and the stability of the next produced nucleus. It occurs if in the process of disintegration an unstable nucleus is formed, which then transforms into basic conditions by emitting photons. Gamma ray is the most penetrating kind of ionising radiation without a specific elimination distance, which therefore means weighty materials of high atomic numbers, e.g. lead (Z=82), must be used as a protection shield for weakening (Borsch et al., 1996).

Radioactive elements can either occur as natural ones or being man-made as artificial ones. The last are mainly due to nuclear energy production or nuclear weapon development. Radioactive elements are also called radionuclides and can be concentrated in solid or liquid materials, in case of radon and its isotope thoron also as volatiles in tight spaces by either natural or human factors. All radionuclides are decaying according to their specific half-life, which means the time passing by to reach the half of the initial activity. A half-life is characterised by an exponential decrease, activity is defined as one decay per second and described by the unit “Bq” (Bequerel).

Natural radionuclides are separated into cosmogenic and primordial ones. The cosmogenic natural radionuclides are continuously created by interactions of cosmic radiation in the atmosphere (e.g. ^{3}H or ^{14}C), whereas the primordial natural radionuclides are still present since the act of nucleosynthesis before the planet earth was formed due to their rather long half-lives. The resulting progenies are defined as radiogenic and can be distinguished into those being part of a decay series and those of just one disintegration step resulting in a stable nucleus immediately (e.g. ^{40}K decaying into ^{40}Ar). There are existing three disintegration schemes classified by the initial decaying radionuclide: ^{238}U, ^{232}Th and ^{235}U (Fig. 1). Each of them results in a stable lead isotope after passing more than a decade of disintegration steps of other elements and their isotopes. Due to the ^{235}U’s very small portion of less than 5% within the uranium’s distribution in the environment (Siehl, 1996), the by far most of it is present as ^{238}U, so that this is the uranium isotope of interest.

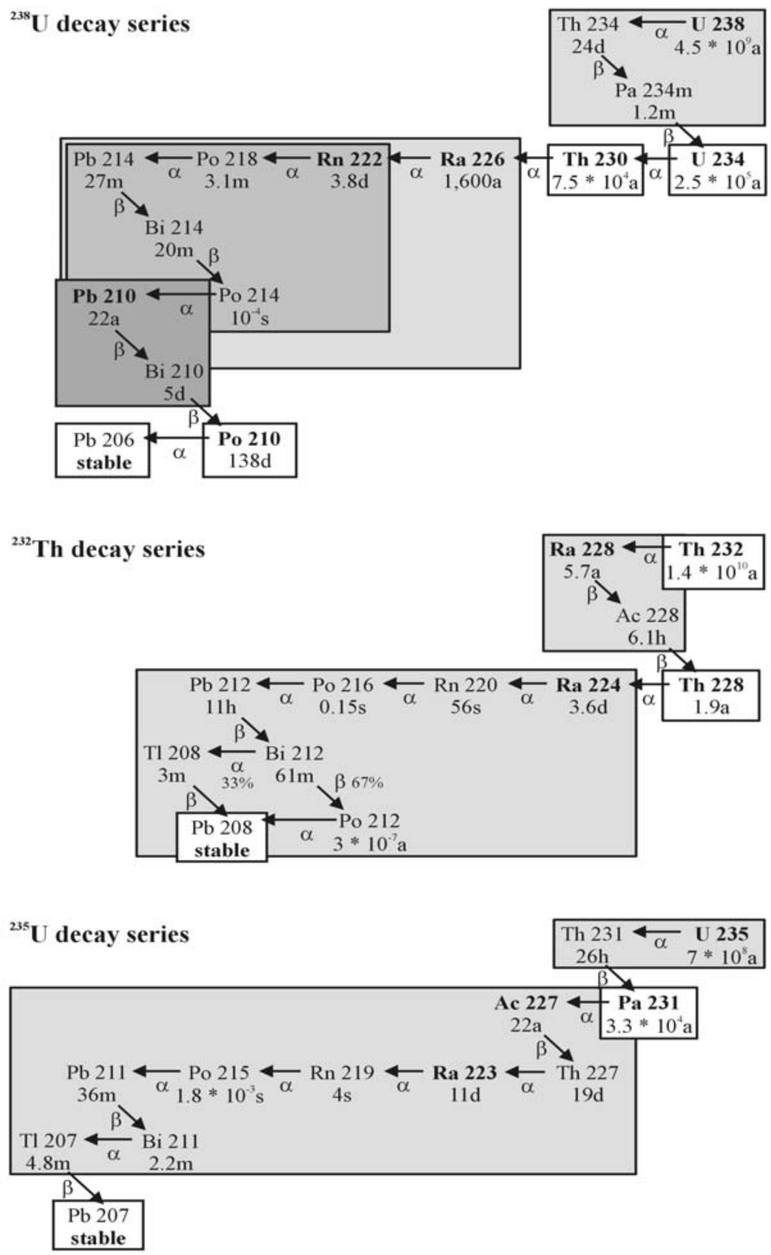

Figure 1. The three natural decay series according to their nucleus' kinds of decay and half-lives.

DEFINITIONS OF RADIOACTIVE MATERIALS

During the last century some substances being used in frame of production processes of certain industry types have been indentified to contain enhanced levels of natural radionuclides. Those types of industries can be summarised as follows:

1. Metal ore processing and metal recycling
   e.g. iron and steel production, reuse of scrap metal
2. Mineral extraction and processing
   e.g. fertiliser production, abrasive and refractory industry
3. Organic material exploitation
   e.g. oil- and gas extraction, coal mining
4. Thermal-electric production
   e.g. coal-fired power plants
5. Water treatment facilities
   e.g. waterworks, geothermal installations
6. Tunnelling and underground workings
   e.g. tunnel/sewer systems, underground caverns

It became useful to classify those substances containing elevated concentrations of natural radionuclides due to their position in the processing schemes. According to Penfold et al. (1999), raw materials can contain activity concentrations of several, even thousands of Bq/kg of naturally occurring radionuclides, often concentrated by the same natural process that concentrates the elements in which the raw material is rich. Such materials are typically extracted and processed in very large quantities; the physical characteristics can range from beach sand to a dense rock. Their processing may concentrate the radionuclides in unwanted by-products in both, technical installations and in the environment as well as in residues. This can occur by means of mass separation (e.g. in processing of monazite/zirconium mineral sands), other physical phenomena (e.g. the volatilisation of lead and polonium in high temperature furnaces) or by chemical reactions (e.g. the precipitation of radium containing scales in tubes). The activity concentration of by-products or residuals may be high as several ten thousands Bq/kg of certain radionuclides. The quantities of such material are often smaller than those of raw materials, particularly those by-products with high activity concentrations. Then, in some cases the resulting products intentionally contain high levels of naturally radioactive elements such as thorium, although not for the radioactive properties of the elements. An example of such a use is that of thorium in welding electrodes, where it aids arc ignition and stability. The activity concentrations of such materials may be quite high, perhaps several hundred thousands of Bq/kg. In summary this gives a total of five groups:

1. Raw materials
   e.g. raw phosphate, manifold types of ores
2. Unwanted by-products (waste) in technical installations
   e.g. scales in the oil & gas industry's tubes, sludge in underground galleries and/or tailings in surface settling ponds
3. Unwanted by-products (waste) in the environment
   e.g. river bottom sediments, flood plain soils or dead rock stockpiles
4. Residuals
   e.g. fly ash, slag
5. Final and intermediate products
   e.g. fertilisers, thoriated welding electrodes, alum earth, building materials

In general, there do exist some different acronyms concerning natural radioactive materials which were introduced by special intentions during time. NORM is most commonly used and comprises all solid ***N***aturally ***O***ccurring ***R***adioactive ***M***aterials being created by natural processes. Rarely, the term NOR is also used for the same meaning (Vandenhove, 2002), but in fact it is slightly different because it stands for ***N***aturally ***O***ccurring ***R***adionuclides and therefore just being focused on the radioactive elements and not on the materials the radionuclides are stored in (Knaepen et al., 1995). The following simplified scenario gives an example of how NORM can be created and can occur. In frame of the geological genesis called magmatic differentiation uranium/thorium (if present) are relatively enriched in the magmatic fluid because they are incompatible elements due to their large ion radius. Therefore, uranium and thorium are then fixed in the crystal lattice of lately solidified minerals such as the heavy minerals zirconium or monazite (Dybek, 1962). Those accessory minerals can show uranium and thorium concentrations of some thousands Bq/kg. In further consequences, the rock types containing those accessory minerals can also show high radionuclide concentrations. If uranium was not enabled to crystallise in those minerals during magmatic differentiation, then it might be forced by decreasing temperatures and pressures to get solidified by oxidation as black spheroid pitchblende e.g. along cracks and grain boundaries in rocks, today maybe outcropping close to the surface. This kind of accumulation mainly occurs in case of silicate rocks (granite or pegmatite) being made of common and frequent minerals (Kemski et al., 1996). Granites exposed to weathering processes may provide the uranium for erosion transports, which further on may lead to an enhanced concentration of heavy minerals in placers along riverbanks or onshore called mineral sands.

Both the acronyms mentioned above concern radioactive materials showing radionuclide concentrations made by natural phenomenon. If the radionuclide content of natural radioactive materials is unintended enhanced by man-made procedures, the acronym TENORM is widely used meaning ***T***echnologically ***E***nhanced ***N***aturally ***O***ccurring ***R***adioactive ***M***aterials for emphasizing the technical factor. Notwithstanding, the terms TENR or ENOR can also be found for the intentions of *Technologically Enhanced Natural Radioactivity* (Edmonson et al., 1998) respectively Enhanced Naturally Occurring Radioactivity. In 2002, Paschoa & Godoy picked up once again the acronym HINAR to determine areas affected by HIgh NAtural Radioactivity, which has been used initially in 1975 within the title of the first international conference dealing with both, NORM and TENORM, held in Brazil.

According to the example for NORM given above, the term is used to describe natural materials such as mineral sands. These placers may exceed background radionuclide concentrations, but they are of natural state. If the human component is interacting by treating the mineral sands resulting in separated materials also of higher radionuclide concentrations than the background, these materials are TENORM. According to EPA (2000), in the past some confusion was created by using the acronym NORM simultaneously for the intention of TENORM, especially before 1998. At the NORM IV conference held in May 2004 in Polish Szczyrk, the simultaneous use of all those different acronyms mentioned above was an important part of the round table discussion. The participants came to the conclusion that despite it is not technically the most accurate term, NORM is the most general and commonly used one (IAEA, 2005). In this study, TENORM is used further on because from the scientific point of view it is the correct term for the presented materials.

All natural solid substances, which are produced or occur in the environment as a result of human activities and may cause enhanced radiation exposure are called TENORM. The enhancement factors can be due to manufacture processes, mining activities and/or water treatment. Therefore, TENORM are characterised by an artificial enrichment or translocation of natural radionuclides and it is out of interest if the factories are still active or were abandoned in the past. A translocation is only considered as a TENORM generating process, if the availability of radionuclides is increased. Per definitionem, the enrichment as well as the translocation are due to physical or chemical processes within the human material treatment. TENORM are accountable for an enhanced radiation against the background in their neighbourhood (Leopold & Wiegand, 2002). A material is to be considered as TENORM if just one radionuclide of the ^{238}U or ^{232}Th decay series is exceeding the threshold of 200Bq/kg dry mass. This threshold value is applied in many EU member states according to Article VII of the Directive 96/29 EURATOM and is justified by the rough correlation of the ambient gamma dose rate[1] of 1mSv/a measured 1m above the ground and the corresponding radionuclide concentration of 200Bq/kg homogenously distributed in the ground.

In 1959 the World Health Organisation (WHO) published a report regarding the genetic effects which might be produced in humans due to the increasing use of ionising radiation in medicine, science and industry (WHO, 1959). In 1975 the first international conference dealing with enhanced natural radioactivity as a result of non-uranium mining was held in Pocos de Caldas, Brazil. Nowadays, international conferences are held continuously in periods of some years such as the TENR- or NORM-conferences.

COAL IN THE SCOPE OF NATURAL RADIOACTIVITY

It is a common geological phenomenon that in the depths especially of hard coal layers highly mineralised waters circulate, which are then no longer called groundwater but deep water, and the occurrence of natural radioactivity is closely connected to those saliniferous waters. This is due to the fact that radium is the first significantly soluble radionuclide within both the decay schemes under those reducing milieus as they are established in coal seams. As mentioned by Wiegand (2003), its precursors uranium and thorium are to be taken for immobile: uranium forms the almost insoluble $U(OH)_4$ (solubility product 10^{-52}) and thorium forms $Th(OH)_4$ (solubility product 10^{-35}). Both elements might have been transported by ascending waters under other chemical conditions from lower layers and then fixed in the organic material. However, the coal's initial uranium and thorium content are usually low (FME, 2007).

[1] Ambient gamma dose rate is defined as the effective gamma dose received at a special location in a specified period, usually hour or year. The effective gamma dose is the sum of all organospecific gamma doses and is given in "Sievert" [Sv=Joule/kg]. The organspecific gamma dose is the energy a human receives by gamma radiation and is classified according to the harm potential for the human tissue/the most important organs, its unit is also given by [Sv]. The pure energy a material is exposed to is called energy dose, its unit is given by [Joule/kg]. According to the EU-directive 96/29 the effective gamma dose shall not exceed 1mSv in a year for members of the public.

The processes involved to enrich radium in highly mineralised deep waters are described in detail by Wiegand (2003), on whom the following paragraphs are based. By looking at the half-lives of both the longest living radium isotopes ^{226}Ra (1,600a) and ^{228}Ra (5.7a) it becomes quite clear that there is no primary radium contained in the rocks' minerals, only a rough maximum of 16,000a can be assumed. This represents 10 half-lives of ^{226}Ra, afterwards its activity is more or less straight and significantly reduced. Therefore, the permanently occurring radium atoms must be generated by the decay of the uranium and thorium precursors. In consequence, the radium's bonding is weakened in comparison with the original uranium or thorium element, because one or several alpha-decays happen until radium is formed and those alpha particles consist of massive helium nuclei resulting in a dislocation of the decaying isotope by recoil. This effect is called "alpha-recoil" and results in a damage of the crystal lattice and a more or less isolated position of the radioactive element. Therefore, radium can occur as an interstitial ion or interact in different manners with anions being set free by radiation damages.

In order to transfer radium from the rock into the surrounding formation water 4 types of processes should be taken into consideration (Kraemer & Reid, 1984): dissolution of minerals, diffusion, leaching and alpha-recoil effect. Both the first ones are not able to explain higher radium concentrations in water sufficiently. Dissollution is not adequate due to very low dissolution products of silicate rocks, which are very common in the neighbourhood of coal seams, and also diffusion is much to slow as calculated by Bloch & Key, 1981 (diffusion distance in minerals $<1.8 * 10^{-10}$m / 10^{6}a). In contrast, a preferred radium leaching and the formation of a soluble radium chloride complex are frequently discussed as an important mobilisation process (Kraemer & Reid, 1984, Ku et al., 1992), the solubility of $RaCl_2 * H_2O$ is given by 245g/l (Gmelin, 1977). Nevertheless, it is well agreed that the above described alpha-recoil effect is the dominating one for transfering radium into water (Thomas et al., 1993). In summary, a mixing of both leaching and alpha-recoil is responsible for radium mobilisation from rocks.

By having a closer look on the radium isotopes within both the ^{238}U and ^{232}Th decay series, the mineral lattice's disturbance by the alpha-recoil effect results in different degrees of their availability. ^{226}Ra is formed after 3 alpha-decays and should therefore be more available than ^{224}Ra after 2 alpha disintegration steps, whereas ^{228}Ra is created after only one alpha decay and should show the lowest availability. Keeping this theory in mind, the mobilisation potential of radium isotopes can be summarised as follows: $^{226}Ra > ^{224}Ra > ^{228}Ra$. In fact, this order was proven correct by different authors: $^{226}Ra/^{224}Ra > 1$ (Wiegand, 2003), $^{224}Ra/^{228}Ra > 1$ (Martin & Akber, 1999) and $^{226}Ra/^{228}Ra > 1$ (Gmelin, 1977). The same ratio is very well known for the higher mobilisation rate of ^{234}U compared with its precursor ^{238}U. But in the same way as the recoil effect leads to enhanced radionuclide availabilities in water it also reduces the mobilisation rate of ^{226}Ra in some extent. In frame of the uranium decay series that ^{234}Th being recoiled into the formation water can be recoiled back into the rock's mineral as ^{230}Th in the course of the ^{234}U decay. This phenomenon leads to the fact that the fraction of mobilised ^{226}Ra is not exactly thrice as the mobilised ^{228}Ra fraction and not 3/2 times of ^{224}Ra, but it should be higher than those of the other radium isotopes due to a better availability as a result of increased crystal damages.

After the cation radium (it mainly appears as a Ra^{2+} cation, Dickson, 1990) has entered the water, a portion will be adsorbed on negatively charged mineral grain surfaces. According to Tanner (1994), the competition of cations for adsorption places regulates that portion or detaches already adsorbed radium isotopes. In frame of that process attention must be paid especially on those bivalent cations like Ba^{2+} and Sr^{2+} which are part of the same chemical group called earth alkaline metals as radium is. Nevertheless, also univalent ions like Na^{+} or K^{+} can interfere by desorbing. But beside the presence of cations also anions can influence the mobilisation of radium, so that NO_3^- sets twice as much radium free than Cl^- due to different states of hydration. Wiegand (2003) discusses those effects deeply and emphasises that the cation competion controls the radium mobilisation whereas anions just modify the conditions for ion exchange. In general, an equilibrium between ad- and desorption of radium is established very quickly after 0.5-2h (Levins et al., 1978). Furthermore, barium tends to precipitate as barite $BaSO_4$ if oxic conditions are established and sulphate is present. Due to the very similar ion radius of barium and radium, also radium is co-precipitated by substitution and the resulting mineral is called radiobarite $Ba(Ra)SO_4$. Pure $RaSO_4$ is not formable, because even high radium concentrations do not come along with high atom concentrations (1Bq/l ^{226}Ra corresponds to $1.2 * 10^{-13}$mol/l, 1Bq/l ^{228}Ra to $4.3 * 10^{-16}$mol/l respectively), so there are not enough particles available. Ra^{2+} is also partly adsorbed on hydroxides such as Mn- and Fe-hydroxides (Wiegand, 2003). For all these reasons the salinity respectively the element load of pit waters are very important parameters to describe their influence on the radium's behaviour.

Saliniferous deep waters contain usually ^{226}Ra and ^{228}Ra concentrations in the order of a few Bq/l up to a few 100Bq/l (Wysocka et al., 1996). In order to design such radium enrichments in the circulating formation waters, only ordinary radionuclide concentrations in the source rocks are required. In fact this statement is proven right by a simple calculation undertaken by Wiegand (2003): a sandstone aquifer with average uranium and thorium activity concentrations of crustal rocks contains 31Bq/kg of ^{238}U and therefore also of ^{226}Ra in equilibrated state and 41Bq/kg of ^{232}Th and ^{228}Ra, respectively, representing a $^{226}Ra/^{228}Ra$ ratio of about 0.75 (not a mobilisation potential). If that sandstone is characterised by a typical density of 2.6g/cm^3 and a relatively high porosity of 20%, 1dm^3 of rock weighs 2,100g roughly and the water volume is of 0.2l. Taking the average ^{226}Ra concentration of 31Bq/kg, the rock contains 65Bq ^{226}Ra. For a relatively high ^{226}Ra concentration of 10Bq/l in the formation water only 3% (2Bq) of the rock's concentration must be mobilised. This is a very reasonable mobilisation portion which would be reduced even more if the porosity or the volumes of cracks are smaller than 20%.

It must be pointed out that the highly mineralised deep waters act as a radium carrier and do therefore interrupt the ^{238}U and ^{232}Th decay series, so that the radium's progenies are also brought to the surface by pit waters. A lot of them have only very short half-lives of just a few seconds or minutes (see fig. 1), but nevertheless two of them must be highlighted. On the one hand there is the noble gas radon as the radium's direct progeny, on the other ^{210}Pb of the ^{238}U decay series shows a rather long half-life of more than 22a.

Radon occurs within all three decay series as an isotope: that of the ^{238}U scheme is called radon (^{222}Rn) and has the longest half-life of 3.8d, that of the ^{232}Th series is called thoron (^{220}Rn) with a half-life less than a minute and the third, actinon (^{219}Rn) being part of the ^{235}U decay series, is characterised by a half-life of only 4s. Therefore, the focus must be set on ^{222}Rn, because as a relative long living and also gaseous radionuclide it is able to migrate by diffusion or convection from solid materials. But despite its higher density (9.73g/l) than air (1.29g/l), it mostly gets distributed homogeneously very quick due to strong convective currents in the atmosphere (Philipsborn, 1990, Porstendörfer, 1996). The release and transport of radon is controlled by three main processes: emanation, migration and exhalation. The emanation rate is given by the radon release from the crystal lattice into the pore space of a solid and if this value, given as [Bq/kg], is related to the solid's ^{226}Ra content, the emanation coefficient of that material is determined as a percentage. This is an important parameter, because it specifies the volatile loss from the ^{238}U decay series. According to White (2001), the physical properties of the ^{226}Ra bearing material largely influence the radon emanation from that material. These physical properties include:

1. the distribution of ^{226}Ra within the material
2. whether the material is massive or granular
3. the type and magnitude of the material's porosity
4. the moisture content in the material
5. the effective ^{222}Rn diffusion coefficient of the material

The maximum emanation rate is reached by water saturation of the solid material, because the liquid slows down the recoil energy of the formed radon atom (alpha decay), so a penetration of the next surrounding grains is interfered, and acts also as a blocking layer for the grains' surfaces resulting in a reduced adsorption (Pellegrini et al., 1996). The second process is the migration, which describes the diffusive and convective transport in the solid. In general, diffusion is caused by temperature, density or concentration gradients. Concerning radon, it describes the amount of ^{222}Rn-atoms perambulating a well defined plane per time and depends on moisture content and pore diameter, because both avoid free movements of radon by collision with other molecules. Convection is the passive transport of ^{222}Rn by a carrier like soil gas or water, e.g. ground water and its ascending or descending, which leads to movements of the air column above (Schachtschabel et al., 2002). The third process is called exhalation, which is the unit for the amount of radon being set free into the atmosphere. It is controlled by the same mechanisms as the migration with the addition of the grain surface's development. Meteorological factors are said to have a strong influence, so rainfall reduces the ^{222}Rn exhalation potential by blocking the surface with water. After the blocking water layer is removed, a rapidly increasing exhalation rate can be observed. This scenario is also transferrable for winter time when snow acts as a blocker (Tanner, 1980). Another interfering parameter is the type of soil, e.g. strongly adhesive types like muddy clay forces the ^{222}Rn to migrate below, which is then exhaled somewhere else where pathways are established. More detailed information about radon and its environmental behaviour is given by Kemski et al. (1996).

The lead isotope ^{210}Pb being part of the ^{238}U decay series has a relative long half-life of more than 22 a. Therefore, it tends to grow again from its precursors ^{226}Ra respectively ^{222}Rn until the same activity concentrations are reached (radioactive equilibrium). Since ^{210}Pb results from the gaseous ^{222}Rn decay, there is also the possibility given of atmospheric transport and enrichment in case of enhanced radon concentrations. Lead is characterised by a rather low solubility of $3.4 * 10^{-28}$, which results in precipitation as PbS or $PbCl_2$ (solubility of 10^{-5}) under reducing milieus very soon. Nevertheless, the ^{210}Pb activity concentration can be roughly used for estimating the age a material (e.g. sediment) got contaminated by radium from the ^{238}U decay series, if the $^{226}Ra/^{210}Pb$ ratio of the initial material (e.g. discharged pit waters) and the permanent fallout from the atmosphere are well known. As pointed out by

Schmidt & Wiegand (2003), the $^{226}Ra/^{228}Ra$ ratio is much more reliable due to the ^{228}Ra's more accurate determination technique, but it demands for the ^{232}Th decay series.

TENORM PRODUCED BY MINING

From the radiological point of view the main problem of coal mining is closely connected with the pumping of the deep formation waters to the surface and the resulting changes in physical and chemical conditions. The waters act as radium carriers and bring that unwanted load to the surface. In order to classify the following given values of ^{226}Ra in water it should be kept in mind that the average ^{226}Ra concentration in untreated German surface water is of about 0.004Bq/l, in a very few geological areas of mainly granitic rock compositions up to 0.4Bq/l (LfU, 2003).

As obvious from Table 1, the different types of coal usually do not contain strongly enhanced radionuclide concentrations. One exemption is reported by Wingender (1995) for hard coal having been extracted in Freital, East Germany. The coal there is interspersed by uranium leading to high ^{238}U concentrations up to 15,000Bq/kg. In the former German Democratic Republic (GDR), those coals have been used for combustion until the 1960's, later on only the uranium content was exploited (Henningsen & Katzung, 1998).

Table 1. Activity concentrations in substances from coal extraction ([1]FME, 2007, [2]Chalupnik et al., 2001, [3]Feige & Wiegand, 1999, [4]Juhasz & Szerbin, 2002, [5]Moravanska & Laciok, 2002, [6]Leopold et al., 2007, [7]Schmidt & Wiegand, 2003)

material	activity concentration [Bq/kg]			
	^{238}U	^{226}Ra	^{210}Pb	^{228}Ra
German brown coal[1]	n.d.	max. 50	n.d.	max. 60
German hard coal[1]	n.d.	max. 150	n.d.	max. 70
Czech hard coal[5]	max. 110	n.d.	n.d.	n.d.
Hungarian hard coal[4]	max. 430	n.d.	n.d.	max. 110
German coke[1]	n.d.	max. 30	n.d.	< 20
German bitumen[1]	n.d.	< 20	n.d.	< 20
German pit waters[3]	n.d.	max. 13 [Bq/l]	n.d.	n.d.
Polish pit waters[2]	n.d.	max. 25 [Bq/l]	n.d.	n.d.
German sediments influenced by pit water[3]	n.d.	max. 32,000	max. 150	max. 6500
Polish sediments influenced by pit water[2]	n.d.	max. 50,000	n.d.	max. 6400
German surface water[7]	n.d.	0.163 [Bq/l]	n.d.	n.d.
Polish surface water[2]	n.d.	1.3 [Bq/l]	n.d.	n.d.
Polish scale in tube[6]	n.d.	100,000	n.d.	62,000
Polish tailings[6]	n.d.	6,000	n.d.	7,200

n.d.: no data available

In Germany, the excavations for brown coal in open pit style demand for well developed water treatment installations in very large areas. The pit waters are usually not very rich in their element load, probably due to the much lower depths and also lower carbon content of the mined brown coal. Therefore, the salinity steps back in its radium control, but nevertheless the waters can contain some ^{226}Ra in concentrations of 0.1Bq/l. This value gets put into perspective by the fact that for the excavations very huge volumes of groundwater (about 1 billion m^3/a) must be pumped to the surface, which then results in high annual emissions of 100GBq/a roughly being released into sewers and/or rivers (Feige & Wiegand, 1999).

In frame of hard coal extraction, the generated pit waters have to be classified as highly mineralised brines, because those are coming from much deeper layers where the circulating formation waters carry a lot of different elements and ions. Therefore, the parameters "presence of barium", "sulphate content" and "reducing milieu" get a high importance for the amounts of radium being brought to the surface. If barium and sulphate are present in the pit water as commonly occurring, precipitations of so called scales can occur in the pumping installations such as tubes or vessels, which then consist of almost pure radiobarite and show high radium activities of both isotopes due to the strong concentration process. Investigations of such material were undertaken by Leopold et al. (2007) in the Upper Silesian Coal Basin (USCB) in Poland, who found activity concentrations ranging between 40,000Bq/kg and more than 100,000Bq/kg for ^{226}Ra and between 27,000Bq/kg and 62,000Bq/kg for ^{228}Ra at a discharge point into the former Rontok tailing pond. As obvious from Figure 2, the red crust covers half of the pipe and the area in front of it. That reservoir in the background is no longer in use and in frame of reclamation activities the former saline water has been replaced by flooding the pond three times being today filled with fresh water, but the tube is still present.

Figure 2. Scales consisting of radiobarite at the discharge point into the former Rontok tailing pond in the USCB in 2005.

In general, the hard coal mining areas in the Polish USCB and the German Ruhr-District (RD) are quite comparable, because in both cases coal layers of the same Carboniferous age having been formed under the same geological regime (Variscian Orogenesis) are mined and also well investigated for their radionuclide content and behaviour. By having a closer look on Table 1, also the radiological data of the mining areas are of similar dimensions: at both locations the pit waters are reported to carry maximum ^{226}Ra load of 13Bq/l (Germany) respectively 25Bq/l (Poland), the surface waters reach maximum values of almost 0.2Bq/l respectively 1.3Bq/l and also the sediments being influenced by dischraged pit waters show similar ^{226}Ra activity concentrations (32,000Bq/kg respectively 50,000Bq/kg).

Despite of radium, the pit waters often contain strongly elevated levels of salinity, for both the RD and the USCB similar maximum concentrations of more than 200g/l are reported (Wedewardt, 1995, Skubacz et al. 1990). Before those saline waters can be discharged into rivers, any suspended load must be removed. For this reason, especially in Poland tailing ponds were built in which the pit water was discharged to allow the suspension to settle on the bottom. As a result of the cleaning process, also much of the radium isotopes (and heavy metals as well) were concentrated in bottom sludge, which is called tailing. As calculated by Michalik (2004), the total volume of such tailings in the USCB where activity concentrations of both radium isotopes exceed 200 Bq/kg (limit to be considered as TENORM) are 5 millions m^3, the outflow of waste waters from about 50 coal mines is given by 800,000m^3 per day.

Figure 3. The 16h tailing pond close to Bojszowy in the USCB in 2005.

The influence of the barium and sulphate content in the brines gets put into perspective once again in the USCB. There, two types of pit water can be distinguished based on their radium isotope ratios and ion content (Lebecka et al., 1994). The water of type A contains radium and barium in high concentrations, but no sulphates are present and the activity ratio of ^{226}Ra:^{228}Ra is of about 2:1. In contrast, type B water shows high radium and sulphate contents, but barium is absent and the ratio of ^{226}Ra:^{228}Ra is the opposite of type A – about 1:2. Up to now, the exact reasons for that difference are not explained satisfyingly, but mineralogical varieties in the coal layers and surrounding rock formations must be taken into consideration. However, those different types of pit waters can be identified on the surface in the tailing ponds. The Bojszowy pond (Figure 3) is of 16h size and was filled with type B water, so that no radiobarite precipitation was enabled and no barium crusts occur. Therefore, the radium load is said to be mostly bond to grain surfaces (Leopold et al., 2007). The high salinity of the formerly discharged water can be easily recognised by white salt crusts on the tailing's surface. The use of this tailing pond was abandoned at the end of the last century's nineties and today, the tailings are covered with a 2m thick layer of sand and other filling materials. In contrast, the Rontok tailing pond has been filled with type A water and that is the reason why such immense crusts of radiobarite were enabled to precipitate inside the tube's wall. Indeed, the sulphate is not carried with the initial formation water, but as soon as there is a mixing with other sulphate bearing natural waters e.g. from higher layers the precipitation takes place.

In Poland, today the pit water is succesfully cleaned for radium in underground installations, where the water flows in turbulent currents in a trough under an automatic feeder and $BaCl_2$ is added as the purification agent in well defined amounts. Afterwards, that water is guided in one of 5 settling galleries, each 1050m long, to allow the radium to co-precipitate with barium on the bottom. The percentage of removed radium is of at least 65%, but dimensions of more than 95% can be temporarily reached (Wysocka et al., 2005). An accompanying effect is that the by far most of other loads is settled on the galleries' bottoms, too. For that reason the surface ponds are now no longer in use.

Finally, also sediments along sewers and rivers the pit water is dicharged in can be affected by enhanced radium concentrations mainly comprising stable radiobarite, which settles as a result of mixing the radium-bearing pit water with oxidisable and barium-bearing water of the river Lippe. As listed in Table 1, the sediments' maximum ^{226}Ra activity concentrations range between 32,000Bq/kg in the RD and 50,000Bq/kg in the USCB whereas the ^{228}Ra concentrations are lower in both countries. This scenario is well investigated in the RD, where sediment samples in different distances from the discharge points and also at different positions from the running water were taken. The maxima are found very close to the discharge points, downstreams the activity concentrations decrease step by step due to attenuation effects, but the sediments are still present as TENORM (>200Bq/kg ^{226}Ra) e.g. for more than 15km along the river Lippe in the RD. Furthermore, river banks being unregularly affected by flood events also show enhanced ^{226}Ra concentrations of almost 400Bq/kg whereas those being hardly flooded have background values (Schmidt & Wiegand, 2003). This is underlined by investigations done at similar sites by Leopold (2007) as can be seen from Figure 4. It becomes obvious that if ^{226}Ra is present also ^{210}Pb occurs in enhanced concentrations due to growing again from its precursor ^{226}Ra. The ^{232}Th decay series is given in equilibrated state by both the same activity concentrations of ^{228}Ra and its next long living progeny ^{228}Th being below the TENORM-limit. The exact indication of the sediment's age when it got contaminated by both the ^{226}Ra/^{228}Ra ratio and ^{226}Ra/^{210}Pb ratio is not reliably enabled, because no proven data about the initial ratios exist (Schmidt, 2001). By taking an initial ^{226}Ra/^{228}Ra ratio of 2 as assumed by Schweer (1995) as an average value, a rough estimation comes to the conclusion of almost 11 years.

In order to verify the hazardeous impact on environment by a re-release of the stored radium isotopes from the different materials, in the RD and the USCB as well some leaching tests have been carried out. In 2003, Schmidt & Wiegand reported results from the application of the 6-step-extraction scheme according to Zeien & Brümmer (1989) on sediments of the RD. They found that the ^{226}Ra's bonding type changes relatively with increasing distances from the dicharge points. Close to those points, the by far most of the radium (85%) is precipitated as radiobarite and therefore left in the residual. With increasing distance, the mobile bond portion representing that radium, which is adsorbed at grain surfaces, increases relatively. This phenomenon has been observed at two discharge points, but can be explained by the fact that the radium's absolute activity concentration decreases significantly with increasing distances whereas the absolute mobile fraction is kept constantly more or less all along the river Lippe. This means that if radium is present in the sediment, there is always the same absolute amount of mobile radium, which is given by 20Bq/kg roughly for that river. Furthermore, available radium will be firstly captured in small amounts in weak and therefore easily constructable bondings such as adsorbed at grain surfaces and finally, it gets fixed in strong ones like radiobarite and bigger portions.

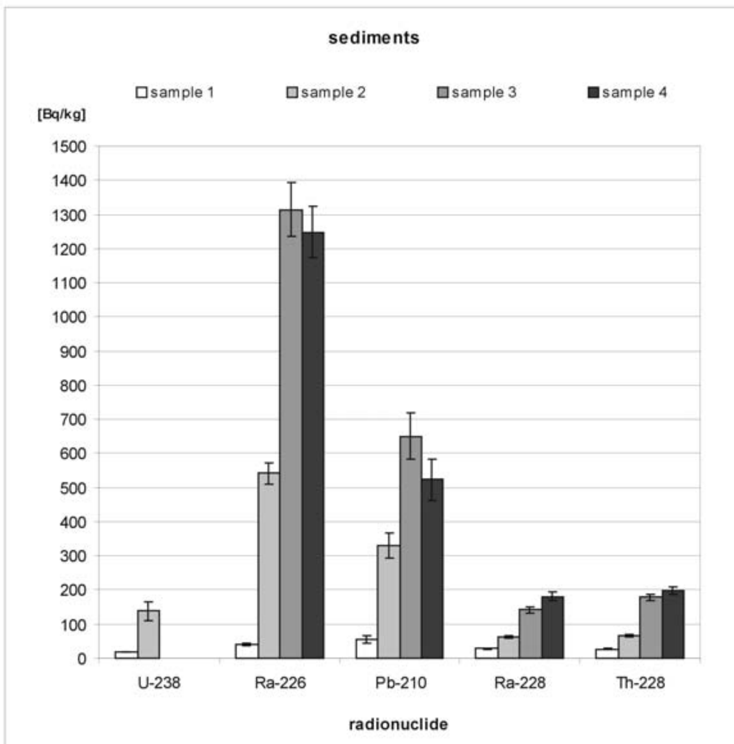

Figure 4. Radionuclide concentrations in sediments being affected by pit waters in the RD, given uncertainty quotes to 2σ-reliability; sample 1: background; sample 2: irregularly flooded; sample 3: slip-off slope; sample 4: undercut slope, same position as sample 3 (Leopold, 2007).

Leopold et al. (2007) applied the 3-step-extraction procedure proposed by the European BCR (Bureau Communautaire de Référence, now Standards Measurement and Testing Programme) as described by Ure et al. (1993) on tailings and scales of the USCB. They also found that almost all the radium is strongly fixed in radiobarite in case of the scales from type A pit water, which is due to the very stable crystalline structure of barite, so that liquids like water (or the used extraction liquids) are not sufficiently aggressive to disrupt and remove compounds. In contrast, the tailings being settled from type B pit water are proven not to consist of any radiobarite, because no barium has been present in the pit water. In that case the radium load is weakly bond to grain surfaces and also to oxidisable components due to the reducing environment established by organic matter in the tailings. The total amount of leached radium is given by almost 25% of the initial ^{226}Ra and 15% of the initial ^{228}Ra content in the tailings.

Table 2. Summarised data about ^{222}Rn in the Lower Rhine area (brown coal) and RD (hard coal) according to Feige & Wiegand (1999)

type of material		^{226}Ra activity concentration [Bq/kg]	^{222}Rn emanation rate [Bq/kg]	emanation coefficient [%]	^{222}Rn exhalation rate [Bq/(m^2 * s)]
brown coal	soil	200-300	-	-	0.1
	sediment	247	98	40	-
	sediment	252	36	14	0.02
	sediment	163	74	45	0.02
	sediment	-	-	-	0.1
	sediment	300	218	73	0.02
hard coal	soil	1,600	62	3.9	0.06
	sediment	23,310	346	1.5	-
	sediment	11,000	38	0.35	0.01
	sediment	32,310	283	0.86	-
	sediment	18255	68	0.37	-
	sediment	13,800	33	0.24	-
	sediment	3,500	6	0.17	-

RADON

Due to its volatile character, radon is enabled to leave the solid materials from coal mining as described above. That gets firstly important on the places where the hard coal is mined: the coal is crushed to pieces and that leads to enhanced surface areas, so radon can exhale from a much greater specific surface resulting in a potential radiation exposure for the miners in case of insufficient ventilation (Chalupnik et al., 2002). By having a closer look on soils and sediments, a difference between those from brown coal and those from hard coal mining becomes obvious (Table 2). As generally one can expect, Feige & Wiegand (1999) found that the ^{226}Ra concentrations in solids influenced by brown coal mining are just slightly enhanced, but the resulting ^{222}Rn emanation coefficients as a function of the emanation rates are remarkable high and this is accompanied by slightly elevated ^{222}Rn exhalation rates (German average is given by 0.015Bq/(m^2 * s)), too. In case of the hard coal mining's solids, the initial ^{226}Ra concentrations are significantly enhanced by a factor of up to 10, but the ^{222}Rn emanation coefficients and exhalation rates are much smaller. Once again radiobarite acts as a moderator: the radon in the hard coal mining's sediments is strongly fixed in the crystal lattice prohibiting any mentionable volatile emission and additionally, the pelitic coal particles tend to adsorb that radon which was free to emanate. In contrast, that ^{226}Ra coming from brown coal mining is mainly adsorbed at the surfaces of ferric hydroxides (no barium is present in those pit waters), so ^{222}Rn can easily emanate. The authors established also a correlation between the exhalation power defined as the quotient of exhalation and emanation and the moisture content of the samples and they observed that higher exhalation rates occur on irregularly flooded riverside deposits than on the highly contaminated, but almost permanently wet sediments on the river banks. Jovanovic (2001) measured ^{222}Rn exhalation rates at a Slovenian site close to an abandoned mine having extracted hard coal with relatively high ^{226}Ra concentrations (no exact data are available). Therefore, beside some coal the produced fly ash heaped up nearby also contains radium, which leads to enhanced ^{222}Rn exhalation rates (0.01 - 0.45 Bq/(m^2 * s)) being higher than those of the German brown coal mining.

As a special character of mining districts, radon can also migrate along open cracks in the underground being caused by mining activities. Klingel & Kemski (2000) mentioned the disruption of the rock system's strength in a deep mining area (Saar Basin in Southwest of Germany) leading to a roof break in the underground stopes. At the surface the area generated by mining subsidence forms a depression zone, on whose margins tectonic faults are frequently established. These fissures are then acting as pathways for radon to be set free in measurably elevated dimensions into the atmosphere, but the absolute amount of released ^{222}Rn strongly depends on the combination of local geological pattern in the whole area.

From time to time coal-fired power plants are accused to emit not only greenhouse gases such as carbon dioxide (CO_2) or methane (CH_4) but natural radionuclides, too. In general, combustion leads to a big reduction of the initial coal mass. Owing mainly to the elimination of organic components of hard coal, during the combustion process there is approximately one order of magnitude enhancement of the radioactivity concentration from coal to ash (Becker et al., 1992, Michalik, 2007). The specific radionuclides being most noticeably expelled via the stack are ^{222}Rn, ^{210}Pb and ^{210}Po, because they are more volatile and vaporise between room temperature (radon) and a few hundred degrees Celsius (lead and polonium) (Martin et al., 1997). In vaporised state it is not possible to filter them out completely by regular ash recovery systems, whereas the gypsum produced by the desulphurisation process is usually not affected by enhanced radionuclide concentrations (Becker et al., 1992). On the particles which escape filtration, there is a tendency for the volatile radionuclides to associate with smaller ones, thus leading to an increased activity concentration with decreased grain size. These aerosols are of highly radiological relevance, because they are within the respirable range below 10µm diameter, which allows them to penetrate into the pulmonary system (Roeck et al., 1987). In 1988, UNSCEAR estimated the influence of such a radionuclide pollution and reported an additional effective dose of 1µSv/a to be due to inhalation of long-living natural radionuclides emitted by coal-fired power plants. Transferring that older model into the presence, the additional dose for the population in the vicinity of such a power plant is less than 0.1% compared with the annual total exposure by natural radiation, which is given for Germany by 2.1mSv/a for the year 2006 (FME, 2007). Rosner et al. investigated yet in 1984 the influence of a coal-fired power plant in Bavaria onto its vicinity including vegetation, but they did not find any elevated level of natural radionuclide concentrations, so the emissions must have been too small to be detected due to the fly ash removal efficiency of more than 99.5%. Nevertheless, Bem et al. found in 2002 some slightly enhanced natural radionuclide concentrations in the Polish Lodz region and attributed them to past emissions in the previous decades from older power plants, but the Polish level for the annual average effective dose from terrestrial radiation given by

0.45mSv/a was never exceeded. There is no doubt, the assessment of the radiological impact of coal-fired power plants on their vicinities is a rather complicated one, but the general statement given at the beginning of this paragraph is not tenable, because a lot of factors (e.g. type of coal, state-of-the-art of the filter installations) influence the sum of emissions a coal-fired power plant is releasing.

CONCLUSION

It becomes obvious that there can occur some enhanced concentrations in natural radionuclides as a result of coal mining activities. Different scenarios have been presented, but each of them must be classified and judged individually.

Brown coal excavations, mostly done in open pit style, lead to just slightly enhanced radionuclide concentrations in the environment. In contrast, hard coal mining activities can cause significant contaminations in different types of media (air, water, soils, sediments) depending on special geological conditions of the mining area.

As explained by Chalupnik et al. (2002), miners can be generally exposed to enhanced radiation in the galleries due to high radon levels and inhalation of that noble gas, if the ventilation power is insufficient.

Since the radium in the German sediments is almost exclusively bond as radiobarite, no significant release potential must be taken into consideration. But if anoxic conditions are enabled, a reduction of the radiobarite and therefore a re-mobilisation of radium must be assumed (Pluta & Trembaczowski, 2001). Therefore, those materials can be kept in their present state, because the resulting ambient gamma dose rates along the riversides are usually just slightly enhanced, only some few hot spots occur in extremely contaminated regions. Nevertheless, one special scenario to be considered in that case is soil ingestion by very young children, which can cause a serious internal exposure (Schmidt & Wiegand, 2003). Since the waters affected by high radium concentrations also show a high salinity, they can not be used as drinking water and a direct impact on humans by ingestion can be excluded, but radium can be concentrated in purification plants by adsorption on iron- and manganese filter. This should be taken into account in such mining areas especially in case of cleaning the filter installations and removing their sand and gravel, so workers can be exposed.

Concerning the Polish tailing ponds, currently all still-working ponds lie in the areas that belong to particular collieries. Access to these areas is restricted to authorised personnel, hence the potential exposure to external radiation is limited only to staff engaged in well-defined practices and ultimately, controlled in the context of occupational risk monitoring. Additionally, during normal exploitation, tailing ponds are filled with water that provides a protection against external radiation from the bottom sediments, but former surface tailing ponds filled to the brim with radium contaminated sediments remain and await land reclamation. The direct radiation risk to people in the vicinity of such ponds results from external gamma radiation. Serious environmental problems occur where there are abandoned tailing ponds, especially those that had been adapted from natural ponds. They were not equipped with any special protective layers, unlike artificial ones, so that the possibilities of pollutant migration exist. However from the environmental point of view, the migration of radionuclides after leaching along with their bioavailability can determine possible detrimental effects. But it must be also emphasised that the detailed investigations of the radium contaminations from Polish mines for almost two decades in combination with a cooperation of the mines finally resulted in a simple but also effective purification process implemented underground, which leads to a strongly significant decrease of the radium emissions nowadays (Wysocka et al., 2005).

In perspective, both workers and members of the public should be completely informed about the problem of enhanced radionuclide concentrations, possible exposure scenarios and where the hot spots are located, which then can result in solutions and findings by authorities on the basis of scientific expertises how to deal with it and if/which remediation actions are to be undertaken.

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Chapter 6

AQUATIC HAZARD OF SELENIUM POLLUTION FROM COAL MINING

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ABSTRACT

Selenium is a chemical element that is found in coal in small amounts. The potential for environmental problems begins when coal-bearing strata are exposed to air and water during the mining process, and when coal is washed prior to transport and distribution. This can mobilize selenium and form contaminated leachate and liquid waste, which often becomes a source of pollution to nearby surface waters. Once in the aquatic environment, selenium can rapidly bioaccumulate in food chains and reach levels that are toxic to aquatic life. Because of bioaccumulation, a small amount of selenium in water can translate to a significant environmental hazard. Case examples show that selenium from coal mining can result in a variety of impacts to fish, ranging from subtle effects on growth to severe deformities and complete reproductive failure. However, despite this negative implication, coal mining can be compatible with environmental needs if adequate steps are taken to prevent or reduce hazard. For prospective mines, this involves conducting a detailed site assessment and then matching operational parameters with environmental requirements. For active or decommissioned mines it is necessary to formulate and implement appropriate waste management and site reclamation plans.

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INTRODUCTION

What Is Selenium and Why Is It a Concern?

Selenium is a naturally occurring chemical element in coal that can be released during the mining process and find its way into nearby aquatic habitats. Selenium in raw coal and overburden is leached out when these materials are exposed to air and water, and the leachate can pose a significant environmental hazard (Lemly 1985a). Once in the aquatic environment, waterborne selenium can enter the food chain and reach levels that are toxic to fish and wildlife (Figure 1). Impacts may be rapid and severe, eliminating entire communities of fish and causing total reproductive failure in aquatic birds (Lemly 1985b, Ohlendorf 1989). Few environmental contaminants have the potential to affect aquatic resources on such a broad scale, and even fewer exhibit the complex aquatic cycling pathways and range of toxic effects that are characteristic of selenium. In recent years there has been an escalation in selenium pollution episodes associated with coal mining in North America and elsewhere (Lemly 2004), which has caused substantial environmental liability issues for coal mining companies, and resulted in regulatory intervention by water quality authorities, natural resource management agencies, and the courts (see for example BC Ministry of Environment 2008, US District Court 2008). With the potential for negative impacts on the coal mining industry as well as the environment, it is essential to recognize and address the selenium threat in the context of active, prospective, and decommissioned mines.

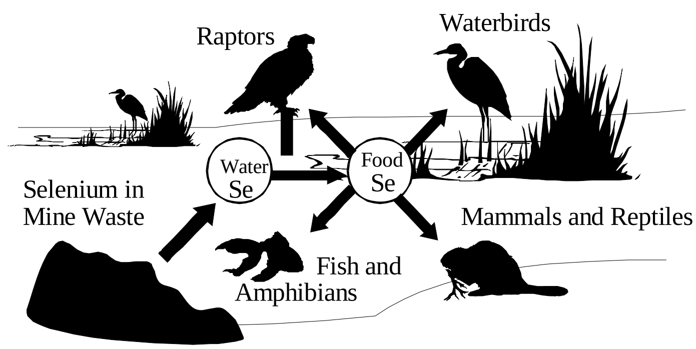

Figure 1. Pathways for selenium movement from coal mine wastes, bioaccumulation in food chains, and dietary exposure of fish and wildlife populations.

Background on Selenium Bioaccumulation, Cycling, and Toxicity

The most important principle to understand when evaluating the hazard of selenium from coal mining is its ability to bioaccumulate. This means that a low concentration of selenium in water has the potential to increase by several orders of magnitude by the time it reaches fish and wildlife. For example, a water concentration of 10 ug/L (micrograms per liter or parts-per- billion) can increase to over 5,000 times that amount in fish tissues. Bioaccumulation causes otherwise harmless concentrations of selenium to reach toxic levels. Although fish do take up some selenium directly from water, most of it comes from their diet.

Therefore, in order to protect fish from selenium poisoning it is essential to keep waterborne selenium below levels that cause bioaccumulation in the food chain (Lemly and Smith 1987). Another important principle is that selenium can cycle in aquatic habitats by moving in and out of sediments. A large portion of the total selenium in a stream or reservoir may be present in sediments, deposited directly from water or from plants and animals as they die and decompose. However, this pool of selenium is not permanently removed from the system. Biological activity, water chemistry changes, and physical disturbance can mobilize selenium back into water and organisms. This means that the selenium in sediments remains active, and provides a significant source of pollution to bottom-dwelling invertebrates and the fish that feed on them. Case studies show that selenium in sediments can recycle into the water and food chain for decades after selenium inputs are stopped (Lemly 1997).

Selenium exerts two main types of effects on fish: (1) direct toxicity to juveniles and adults, and (2) reproductive impacts from selenium that is passed from parents to offspring in eggs. Both of these modes of toxicity can occur at the same time so the threat from selenium poisoning is multifaceted. Type 1 toxicity can begin to occur if concentrations in the food chain reach 3 ug/g dw (micrograms per gram or parts-per-million, dry weight) and whole-body residues in fish reach 4 ug/g dw (Cleveland et al. 1993, Lemly 1993a, Hamilton 2003). This form of selenium poisoning involves changes in physiology that causes damage to gills and internal organs, ultimately resulting in death of the fish (Sorensen 1986). There may be no outwardly visible symptoms in this type of selenium toxicity or, if selenium concentrations are high enough, some fish may appear swollen from accumulation of fluid (edema) or have cloudy lenses (cataracts) in their eyes (Lemly 2002a). Type 2 effects occur when selenium present in egg yolk is absorbed by the developing embryo. A variety of developmental abnormalities can result in newly hatched larval fish, such as teratogenic deformities of the spine, head, and fins (Lemly 1993b, see Figure 2). Other toxic symptoms include hemorrhaging and swelling or edema (Gillespie and Baumann 1986, Hermanutz et al. 1993, see Figure 2). Most of these effects are lethal because they either kill young fish just after hatching or, in the case of some teratogenic deformities, prevent them from feeding normally and escaping predators as they grow (see Figures 3-4). Type 2 effects (reproductive failure) begin to occur at egg selenium concentrations of about 9 ug/g dw, which is equivalent to about 16 ug/g dw whole-body in the parent (Coyle et al. 1993, Hermanutz et al. 1993). Adult fish may be unaffected by selenium concentrations that impair their ability to reproduce so the threat of selenium impacts on a fish population must be assessed by something more than routine monitoring surveys, that is, simply finding fish does not indicate the absence of selenium toxicity (Lemly 2002b). Waterborne concentrations of selenium in the 1-5 ug/L range can bioaccumulate and begin the Type 1 and/or Type 2 effects. The exact number is site-specific, and depends on the kind of aquatic system (stream, reservoir, wetland), its biological productivity, and the chemical form of selenium present in the water. Case studies show that if waterborne selenium reaches 10 ug/L, complete reproductive failure can occur in reservoirs, and reproduction may be reduced by 40% in streams (Cumbie and Van Horn 1978, Lemly 1985b, Gillespie and Baumann 1986, Hermanutz et al. 1993). Selenium concentrations in coal mine wastewater can far exceed these toxic thresholds, and are particularly high in coal cleaning process water (up to 63 ug/L) and coal cleaning solid waste leachate (up to 570 ug/L, Lemly 1985a).

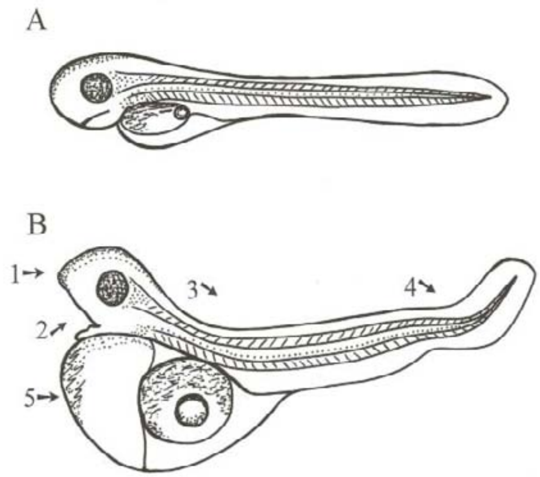

Figure 2. Typical appearance of larval fish at about 2-4 days after hatching. (A) Normal larva with yolk absorption nearing completion and straight, developing spine, (B) Abnormal development due to selenium-induced terata: (1) deformed, pointed head; (2) deformed, gaping lower jaw; (3) kyphosis (curvature of the thoracic region of the spine); (4) lordosis (concave curvature of the lumbar and/or caudal region of the spine). Other symptoms of selenium poisoning that usually accompany terata include (5) edema (swollen, fluid-filled abdomen) and delayed yolk absorption (drawing by A.D. Lemly).

Figure 3. One of the most common and outwardly visible teratogenic effects of selenium in fish is deformity of the spine. Shown here are examples of dorso-ventral abnormalities known as kyphosis and lordosis (photo by A.D. Lemly).

Figure 4. Lateral curvature of the spine (scoliosis) caused by exposure to elevated selenium. Individual on the right is normal (photo by A.D. Lemly).

CASE EXAMPLES OF IMPACTS ON FISH

Elk Valley, British Columbia, Canada

The Elk River watershed is located in the extreme southeastern portion of the province and lies in an area of naturally seleniferous soils and underlying coal deposits known as the Kootenay geological formation. Recent studies have determined that elevated concentrations of selenium are present in some areas of the watershed (EVS 2002a). Five active open-pit coal mines operate within the watershed and produce wastewaters containing selenium in concentrations that can exceed 200 ug/L (EVS 2002a, 2002b). Elevated selenium is present in water, sediments, and biota downstream of the mines relative to undisturbed sites (EVS 2004, Minnow 2004, 2007, Orr et al. 2006, Golder 2007). Experimental reproduction studies using field-exposed fish show that selenium toxicity associated with coal mine discharges has taken place in populations of cutthroat trout (Oncorhynchus clarki lewisi, Rudolph et al. 2006) and longnose sucker (Catostomus catostomus, Minnow 2005, 2006) in the Elk River watershed. Figures 5-6 illustrate the magnitude of these effects. The severity of impacts increases as egg selenium concentrations rise, culminating in complete reproductive failure.

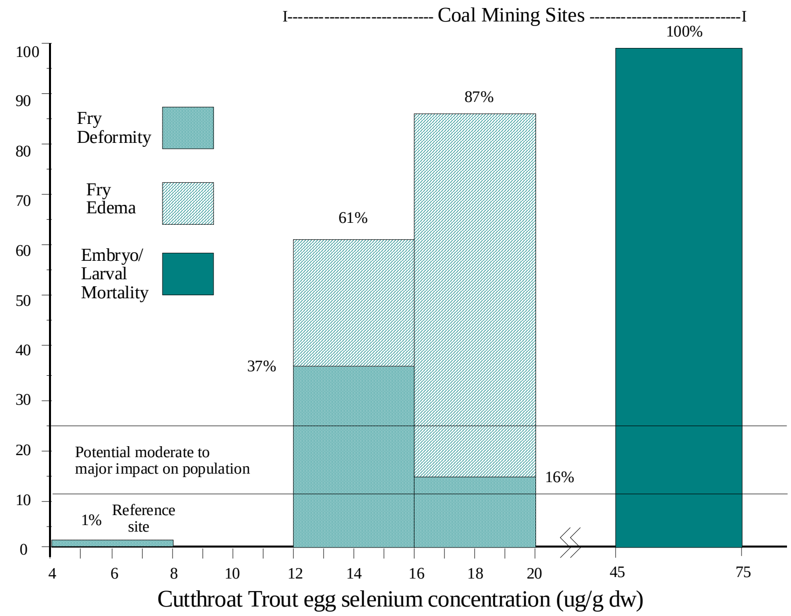

Figure 5. Effects of selenium on reproductive success in Westslope Cutthroat Trout (Oncorhynchus clarki lewisi) exposed to coal mining effluents in the Elk River watershed, British Columbia, Canada (data compiled from Rudolph et al. 2006). An effect level of 12-25 % or greater would be expected to result in moderate to major impacts on the population.

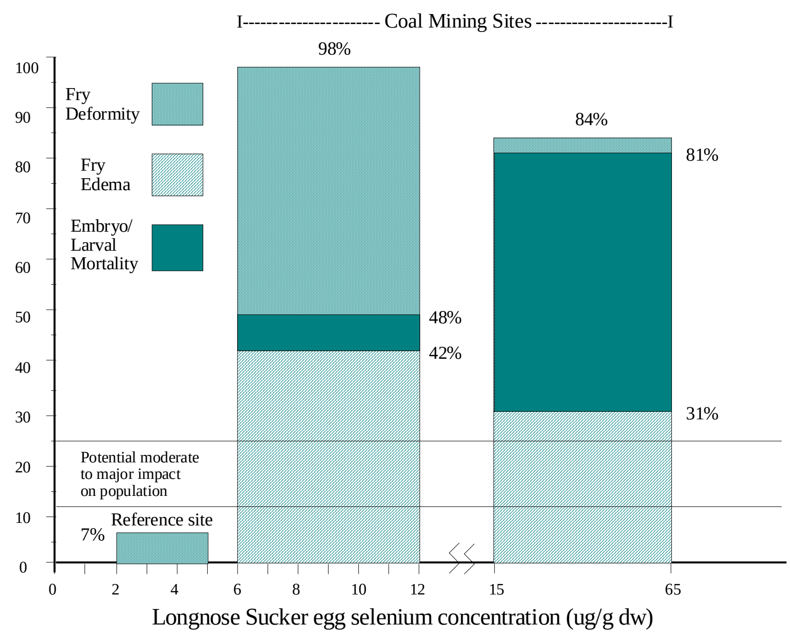

Figure 6. Effects of selenium on reproductive success in Longnose Sucker (Catostomus catostomus) exposed to coal mining effluents in the Elk River watershed, British Columbia, Canada (data compiled from Minnow 2005, 2006). An effect level of 12-25 % or greater would be expected to result in moderate to major impacts on the population.

Mud River Watershed, West Virginia, USA

Coal mining has a long history in this state but until recently, little attention was paid to water quality issues other than acid drainage and sedimentation. Selenium was raised as a concern by local and regional nonprofit environmental conservation groups in the 1990's. Subsequent water quality monitoring conducted as part of mine wastewater discharge permit requirements under USEPA's National Pollution Discharge Elimination System revealed that frequent violations of the surface water quality criterion (5 ug/L) were taking place (WVDEP 2007a). This led the West Virginia Department of Environmental Protection to initiate an aquatic monitoring program aimed at evaluating the extent and severity of selenium pollution from coal mining (WVDEP 2007b). Results of this effort in one of the key mining areas (Mud River watershed) are depicted in Figures 7-10, and reveal that selenium levels in water, fish tissue, and invertebrate food organisms exceed toxic thresholds for fish. As a supplement to this routine monitoring, a fish reproduction study was conducted in 2007 to determine if selenium-related abnormalities were present in the fish population of Upper Mud River Reservoir in Lincoln County (WVDEP 2007c). This reservoir receives selenium-laden discharges from a surface coal mining complex that has several active mine sites upstream in the watershed. The tell-tale signs of selenium toxicity (spinal deformity and edema) were evident in larval fish, indicating that significant biological impacts have occurred. Figures 11-12 illustrate the appearance of normal and affected individuals from this study.

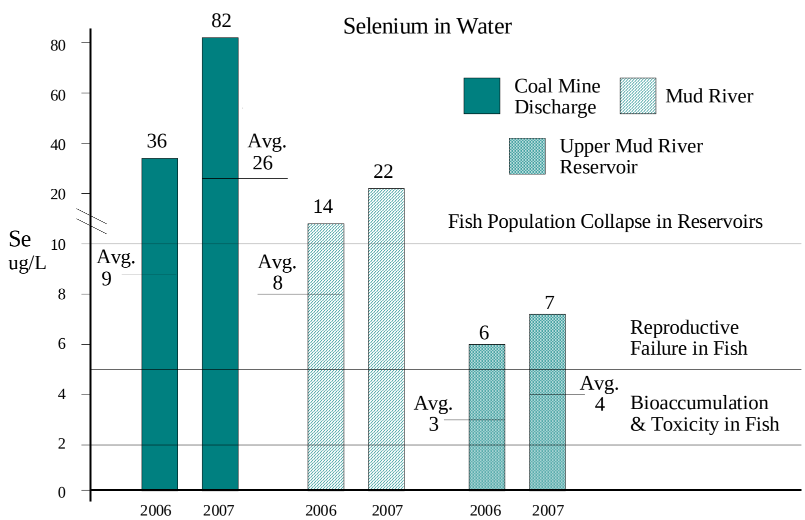

Figure 7. Selenium concentrations (ug/L or parts-per-billion) measured in coal mine discharges and surface waters of the Mud River ecosystem, West Virginia, relative to levels that can bioaccumulate and become toxic to fish (data compiled from WVDEP 2007a, 2007b).

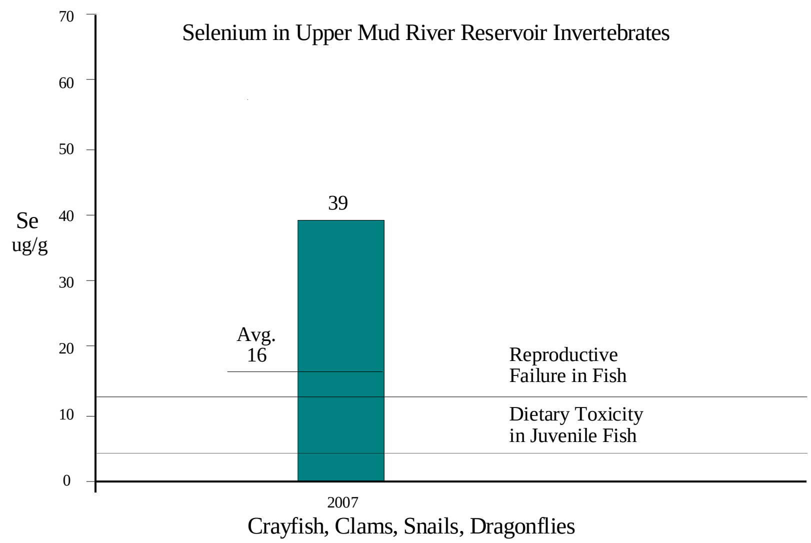

Figure 8. Selenium concentrations (ug/g or parts-per-million, dry weight) in fish food organisms of Upper Mud River Reservoir, West Virgina, relative to known toxic effect levels (data compiled from WVDEP 2007b).

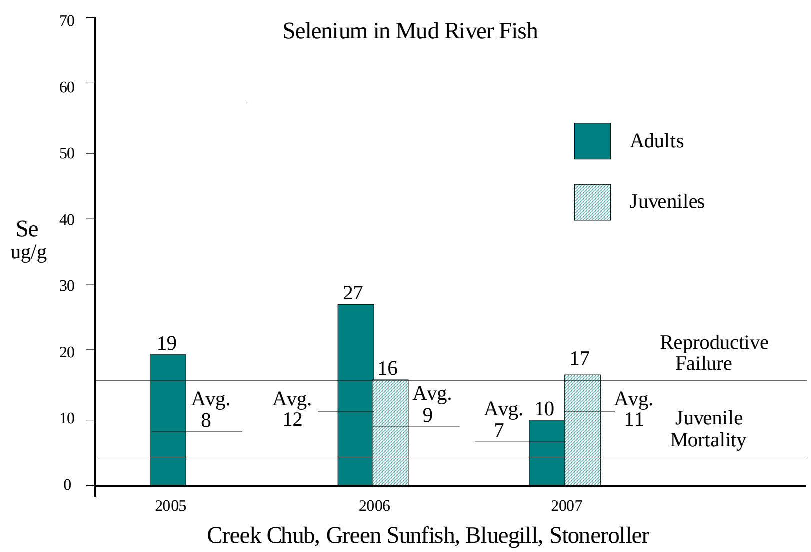

Figure 9. Selenium concentrations (ug/g or parts-per-million, dry weight) in fish from Mud River, West Virginia, relative to known toxic effect levels (data compiled from WVDEP 2007b; data are for creek chub, Semotilus atromaculatus, bluegill, Lepomis macrochirus, green sunfish, Lepomis cyanellus, and stoneroller, Campostoma anomalum).

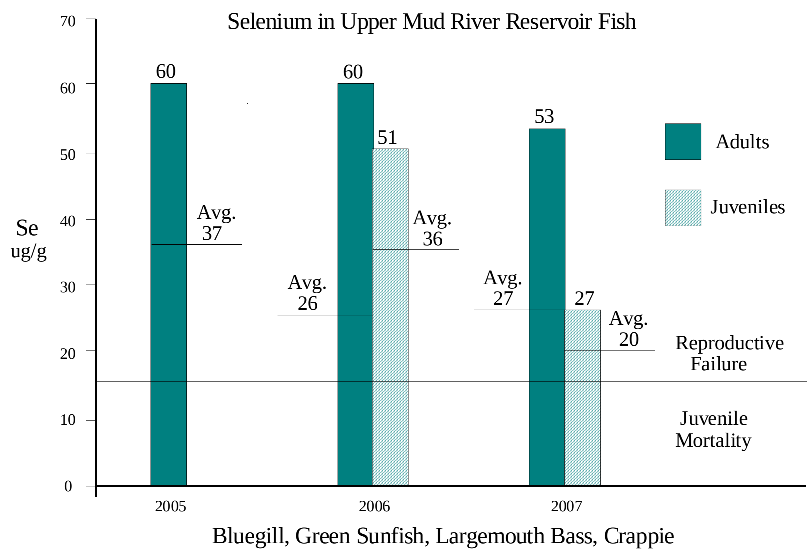

Figure 10. Selenium concentrations (ug/g or parts-per-million, dry weight) in fish from Upper Mud River Reservoir, West Virginia, relative to known toxic effect levels (data compiled from WVDEP 2007b; data are for bluegill, Lepomis macrochirus, green sunfish, Lepomis cyanellus, largemouth bass, Micropterus salmoides, and crappie, Pomoxis sp.).

Figure 11. Side view of normal fish larva from Upper Mud River Reservoir, West Virginia, June 2007 (photo by West Virginia Department of Environmental Protection). Note normal eye development, straight spine, and complete yolk absorption with no evidence of edema or a swollen, deformed yolk sac.

Figure 12. Side view of abnormal fish larva from Upper Mud River Reservoir, West Virginia, June 2007 (photo by West Virginia Department of Environmental Protection). Note the distended, fluid-filled yolk sac (edema) with delayed yolk absorption. This individual also has dorso-ventral curvature of the spine (kyphosis) and deformed pectoral fins and eyes (both eyes are on the same side of the head). All of these abnormalities are characteristic biomarkers of selenium poisoning.

How to Reduce Risks to Aquatic Life

For Coal Mines in the Planning Stage

Adequate pre-mine evaluation and planning are critical to prevent selenium pollution. Lemly (2007) provides a detailed procedure for accomplishing this task. The reader should refer to that publication for specific information, as only a general overview is given here. There are five major components to the procedure (Figure 13), which is designed to gather information on operational parameters of the proposed mine as well as key aspects of the physical, chemical, and biological environment surrounding it. 1) Geological assessment is the first step to understanding the environmental risk of selenium at prospective coal mines. It is essential to characterize the amount of selenium present in the geologic strata that are to be disturbed because once these materials are exposed to air and precipitation they can leach substantial quantities of selenium, which begins the mobilization process and threat to aquatic life. Because selenium concentrations vary widely in the target matrix and waste rock at a mine site, an accurate representation of the intended geographic area and depth of disturbance by mining must be made. This projection, in combination with analyses of selenium content and leachate parameters, will provide key information on selenium quantity and mobility. 2) Mine operation assessment is the next component. The disposal method(s) used for solid and liquid wastes at a mine greatly affect the potential amount of selenium released and thus the risk of ecological damage (Lemly 1994). It is important to know approximately how much excavated solid material will be exposed to weathering at any given time, as well as how much liquid will be produced, whether held in tailings ponds or directly discharged into receiving waters. The engineering design should be examined closely to provide waste volume estimates that are as accurate as possible. Once these numbers are obtained, some calculations will provide estimates of daily selenium production, that is, how much selenium is available for potential release to the surrounding environment. 3) Hydrological assessment is necessary to reveal key pathways for selenium movement and accumulation. The surface water hydrology of the basin surrounding the proposed mine must be carefully examined in order to identify all potential receiving waters for selenium discharges. Because of hydrological connections between the various aquatic habitats that may be present in a watershed basin, the toxic threat from selenium contamination is also connected. The hydrologically linked parts of a watershed that are down-gradient of the mine site, extending to the point at which outside water sources dominate the hydrology (for example, confluence of the watershed with a larger drainage basin) should be the area evaluated. This physical area constitutes a hydrological unit (HU). The protocol given by Lemly (2007) aims to protect the weakest link in the HU, that is, habitats where the risk of selenium accumulation and toxicity to aquatic life are greatest. In order for the assessment and resultant mine operation decisions to be environmentally sound it is necessary to map and characterize the aquatic system of the HU, estimate its selenium retention capacity, and project selenium concentrations in water and biota. 4) Biological assessment is needed because is important to have a complete inventory of the aquatic resources that may be threatened by mine development in order to obtain a comprehensive and ecologically relevant hazard assessment. This entails making a list of fish and aquatic-related wildlife present in the HU, characterizing fish and wildlife uses of the habitat (feeding, spawning, nesting, migratory stop-overs, etc.), and identifing biota of special concern such as endangered or threatened species and management priority species. It is also necessary to document the presence of, and habitat used by, selenium-sensitive species and identify habitats where bioaccumulation would likely be greatest, that is, in locations with high primary productivity and slow-moving or impounded waters (reservoirs, ponds, wetlands, marshes, etc.). The reason for collecting this information is so that any biological issues or concerns can be identified and factored into the formulation of a Total Maximum Daily Load (TMDL) of selenium that is sustainable for the HU. The TMDL will be useful as guidance for developing and refining mine operation parameters needed to meet environmental quality goals. Information from the biological assessment will also aid in focusing monitoring efforts on the habitats and species of greatest priority and sensitivity to selenium. 5) Hazard assessment is the final and most crucial step. At this point, having completed the preceding four steps, the planner/evaluator will have gathered all of the information necessary to evaluate the ecological risk posed by the prospective mine. Hazard is determined by comparing the projected water and tissue selenium concentrations to published toxicity levels and then rating the degree of hazard using interpretive guidelines (Lemly 2007). Five degrees of hazard are possible: none, minimal, low, moderate or high. The initial ratings may be modified based on other information such as presence of endangered or threatened species, resource management agency priorities, and other local, regional, or national regulatory control considerations. If the hazard level is low, moderate, or high, a TMDL needs to be developed and then reviewed in the context of the mine operation parameters to identify options for meeting environmental quality goals. If modifications are needed, there are several options for reducing the exposure and weathering of selenium-laden solid materials, and minimizing the amount of wastewater produced (Lemly 1994). Practices such as backfilling, water recirculation/reuse, and containment leaching are just a few of the possible ways to lower selenium discharges. Chemical/physical treatment of liquid waste to lower selenium concentrations in the discharge is another step that can be taken. Some flexibility on the part of the mining company may be all that is necessary to meet the TMDL and gain approval for the project. Monitoring of water, fish, and birds should be done once mining begins to verify that selenium levels in aquatic habitats remain at safe levels. Monitoring is needed to make sure that the mine is meeting its discharge limits and also as a check on how well the TMDL fits the ecosystem. The TMDL is generated from calculations that are based on projected selenium levels, not actual concentrations. Therefore, it may not be a perfect fit to the HU once site-specific environmental conditions that regulate selenium cycling and biological uptake come into play. It is possible that some adjustment of the TMDL may be necessary because of mine-related and/or environmental-related factors.

For Active Coal Mines

Waterborne selenium should be measured routinely as part of a mine's overall environmental accountability reporting. In the US, this would fall under the monitoring requirements for discharge permits issued as part of EPA's National Pollution Discharge Elimination System or other state and local monitoring efforts. If monitoring reveals elevated selenium concentrations in water (2 ug/L or greater), follow-up monitoring of biota is needed. If levels of selenium are also elevated in biota (3 ug/g dry weight in benthic invertebrates, 4 ug/g dw in fish whole-body samples or 8 ug/g dw in fish muscle fillets, 10 ug/g dw in fish eggs, 7 ug/g dw in aquatic bird eggs), steps should be taken to reduce wastewater and leachate discharges. This would typically involve the TMDL process discussed above, which would identify HU's and develop maximum sustainable discharge limits based on site-specific selenium retention capacity. There are several options for reducing selenium discharges. Perhaps the most basic is to simply reduce the amount of surface residuals, waste rock, and raw coal that are exposed to precipitation. This could involve increased use of backfilling for all solid wastes, and measures to reduce the residence time and aerial extent of tailings piles, raw coal storage areas, and cleaning/preparation/loading sites. Disposal of coal cleaning waste should be done so as to prevent movement of solids or liquids off-site, as this waste can contain very high concentrations of selenium. Recirculation and reuse of water should be done to the extent possible in order to reduce the amount of liquid waste produced. Finally, chemical and/or biological treatment can be used to remove selenium from liquid waste and precipitation-derived leachate before it is discharged to surface waters. The overall target should be a final effluent concentration of 5 ug/L or less. Success of treatment will depend on determining the chemical form of selenium in the wastewater and then matching an appropriate technology. For example, if it is predominantly selenite, treatment with ferrihydrite can reduce concentrations by 85-90%, and achieve final values in the range of 3-6 ug/L (Rosengrant and Fargo 1990). If it is selenate or organic, biological removal methods such as BSeM may be more effective and less expensive than chemical treatment. For more information on the use of ferrihydrite to pre-treat the discharge, see Rosengrant and Fargo

(1990). For comparison of ferrihydrite and less expensive biological options, including BSeM, see USEPA (2001) and Microbial Technologies (2005).

SELENIUM DECISION TREE FOR COAL MINES

1. GEOLOGICAL ASSESSMENT
▼
Core sampling and analysis of ore and overburden
▼ ▼
$\geq$1 µg/g Selenium | <1 µg/g Selenium
▼ ▼
Passive leaching test | Begin mining
▼ ▼
Selenium mobility characterization | Environmental monitoring
▼
2. MINE OPERATION ASSESSMENT
▼
Waste disposal methods
▼
Waste volume projection
▼
Daily selenium load projection
▼
3. HYDROLOGICAL ASSESSMENT
▼
Delineate and characterize Hydrological Unit (HU)
▼
Estimate selenium retention capacity of HU
▼
Projected selenium concentrations
▼
4. BIOLOGICAL ASSESSMENT
▼
Inventory of aquatic life present in HU
▼
Characterize sensitivity to selenium
▼
Identify priority species
▼
5. HAZARD ASSESSMENT
▼
Determine hazard level of projected selenium concentrations
▼ ▼
High, moderate, or low hazard | Minimal or no hazard
▼ ▼

Figure 13. Continued on next page.

▼ ▼

Determine allowable selenium load (TMDL) | Begin mining

▼ ▼

Identify mine operations needed to meet load | Environmental monitoring

▼

Evaluate feasibility of mine meeting environmental goals

▼ ▼

Environmental goals met | Goals not met

▼ ▼

Begin mining | Do not begin mining

▼

Environmental monitoring

Figure 13. Framework for identifying and interpreting selenium hazards associated with coal mining.

For Decommissioned Coal Mines

Once a mine is closed, actions are necessary to reclaim and vegetate all exposed areas to stabilize them and minimize further leaching of selenium. However, it should be noted that even with typical mine reclamation and revegetation efforts there may still be substantial selenium exposure risks to upland wildlife and livestock (Steele 2003), that would have to be avoided through additional measures such as capping the waste spoils with several feet of clay to reduce water infiltration and prevent selenium uptake by plants, containment and treatment of leachate, etc. Thus, there may be a need for long-term site management and environmental monitoring at decommissioned coal mines.

Conclusion

Until recently, most environmental concerns associated with coal mining were focused on sedimentation and acid drainage. However, selenium pollution should also be a major concern and, in fact, all coal mines have the potential to release hazardous amounts of selenium. Case examples show that selenium pollution from coal mining is widespread, and is capable of causing extreme toxicity to fish. The need for coal as a source of energy is growing steadily, as is the need for coal mining companies to display prudent environmental stewardship. It is both essential and quite feasible to recognize and deal with selenium pollution from coal mining, thereby allowing expansion of the industry while also protecting aquatic life.

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Chapter 7

FLUORINE IN COAL: A REVIEW

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ABSTRACT

The World average F content in coals (coal Clarke of F) for the hard and brown coals are, respectively, 82±6 and 90±7 ppm. On an ash basis, these contents are greatly increased and are 580±20 and 630±50 ppm, respectively. As an average, F content in ash is 605 ppm (lower than the Clarke value for sedimentary rocks, 650 ppm). F is, on average, *not a coalphile element.*

Nevertheless, some coals are known to have a F content one order of magnitude more than the coal Clarke level. In general, these are either high-ash or high-phosphorus coals, with both the features often combined. This (and some others) features show some similarity between F and P geochemistry in coal. In particular, F, like P, seems to be depleted from the buried peat during diagenesis toward hosting rocks.

No less than three F-forms (modes of occurrence) may be present in coal: phosphatic (F_{phosph}), silicatic (mostly F_{clay}), and organic (F_{org}). It can be suggested that F_{clay} dominates in high-ash coals, F_{phosph} in high-P coals, and in ordinary coals with moderate ash yield and near-Clarke P and F contents, F_{org} may be dominant. There is no information concerning chemical species of the F_{org} form. However, by an analogy with P, it seems to exist as an F compound with Ca_{org}, not with organics itself.

It is yet not clear, if F is in authigenic CaF_2 and what could be a contribution of such a form to total F content. It seems not to be excluded that such form may have genetic relation with F_{org} (diagenetic or catagenetic transformation, $F_{org} \Rightarrow F_{min}$?).

There are no clear relationships concerning F enrichment in coals. Plausible hypothesis is that F might be syngenetically enriched in coals (a) in paralic (near-marine) coals, and (b) in coals formed with a volcanic activity background. On the other hand,

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some F anomalies (like that in some Alabama coals) may resulted from epigenetic hydrothermal F-input, during (or after) coal metamorphism.

Keywords: fluorine, coal, geochemistry, environmental impact

1. INTRODUCTION

Some notes concerning F presence in coalified plant residues appeared in the middle of the 19th century (see references in Dässler et al., 1973). However, the first paper on F in coal was, probably, Lessing's (1934), in which he noticed a strong corrosion of the ceramic fillings in gas-generating installations. He supposed that it was due to fluorine and, in reality, he found nearly 80 ppm F in ammonium waters. He concluded that F could have originated only from coal. Qualitative analyses showed that F was contained in all the British coals studied; a coal dust enriched in fusain contained much more F than a lump coal. McIntyre et al.'s (1985) microprobe study suggested F enrichment in fusinite. Fluorine was only weakly extracted by water but was appreciably extracted by 1 % NaOH. Lessing (1934) concluded that the main mode of F occurrence in coal is fluorspar, CaF_2. As the ratio F/Cl in one sample was the same as in sea water, he supposed that F entered coal from marine waters in the peat stage, in the same manner as Cl[1].

Unfortunately, due to analytical problems, we still know little about F geochemistry in coal. In ashing, much F may be volatilized as HF or SiF_4; the retention of F in ash needs much CaO, MgO, or K_2CO_3 in ash (either natural or added), at careful low-temperature ashing. In addition, the older analytical method of atomic emission spectral analysis does not work for F determination; however, F-analysis based on the CaF^+ molecular band is a rather new technique, although not in wide use. Besides, this procedure needs some CaO addition into ash. Many F-determinations made before end of 1980's by means of the ASTM method (bomb oxidation following ion-selective electrode [ISE] F-determination), resulted in appreciable underestimates due to incomplete decomposition of the F-bearing minerals. Godbeer and Swaine (1972) showed that such an underestimation ranged from 28 up to 72 %; in general, the error increased along with ash yield of coal analyzed (Godbeer, 1987; Martinez-Tarazona et al., 1994). So, for the reliable F-analysis, some intricate chemical procedures are needed (such as pyro-hydrolytic etc.), as discussed by Swaine (1990, p. 109, 112–113).

Coals can now be analyzed for F by means of PIGE method (proton-induced gamma-ray/X-ray emission analysis), described, for example, in Wong and Robertson (1993). This modern procedure gets good results (see, for example, some figures in Hower et al. [1997]).

[1] There were romantic times of the geochemistry: the issues based on only one analysis were taken by the scientific community as quite valid data!

2. Fluorine in Environment

Fluorine has a high marine-affinity, with its Clarke value in sea water being as high as 1300 mg/L, much more than in fresh waters (100 mg/L). In the hypergene zone, F is mobile in acid environments but can be trapped with pH increase on three geochemical barriers: Ca-bearing, phosphatic, and silicatic. Thus, in near-neutral and alkali milieus, dissolved F^- may be extracted by carbonates (resulting in CaF_2), phosphates (entering apatite structure), and clay (entering hydromica structure).

Ivanov (1994, p. 274), based on more than 3000 analyses of sedimentary rocks from the Transbaikal region Russia, found the average F content in terrigenous continental strata to be 170 ppm, i.e. much less than in marine strata (300 ppm), reflecting the "marine-affinity" of fluorine. This has also been observed in pelitic fractions from the Mesozoic strata in the Tadzhik depression: 440 ppm (continental strata) versus 1200 ppm (marine strata) (Pachadzhanov, 1981).

In wet landscapes, F actively moves; its contents in surface and ground waters are related to the organic matter contents (Perel'man, 1972, p. 207), suggesting that F forms soluble complexes with organics. Waters in arid and volcanic landscapes are enriched in F. Arid-landscape waters concentrate F due to evaporation, and volcanic-derived waters concentrate F due to acid exhalations, such as HF. As important F source for water may be an erosion of the F-bearing sedimentary rocks, such as phosphates. However, not all volcanic waters are enriched in F; for example, in the Kamchatka Peninsula (Russia), volcanic hydrotherms show near-background F contents in the range of 1.4–3.0 mg/L. Similar F concentrations are known in USA and New Zealand Cl-Na thermal waters (Trukhin, 2003). Although the data are scattered, Ivanov (1994, p. 278–279) noted a general regularity: F contents in water are positively correlated with a Na/Ca ratio.

Fluorine has a rather low bio-affinity: its bio-affinity index being lower than for chlorine. It is unclear what a biological role F plays in plants. However, in animals, such role is well known: F is an obligatory constituent of the bone skeletons, teeth, nails, plumes, hair and horns, entering biogenic F-OH-apatite.

It is worth noting, that according to Kowalevsky (1991 and others), an appreciable part of F in plants (up to 84 % on dry basis) is water-soluble; implying that such F may be leached in the peatbog.

There is an important question: may organics in marine or continental sediments scavenge F? Even in the modern Belorussian monograph (Evtukhovich and Lukashev, 2001) there are no figures on F content in peats. Only for the *peaty-soils* (horizons A_1 and $B_{1\text{-}2}$), some data are reported (p. 48): on average 63 ppm (the range 23–91 ppm) and 56 ppm (29–132 ppm). Pore waters of Recent carbonaceous sediments in the Black Sea contain more F than near-bottom sea water (Shishkina et al., 1969); indicating a F-input from the sediment, rather than an accumulation. Along with sediment diagenesis, F content in pore water (due to water metamorphization) decreases; however, F goes out as CaF_2, not as F_{org}.

3. An Estimation of Coal Clarke Value of F

In 1985, coal Clarke values (World averages) of F were calculated based only on 370 analyses, as follows (Yudovich et al., 1985, p. 133):

- 80±20 and 110±30 ppm for lignites and bituminous coals,
- 500–1000 ppm for their ashes.

In 2004, the Clarke value for F in coal was recalculated by Marina Ketris. The detailed calculation procedure was published elsewhere (Ketris and Yudovich, 2002), but the main idea is outlined here.

The concept involves *stepped (successive) averaging*, from minor to large: one coal bed ⇒ several coal beds ⇒ coal field (deposit) ⇒ coal area (several coal fields) ⇒ coal basin or province ⇒ totality of the coal basins, i. e. Clarke value totality, comprising several dozen random samples representing thousands of analyses. As a rule, the median is used for the Clarke estimation because it is very stable statistical parameter, only little influenced by large sample dispersion.

Modern estimations of F Clarke values are based on approximately 115 random samples, derived from nearly 11250 analyses (Figure 1):

- 90 ± 7and 82 ± 6 ppm for brown and hard coals,
- 630 ± 50 and 580 ± 20 ppm for their ashes.

In comparison with the 1985 figures, the F Clarkes for hard coals have been some lowered (110 ⇒ 82 ppm) and for lignites (brown coals) – some increased (80 ⇒ 90 ppm). However, averages for ashes were estimated more correctly; though, they may be underestimated because of above-noted F loss in coal ashing.

In most coal basins, average F contents are rather near to the Clarke values. There is some relation between F content and ash yield of the coals, more correctly – with their hydromicas contribution, as main carriers (sites) of F in coal.

According Swaine (1990, p. 109), world average F content is 150 ppm, ranging from 20 to 500 ppm. It is obvious now that this figure was overestimated. The background F estimation of Kler (1988, c. 68) for the former USSR coals was 100 ppm, much closer to our Clarke value. Based on 2469 analyses of World lignites, Bouška and Pešek (1999) calculated average content as 58 ppm F, and for Miocene lignites of the North Czech basin – 110 ppm (56 analyses).

Miocene lignites to the east of Elba River (Germany) contain 6–50 ppm F, and Eocene ones to the west – 2–178 ppm (Dässler et al., 1973). In the commercial bituminous coals of the Appalachian region, USA, the average F content is 80 ppm (Kopp et al., 1989). In Australian coals, average F contents strongly vary from 20 to 300 ppm, on average 110 ppm. In bituminous coals of New South Wales, F content ranged (over 90 % of the analyses) from 15 up to 458 ppm (on average 119 ppm). Queensland coals have an average of 108 ppm (21–243 ppm). Brown coals contain on average in the range from 42–130 ppm but Victoria lignites are quite poor in F: on average 8–18 ppm, in the range from 4 up to 79 ppm (Godbeer and Swaine, 1987).

According to 448 analyses of some Chinese coals, the background A contents are from 20 up to 300 ppm, with arithmetic mean of 140 ppm (Huang, Che, Tang, 2003, p. 45).

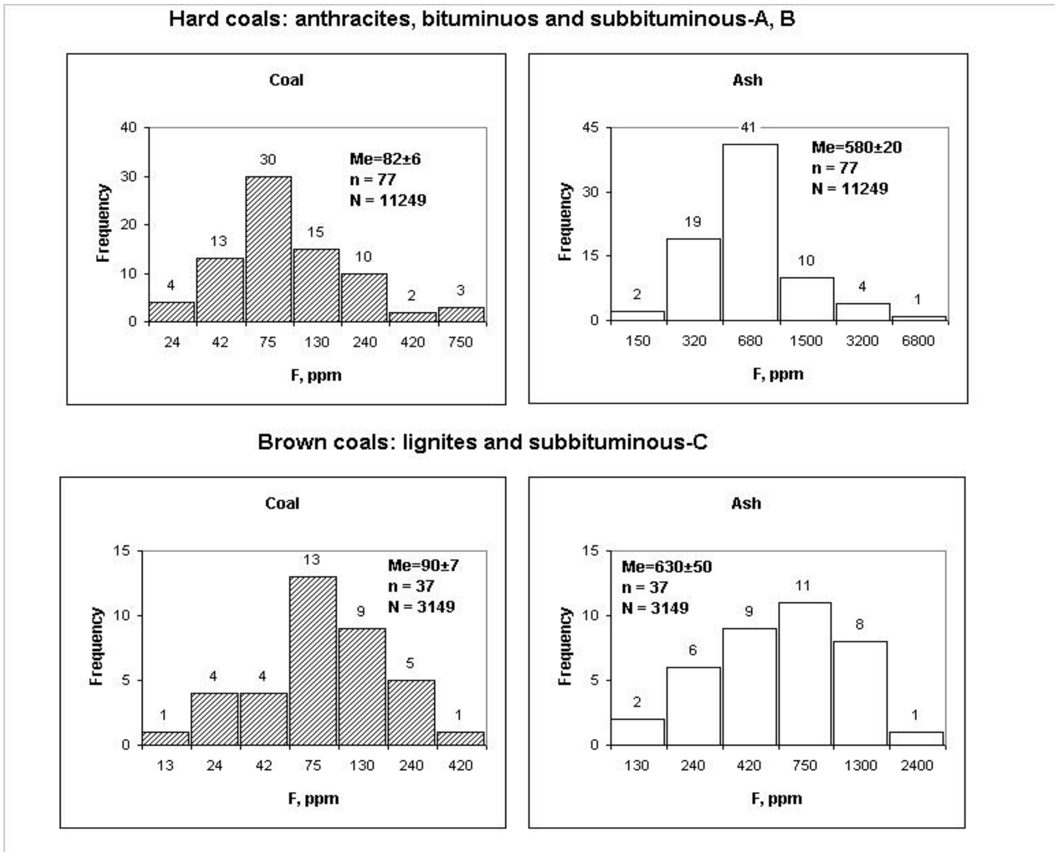

Figure 1. Frequency distribution of F in World coals.

N – number of analysis, *n* – number of random samples, *Me* – a median content.

4. "Coal Affinity" Index (Coalphile Index) of F

The Clarke value of concentration (the term of V.I.Vernadski) of F in coal ash (i.e. coalphile index or "*coal affinity index*" [2]) is 605 ppm (average F content in coal ash) / 650 ppm (F Clarke value in sedimentary rocks) = 0.93.

Therefore, according to modern F coal Clarke value, fluorine is *non-coalphile element* (see monograph by Yudovich and Ketris, 2002, for details).

[2] It is of note, that "*coal affinity*" is *not* the same thing as "*organic affinity*"! Coal affinity means an element affinity to all *authigenic* coal matter (organics and inorganics, including sulphides, carbonates, silicates etc., and excluding extraneous terrigenous or volcanogenic mineral clastics).

5. SOME COALS ENRICHED IN F

The coals notably enriched in F above the coal Clarke level are known in Russia, Greece, China, USA, and Canada. However, there is no doubt that such coals are widespread much more over the World, but were not analyzed up to date.

5.1. Russia: Various Coals

In the Jurassic Irkutsk basin coals, the highest F content is in the Cheremkhovo coal field: up to 1000 ppm in coal and up to 6000 ppm in coaly partings. Vyasova et al. (1989, p. 746) noted that Cheremkhovo and Voznesensk coals are much more enriched in F than many coals of the former USSR, USA, and former East Germany, and *"fit to the probably dangerous concentration level of 0.05 %"*

In drillholes penetrating coal beds of the east part of the Ulughem basin (Tyva Republic), F content reaches up to 300 ppm (and 54 ppm on average). In the Ulug seam, Mezhegeisk and Elegetsk coalfields, F content is up to 500 ppm (only 20 ppm on average) (Bykadorov et al., 2002).

Some F-anomalies reaching up 5500 ppm (ash basis) are found in Gusinoozersk Lower Cretaceous subbituminous coals, south Transbaikal region. F-enrichment seems to be related with *"known manifestations and deposits of fluorspar in near and distant bordering of the* (Gusinoozersk) *depression"* (Osokin, 1993, p. 117).

Some lignites of the Pacific Coast are enriched in F. For example, in the Shkotov deposit (Uglovsk basin), there are F-anomalies ranging from 300–600 ppm (Sedykh, 1997, c. 173). In the Ge-bearing Miocene Pavlovsk lignites (Khankaisk basin), some analyses showed up to 500 ppm F (Medvedev et al., 1997, c. 190). In the REE-bearing lignites, F contents may be as much as 1000–2000 ppm (Seredin et al., 1997, 1999; Seredin and Shpirt, 1995).

5.2. Greece: Neogene Lignites

F content in ash is negatively correlated with ash yield: $r(A^d - F_A{}^d) = -0.95$. Such relation is explained as F bonding with coal organics (Iordanidis, 2002). At the same time, F is positively correlated with Sr; this may have two explanations: (a) Sr is also bonded with coal organics; (b) Sr and F enter apatite but the ashes of low-ash lignites contain more apatite than the ashes of high-ash lignites (?).

5.3. China: Various Coals

Some Chinese coals are F-bearing. For example, eight (typical?) coals have high geometric average: 729 ppm F (ranging from 100 up 3600 ppm) (Ren et al., 1999). Compared to the average F content for Chinese coals of 248 ppm (based on 328 analyses), coals from Fuling prefecture, Sichuan province have on average 866 ppm (up to 1488 ppm), and in Baoching, Xianxi prefecture – 1411 ppm (up to 2350 ppm) (Zheng et al., 1999).

Enhanced F contents in coals are found in Quanxi Fault Depression Area, SW Guizhou province, where Upper Permian coals (12 samples) have on average 693 ppm F (Zhang et al., 2004, p. 55–56), or 2390 ppm F calculated on an ash basis[3]. Here, three areas are contoured with coals containing more than 1000 ppm F. In particular, in Liuzhi area, average F content is 1797 ppm, and the highest – 2544 ppm (Zhang et al., 2004, p. 58).

5.4. USA: Alabama Pennsylvanian Coals

The main part of coals enriched in F compared to US average level is in Warrior basin, in the marginal south of the Appalachian basin. The highest F content reaches here up to 4900 ppm and relates to later hydrothermal processes (Goldhaber et al., 1997; Oman et al., 1995).

5.5. Canada: Cretaceous Coals

In British Columbia subbituminous coals, on average over 30 coal beds, F content is enhanced compared to coal Clarke level – 518 ppm (Grieve and Goodarzi, 1993).

6. MODE OF FLUORINE OCCURRENCE IN COAL

One can think that F modes of occurrence are different in coals with near-coal Clarke F-content level, and in coals enriched in F.

At near-Clarke F-contents, the contributions of various F-sites, such as phosphatic, silicatic, and organic, may be commensurable. By this, low values of the P/F ratio may indicate the F_{org} site, as well a dominant F_{sil} site in hydromicas (Beising and Kirsch, 1974), or in other clay minerals. Swaine hypothesizes even such exotic accessory F-carriers (contributors) as tourmaline and topaz (Godbeer and Swaine, 1987; Swaine, 1990).

For example, in Utah coals, the contents of P are 70–180 ppm and of F – from 53 up to 132 ppm, at a P/F ratio ranging from 0.7 up to 2.0 (Bradford, 1957). If F-apatite has the highest (as possible) F content, the contribution of such phosphatic F (F_{phosph}) will be 0.2xP. A contribution of terrigenous silicatic F (F_{clay}) can be estimated assuming that such fraction remains in ash, by high-temperature ashing (800 ^{o}C). At last, a contribution of organic F (F_{org}) can be calculated by the difference between total F and the sum of (F_{phosph} and F_{clay}).

The calculations show that F in Utah coal is a sum of three F-forms with F_{org} as a dominant form: F_{phosph} = 24–28 %, F_{clay} = 20–25 %, and F_{org} = 56–47 %. Note that such calculations are only very approximate because of a set of suggestions were made: a) all the P is in Ca-phosphate; b) Ca-phosphate is fluorapatite with maximal possible F-content; c) in the ash (800^{o}C), only F_{clay} remains. Actually, there may be no Ca-phosphate at all, or it could have other F-content; the ash may capture a part of F_{org} or F_{phosph} (by reaction of F with CaO). The suggestion (a) and (b) would overestimate F_{org} contribution, whereas the suggestion (c) would underestimate it.

[3] Our calculation based on average ash yield of Permian (25 analyses) and Triassic (10 analyses) coals of 29.0 and 14. 5 %, respectively.

Finkelman (1980) found fluorapatite in the majority of the 79 coal beds examined (from USA and other countries). However, the amount of fluorapatite is, in general, too minor to be a real F-contributor in coal. As a result, Finkelman concluded:

"The problem of the mode of occurrence of F remains unresolved. It is possible that this element has a very complex mode, occurring in apatites, fluorites, amphiboles, clays and micas. In individual coals one form may dominate over the others" (Finkelman, 1980, p. 154).

In two Kuzbas coals as much as 87 % F_{org} is estimated (Khrustaleva et al., 2001, p. 40), but this figure seems to be some questionable.

In general, one can suppose that a contribution of the silicatic F_{clay} must be the highest in high-ash coals with abundant hydromicas, F_{phosp} highest in high-ash phosphate-bearing coals, and F_{org} highest in low-phosphorus coals with low and moderate ash yield.

6.1. Silicate Form

Illites from German bituminous coals contain from 600 to 1600 ppm F. This means that 5 % of such illite in coal may result in, for example, 50 ppm F, that is rather near to the observed F contents in these coals (15–120 ppm). It is of note that some part of F (nearly 3 %) is water-leachable and can be attributed to a sorbed ion-exchange form, F_{sorb}. The water-extract becomes alkali (pH = 9) probably due to OH^- leaching from coal along with F (Beising and Kirsch, 1974).

In Rhine (German) lignites with 3–28 ppm F, most of the F is in illite; however, the regression line "F in coal – ash yield" does not start from zero ash and has an absolute term. This may indicate some F_{org} presence.

In "Vostochny" (East) brown coal open pit (East Siberia), average ash yield is 8.34 % with 550 ppm F (coal basis). The same F content is found in the overburden silty clays with nearly 5 % C_{org}. These rocks consist of quartz (32 %), mixed-layer clay minerals (27 %), kaolinite (21 %), feldspars (10 %), siderite (4.5 %), dolomite (2 %), calcite (1 %), and magnetite (2.5 %) (Shpirt et al., 1994). The carrier of F is likely to be only mixed-layer illite-montmorillonite minerals, of, possibly, pyroclastic origin. Equal F contents in coal and its roof means that coal has to contain a substantial part of F_{org} form.

Among the silicatic F-contributors may be also non-clay minerals. For example, in the non-magnetic fraction of the Pennsylvanian Waynesburg seam low-temperature ash (West Virginia), olive-green grains of hornblende with ~0.2 % F were found. Finkelman (1980, p. 42) argued that the F-contribution of hornblende is far more than that of the rarer apatite.

Some F-enrichment is found in the most heated (coked) contact coal in Colorado, USA (Finkelman et al., 1992). Here, F seems to be contained in silicatic form.

6.2. Phosphatic Form

A presence of F_{phosph} may be supposed by P/F ratio and some correlations, as well as estimated by means of stepped leaching.

For example, in above mentioned relatively F-enriched low-ash Rhine lignites, fluorapatite may be the real F-contributor. The calculation shows that at 2 % P_2O_5 in ash, fluorapatite may result in up to 170 ppm F in ash (Beising and Kirsch, 1974).

The first studies of Australian coals (Phosphorus… , 1963) showed large variations of the P/F ratio (despite of general positive F-P correlation), which shifted from the 4.9 value (fluorapatite) to more (up to 6.6) or (rarer) lesser side (up to 4.6). The ratios more than 4.9 were explained by the contribution (along with fluorapatite) of hydroxyl-apatite. For the P/F <4.9 ratios no explanations have been offered. However, at least two explanations are possible: a presence of the part F as F_{sil} (in micas), or as F_{org}. In two high-ash coaly shales, much P (1.94–2.03 %) and F (3930–4860 ppm) were found. It is obviously, this is due to fluorapatite, because P/F ratios are 4.9 and 4.7.

The experiments with Australian F-bearing coals showed that Ca-phosphatic F may be fully extracted by the ion-exchange resin at heating up to 80 ^{o}C. From other phosphates (Fe, Al), fluorine can be extracted to a lesser extent, and F_{org} cannot be extracted. For example, from the low-ash Bulli coal seam, New South Wales (A^d = 6.7 %, P = 0.94%, F = 100 ppm), neither P nor F were extracted, and from other coals, no more than 30 % F were, on average, extracted (Phosphorus …, 1963).

6.3. Fluorite Form

Large excess F above P may imply fluorite presence, as proposed by Lessing (1934), and is assumed concerning some South African coals (Kunstmann et al., 1963).

Theoretically, CaF_2 may be formed during coal metamorphism due to Ca^{2+} and F^- interaction, both being liberated from the brown coal organics. Besides, in weathered coals, epigenetic fluorite may be, perhaps, present. If these processes operated, so a contribution of fluoritic F (F_{fl}) must be lesser in low-rank coals than in high-rank ones.

Besides, primary biogenic form, F_{bio}, may be, theoretically, also retained in coal. In ash of the so-called “phyto-schlichs” (the concentrate of the phytoliths, extracted from the living plants), containing 1–10 % F, very large fluorite particles, up to 0.2–0.5 mm, were found (Kowalevsky and Prokopchuk, 1999, p. 103).

6.4. Organic Form?

Finkelman (1980) considered only mineral forms of F in coals. F in natural environments has only anion F^- which appears to be not bonded with negatively-charged humic organics. However, it is well-known that peats and some coals may be enriched in P and Cl, which are also only anionic species. At least for P in peats, it is found that it bonds not with the peat-organics but with organic-peat Ca (i.e. Ca_{org}) (Ivanov, 1962). On the other hand, F may not be a “true” organic (F_{org}), not in F-organics chemical compounds but rather only sorbed on the organic matter surface (F_{sorb}). For example, in the fusain from a US coal, by means of XPS-method (X-ray photo-electronic spectroscopy), positive F–C correlation was found and was explained as an indication of F_{org} form (McIntyre et al., 1985). However, by analogy with results obtained for Cl (Huggins and Huffman, 1995), only organics-sorbed F (not firmly organic-bound) should be present.

An organic form of F always "appears" in our interpretations if the known (or supposed) mineral forms of F seem to be insufficient for the total F amount. For example, the F enrichment in low-ash coals may indicate organic F.

7. FACTORS AFFECTING FLUORINE DISTRIBUTION

The distribution of F in the given coal bed is influenced mostly by the ash yield, and in some high-F coals – also by P-content, due to appearance of the F_{phosph} form. Two other factors (coal petrographic composition and position of a bench within coal bed column) are usually masked by the two former factors.

7.1 Ash Yield

Fluorine entering clay matter depends on positive correlation «F in coal[4] – A^d». Such data are known for coals of Russia, Germany, Spain, and USA.

7.1.1. Russia: Eastern Donbas and Irkutsk Basin

In the statistical sample of the 65 Eastern Donbas bituminous coals, an exponential regression equation was obtained:

$$F\ (ppm) = 91.03\ A^d\ (\%)\ \exp\ (0.01062\ A^d,\%)$$

Calculated average F content (107 ppm) very good matches to the analytically determined value of 109 ppm for the 240 samples (Kizilstein, 2002, p. 111–112).

In Jurassic Irkutsk basin coals, F content in high-ash tailings was 1.5–2 times than in raw coals. In the Voznesensk coalfield, F is enriched the 1.7–1.8 g/cm^3 fraction, especially in high-ash raw coals. These relations, and a positive "F in coal – A^d" correlation in Cheremkhovsk and Voznesensk coals, allow the conclusion: " *in general, fluorine is bound with the mineral part of coal*" (Vyasova et al., 1989, p. 747).

7.1.2. Germany: Pennsylvanian Ruhr Coals

In bituminous coals containing from 15 to 120 ppm F, a strong positive correlation «F in coal – A^d» is found, as well as F–K_2O and F–Al_2O_3 correlations, resulting from F entering illite. In ash, F contents have a rather minor range of 600–900 ppm (Beising and Kirsch, 1974).

7.1.3. Spain: Pennsylvanian Asturian Coals

Study of 69 bituminous and anthracite coals showed strong positive correlation of «F in coal – A^d» in gross coal samples as well in sink-float fractions (Martinez-Tarazona et al., 1994). In low-ash fractions (A^d <3 %), F contents are <100 ppm, whereas in high-ash ones (A^d >60 %) they reach up to 800 ppm. Nearly the same F contents (700–800 ppm) are

[4] All the figures are on whole coal basis if other is not specified.

observed in coaly shales with an ash yield of more than 60 %. The ratio P/F is far less than for fluorapatite (4.9), sometimes it is as low as 0.5, therefore, it is obvious that apatite is not the primary F-carrier. The regression line «F in coal – A^d» goes to zero, therefore, F_{org} form seems to be absent. All these data suggest that illite is the main F-carrier.

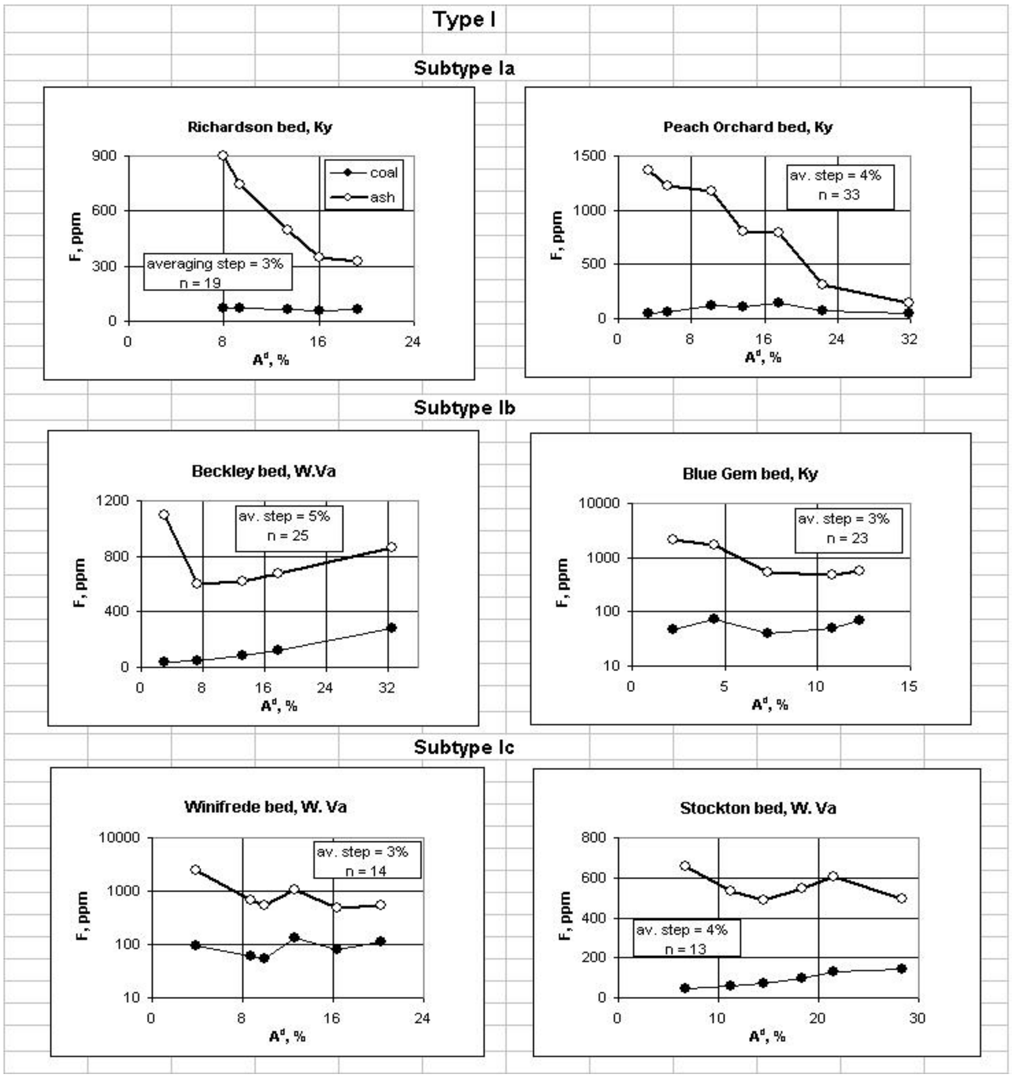

Figure 2. Type-I plot of F contents in coals of the central Appalachian basin. (See Table 1 for description.)

7.1.4. USA: Pennsylvanian Central Appalachians Coals

Using the U.S. Geological Survey Database (Bragg et al., 1998), we examined the correlations «A^d, % – F, ppm in coal» and «A^d, % – F, ppm in ash (calculated)». Altogether, 63 coal beds and nearly 1300 F determinations (and approximately the same number of P determinations) were studied, for coal beds in Virginia, West Virginia, and Kentucky. For small-body statistical samples (5–15 analyses), the data were directly plotted; for more numerous (>20 analyses) – the data were previously grouped over 2-, 3-, 4- or 5 %- intervals of ash-yield, and the averaged data were plotted. In general, several types of plots were obtained – Figures 2–4 and Table 1.

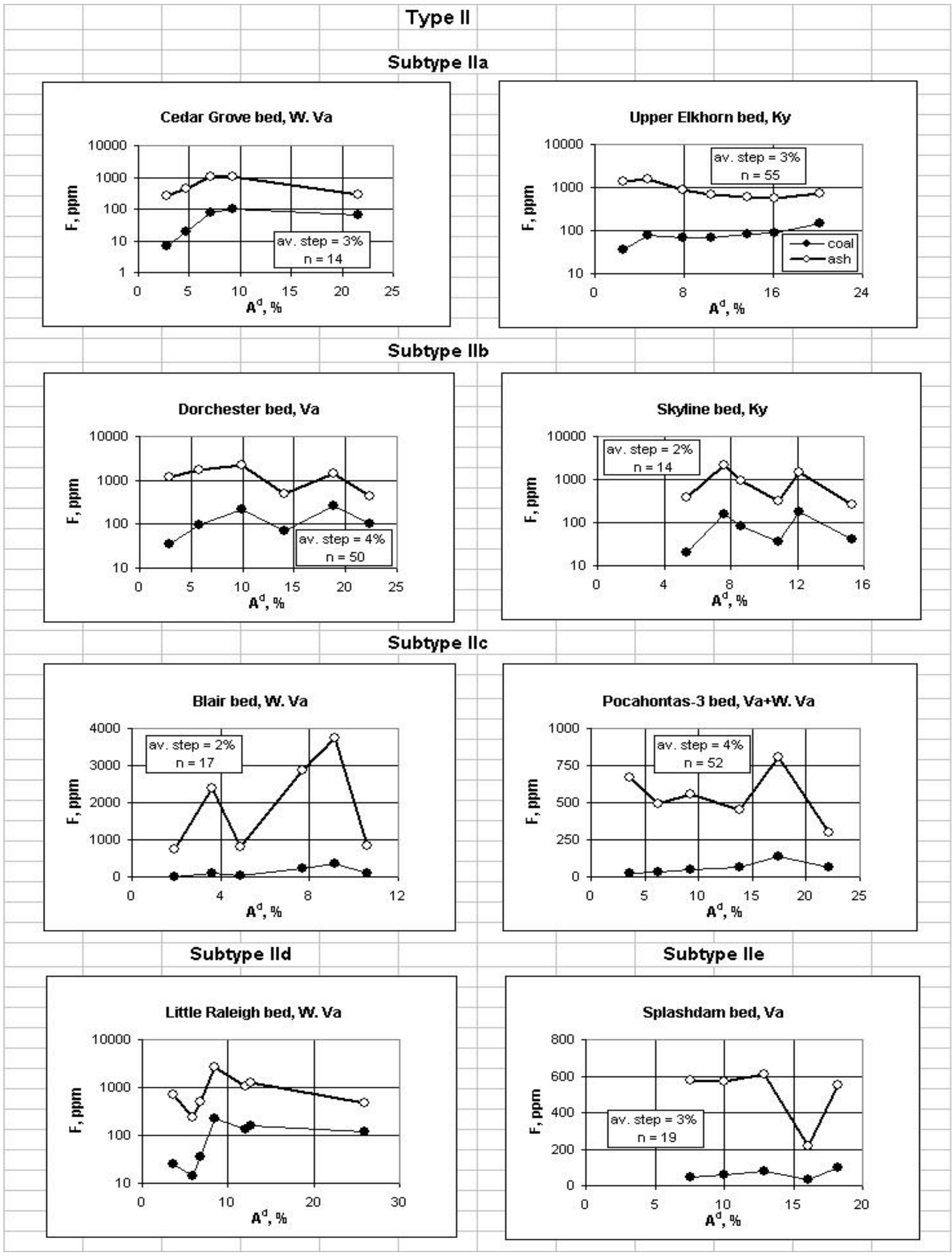

Figure 3. Type-II plot of F contents in coals of the central Appalachian basin. (See Table 1 for description.)

Table 1. Typization of the "F–Ash" Correlations for Central Appalachian Coals

Plot subtype	Description	Coal beds	Comment
Type I. F-contents (ash basis) of coals with the least ash yield are much more than of coals with the greatest ash yield[5]. F-contents (coal basis) do not correlate with an ash yield, or positively correlate. There are three subtypes:			
Subtype Ia	F-contents (ash basis) sharply monotone decrease along with ash yield increase; F-contents (coal basis) show no correlation with ash yield, or the correlation exists – linear or non-linear (with intermediate extremes)	Kentucky: Richardson and Peach Orchard.	No correlation "F–P" is observed
Subtype Ib	F-contents (ash basis) fast decrease along with ash yield increase from the beginning and further again increase but far not reaching the values of low-ash coals; F-contents (coal basis) show in general linear positive correlation (and rarer non-linear)	Tennessy: Big Mary; West Virginia: Beckley, Sewell (including Virginia); Kentucky: Fire Clay, Blue Gem, Jellico, Hazard.	More than 50 % beds show positive correlation "F–P"
Subtype Ic	F-contents (ash basis) show the same picture but **with intermediate maximum** in rather ash-enriched coals; F-contents (coal basis) show mostly non-linear positive correlation	Virginia: Upper Banner, Lowe; West Virginia: Stockton, Campbell Creek, Eagle, Winifrede, Bens Creek, Coalburg, Pocahontas-4 (including Virginia); Kentucky: Lily, Hazard-7, Unnamed, Alma (including West Virginia)	40 % beds show positive correlation "F–P"
Type II. F-contents (ash basis) of low-ash coals are some more (or even no more) than of high-ash coals but **pass maxima** on moderate- and/or high-ash coals. F-contents (coal basis) do not correlate with an ash yield, or positively non-linear correlate. There are five subtypes:			
Subtype Iia	F-contents (ash basis) weakly decrease along with ash yield increase and pass only **one maximum** on the middle-ash coals. F-contents (coal basis) show mostly non-linear positive correlation	Virginia: Lyons, Kennedy, Clintwood; West Virginia: Cedar Grove, Fire Creek; Kentucky: Hindman, Upper Elkhorn, Fire Clay Rider. 3.2 %.	Clintwood bed is included conditionally; it stands out by sharp F anomaly: 27500 ppm in ash (coal with an ash yield of 3.2 %). Only Fire Clay Rider bed shows positive correlation "F–P"

[5] These terms are only relative because, in general, rather low ash yield of the Appalachian coals. For example, "low-ash" means there up to 6 %, "moderate-ash" – 6–12 % and "high-ash" – more than 12 % ash yield.

Table 1. Typization of the "F–Ash" Correlations for Central Appalachian Coals (Continued)

Plot subtype	Description	Coal beds	Comment
Subtype IIb	F-contents (*ash basis*) weakly decrease along with ash yield increase and pass ***two maxima on the middle-and high-ash coals, and the first maximum is more high than the second.*** F-contents (*coal basis)* show no correlation or non-linear positive correlation.	Virginia: Dorchester; West Virginia: Peerless; Kentucky: Skyline, Manchester, Amburgy, Princess 3-9, Upper Peach Orchard.	Two beds from seven studied show positive correlation "F–P"
Subtype IIc	F-contents (*ash basis*) show similar picture but ***the second maximum is more high than the first.*** F-contents (*coal basis)* show no correlation or non-linear positive correlation	Virginia: Jewel; West Virginia: Blair, Pocahontas-3 (including Virginia)	Two beds from tree studied show positive correlation "F–P"
Subtype IId	F-contents (*ash basis*) weakly decrease along with ash yield increase and pass ***absolute minimum on the low-ash coals.*** F-contents (*coal basis)* show no correlation with an ash yield.	The only example: Little Ralegh bed, West Virginia	
Subtype IIe	F-contents (*ash basis*) weakly decrease along with ash yield increase and pass ***absolute minimum on the high-ash coals.*** F-contents (*coal basis)* show no correlation with an ash yield.	The only example: Splashdam bed, Virginia	
Type III: F-contents (*coal basis*) increase along with ash increase (that is normal); F-contents (*ash basis*) also increase (that is very unusual). There are two subtipes:			
Subtype IIIa	F-contents (*ash basis*) droningly increase	The only example: Pocahontas-6 bed, West Virginia	
Subtype IIIb	F-contents (*ash basis*) increase with intermediate maximum	The only example: Broas bed, Kentucky	

Re contents in the epigenetic zonality column, on Low-Ili (?) uranium-coal deposit.
Compiled from the data of *Maksimova and Shmariovich* (1982, p. 74).

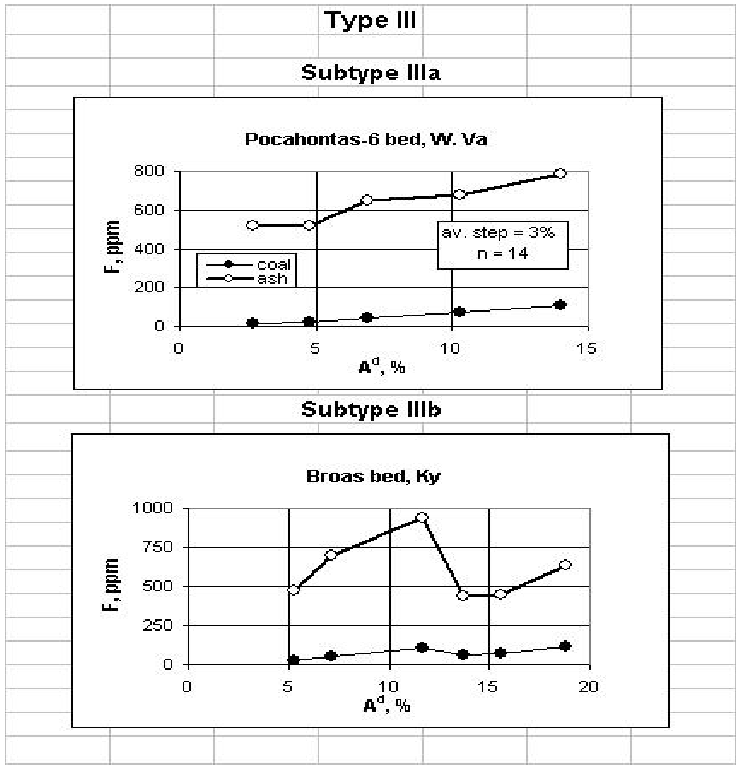

Figure 4. Type-III plot of F contents in coals of the central Appalachian basin. (See Table 1 for description.)

It is evident that a plot type is due to the ratios of three main F-forms: F_{org}, F_{clay}, and F_{phosph}. If F_{org} predominates, the *plot types I* are observed; if F_{org} and F_{clay} , or F_{org} and F_{phosph} are similar, then the *plot types II* are the most characteristic. Only very rarely is the *plot type III*; in such coals, inorganic F seems to be dominant, and the more, the more an ash yield.

7.1.5. USA: Pennsylvanian Illinois Basin Coals

In two Kentucky power plants, a blend of Pennsylvanian bituminous coals from western Kentucky and Indiana is burned. The data from Wong's dissertation (1994) show some correlation «F in coal – A^d» for feed coals collected in 1978 – Figure 5. Compared to the Appalachian plots (see fig. 3 for comparison), such a type of plot may be attested as *IIe typ*e.

7.1.6. USA: Eocene Green River Lignites

In the Vermillion Creek coalfield Wyoming (Green River basin), the relation of the F content with ash yield (Hatch, 1987) is complicated (Figure 6). It is of note, the highest F content is in coal with high, but not the highest, ash yield. Such a picture is typical for the most of *coalphile elements* and indicates several (two or more) elemental mode of occurrence (Yudovich, 1978; Yudovich and Ketris, 2002). Based on the Appalachian plots (see Figure 3 for comparison), such a type of plot may be described as the *IIc typ*e.

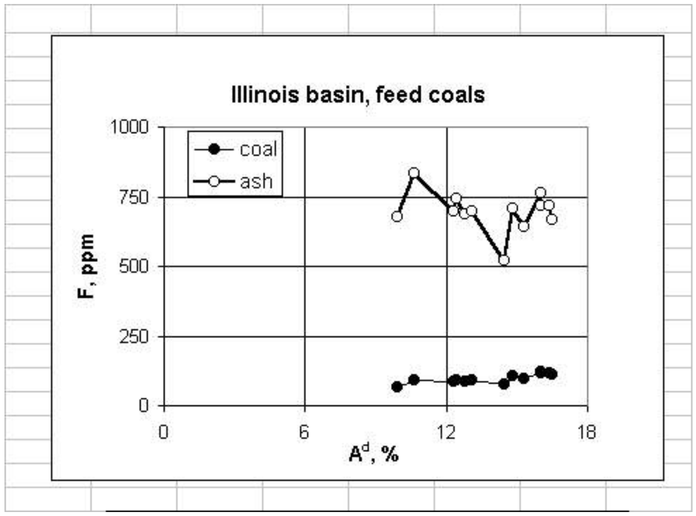

Figure 5. Plot of F contents in coal and ash (calculated) of the Illinois basin. (Plotted from the A.Wong's (1994) dissertation unpublished data.)

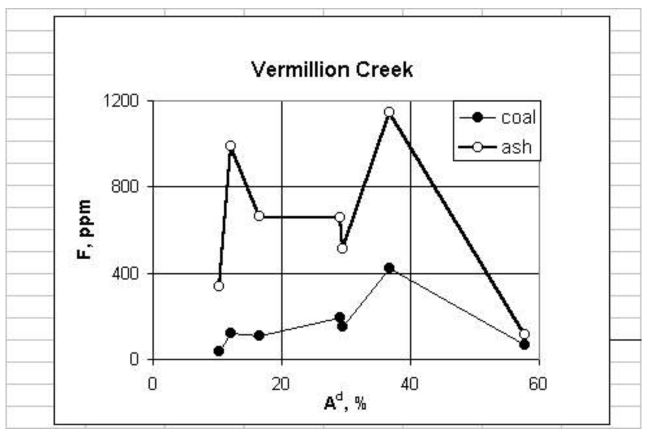

Figure 6. Plot of F contents in coal and ash (calculated) of the Vermillion Creek coals. (Plotted from the data of Hatch (1987).)

7.2. Content of Phosphorus

In coals with enhanced P content, a positive F–P correlation may occur, first noted by Crossley (1946) for British coals. Crossley even assumed that F-content could be predicted by the easier-to-determine P-content. However, the latter issue was later disputed by Bethell (1962), who emphasized that, in many coals, the correlation between F and P is not significant. For example, although in high-P Queensland coals high P-content (3.45 %) is accompanied by the F-enrichment (7360 ppm), the P/F ratio is 7.9 (far more than in fluorapatite). In other P-bearing Australian coals P/F ranges from 2.06 (New South Wales) to 10.2 (South Australia) (Durie and Schafer, 1964). It is worth noting also, a P/F ratio deviation from fluorapatite may be due to the presence of F-deficient phosphate, for example, Al- or Fe (also Sr, Ba, REE)-phosphate known in some coals.

7.3 Position of a Bench within Coal Bed Column

In an East German brown coal deposit, F is enriched in coaly-clay partings, as well as in coaly clays of the coal bed roofs and floors (Dässler et al., 1973). In the subbituminous Highvale Mine coals (Alberta, Canada), some F-anomalies are noted: 116–142 ppm against of background of 31–97 ppm. The anomalies are related to high-ash coals and/or to the upper part of the parting (in one coal bed) (Gentzis and Goodarzi, 1995, p. 62).

Such pictures are very similar to vertical distribution of P. As it is well known, phosphorus moved from the buried peat-bed to the nearest alkali barriers, where it was fixed in phosphate (and Al-phosphate) form (Yudovich et. al., 1985, p. 127–129). The same process may be assumed for fluorine. Low coalphile coefficient of F (its minor “coal affinity”) may be, like P, partly due to F output from the peat beds during diagenesis.

8. GENETIC PROBLEMS

The distribution of F in coal is poorly studied; this forces to use some analogies and suggestions concerning F genesis in coal.

8.1. Does F Have an Organic Affinity?

There are no known experimental data about F capture by peat. However, a “F – organics” correlation is found in surface waters due to *soluble* F-organic compounds formation. Could *insoluble* F-organics compounds also be present? At least, the co-precipitation of F with organic-mineral gels in podzol soil illuvial horizons were found (Perel’man, 1972, p. 206–207). Could a similar process can explain a F-enrichment in high-ash coals? As was above noted, F, like P, may be mobile in diagenesis; possibly accounting for the F accumulation in partings and high-ash coals.

8.2. May F be Facies Controlled?

As was shown above (see Section. 2), an important geochemical feature of F is its “marine-affinity” (“thalassophile” property): an average F concentration in sea water is 1–2 orders-of-magnitude higher than in river water (in humid zone environments) (Perel’man, 1972). Therefore, like boron and sulfur, fluorine contents in coal may be influenced by peat-forming facies: to be higher in paralic (marine influenced) than in limnic (intracontinental) environments. At least, the data about enhanced F-contents in paralic Donbas coals (Gulyaeva and Itkina, 1962) do not contradict this suggestion.

In south Greece, some relatively high F contents (132–258 ppm) are found in Pleistocene (Megalopolis, Peloponnes) and Pliocene (Peloponnes, Kalavrita) lignites. This may indicate the near-sea peat-forming facies (Foscolos et al., 1989).[6]

8.3. May F Be Volcanic Controlled?

Theoretically, F entering volcanic exhalation may result in syngenetic F-enrichment in nearby peatbogs. For example, high F-contents in Guizhou Permian coals seem to be directly related with Emeishang basalt flow (Zheng et al., 1999). Moreover, the authors think that F was mainly captured by the peat-forming plants from air, i.e. F in coal may be attested here as primary F_{bio} form!

In general, all these syngenetic mechanisms appear to be probable but data deficiency makes them only hypothetical.

8.4. Epigenetic F-Enrichment

In the Warrior basin, zones of enhanced F (and As) contents are controlled by two cross faults of the Appalachian folded belt and are displayed above the basement uplifts. Coal mineralization is similar to the hydrothermal vein Au-Sb-Cu-mineralization that occured in the southern Appalachians. In contrast to Mississippi Valley Type mineralization resulting from descending brine movement, this mineralization is clearly influenced by the burial metamorphism. As seen from the vitrinite reflectance picture, a heat flow maximum (perhaps, related to the hot fluids input into the coal-bearing strata) was situated on the eastern margin of the Southern Appalachian coal-bearing basin, near the Blue Creek anticline (Goldhaber et al., 1997).

9. Behavior of F in Coal Combustion

During a coal burning in electric power plants (EPP), volatile HF is formed and escapes the combustion in flue gases. A part of evaporated F may be captured by fly ash collected on ESPs (electrostatic precepitators); this part is greatly influenced by CaO content in fly ash which may bond F as CaF2 compound.

9.1. Pulverized Coal Combustion

In Novo-Irkutsk EPP, Jurassic Azeisk brown coals with near-Clarke F contents are combusted. In ash wastes, F is distributed as follows (Boiko and Suturin, 1994, p. 106):

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[6] An alternative explanation is epigenetic one: influence of the F-bearing ground waters derived from evaporites.

precombustion chamber slag …………………………….…….. 300 ppm F
fly ash, three ESP fields..……………………...… ..0–630 ppm F
ash disposal …………………………………………… .440 ppm F

Therefore, F is enriched in fly ash but no more than twofold.

In the Mojave EPP (near Bullhead, Arizona), there is alkali fly ash disposal containing 70 ppm F. Fluorine distributes over the ash size fractions (μm) as follows:

72 ppm (>250 μm) → 66 ppm (250–105 μm) → 68 ppm (105–53 μm) → 83 ppm (<53 μm)

Therefore, in these alkali fly ash, F is not substantionally fractionated (Phung et al., 1979).

9.2. Cyclone Burning

In cyclone burning (with known minor yield of fly ash), F is also fully evaporated as HF and only partly captured by fly ash. This is logical because T is here much higher. The laboratory ash from Ruhr bituminous coals contains 600–900 ppm F, and their cyclone fly ash contains some more, up to 1100 ppm. In this-low-Ca ash, F enters silicate spheres, although its form was not established. However, in the cyclone burning of high-Ca Rhine brown coals, ¾ of initial F pass into the slag, and up to 2200 ppm F – into fly ash. A general trend is noted of evaporation of F controlled by flue gas temperature (Beising and Kirsch, 1974).

9.3. Semicoking

A redox medium of the burning and pyrolysis is of value. For example, in the Irkutsk basin coal burning with average F content of 800 ppm, up to 90 % from initial F volatilize and only 100–200 ppm F retained in ash. However, in semicoking (i.e., in more reducing medium), almost all F retains in semicoke and begins to evaporate only at T >1000 ^{o}C. After coal and coaly argillite semicokes were calcined up to 1200 ^{o}C, 25 % and 40 % initial F were retained (Khankhareev et al., 2002, p. 398).

10. Technological Injurious Action

Fluorine in coal is an unwanted admixture. It complicates coal burning and processing due to corrosion of the scrubber ceramic fills and silica deposition on the cold sides of the installations heated by flue gases. According Crossley (1946), refractory crubbers were corroded even at slightly enhanced F contents of 120–140 ppm (against <40 ppm F as British coals background (Wandless, 1957). Wong et al. (1994, p. 86) noted:

> "One of the major concerns for a coal-fired power plant equipped with a FGD system is corrosion in the duct work and the tail-end of the air preheater. Corrosion of refractory materials in contact with flue gases has been attributed to the small amounts of fluorine present in the coal and scrubber sorbent. The metal surfaces (Ti metal, carbon steel, and stainless steel) of the duct work and air preheater have already been abraded by the mass flow of fly ash particles which are mainly composed of small, abrasive silicate glasses. This roughness on the surface provides a very good opportunity for corrosive gases such as HF, HCl and H_2SO_4, which are present in the stream of flue gases, to diffuse into the surfaces and attack the metals".

11. ENVIRONMENTAL TOPICS

Atmospheric F emission may create some environmental problems at coal industrial and domestic burning because of fluorine toxicity.

11.1 Toxicity

In coal burning, high toxic compounds, such as CaF_2, SiF_4 and Na_2SiF_6 may be formed. In the air of populated areas, their permissible limit (calculated on F) has to be no more than 0.005–0.03 mg/m^3. In drinking water, permissible F concentration must be no more than 2 mg/L – that is near the F content in sea water (if more, fluorosis may be caused) (Perel'man, 1972, p. 210).

According the Russian sanitary standards (Belyaev et al., 1993) F concentrations must be no more than (all figures calculated on F):

the air of the populated areas (gaseous HF and SiF_4)
simultaneous concentration…………………………0.02 mg/m^3
average daily norm …………………………..0.005 mg/m^3

well soluble compounds (NaF et al.)
simultaneous concentration…………………….……0.03 mg/m^3
average daily norm …………………………..0.01 mg/m^3

weakly soluble inorganic fluorides (AlF_3, CaF_2, et al.)
simultaneous concentration…………………………..0. 2 mg/m^3
average daily norm …………………………..0.03 mg/m^3

drinking water (F and F in compounds)………...1.5 mg/l

In one Chinese village in 1986 a fluorosis event was described, the result of burning of F-bearing coal (170–1026 ppm F) for stove heating and coking (Dai et al., 1986). Further publications (Zheng et al., 1999) highlighted a serious problem; extremely high endemic fluorosis levels (dental and skeleton disability) in south and south-east China. Endemic fluorosis were noted in an area of 14 provinces populated with 30 million people, and more than half of them were ill.

Special study (Zheng et al., 1999) showed that F-contents in the environment was not higher than in other provinces. The point was that, the rice drying performed in open, without flues home stoves heated by coal. The burned coals contained up to 2000 ppm F and the rice captured F from air. For example, after three-day-drying, in the rice with a moisture value of 21 % was 6.1 ppm F. After 210-day-drying, the moisture decreased up to 12.4 %, and F content increased up to 130 ppm. The same duration of the drying but using wood-burning stove, at similar initial moisture of 13.7 %, resulted in F content of the rice only 2.5 ppm. The indoors air with coal-burning contained up to 143.5 $\mu g/m^3$ F (Zheng et al., 1999).

11.2. Atmospheric Emission

Feed coals imported into Netherlands from Australia and USA have, on average, 11 % ash and 80 ppm F (or 727 ppm on an ash basis). Over 16 analyses series for all Dutch EPPs with pulverized coal combustion, the following F distribution was observed (Meij, 1994):

727 (feed coal ash) $\Rightarrow$ 55 (bottom ash) $\Rightarrow$ 127 (fly ash from four rows of EPS, with median diameter from 22 down to 3 μm) $\Rightarrow$ 1090 (emitted finest fly ash, three fractions with median diameter from 3 down to <0.3 μm).

Therefore, F is depleted in bottom ash and sharply enriched in finest fly ash – an indication of the evaporation followed by the condensation, with partial solid-phase emission. Further, in flue gas clean up by wet scrubbers, F emission may be two-fold decreased (Meij, 1994).

As it exemplified by the German coals combustion (Brumsack et al., 1984), solid-phase F emission is influenced by coal rank. In brown coal burning, enrichment ratio (F content in finest emitted fraction of fly ash / F content in collected fly ash) is far lesser than in bituminous coals burning: 4.6 vs. 12–14[7]:

	collected fly ash	emitted fly ash
brown coals …………………....	249 ppm F	1144 ppm F
bituminous coals……………..	165–196 ppm F	2307–2548 ppm F

These data imply that mode of F occurrences in brown and bituminous German coals are appreciably different.

11.3. Fluorine Poisoning of Surface Waters

In 11 Bulgarian ash disposal ponds, F content reaches up to 13.3 mg/L (Bobov Dol EPP); this two orders of magnitude more than F background in surface waters (Bowen, 1966), and

[7] two figures mean two burning regimes: dry and wet bottom.

more than 25 times – the European Council permissible concentration, 0.5 mg/l (Vassilev and Vassileva, 1992).

Typical F-content range in British fly ash disposals is from zero to 200 ppm. Experimental leaching of the fly ash showed F contents ranged from 0.2 to 2.3 mg/L (Sear et al., 2003). These figures are higher than permissible water concentrations.

11. 4. "Threshold of F Toxicity" in Coal

According Russian official norms, the "coal threshold of toxicity" is 500 ppm F (Zharov et al., 1996, p. 15), but Kizilstein et al. (1989) note that the figure *"has no scientific basis"*. That is correct; for example, in the eastern Germany, were bees mortality was described in the vicinity of the EPP burning the coals containing no more than 178 ppm F (Dässler et al., 1973). It is evident that F-emission depends on not only F-content but also on F mode of occurrence and the combustion temperature. Therefore, the F threshold yet has to be determined, for reasons of these considerations.

12. Coal Cleaning and Flue Gas Clean Up

As F has low coal affinity ("coalphile index"), the mineral site of F is dominant in coal, mostly as F_{clay}. Only in high-P coals, one can predict an appreciable contribution of phosphatic fluorine, F_{phosph}, whereas a F_{org} contribution is, in general, minor. All this means that routine coal cleaning could be an effective method for decreasing the F content. For example, in the Upper Freeport coal seam, clay matter is main F contributor; industrial coal cleaning could decrease F content up to 50 %. In the lab cleaning, F content was decreased even on 78 % (Finkelman, 1993).

As was seen from the Dutch data (Meij, 1994), the wet scrubber flue gas desulfuration (FGD) leads to appreciable lowered F emission. Similar results were obtained in Kentucky EPPs, where a blend of high-sulfur coals of the Illinois basin was burned (Wong et al., 1994; Hower et al., 1997). The feed coals contained on average 3.7 % S and 12.6 % ash. The solid FGD wastes (after vacuum filtration) are composed mostly by $CaSO_3$ with 47.35 % CaO. The final wastes (named as "Poz-o-tec") are the blend of $CaSO_3$+$CaSO_4$, fly ash and some $CaCO_3$ remainders. They contain (on average) 6.58 % Fe_2O_3 (magnetite), 24.36 % SiO_2, 8.58 % Al_2O_3, 27.10 % CaO, and 31.50 % SO_3. Their appreciable part is represented by new-formed ettringite, $Ca_6Al_2(SO_4)_3(OH_2)$ 26 H_2O, filling the pores between the fly ash silicatic glass spheres. In the technological chain, F is distributed as follows [8]:

94 ppm (feed coal ash) ⇒ 124 (fly ash) ⇒ 85 (bottom ash) ⇒ 898 (FGD wastes) ⇒ 501 (final wastes)

[8] Our averaging based on four analyses performed during 4-months-long monitoring; all the figures are on dry matter [Hower et al., 1997].

Therefore, F in ash wastes relatively enriches in fly ash, and in FGD wastes is sharply enriched. Such F accumulation results from, perhaps, interaction F + CaO (with fluorite formation?)

13. CONCLUSION

1. The World average F content in coals (coal Clarke of F) for the hard and brown coals are, respectively, 82±6 and 90±7 ppm. On an ash basis, these contents are greatly increased and are 580±20 and 630±50 ppm, respectively. As an average, F content in ash is 605 ppm (lower than the Clarke value for sedimentary rocks, 650 ppm). F is, on average, *not a coalphile element.*

2. Nevertheless, some coals are known to have a F content one order-of-magnitude more than the coal Clarke level. In general, these are either high-ash or high-phosphorus coals, with both the features often combined. This (and some others) features show some similarity between F and P geochemistry in coal. In particular, F, like P, seems to be depleted from the buried peat during diagenesis toward hosting rocks.

3. No less than three F-forms (modes of occurrence) may be present in coal: phosphatic (F_{phosph}), silicatic (mostly F_{clay}), and organic (F_{org}). It can be suggested that F_{clay} dominates in high-ash coals, F_{phosph} in high-P coals, and in ordinary coals with moderate ash yield and near-Clarke P and F contents, F_{org} may be dominant. There is no information concerning chemical species of the F_{org} form. However, by an analogy with P, it seems to exist as an F compound with Ca_{org}, not with organics itself.

4. It is yet not clear, if F is in authigenic CaF_2 and what could be a contribution of such a form to total F content. It seems not to be excluded that such form may have genetic relation with F_{org} (diagenetic or catagenetic transformation, $F_{org} \Rightarrow F_{min}$?) (See (Yudovich, 1978) for details).

5. There are no clear relationships concerning F enrichment in coals. Plausible hypothesis is that F might be syngenetically enriched in coals (a) in paralic (near-marine) coals, and (b) in coals formed with a volcanic activity background. On the other hand, some F anomalies (like that in some Alabama coals) may have resulted from epigenetic hydrothermal F-input, during (or after) coal metamorphism.

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Chapter 8

ENVIRONMENTALLY COMPATIBLE LAND USE ZONING IN A REPRESENTATIVE POWER GRADE COALFIELD IN INDIA: A MULTI-CRITERIA OPTIMIZATION APPROACH

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ABSTRACT

Land use zoning is gaining increasing popularity in India, amongst environmentalists and planners alike, as an important instrument governing siting of industrial, commercial, residential and other uses of land. 'Environmentally compatible land use zoning' is gaining increasing acceptance as an essential tool for effecting environmentally sustainable development. Most of the environmental problems in mining/ industrial regions can, in one way or the other, be related to improper land use zoning. Through an implicit integration of environmental constraints into the basic planning procedure, the zoning system arrests an otherwise (business-as-usual scenario) spiralling environmental management cost. However, environmentally compatible micro level zoning system is yet to find its right place in Indian planning set-up.

Land use is expected to be altered significantly in power grade coal bearing regions in India that typically have a mix of large opencast mining projects, thermal power plants and other associated industries in coalfields. Power grade coalfields in the country are in river valleys that host rivers and large tract of forests and agricultural lands amid a majority of tribal population. A need to carry out a scientific inquest into zoning study in the power grade coalfields in the country can hardly be over emphasized. The chapter

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discusses a new micro level zoning method applied for a representative power grade coalfield in the country. The authors have attempted to devise a mechanism for optimizing spatial zoning as per need based zoning policy. The study area was divided into segments of land parcels for spatial analysis of each parcel. Behaviour of infrastructural, socio economic and environmental attributes was studied to identify the underlying economic forces and environmental need. Land use forms of segments or land parcels were logically integrated to evolve overall land use zoning.

Keywords: zoning, land use suitability, environmental sustainability, analyzing framework, GIS, incompatibility, India

1. Introduction

Power grade coalfields in India are gradually being subjected to compounded environmental pressure due to rapid rise of demand for power grade coal in India. A huge energy demand projection (by the year 2012, India's peak demand would be 157,107 MW with energy requirement of 975 BU) sets out phenomenal rise of demand for indigenous power grade coal production (Bhaskaran and Ravikumar, 2002). In 2005-06, of the total 407.02 million tonnes of indigenous coal off take, more than 70% was power grade coal (Anon, 2007a). Coal is the most important and abundant fossil fuel in India and accounts for 55% of India's energy need (Anon, 2007b). A share of such magnitude in the commercial energy spectrum of the country is in conformity with comparatively favourable reserve potential of coal vis-à-vis other energy resource like oil, natural gas or hydropower. As a measure to jack up productivity in coal sector, government of India has planned for liberalization of the coal sector to private sector players including the MNCs. Private and public sector entrepreneurs, mostly power plant operators, are being allotted coal blocks for captive mining.

Typically, power grade coalfields in the country are in river valleys that host dense forests and fertile agricultural land amid a majority of tribal populace. The pristine environmental setup are feared to be impacted significantly due to large scale exploitation of surface land by open cast coal mining and downstream coal based industries - thermal power plants in particular. Tchno-economic factors tend to favour location of coal based industries at sites close to coal resources and water supply base. In addition to the physical pollution potential, the areas in and around the coalfields is prone to significant socio-economic impacts due to large-scale economic in-migration and de-settlement of population.

In order to ensure that developmental projects do not inflict environmental stress beyond supportive and assimilative capacity of receiving environment, it has been found useful to carry out at first, an appropriate land use exercise so as to distribute the activities over space and time to ensure optimum resource allocation at minimum pollution contribution. Environmentally compatible spatial zoning is a possible method for effecting environmental sustainability of an environmentally subdued region. Through an implicit integration of environmental constraints into the basic planning procedure the zoning system fulfils long-term environmental goals.

1.1. Land Use Models and Recent Approach

The twentieth century witnessed significant development in the area of modelling land use structure. Burgess (1925; cited in Rhind and Hudson, 1980) suggested that the urban areas may be conceived as five concentric rings of different types of land use. According to Burgess the central most area of a city is generally occupied by the Central Business District (CBD), - the focal point of commercial, civic and social life in the city. Transport routes converge on CBD, which is thus the most accessible location within the urban area. The second zone is the transition zone, an area characterized by blighted conditions and the penetration of commercial and industrial uses into residential areas. The remaining three rings of (i) zone of working men’s homes, (ii) residential zone and (iii) commuters’ zone are purely residential with the quality of residential areas increasing with distance from the centre of the city. These phenomena are seen as response to the differential ability of groups of people to be able to afford the cost of travel to work. Hoyt (1939) specified directional as well as distance component from the city centre to urban land use patterns. Harris and Ulman (1945) proposed a composite model of urban structure, which reconciled of those of Burgess (1925) and Hyot (1939) together with the addition of multiple nuclei to display functional specializations. Berry *et al.* (1963; cited in Rhind and Hudson, 1980) have shown a relationship between the relative importance of road intersections and localized peaks in land value. With respect to manufacturing industry Hamilton (1968) proposed a model of the spatial industrial structure of a metropolis, which distinguishes between four categories of manufacturing industries, each with distinct site requirements. In the last few years, Cellular Automata (CA) has gained popularity as modelling tools for urban process simulation. Barredo *et al.* (2003) explained that from a practical point of view, the process of urban dynamics can be defined as an iterative probabilistic system (White *et al.*, 1999) in which the probability that a place in a city is occupied by a land use in a given time, is a function of the concerned factors measured for that land use: suitability, accessibility, land use zoning status, neighbourhood influence and a stochastic perturbation.

Grabaum and Meyer (1998) introduced a novel way of using GIS to support decision making in the planning process and to develop regional guidelines. The method of ‘multicriteria optimisation' helps new methodological standards to be established for integrating the various results of functional landscape ecology assessments of the type usually carried out in ecological planning, and enables the overall comparison of competing aims. This technique allows different aims in a geographical region to be quantified and takes into account different weightings of scenarios. They carried out different functional assessments and an assessment of the agricultural production function using GIS for a test site in Saxony, Germany and presented the results in the form of ordinal assessment classes, which express tendencies. On the basis of the assessment results, objectives for the calculation of an optimal land-use pattern were defined and weighted in different scenarios.

The authors have attempted multi-criteria optimization approach with an optimization strategy suitable for environmentally compatible micro level land use zoning applicable for a representative power grade coalfield in India. The research work undertakes (i) identification of principle attributes and their functionality that governs land use forms in subject area (ii) development of criteria (goal function values) for deciding optimal land use that fosters economic development without sacrificing environmental sustainability goals, and (iii) devising a mechanism for optimizing spatial zoning based on understanding of impacting attributes. A step-by-step application of the suggested zoning strategy is presented in this paper with the help of an in-depth analysis of various techno-economic, environmental and social attributes.

1.2.The Representative Power Grade Coalfield

Physiographical and Geomorphologic characteristics of power grade coalfields in the states of Orissa, Madhya Pradesh, Bihar and Jharkhand present significant similarity. The coalfields are drained by major rivers that serve as water sources for thermal power plants and downstream coal based industries. Over the years good communication network through rail and road links have developed in these coalfields. Common site related features exhibited by Indian power grade coalfields include (i) valleys amid undulated hilly topography (plains have elevation range of 250-300 mRL and the hill tops are, in general, at 500-600 mRL) (ii) protected and reserve forest cover especially in the hill tops (iii) substantial agricultural fields because of good drainage at river basin (iv) similar socio-economic profile with predominance of migration economy and agriculture as the second alternative employment, and (v) plenty of rainfall (1200-1600 mm annually) through a distinct south west monsoon ranging predominantly from June to August.

The Talcher coalfield, a truly representative power grade coalfield was chosen for the study because:

- All governing attributes related to environmental, infrastructural, industrial and socio-economic aspects are well exhibited in the coalfield. Huge unexploited reserve calls for a long term infrastructure planning. This coalfield has a mix of opencast and underground (very less underground typical to power grade coalfields) mines, government and private ownership (coal blocks have been allotted by government of India for captive lease), rural and urban character.
- Talcher coalfield, better known as Angul-Talcher area, has been identified by Central Pollution Control Board (CPCB) of India as a critically polluted area. Angul-Talcher area is identified for assistance by Norwegian Agency for Development Co-operation (NORAD).
- Land use zoning requires an extensive large database on a variety of aspects. Substantial secondary data is available for Angul-Talcher area.

The coalfield, covering an area of about 1815 sq km is connected with the Puri-Talcher branch line of south-eastern railway and the connected road network includes NH-23 and NH-42. The area is drained by the Brahamani river flowing in the eastern extremity of the coalfield. About 400 sq km areas on eastern part have coal-bearing exposure of Barakar and Karharbari formation. History of coal mining in the coalfield dates back to 1921 whereas coal based thermal power generation took off in 1967. Existing large opencast coal mines are located at Bharatpur, Jagannath, South Balanda, Anant and Lingraj. The coal production of Talcher Coal field has attained phenomenal growth from 0.91 million tones in 1972-73 to 50.582 million tones in 2006-07. A rapid growth of industrial activities has taken place in the region because of favourable market condition backed by ready availability of resources and cheap labour force.

More than a decade back a regional EIA study carried out on Talcher coalfield identified a plethora of serious environmental issues that included: deposition of fly ash and air pollution, deterioration of water quality of Brahamani river, deforestation and degradation of forests and, change of land use etc (Anon, 1994). Major industries located in the coalfield are (i) coal mines operated by the Mahanadi Coalfields Limited (MCL), mostly large open cast coal projects; (ii) thermal power stations of National Thermal Power Corporation (NTPC) at Talcher and Kaniha; (iii) Aluminium smelter of National Aluminium Company (NALCO), NALCO has Captive power plant also; (iv) Chemical plant of Orichem Limited to manufacture sodium dichromate and basic chromium sulphate. Basic fuels burnt in the industries are coal, HSD, Furnace oil, LDO and Synthetic gas. A variety of chemicals *viz.* sulphuric acid, alum, caustic soda, lime, methanol, ammonia etc. and ores viz. limestone and chromite are used as raw materials. Status of coal mining in Talcher coalfield is elaborated in Table 1. Besides, there are about 35 small-scale industries mostly engaged in mechanical and fabrication works, carpentry, manufacture of food products, aluminium utensils, electronic equipment etc.

Table 1. Status of coal mining in Talcher coalfield

Mining/exploration	Total area (sq. km)	Type of mining	Coal reserves (Mt)
Existing Underground Mines	25.00	Underground	440.71
Existing Opencast Mines	28.37	Opencast	821.13
Mines for which Detailed Exploration Completed	8.07	Opencast & Underground	528.00
Mines for which Semi-detailed Exploration Completed	48.92	Opencast	1,720.08
Mines for which Detailed Exploration in Progress	32.00	Opencast	1,677.50

Coal projects and associated industries are located in a broad valley between the hilly terrains on the north-eastern and south-western parts of the coalfield. River Brahamani traverses the valley from north to southeast and drains directly into the Bay of Bengal. The major part of the area forms the plains of river Brahamani and its tributaries *viz*., Nandira jhor, Singhada jhor and Tikra nala. The western and southern hill ranges form watershed between river Brahamani and Mahanadi whereas the eastern hill ranges divide the catchments of river Brahamani and river Ramaila. Most of the hill slopes are covered with forests and scrubby vegetation. Figure 1 and Figure 2 show Physiography and land use of the area respectively. The area has the following socio-environmental characteristics:

- In the pre-industrialization era (1960-70), the area had predominantly rural character with scattered small villages in the valley between forested hill ranges. Population density of the region was very low. Agriculture was the only means of livelihood.

- Large-scale industrialization has taken place due to availability of suitable resources and infrastructures e.g., coal (from Talcher coalfield), water (from Brahamani river and its tributaries), communication link (NH-33, 42 and well developed state highway networks) etc.
- After industrialization, air pollution (majority of industrial area has ground level concentration of suspended particulate matter, more than 500 $\mu g/m^3$), water contamination (in Nandira jhor and Brahamani river downstream of confluence with Nandira jhor), Soil contamination (storage area, workshops, waste disposal area in industries) and land degradation (opencast coal mines) have increased. Large-scale immigration has taken place.
- With development of industries although the natural resources have been subjected to taxing, social capital resources have improved. Medical facilities have increased (although health status has deteriorated due to increased air pollution related diseases) and educational facilities have improved (literacy rate has increased). Although substantial prime agricultural land is under pressure, agriculture is still an important occupation in the region. Increased earning from industry and business activity has resulted in increased investment in agriculture.
- A number of environmental and social assets e.g., stretches of reserve and protected forests, water quality of Brahamani river, a good stretch of prime agriculture land, a few places of historical importance and, ambient air quality at a few location are in urgent need of protection.
- Large-scale land use alteration is inevitable in and around the ongoing and potential coal mining areas due to massive opencast excavation.

2. Land Use Zoning Objectives for the Representative Power Grade Coalfield

Appropriate land use zoning facilitates formulation of an optimum resource utilization policy within the environmental carrying capacity of the region thereby encouraging intended land uses and or discouraging yet another set of land uses, and thus ensuring an optimized environmental performance, on a continual basis. The broad environmental zoning policy for the representative study area aims:

I. to recognize economic, social and environmental aspects of the power grade coalfield and to plan coal mining and associated development in an environmentally sustainable way through optimization of land uses with the objectives of (i) having long term suitability of land uses from economic and social perspectives on sustainable basis; (ii) rendering minimum possible pollution load to human habitats - local or distant; and, (iii) maximize generation of social, capital and environmental resources as much as possible.

II. to protect and improve the specific natural resources viz., reserve forest areas, protected forest areas, biosphere reserves and wetlands in line with national policy.

III. to protect areas with unique features of social/cultural, commercial interest viz., historical monuments, specific faunal/floral habitat etc.

The policy framework for zoning recognised that coal mining,- being the host economic attribute for the power grade coalfield, is central to the zoning exercise and zoning criterion should be liberal on coal mining.

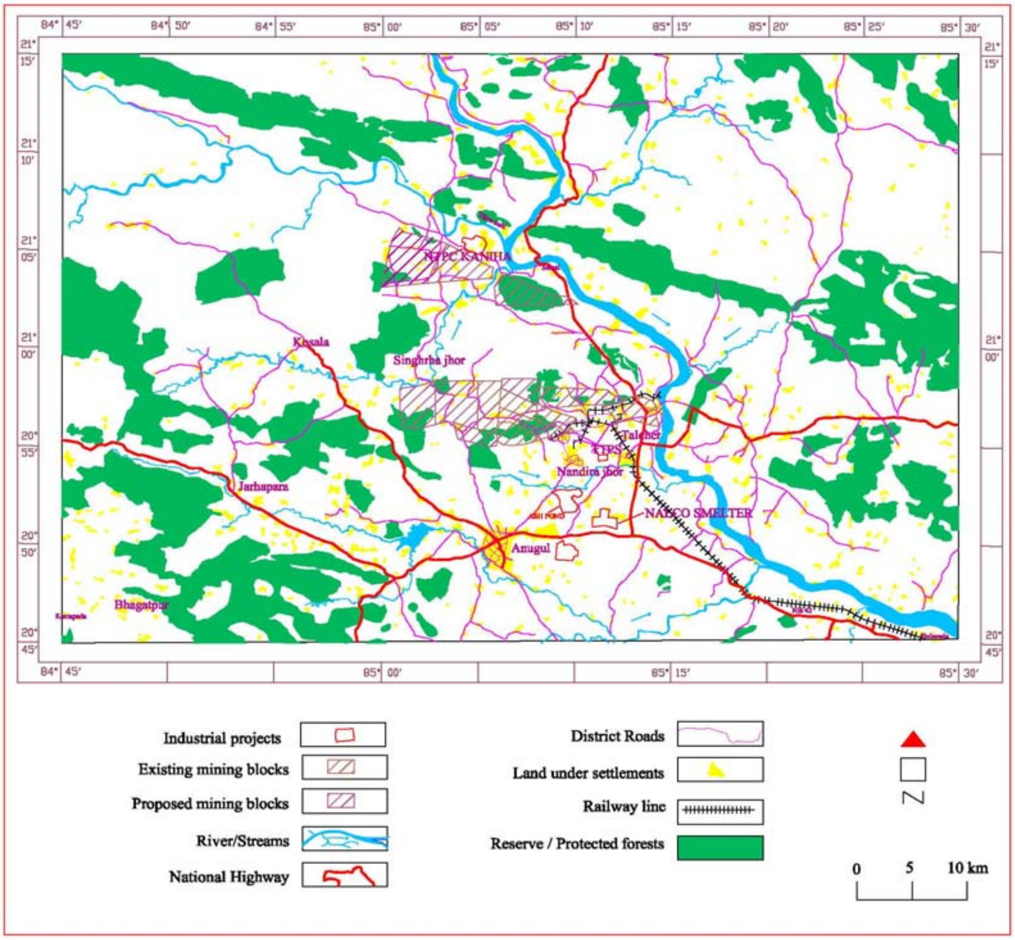

Figure 1. Physiography of the Angul -Talcher area

3. Resource Based Land Use Suitability and Environmental Sustainability

Prevailing land use of any land parcel is governed by a host of techno-economic factors with a view to optimise maximum yield of economic rent (Mukhopadhyay and Sinha, 2005). The prevailing land use type requires a certain degree of socio-infrastructural resource requirement for socio-economic viability. In order to ensure environmentally sustainable development of a region is to maintain an uninterrupted supply of acceptable quality of input resources. For continuing suitability of a land use type it is important that the site meets long-term resource requirements for the type of land use. Continual over exploitation of resources by an existing or adjoining land use type may gradually render the land use unsuitable due to unavailability of required resources. This, in environmental parlance, is called reduction of supportive capacity. The degraded or altered resource combination, then, attracts a different land use category. Land use changes in coalfield areas may be triggered due to overuse of resources (*e.g.*, drawal of ground water beyond natural yield capacity creating a draft) or contamination of resources (*e.g.*, contaminating ground water, surface water and soil through effluents from industrial land use, pesticides from agricultural land use, untreated sewage from residential land use *etc*.). Recent years have seen growing interest in the identification and encouragement of economic development strategies that are environmentally and socially sustainable (Serageldin, 1996; Vosti and Reardon, 1997). Key infrastructural resource requirement for common land use categories (industrial, commercial, residential, agricultural, forestry and pasture) are shown in Table 2. Table 3 explains environmental risks associated with the land use forms with respect to environmental attributes. Socio-infrastructural (or economic) suitability factors are elaborated at Table 4.

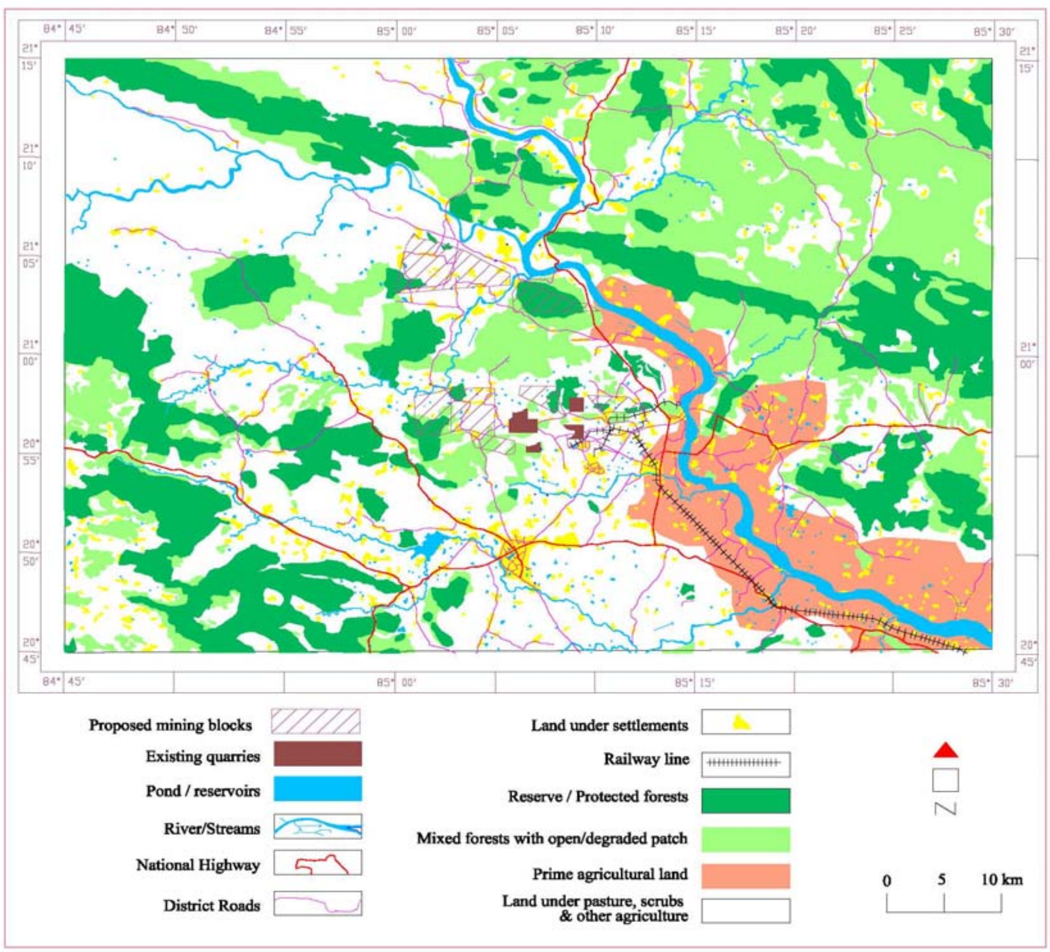

Figure 2. Land use of the Angul- Talcher area

Table 2. Key resource indicators for common land use categories

Land use category	Resource requirement	
	Natural	**Infrastructural and socio-economic**
Industrial (TPPs and other processing and manufacture industries)	Water, large flat land area	Cheap labour, a good communication network, proximity of coal base as raw material resource, proximity of market for the product
Commercial	Large flat or moderately flat land area	Sizeable population density around, good communication
Residential	Proximity of agricultural resource, water source, flat or moderately flat area	Proximity of earning source, proximity of medical facilities, proximity of educational facilities, communication, electricity, sewerage connection
Agricultural	Good soil capability, flat or moderately flat area, water source	Cheap labour, electricity, proximity of market for the product
Forestry	Adequate soil capability, adequate spatial or altitudinal distance from habitation area.	Arrangements such as “social forestry” or “joint forest management”
Pasture	Flat or sloped area	Proximity to habitation area

Table 3. Environmental risk issues associated with common land uses

Attributes	**Environmental risk issues**
Erosion proneness	Increased erosion affects agriculture and forestry
Background particulate level	Maximum permissible limit (as per CPCB) is 200 $\mu g/m^3$ for residential area and 500 $\mu g/m^3$ for industrial area
Background SO_2 level	Maximum permissible limit (as per CPCB) is 80 $\mu g/m^3$ for residential area and 120 $\mu g/m^3$ for industrial area
Background NO_x level	Maximum permissible limit (as per CPCB) is 80 $\mu g/m^3$ for residential area and 120 $\mu g/m^3$ for industrial area
Water contamination	Critical with Residential and agriculture land use
Background noise level	Maximum permissible level (as per CPCB) is 45 dB(A) for residential area (night time); 55 dB(A) for commercial area (night time), and 65 dB(A) for Industrial area (night time)
Soil contamination	Risk more with Residential and Agriculture land uses
Soil capability	Poor soil capability affects Agriculture and Forestry

Table 3. (Continued)

Attributes	Environmental risk issues
Proximity to hazardous material storage	Risk increases with proximity. Particularly important for Residential, Commercial and Agriculture
Proximity to religious, historic or archaeological monuments	Risk increases with proximity to Industry.
Proximity to biosphere reserves, sanctuaries, national parks	Risk increases with proximity to Industry.
Proximity to defence installations	Safety/security matters with proximity to Industrial, Commercial and Residential land uses.
Proximity to active surface mine	Risk increases with proximity to Residential zone.
Impounded water on upstream side nearby	Risk of flooding increases when high quantities of water is impounded on nearby upstream side with respect to Residential or Commercial zone.
Subsidence /landslide prone zone	Critical when history of subsidence is present in Residential and Commercial land use.
Proximity to tribal/ethnic people's habitation	Possibility of dilution of ethnic culture increases with proximity to ethnic people's habitation to Industry, Commercial and Residential zone.
Flooding hazard from river	Critical when history of flooding is present in Residential and Industrial zone
Proximity to Reserve and Protected forest area	Risk increases with proximity to Residential and Industrial zone
Prime agricultural land	Conversion to any other type of land use is unwanted.

3.1. Land Use Suitability Evaluation

Chen and Verburgi (2000) explored the relationships between land use and the factors that can be used to predict it. They used correlation and regression analyses to identify the most important explanatory variables from a large set of factors and found that the spatial distribution of all land use types is best described by an integrated set of biophysical and socio-economic factors. They called for prudence and postulated that relationships obtained at a certain scale of analysis should not be directly applied at other scales or in other areas.

Table 4. Economic/infrastructural suitability factors associated with common land uses

Attributes	**Economic/ infrastructural risk issues**
Proximity to city/town	Suitability for Industrial land use decreases and suitability for Residential, Commercial and Agriculture zone increases
Distance from Highway	Suitability for Industrial, Residential and Commercial zone decreases with distance from highway
Access to river or lake	Suitability for Industrial land use decreases with distance from river/lake
Access to public sewer system	Suitability for Residential land use decreases with distance from public sewer system
Distance from market (domestic)	Suitability for Residential and Agricultural land use decreases with distance from market (domestic)
Distance from railroad	Suitability for Industrial and Commercial land use decreases with distance from railroad
Slope of the area	Suitability decreases with steepness for Industrial, Commercial and Residential land use
Ground water availability	Poor ground water availability affects Agricultural and Residential land uses
Distance from colliery (coal supply)	Suitability for Industrial land use decreases with distance from coal supply base
Availability of labour	Suitability decreases if skilled/unskilled labour is not available for Industry and Agriculture
Distance from important medical base	Suitability for Residential land use decreases with distance from medical base
Distance from High school	Suitability for Residential land use decreases with distance from educational facilities
Population density	Suitability for commercial and Residential land use decreases with decrease of population density

From practical point of view, several land use allocation factors have been identified in the science of spatio-temporal decision-making (Eastman *et al.*, 1993; Voogd, 1983; Carver, 1991). Barredo *et al.* (2003) identifies five groups of factors: (i) environmental characteristics, (ii) local-scale neighbourhood characteristics, (iii) spatial characteristics (i.e., accessibility), (iv) urban and regional planning policies, and (v) factors related to individual preferences, level of economic development, socio-economic and political systems.

Lawrence *et al.* (1986) have stated to define the scale of investigation (global, regional, local) prior to selecting factors for land use study. Herzog and Buhler-Natour (1999) give importance to certain points regarding criteria selection at regional level, such as: (i) analysis of the main characteristics of the region including its history (ii) all dimensions of sustainability should be taken into consideration, *e.g.,* the agro-ecological, socio-economic and cultural aspects (iii) the criteria should be suitable for simple application in political decision making processes (iv) criteria from the global level should be differentiated and criteria from the local level should be aggregated (v) interaction and interdependence between the criteria should be formulated, to facilitate substitution; and, (v) criteria for analyzing the study site should be applied.

Pauleit and Duhme (2000) demonstrate that environmental quality targets and standards applied to different types of land uses would provide a clear framework and guidance for innovative planning and design on a more detailed level. Allocation of space to the different human activities in a city and prescriptions to their physical design are the principal means of development plans and control. Environmental, social and economic implications of the spatial pattern of human activities in the city must be understood to integrate sustainability principles into development practice.

It is established that adequate supply of socio-infrastructural resources assure better economic return and increased unsuitability of environmental aspects call for additional costs for damage repairing (to comply with regulatory standards) which the economists term as “environmental externalities”. Increased “environmental externalities” mar the economic prospect of a practising land use. The concept of “damage repair cost” is not workable for certain environmental conditions when damage repairing is not possible because of non-availability of a viable mitigation measure. In the present case of Talcher coalfield, environmental and socio-infrastructural attributes have been dealt with side by side. Environmental incompatibility has been identified with respect to varying levels of socio-infrastructural development.

The subject area was divided into small land parcels for analysis using GIS. Environmental and socio-infrastructural factors applicable for all the land parcels were studied. A framework (Table 5) for analysis of environmental suitability has been prepared based on Table 3. Environmental conditions, in applicable ranges, are listed against land use categories. Rationale for scoring environmental attributes is given in Table 6. The scoring pattern points to a logical, though hypothetical, economic cost indicator for damage repairment. Lesser the score better is environmental suitability. Table 7 shows another framework (prepared based on Table 4) for analysis of socio-infrastructural resource requirement where applicable ranges of resource attributes are listed against land use categories. A scoring pattern (0 to 4) has been evolved that suggests 0 for best suitability to 4 for moderate suitability and R (Restrict) as unsuitable condition. Lesser score indicates lesser resource requirement and ensures better suitability (conversely, greater score implies absence of a required resource and takes into account an imaginary economic cost for its establishment). Rationale for scoring pattern is given at Table 8.

Following stepped tasks were carried out to ascertain degrees of land use suitability:

I. Classification of Spatial Information:

- About 4500 sq.km area with the coalfield at center was divided into 3141 land parcels of each 1.2 km x 1.2 km for analysis using GIS.

- Infrastructural and social requirements and environmental characteristics of the individual land parcels were identified using GIS. Existing land use of the parcels was noted.

Land use restrictions of land parcels were noted based on legal non-compliance, intense environmental degradation or intense resource consumption beyond natural regeneration potential or infrastructural incapability beyond investment cut off.

II. Statistical Analysis of Spatial Information:

Degrees of land use incompatibility of the land parcels for environmental as well as infrastructural issues were ascertained through a structured framework (Table 4 and Table 6) and compared with existing land use. Scores of each land parcel is summed up separately for aggregate scores on environmental and socio-infrastructural accounts. A statistical summary of the land parcels is given in Table 9.

III. Identification of levels of infrastructural and environmental incompatibility:

The land parcels meeting environmental and socio-infrastructural incompatibility on strategic limiting cut-offs were mapped using GIS AutoDesk Map 6.0. The strategic cut-offs used are defined in Table 10 and Table 11 for environmental and infrastructural resource linked incompatibility, respectively.

IV. Optimization of infrastructural and environmental indicators to develop integrated zoning alternatives:

By combining/querying the infrastructural incompatibility scenarios with the environmental incompatibility scenarios for a specific land use category, land parcels with 20, 50 and 80 percentile *environmental incompatibility* at 20, 50 and 80 percentile *infrastructural incompatibility* were identified. For all land use categories such incompatibility scenarios were prepared. By combining/querying all such incompatibility information (infrastructural as well as environmental), for all land use categories, it was possible to generate nine different zoning scenarios with combination of different environmental and infrastructural incompatibilities of land use categories. For the Talcher coalfield case, the following three strategic zoning scenarios were developed:

Scenario I: 20 percentile environmental incompatibility at 50 percentile infrastructural incompatibility

Scenario II: 20 percentile environmental incompatibility at 80 percentile infrastructural incompatibility

Scenario III: 50 percentile environmental incompatibility at 50 percentile infrastructural incompatibility

Scenarios I, II and III have been shown in Figure 3, Figure 4 and Figure 5, respectively.

Table 5. Framework for analyzing environmental issues

Issues	Unit	Parameter rankings		Industrial	Commercial	Residential	Agriculture	Forestry	Pasture
				Land use applicability score					
Erosion proneness		Slight		0	0	0	1	0	0
		Less		0	0	0	2	0	0
		Moderate		0	0	1	4	2	1
		Severe		1	2	2	R	3	2
Background particulate level	$\mu g/m^3$	<200 and	Low dispersion potential	0	0	0	0	0	0
			High dispersion potential	0	0	0	0	0	0
		200– 400 and	Low dispersion potential	1	2	R	1	0	0
			High dispersion potential	1	2	R	1	0	0
		>400 – 500 and	Low dispersion potential	2	2	R	2	0	0
			High dispersion potential	2	2	R	1	0	0
		>500 and	Low dispersion potential	R	R	R	3	1	1
			High dispersion potential	R	R	R	2	1	1
Background SO_2 level	$\mu g/m^3$	<80 and	Low dispersion potential	0	0	0	0	0	0
			High dispersion potential	0	0	0	0	0	0
		80 – 100 and	Low dispersion potential	1	2	R	2	1	0
			High dispersion potential	0	2	R	1	1	0
		>100 – 120 and	Low dispersion potential	2	2	R	2	1	0
			High dispersion potential	2	2	R	2	1	0
		>120 and	Low dispersion potential	R	R	R	3	1	1
			High dispersion potential	R	R	R	2	1	1
Background NO_x level	$\mu g/m^3$	<80 and	Low dispersion potential	0	0	0	0	0	0
			High dispersion potential	0	0	0	0	0	0
		80 – 100 and	Low dispersion potential	1	2	R	2	1	0
			High dispersion potential	0	2	R	1	1	0
		>100 – 120 and	Low dispersion potential	2	2	R	2	1	0
			High dispersion potential	2	2	R	2	1	0
		>120 and	Low dispersion potential	R	R	R	3	1	1
			High dispersion potential	R	R	R	2	1	1
Water contamination		Absent		0	0	0	0	0	0
		Present		1	2	4	R	2	2
Background noise level	dB(A)	<40		0	0	0	0	0	0
		40 - 55		0	0	2	0	0	0
		>55 - 75		1	3	R	0	0	0
		>75		4	4	R	0	0	0

Table 5. Framework for analyzing environmental issues (continued)

Issues	Unit	Parameter rankings	Land use applicability score: Industrial	Commercial	Residential	Agriculture	Forestry	Pasture
Soil contamination		Absent	0	0	0	0	0	0
		Present	1	1	3	R	3	2
Soil capability (for agriculture and forestry)		Good	0	0	0	0	0	0
		Fair	0	0	0	2	1	1
		Bad	0	0	0	R	R	2
Proximity to hazardous material storage	**km**	>5	0	0	0	0	0	0
		>2 - 5	0	1	2	1	0	0
		1- 2	1	2	4	3	0	0
		<1	3	4	R	R	0	0
Proximity to religious, historic or archaeological monuments	**km**	>10	0	0	0	0	0	0
		>5 - 10	0	0	0	0	0	0
		2 - 5	2	0	0	0	0	0
		<2	4	0	0	0	0	0
Proximity to biosphere reserves, sanctuaries, national parks	**km**	>10	0	0	0	0	0	0
		>5 - 10	0	0	0	0	0	0
		2- 5	2	0	0	0	0	0
		<2	4	0	0	0	0	0
Proximity to defence installations	**km**	>10	0	0	0	0	0	0
		>5 - 10	0	0	0	0	0	0
		2 - 5	2	3	2	0	0	0
		<2	R	R	R	0	0	0
Proximity to active surface mine	**km**	>4	0	0	0	0	0	0
		>2- 4	0	0	1	0	0	0
		1 - 2	0	0	2	0	0	0
		<1	0	1	3	0	0	0
Impounded water on upstream side nearby		Absent	0	0	0	0	0	0
		Present but less quantity of water	0	0	1	1	0	0
		Present and high quantity of water (>5 lakh m^3)	2	1	3	1	1	1
Subsidence /landslide prone zone		Absent	0	0	0	0	0	0
		Has potential but no incidence	R	1	R	0	0	0
		Has potential and incidence present	R	2	R	0	0	0

Table 5. Framework for analyzing environmental issues (continued)

Issues	Unit	Parameter rankings	Land use applicability score: Industrial	Commercial	Residential	Agriculture	Forestry	Pasture
Proximity to tribal/ethnic people's habitation	**km**	>10	0	0	0	0	0	0
		>5 - 10	1	0	0	0	0	0
		2 - 5	2	1	2	0	0	0
		<2	3	3	3	0	0	0
Flooding hazard from river		Absent	0	0	0	0	0	0
		Has potential but no incidence	4	1	4	1	0	0
		Has potential and incidence present	R	2	R	2	1	1
Proximity to Reserve and Protected forest area	**km**	>4	0	0	0	0	0	0
		>2- 4	0	0	0	0	0	0
		1 - 2	0	0	0	0	0	0
		<1	2	1	3	0	0	0
Prime agricultural land		Absent	0	0	0	0	0	0
		Present	R	R	R	0	R	R

Table 6. Rationale for scoring environmental issues

Score	Areas other than regulatory compliance		Areas where regulatory compliance is compulsory
R (Restrict)	Severe impact; complete mitigation not possible	**AND/ OR**	Non compliance of regulatory requirement
4	Strong impact; complete mitigation possible at huge cost	**AND/ OR**	Close to upper threshold of regulatory requirement
3	Moderate impact; complete mitigation possible at moderate cost		
2	Less impact; complete mitigation possible at comparatively lesser cost		
1	Minor impact: complete mitigation possible at minor cost		
0	Acceptable with no remediation or compensation		

Table 7. Framework for analyzing Infrastructural requirement

Issues	Unit	Parameter rankings	Land use applicability score: Industrial	Commercial	Residential	Agriculture	Forestry	Pasture
Proximity to city/town	**km**	>6	0	3	3	2	0	1
		>3 - 6	1	1	2	1	0	1
		1- 3	3	0	1	0	0	0
		<1	4	0	0	0	0	0
Distance from Highway	**km**	>10	4	4	4	2	0	0
		>5 - 10	3	3	4	2	0	0
		2 - 5	1	2	3	1	0	0
		<2	0	0	0	0	0	0
Access to river or lake	**km**	>10	R	0	2	3	0	0
		>5 - 10	3	0	1	2	0	0
		2 - 5	1	0	0	1	0	0
		<2	0	0	0	0	0	0
Access to public sewer system	**km**	>6	2	2	4	0	0	0
		>3 - 6	1	1	3	0	0	0
		1 - 3	1	1	1	0	0	0
		<1	0	0	0	0	0	0
Distance from market (domestic)	**km**	>10	0	0	4	4	0	0
		>5 - 10	0	0	3	2	0	0
		3 - 5	0	0	1	1	0	0
		<3	0	0	0	0	0	0
Distance from railroad	**km**	>10	3	3	2	0	0	0
		>5 - 10	2	2	1	0	0	0
		2 - 5	1	1	0	0	0	0
		<2	0	0	0	0	0	0
Slope of the area		Steep slope	4	3	3	2	0	3
		Moderate slope	2	1	1	0	0	3
		Flat	0	0	0	0	0	0
Ground water availability		Poor	3	1	4	4	3	2
		Moderate	2	1	2	2	2	1
		Good	0	0	0	0	0	0
		Excellent	0	0	0	0	0	0

Table 7. Framework for analyzing Infrastructural requirement (continued)

Issues	Unit	Parameter rankings	Land use applicability score: Industrial	Commercial	Residential	Agriculture	Forestry	Pasture
Distance from colliery (coal supply)	**km**	>10	3	0	0	0	0	0
		>5 - 10	2	0	0	0	0	0
		2 - 5	1	0	0	0	0	0
		<2	0	0	0	0	0	0
Availability of labour		Not available	4	0	0	3	0	0
		Only skilled labour available	2	0	0	3	0	0
		Both skilled and unskilled labour available	0	0	0	0	0	0
Distance from important medical base	**km**	>10	2	2	4	0	0	0
		>5 - 10	1	1	2	0	0	0
		2 - 5	0	1	1	0	0	0
		<2	0	0	0	0	0	0
Distance from High school	**km**	>6	0	0	4	0	0	0
		>4 - 6	0	0	3	0	0	0
		2 - 4	0	0	1	0	0	0
		<2	0	0	0	0	0	0
Population density	**Persons/km^2**	<200	0	4	3	1	0	0
		200-400	0	2	2	1	0	0
		>400-600	0	1	1	0	1	0
		>600	0	0	0	0	2	0

Table 8. Rationale for scoring infrastructure based issues

Score	Scoring rationale
R (Restrict)	Not acceptable due to resource constraints/High risk
4	Very Less suitability. Acceptable at huge cost
2-3	Less suitability. Acceptable at higher cost
1	Moderate suitability. Acceptable at moderate cost
0	Best suitability. Acceptable without appreciable cost towards arrangement for resource availability

Table 9. Statistics of the Range of scores on infrastructural and environmental aspects

	Industrial		Commercial		Residential		Agricultural		Forestry		Pasture	
	Env	**Infra**	**Env**	**Infra**	**Env**	**Infra**	**Env**	**Infra**	**Env**	**Infra**	**Env**	**Infra**
Total no of parcels*	1450	2610	3141	2805	3141	1730	3141	3045	3141	2808	3141	2808
Minimum	5	0	2	0	7	0	0	2	0	0	0	0
Maximum	22	8	20	12	35	12	16	8	4	8	6	5
Average	14.76	0.70	16.08	1.20	29.59	1.99	12.98	3.91	2.65	2.11	3.43	0.73
St.Deviation	3.77	1.13	3.70	1.58	5.58	1.54	3.33	1.28	1.061	1.49	1.63	0.60
20 percentile	11	0	13	0	25	1	10	2	3	0	2	0
50 percentile	15	0	17	1	31	2	14	4	3	3	3	1
80 percentile	18	1	19	2	34	3	16	5	3	3	6	1
95 percentile	20	3	20	3	35	4	16	6	4	3	6	1
98 percentile	21	4	20	5	35	5	16	6	4	4	6	2
99 percentile	22	5	20	8	35	7	16	7	4	5	6	3

* total number of parcels with no restriction; Env = Environmental issues; Infra = Infrastructural issues

Table 10. Degrees of environmental incompatibility

Cut-off indicator	Cut-off percentile score	Definition of cut-off percentile level	Significance	Comparison with site condition	Indicated level of investment
20 percentile on aggregate score of environmental issues w.r.t. a specific land use	Ind :0 Com 0 Res: 1 Agr:2 For : 0,Pas : 0	20 percentile environmental incompatibility	Low level of incompatibil ity	Comfortable gap between existing pollution level and permissible limits	Low
50 percentile on aggregate score of environmental issues w.r.t. a specific land use	Ind :0,Com :1 Res: 2 Agr:4 For : 3 Pas : 1	50 percentile environmental incompatibility	Average level of incompatibil ity	Moderate gap gap between existing pollution level and permissible limits	Average
80 percentile on aggregate score of environmental issues w.r.t. a specific land use	Ind :1 Com :2 Res: 3 Agr:5 For : 3,Pas : 1	80 percentile infrastructural incompatibility	High level of incompatibil ity	Narrow gap between existing pollution level and permissible limits	High

Note : Ind =Industrial; Com = Commercial; Res = Residential; Agr = Agricultural; For = Forestry; Pas = Pasture land uses

Table 11. Degrees of infrastructural resource linked incompatibility

Cut-off indicator	Cut-off percentile score	Definition of cut-off percentile level	Significance	Comparison with site condition	Indicated level of investment
20 percentile on aggregate score on infrastructural issues w.r.t. a specific land use	Ind :11 Com :13 Res: 25 Agr:10 For : 3 Pas : 2	20 percentile infrastructural incompatibility	Low level of incompatibility and hence low level of additional resource requirement	Small gap between resource based demand and supply	Low
50 percentile on aggregate score on infrastructural issues w.r.t. a specific land use	Ind :15 Com :17 Res: 31 Agr:14 For : 3 Pas : 3	50 percentile infrastructural incompatibility	Average level of incompatibility	Moderate gap between resource based demand and supply	Average
80 percentile on aggregate score on infrastructural issues w.r.t. a specific land use	Ind :18 Com :19 Res: 34 Agr:16 For : 3 Pas : 6	80 percentile infrastructural incompatibility	High level of incompatibility and hence high level of additional resource requirement	Wide gap between resource based demand and supply	High

Note : Ind =Industrial; Com = Commercial; Res = Residential; Agr = Agricultural; For = Forestry; Pas = Pasture land uses

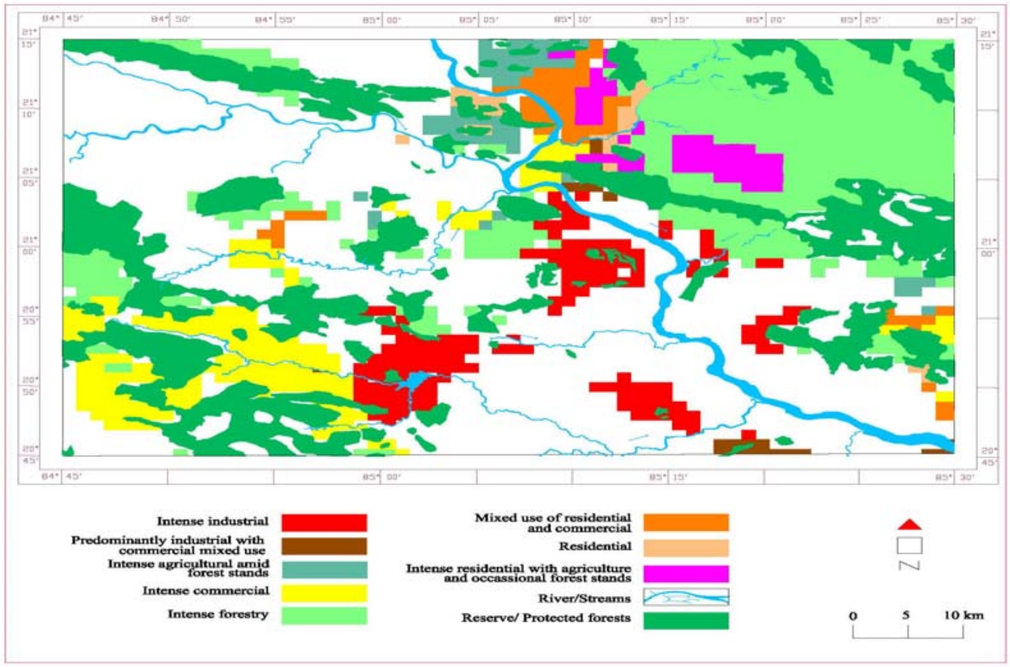

Figure 3. Zoning with 20-percentile environmental and 50 percentile infrastructural incompatibility cut-off

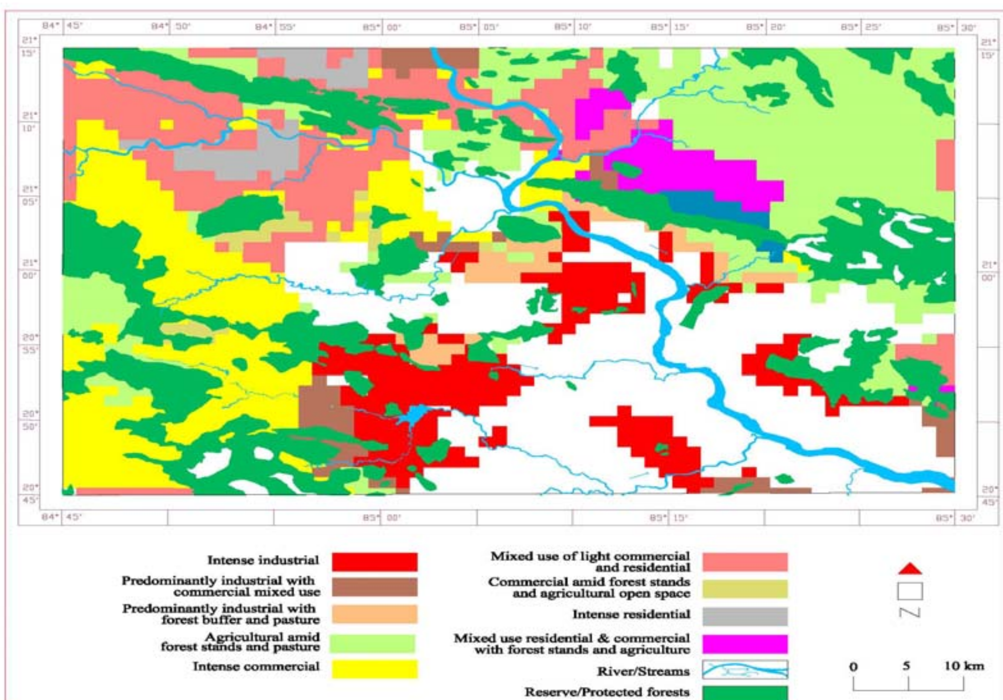

Figure 4. Zoning with 20 percentile environmental and 80 percentile infrastructural incompatibility cut-off

4. RESULTS AND DISCUSSIONS

Following significant observations were made from the developed zoning maps:

- All the alternative zoning scenarios show combination of the zones of mixed land use of specified categories and single land use zones. The mixed land use zones are, in fact, zones of superimposition of suitable land uses classes.
- Incidence of mixed land use zones is higher at higher percentile of incompatibility. Theoretically, at the highest level of incompatibility there will be just one mixed zone for all the land use classes (at no restriction level).
- All the scenarios follow a basic pattern. Merging of zones (forming mixed use zones) increases at higher level of incompatibility.

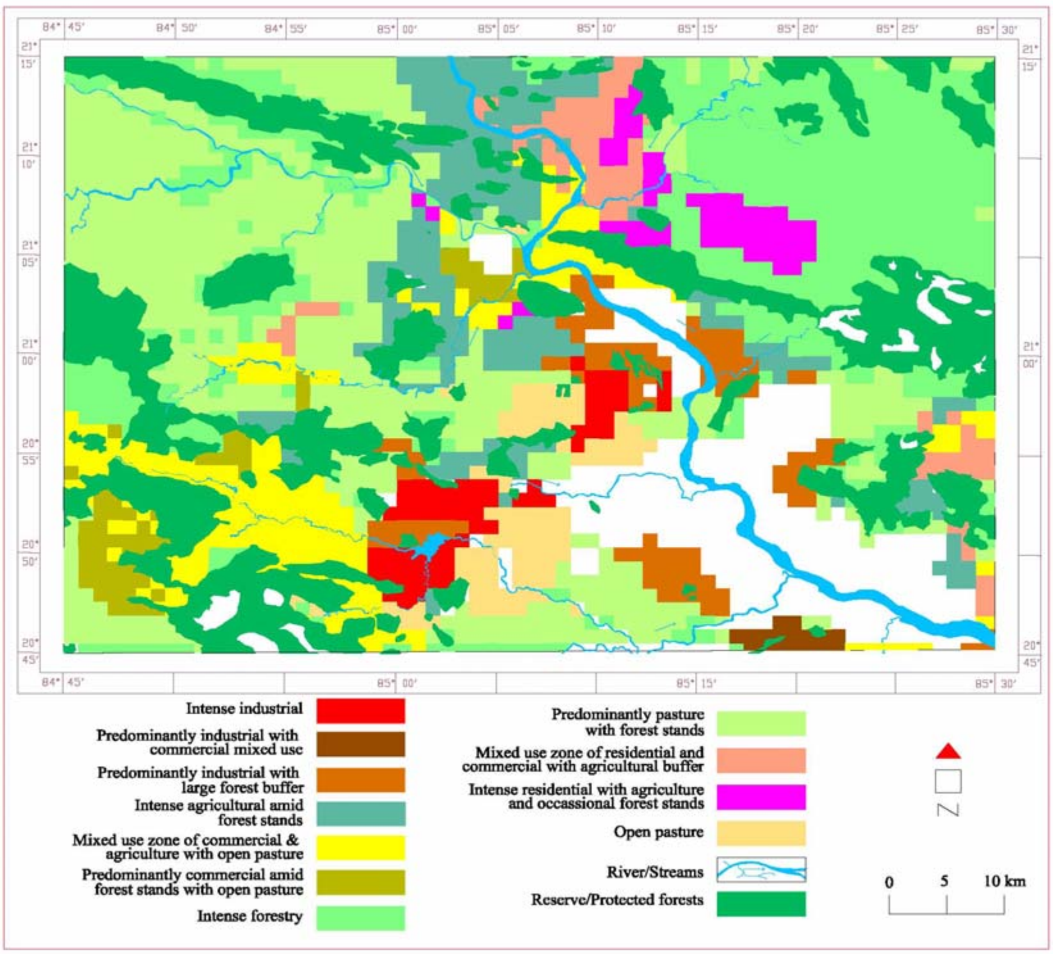

Figure 5. Zoning with 50 percentile environmental and 50 percentile infrastructural incompatibility cut-off

- Deciding the appropriate cut-off combination is of paramount importance to arrive at the desired zoning scenario. Appropriate cut-off combination should depend on the state of infrastructural and environmental development.
- A lower to moderate infrastructural incompatibility cut-off depicts a realistic scenario (for a developing economy, as in India) and a lower environmental incompatibility cut-off assures stringent environmental safeguard. Land use operators discourage higher infrastructural incompatibility zones, as it demands a higher investment input to bridge the infrastructure demand gap. A stringent environmental cut-off, however, has the risk of restricting infrastructural development. While planning land use zoning in predominantly virgin area, a strict environmental cut–off can be employed to begin with, whereas for the areas where pollution level is already high a moderate environmental cut-off (that does not compromise with environmental performance) can be planned. Infrastructural and environmental cut offs may vary from country to country based on existing infrastructural development, environmental performance and strength of economy of the country.
- Certain extent of land parcels is not selected by any of the scenarios. The land parcels have land use restrictions. Open space zoning is suggested to be practiced there.

An 80-percentile infrastructural incompatibility scenario, even if combined with the best environmental scenario does not show enough promise. Zoning based on 50 percentile environmental scenario combined with 50 percentile infrastructural scenario is poised optimally to handle environmental and resource based issues in polluted coalfields, at least to ensure regulatory compliance of environmental issues and a level of resource conservation without compromising environmental sustainability. Even 99 percentile cut-offs filter only such land parcels that conform to regulatory limits, as non-compliant parcels are restricted *a priori* from selection. Combination of the 20-percentile environmental incompatibility and 50-percentile infrastructural incompatibility scenario more than fulfils the zoning policy commitments for the virgin power grade coalfields, at least in the present Indian situation.

The optimal strategy would be to initially develop a low level of infrastructural and environmental incompatibility scenario to isolate the core land use centres. It may be followed by a moderate level of infrastructural incompatibility combined with lower/moderate environmental incompatibility to identify the future growth directions. Fig.3 (20 environmental: 50 infrastructure) indicates the core land use centres. Fig.5 (50 environmental: 50 infrastructure) includes peripheral permissible buffers with mixed-use zones beyond the core land use centres Since mining activities occupy the centre-stage of economy in a coalfield, the zoning exercise may not impose any restriction on coal mining in any of the land parcels. Instead of keeping the land parcels from purview of the GIS analysis (similar to land parcels under river, protected and reserve forests etc which are not intended for change and hence were not analysed) the coal bearing land parcels were subjected to land use suitability analysis with an objective to identify interim land uses, and a logical buffer land use selection. Predicted optimum land use (other than industrial) over coal bearing parcels are suggested to be practised as interim land use only, till coal mining commences in the parcels. Cut-off percentile for infrastructural aspects should ideally depend on:

- degree of existing demands or linking of available resources viz., availability of river water, road traffic density, railway goods carrying capacity, soil capability or agricultural productivity etc. In the Talcher coalfield case, the principal cut-off deciding criteria should be the peak season availability of water from Brahamani river and unhindered supply of required quality of coal. Government of India is granting captive coal blocks to private entrepreneurs but river water allocation remains an important concern. A safe cushion is required to be planned between availability and exploitation of resources. Permissible infrastructural development can be decided based on allowable environmental performance cut off.

- an optimistic infrastructural planning at which entrepreneurs stay invested

Cut-off percentile on environmental account should trade off to ensure adequate margin from environmental regulatory limits. A comparison of the developed scenarios with the existing land use at Talcher site reveals the following:

- All the three scenarios follow a basic pattern and conform, by and large, to the existing land uses. Existing central industrial zone, forest buffers at corners and residential and commercial land use at the outer ring of industrial zone is noted in the developed scenarios especially at scenario I and III. Significant conformity exists between predicted and existing profile of industrial zone. Given that a number of parcels remained unselected due to environmental unsuitability in the vicinity of predicted/existing industrial zone, only low air pollution potential, low water pollution potential and low land contamination potential industries are admissible in hitherto unoccupied industrial parcels. Such low pollution prone industries should be adequately buffered by forestry/pasture.
- Zone with prime agricultural land is not selected in any of the scenarios. The reasons are (i) the zone is identified as water contamination area, at the same time, and (ii) change of land use is restricted as this area is the only prime agricultural area (a high degree of water contamination control is the only feasible solution).
- Another notable point of disagreement is land parcels near Talcher Super Thermal Power station at Kaniha. Because of presence of a place of religious importance nearby, the land parcels have not been selected as Industrial land use (indicating unwise land area selection for the Thermal Power Plant)
- Present SPM level in residential areas of Angul exceeds the permissible limits. The areas, which exceed permissible thresholds, have not been selected by the zoning scenario. The cases where a land use change is not possible call for a stricter management of issues.

5. Conclusions

Work on macro level zoning study and preparation of zoning atlas for industrial land use is nearing completion in India. The next important task would be to devise micro level zoning mechanism in the identified critically polluted areas. This study presented a step-by-step detail of identification and optimization of various environmental, socio-economic and infrastructural attributes to devise micro level zoning in the context of a power grade coalfield, which is identified as a critically polluted area by CPCB of India.

The developed zoning scenarios are dependent on the land use suitability framework. Certain degree of subjectivity is associated while assigning the comparative scores for assessing land use suitability. The subjectivity can be minimized by developing detail scoring rationales. For land use applicability scoring (0-4, R) a better result may be possible if weighted average of expert opinions (scores) are considered.

Societal information base and public participation should be an important element of the zoning study. In the present case societal attributes of the coalfield could not be considered due to paucity of relevant information. Village level workshops will give better insight into socio-economic, infrastructural and environmental needs of the region.

The work methodology presented in the study can be adopted suitably while developing zoning methodology in other environs also, with selection of an applicable set of attributes following a suitable zoning policy. It is important to carry out similar exercise in the identified critically polluted areas in India and other developing countries where growth possibilities exist. Putting in place a reliable system of data base development and management may go a long way in facilitating undertaking of similar exercises in other environs.

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Chapter 9

PATHOGENESIS, ASSESSMENT AND DIAGNOSTICS OF RESPIRATORY DISORDERS IN COAL MINERS

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ABSTRACT

The long-term exposure of coal miners to respirable dust containing crystalline silicon dioxide (silica; SiO_2) causes a chronic inflammatory process in the alveoli, interstitial lung tissue and bronchi, which ultimately result in coal workers' pneumoconiosis (CWP), progressive massive fibrosis of the lung (PMF), as well as chronic obstructive pulmonary disease (COPD) and emphysema. These health disorders show a close pathogenetic and pathophysiological association and should not be considered individual entities. Many coal miners subjected to long-term exposure demonstrate several of these pathological findings in parallel, although their absolute degree may differ for each individual. Some individuals are rather resistant and others show severe effects, presumably because of variations in genetically based susceptibility. The risk of respiratory impairment in coal miners increases with increasing dust exposure in a dose-dependent manner, regardless of radiologically demonstrated CWP/PMF or not. Thus, COPD and emphysema should be added to CWP and PMF as occupational diseases arising from long-term employment in coal mines, even in the absence of pneumoconiosis.

CWP patients are susceptible to mycobacterial infections (tuberculosis as well as atypical mycobacterial infections; so-called silicotuberculosis). Another related disorder is Caplan syndrome which is characterized by large pulmonary nodules and mostly seronegative rheumatoid arthritis. The recently established increased risk of developing lung carcinoma after exposure to crystalline silica should also be considered. No definitive data for coal

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miners is available as yet. Conversely, there are persistent reports of an increased risk of stomach cancer.

It is important to recall that conventional chest X-ray of coal miners has low diagnostic sensitivity and specificity, especially in comparison with fibrotic as well as emphysemous lesions in CWP verified pathologically or by high resolution computed tomography. The same is true for lung function deficits or dyspnea symptoms.

Since there are dose-response relationships between dust load and severity for all of the above mentioned disorders, the only appropriate primary prevention is a significant reduction in exposure to dust (to levels below the NIOSH REL of 1 mg/m^3 for respirable coal mine dust).

OBJECTIVE

The objective of this review article is to summarize present knowledge on the pathogenesis of respiratory disorders in coal miners, facilitating their expert diagnosis in a standardized professional manner.

1. INTRODUCTION

Coal was the major energy source in the last century and millions of workers were engaged in mining this resource. In recent decades, coal extraction has been mainly transferred to the new economies with their lower wages, such as South Africa, China and South American countries, resulting in a steady decline in the number of coal miners in most Western countries. Further, a significant reduction of the dust load in coal mines in Western countries has improved working conditions, in association with better dust monitoring, airborne dust control regulations and the introduction of health surveillance. As a consequence, the prevalence of CWP has fallen in these countries, for example, from 12% in 1954–1957 to 0.2% in 1959–1963 in the UK and all of these latter 13 cases assigned to the lowest ILO category 1 (National Institute for Occupational Safety and Health 2003). Further, PMF (Progressive Massive Fibrosis) has become an extremely rare disorder (Afacan and Scarisbrick 2001). In the USA, CWP rates fell from >10% in the early 1970s to <2% in the late 1990s, which is similar to the level of incidence reported for South Africa (2.6 %), (Naidoo et al. 2001), and Europe (International Labour Office 1997, Meyer et al. 2001). The permissible exposure limit (PEL) for respirable coal dust in the USA is 2 mg/m^3 (National Institute for Occupational Safety and Health 2002) and in Germany the threshold limit value (TLV) is 3 mg/m^3 as an annual average (Technical Rules for Hazardous Substances, TRGS, 900). A quarter of coal mine dust exposure recorded by the Mine Safety and Health Administration (MSHA) in the USA do still exceed the NIOSH recommended exposure limit (REL; 10-hour time weighted average, TWA) of 1 mg/m^3 (National Institute of Occupational Safety 2003).

The International Agency for Research on Cancer (1997) has summarized the known health disorders in coal miners as follows: "some biological effects of coal mine dust in coal miners include simple coal workers' pneumoconiosis (CWP), progressive massive fibrosis

(PMF), emphysema, chronic bronchitis and accelerated loss of lung function". Rare disorders include the Caplan syndrome and mycobacterial infections.

In Germany, where up to 500,000 coal miners worked underground in the 1950s, nowadays there are only about 45,000 and, currently, about 1,100 cases of CWP (including a few with PMF) and 800 cases of COPD (mainly without abnormal radiological findings) are reported annually. Non-pulmonary occupational diseases include such rare diseases as gonarthrosis and impairment of hearing. Figure 1 shows the course of compensated cases related to individual occupational diseases in the German mining industry from 2001 to 2006 (Statutory Accident Insurance Institutions for the Mining Industry 2007).

CWP and PMF are generally accepted as occupational diseases in workers exposed to respirable coal mine dust containing crystalline silica (i. e. quartz). However, only a few countries (e. g. France, Great Britain, Germany, South Africa) recognise chronic obstructive bronchitis and/or emphysema in coal miners as occupational diseases in the absence of radiologically detectable pneumoconiosis, as well as regarding them as targets for preventive measures.

In addition to coal mining, other occupations at risk for CWP include coal trimming, the loading and stowing of coal in stores or the holds of ships, as well as the mining and milling of graphite.

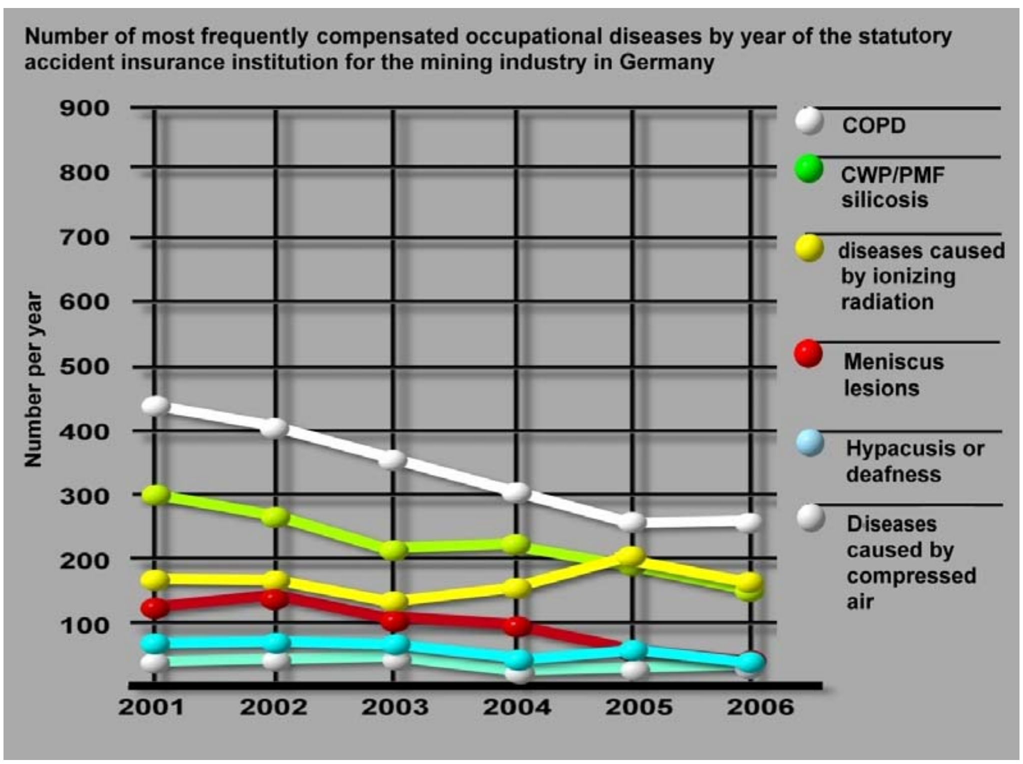

Figure 1. Annual numbers of occupational disases compensated by the German Statutory Accident Insurance Institution for the mining industry from 2001 to 2006. 79 % of the employees of the mining industry work in coal mine facilities.

2. Definitions of Anthracosis, Silicosis, CWP, PMF and Other Disorders in Coal Miners

Long-term exposure to coal dust is the cause of *anthracosis* in coal miners. Carbon deposits throughout the lung can be seen at autopsy and, although carbon is relatively inert, extensive long-term exposure may result in emphysematous lesions and mild fibrosis of the lungs.

Aetio-pathologically, *silicosis* is a pneumoconiosis induced by the inhalation of respirable dust containing a high proportion of crystalline silica, SiO2, mainly as quartz and to a lesser extent the high temperature forms, cristobalite and tridymite (Mossman and Churg 1998, Fubini and Hubbard 2003, Rimal et al. 2005, Hamilton et al. 2008). These particles of tetratechnical crystals between 1 and 5 µm in size have fibrogenic effects.

Exposure to the high concentrations of inhaled crystalline silica that occurs in different occupational settings (such as tunnelling, gold mines, quarries, sandblasting, processing of silica and scouring powders) results in a dose-dependent deposition - when the clearance mechanism of the respiratory tree is overwhelmed – which leads to the chronic inflammatory and fibrotic processes that result in silicosis. Quartz-containing dust particles that reach the alveolar area are phagocytized by macrophages and partially transported to hilar and mediastinal lymph nodes, which may calcify producing the characteristic “eggshell silicosis”. The macrophagocytic inflammatory reaction in the lung tissue is associated with fibroblast proliferation and increased production of collagen. The classical nodules induced by dust with a high crystalline quartz content have an “onion skin”, i.e. a more or less concentrically layered centre consisting of collagen fibres, surrounded by an annulus of loose dust representing the “growth zone” of a recycling process that releases silica crystals. This aspect explains the progression of silicosis even after cessation of exposure.

Histologically, the dust deposits are present in the interstitium, bound to macrophages to a variable extent, and can also be seen in fibrotically extended septa. Microscopic examination with polarized light permits estimation of the birefringent (doubly refractile) particles which represent quartz (but may also be other silicates). The nodules typically surround the respiratory bronchioles which predominate in the upper lung zones. Superimposed nodules appear on a chest X-ray mainly as rounded small opacities with a diameter of 3 – 10 mm, with large opacities resulting from the coalescence of smaller ones. The visualization of lung scarring in coal miners by chest X-ray should be performed according to the ILO International Classification of Radiographs of Pneumoconioses (International Labour Office (ILO) 2000). The centre of callosities can soften by ischaemic necrosis. In addition to the classical nodular appearance of silicosis, pinhead silicosis (see below) associated with severe emphysema can be observed.

In contrast to “pure“ silicosis caused by dust with a high quartz content, the changes of the lung parenchyma caused by dust mixed with progressively lower quartz content are much more dependent on the accessory dust components. Most presenting silicoses are generally called *mixed dust pneumoconioses* and this also applies to coal mining in the development of *coal workers’ pneumoconiosis* (CWP).

The dust in coal mines is dominated by carbon particles but it can contain between 8 and 18% crystalline silica as quartz. This combined exposure effectively determines that CWP presents as a mixture of anthracosis and modified silicosis. The mainly centrilobularly and subpleurally located nodules do not show the concentric formation of collagen fibres ("onion skins") typical of silicosis and, instead, collagen is arranged in interlacing bundles lacking orientation (Figure 2). Initially, when the mucociliary escalator of the ciliated lower airways and the macrophage clearance mechanism in the alveolar region are overwhelmed by the coal dust load, then carbon-filled macrophages are deposited and incorporated into the walls of the alveoli adjacent to the respiratory bronchioles and alveolar ducts. These macrophages form coal dust macules, i.e. fibroblasts and closely packed dust particles , either within macrophages or free, bound by reticulin but with little deposition of collagen, and centered around the respiratory bronchioles mostly in the upper lung lobes. They are the primary lesions in CWP and may be distributed extensively throughout the lung, although usually dominating in the upper lobes and the upper zones of lower lobes. The macules measure 1 to 2 mm in diameter, are non-palpable and not resolved on X-rays. Formation of these macules is associated with bronchiolar dilatation (focal emphysema).

Chronic inflammatory and fibrogenic processes in these macules may lead to the development of stellate-shaped centrilobular emphysema and dysfunctions, i. e. reduced maximal expired and inspired volume (vital capacity, chronic airflow obstruction, hyperinflation) impaired gas exchange and ventilation-perfusion mismatch.

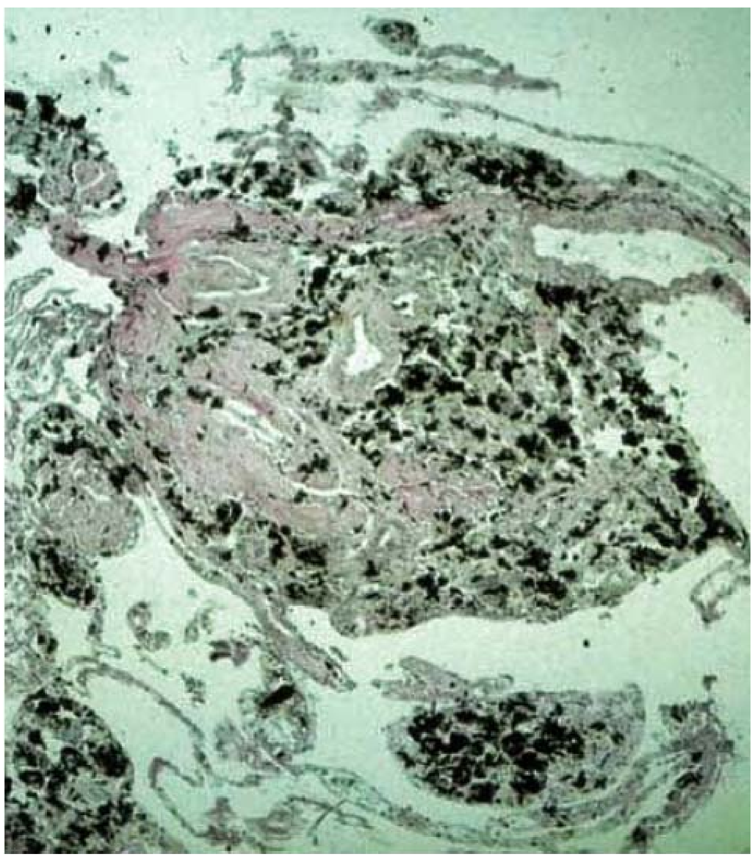

Figure 2. Histopathology of lung specimen of a CWP patient who had worked underground in a coal mine for 22 years. Note the destroyed lung structure, deposition of carbon (black), coal macules and a nodule showing irregular bundles of collagen fibers and carbon.

While macroscopically, the foci in pure or predominantly quartz dust are silver, the nodules become increasing black as the coal dust content increases at the expense of the quartz.

Interstitial disseminated *pinhead silicosis* may appear clinically as unspecific interstitial lung fibrosis and is only revealed on detailed microscopic investigation. A rare extreme type appears as a massive dust emphysema with a partially diffuse pinhead anthracosis and anthracofibrosis in combination with a mostly disseminated deposition of anthracotic pigment in alveolar septa. This finding is peculiar to the inhalation of dust with a high coal content, resulting in relatively sparse nodule formation.

In addition to small rounded opacities, predominantly basilar located small irregular opacities that are visible in the chest X-rays of miners with CWP, are often related to fibrosis, emphysema and lung function impairment (Amandus et al. 1976, Cockraft et al. 1982, Muck et al. 1981).

Caplan's syndrome (rheumatoid pneumoconiosis) is characterized by large necrobiotic nodules (up to 5 cm in diameter) typically associated with rheumatoid arthritis. It shows little relationship to the coal dust burden or rheumatoid factor positivity (Caplan et al. 1962).

The recently established increased risk of developing lung carcinoma from exposure to crystalline silica should also be mentioned, although whether this also refers to coal miners is not definitive as yet (International Agency for Research on Cancer 1997, Borm and Tran 2002). Conversely, an increased risk of stomach cancer in coal miners has been consistently reported (Swaen et al. 1995).

3. Pathogenetic Aspects

The central pathogenesic mechanism of CWP is a chronic inflammatory process in the alveoli (alveolitis), lung tissue, and airways caused by an overload of respirable coal dust deposits, leading ultimately to a restrictive as well as chronic obstructive pulmonary disorder, and emphysema. The rate of clearance of dust particles deposited in the alveolar (transport by macrophages to the ciliated airways) region involves an alveolar and a slow interstitial component (sequestration compartment), with a very slow translocation route to the lymph nodes (Kuempel et al. 1997, Kuempel 2000). The phagocytosis of crystalline silica by macrophages is followed by cell damage and the release of proteases, lipases, growth factors, and proinflammatory cytokines, such as TNFα, IL-1, IL-6, fibroblast growth factor, platelet-derived growth factor and insulin-like growth factor, followed by a rapidly increased production of fibronectin and collagen. It has been reported that TNFα polymorphisms in positions -238, -376, -308 of the promoter region are associated with severe silicosis. These TNFα-variants were also significantly increased in coal miners with CWP. The same is observed for certain polymorphic chemokine and chemokine receptor genes (CX3CR1 V249I or CCR5 Δ32 alleles) (Nadif et al. 2006, Yucesoy and Luster 2007). The cytokine microenvironment induces an inflammatory process associated with the formation of reactive oxygen species (ROS). This results in oxidative stress which overwhelms antioxidant defences and affects lipid peroxidation, protein nitrosation, fibroblast proliferation, cell injury, and apoptosis (Matruzzo et al. 2002, Schins and Borm 1999). Genetic polymorphisms in antioxidant enzymes (components of the lung defence against oxidative stress), such as manganese superoxide (MnSOD) and glutathione S-transferase (GSTM1, GSTT1), obviously play a limited role in the ROS-induced damage in CWP development (Zhai et al. 2002).

The surface characteristics of quartz crystals are thought to be involved in the fibrogenic process by mimicking the features of a semiconductor. Electron transfer between the crystal surface and the phagolysosome membrane is believed to initiate the release of lytic enzymes leading to cell death. Denatured proteins, fractured cell components and crystalline silica encapsulated by proteins may influence the pathogenetic processes and be associated with an activation of the immune system. These factors may contribute to the increased incidence of rare autoimmune disorders in coal workers, such as Caplan syndrome, scleroderma, systemic erythematodes, small vessel vasculitis, and maybe also diffuse interstitial lung fibrosis (Parks et al. 1999).

The profusion categories of CWP, and the development of PMF, are related to the intensity of dust exposure, age, the proportion of inhaled silica in the dust and its surface bioactivity, including numerous immunological and genetic factors. Histopathologic studies demonstrate that the degree of lung fibrosis is associated with lung deposition of crystalline silica.

4. Clinical Findings

a) Chronic Bronchitis

The prevalence of chronic bronchitis, as defined by the WHO ("a condition associated with excessive tracheobronchial mucus production sufficient to cause cough with expectoration for at least three months of the year for more than 2 consecutive years"), clearly shows a positive response relationship with dust exposure in coal miners (Marine et al. 1988, Leigh 1990). As reported by Marine et al. (1988) for British miners after exposure to 122.5 gh/m^3 dust, 45 out of 1,000 non-smokers developed chronic obstructive bronchitis (COPD) attributable to this effect, while 74 out of 1,000 was observed for smokers. Similar findings were obtained by the German Bronchitis and Occupational Dust Exposure Research Program (German Research Foundation 1971, 1975).

b) Lung Function Impairment in Coal Miners

Cross-sectional and longitudinal studies demonstrate reduced values for forced expiratory volume in 1 sec (FEV_1), vital capacity (VC), CO diffusion capacity, arterial oxygen partial pressure and ergospirometric parameters, as well as increases in airway resistance and thoracic gas volume (Musk et al. 1981, Marine et al. 1988, Leigh 1990, Smidt 1974 (Figure 3), Reichel 1989, Bates et al. 1985, Minette 1986, Nemery et al. 1987, Coggon and Newman Taylor 1998, Isidro Montes et al. 2004, Bauer et al. 2001, Bauer et al. 2007, Bégin et al. 1988, Bégin et al. 1995, Collins et al. 1988, Cowie and Mabena 1991, Gevenois et al. 1998, Irwig and Rocks 1978, Koskinen et al. 1985, Ng and Chan 1992, Reichel 1976, Reichel 1989, Rogan et al. 1973, Smidt 1974, Tjoe-Nij et al. 2003, Wang et al. 1999a, Wang and Yano 1999b, Worth and Smidt 1974, Seixas et al. 1993, Carta et al. 1996, Smidt 1974, Lewis et al.

1996, Neukirch et al. 1994, Wang et al. 1999a, Wang et al. 1999c, Hnizdo and Vallyathan 2003, Soutar and Hurley 1986, Henneberger and Attfield 1996, Leung et al. 2005, Cockcroft et al. 1982, Lapp and Morgan 1975, Nemery et al. 1987, Gevenois et al. 1998, Cowie et al. 2006, Attfield and Hodous 1992, Carstens et al. 1958).

Impairments were shown to be related to the dust load occurring in the coal mines (Soutar et al. 1993, Oxman et al. 1993) and were more distinct in smokers than in non-smokers, indicating that the adverse effects of smoking and working in a coal mine are additive. These relationships have been shown in coal miners both with and without CWP/PMF and they parallel to some degree the pneumoconiosis profusion categories verified radiologically (International Labour Office (ILO) 2000).

According to Seixas et al. (1992), the FEV_1 loss in US American coal mines is – 0.0034 L per mg/m³ per year. On the basis of an average respirable dust concentration of 4 mg/m³, non-smokers had an annual FEV_1 and VC loss of – 0.010 L each per year (Collins et al. 1988).

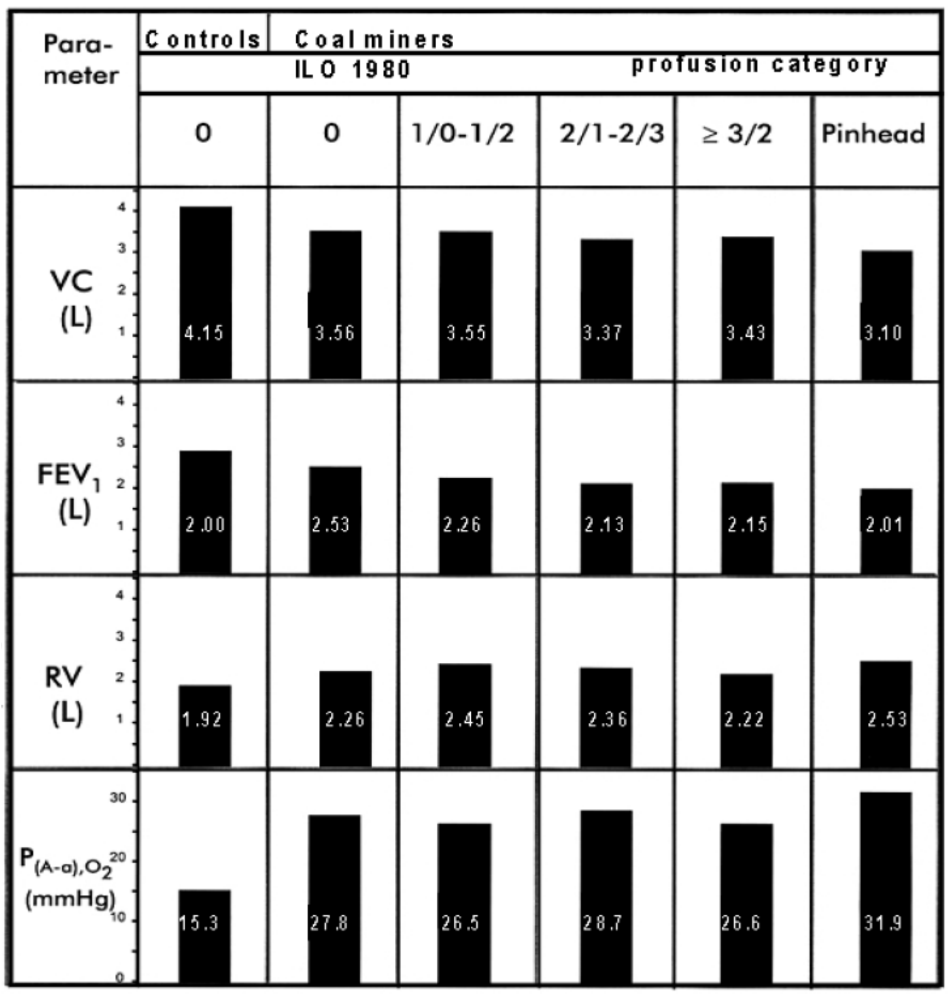

Figure 3. Lung function data of German coal miners belonging to different ILO 1980 pneumoconiosis profusion categories compared with unexposed controls (Smidt 1974).

At a cumulative exposure of 100 respirable dust years (i.e. 100 mg/m^3 x years, corresponding to 175 gh/m^3), non-smokers working in coal mines have a doubled risk of contracting COPD (German Federal Ministry of Labour and Social Affairs 1995; Figure 4). The respirable dust dose for smokers corresponds to a value 20 to 60 % higher, as reported by Marine et al. (1988), Lange and Ulm (1983), Lange and Pache (1991), Attfield (1985), Attfield and Hodous (1992) and by Collins et al. (1988), who observed an FEV_1 loss of - 0.156 L (- 0.164 L for smokers and - 0.118 L for non-smokers) as well as a VC loss of - 0.151 L per 100 gh/m^3.

Sircar et al. (2007) found the FEV_1 loss of smokers to be - 0.052 L/year and that of non-smokers - 0.038 L/year.

In silicotics from South African goldmines, a reduction of – 0.060 L/year led to increased mortality (Hnizdo 1992).

A detailed investigation by the Pneumoconiosis and Field Research of the U. K. National Coal Board should be particularly emphasized. Marine et al. (1988) reanalysed data on 3,380 coal miners without PMF to determine the extent of pulmonary impairment, collecting data on “chronic bronchitis” and FEV_1 measurements. The cross-sectional analysis was performed using linear logistic models involving age and dust exposure, studying residuals and incorporating interaction terms. Significant influences of dust were found for each investigated objective and they were independent of smoking habits. Clinically important lung function (FEV_1) reductions of 20 % had a prevalence of 15.5 % in non-smoking miners and 27.2 % in those who smoked, with each group exposed to a cumulative respirable dust dose of 174 gh/m^3. The values for a higher cumulative respirable dust exposure of 348 gh/m^3 were 23.9 % and 40 %, respectively.

Summarizing the literature, the average FVC and FEV_1 losses were found to be mainly in the range of 0.069 to 0.096 L/100 gh/m^3 (Soutar and Hurley 1986, Heederik 1990, Attfield 1985, Attfield and Hodous 1992).

Longitudinal studies in the German, UK and US coal mining industries clearly demonstrated dose-response relationships between dust exposure and the occurrence of chronic obstructive pulmonary disease (German Research Foundation 1971, 1975, Lange and Ulm 1983, Lange and Pache 1991, Marine et al. 1988). The greatest exposure-related effects were reported by Seixas et al. (1992), (1993) (Figure 4).

Additional investigations revealed that there is not a close relationship between dyspnea degree (which varies considerably between individuals) and standard lung function tests. CO diffusion capacity and submaximal ergospirometry parameters correlate better with dyspnea than do spirometry and body plethysmography parameters (Bauer et al. 2007).

In conclusion, information accumulated on the cumulative dust exposure in coal mines and consequent health disorders can be integrated with all relevant diagnostic findings to make the following points.

- The cumulative respirable coal mine dust load plays an important role in the development of functional impairment (Attfield and Hodous 1992, Cowie et al. 2006, Carta et al. 1996); in some individuals a relatively low exposure may already result in health complaints and functional disturbances (Carta et al. 1996).
- The radiographic profusion categories (ILO 2000) are rough exposure markers but do not provide essential information on the degree of functional impairment. Therefore, the degree of pulmonary function impairment in coal miners should not only be

assessed from radiography findings but be based on comprehensive lung function and gas exchange measurement data.

- Lung function is impaired in coal miners without CWP and it is somewhat more distinct in those with CWP/PMF (Reichel 1989, Koskinen 1985, Smidt 1974).
- According to Collins et al. 1988, lung function loss is more pronounced if the X-ray shows irregular opacities.
- The estimation of resilience or exertional dyspnea, the dominating symptom in coal miners, is best achieved by measurement of CO diffusion capacity and ergospirometry.
- In the case of an exertional dyspnea or radiologically proven CWP then comprehensive lung function testing, including the determination of CO diffusion capacity and gas exchange during exercise, should be performed to obtain a complete picture and differential diagnostic evaluation.
- A decline in CO diffusion capacity, ergospirometry parameters and FEV_1/VC correlates with the HRCT emphysema score.
- Progression of CWP may continue even after cessation of exposure; the risk is positively related to the intensity and duration of exposure and the percentage of free silica incorporated.

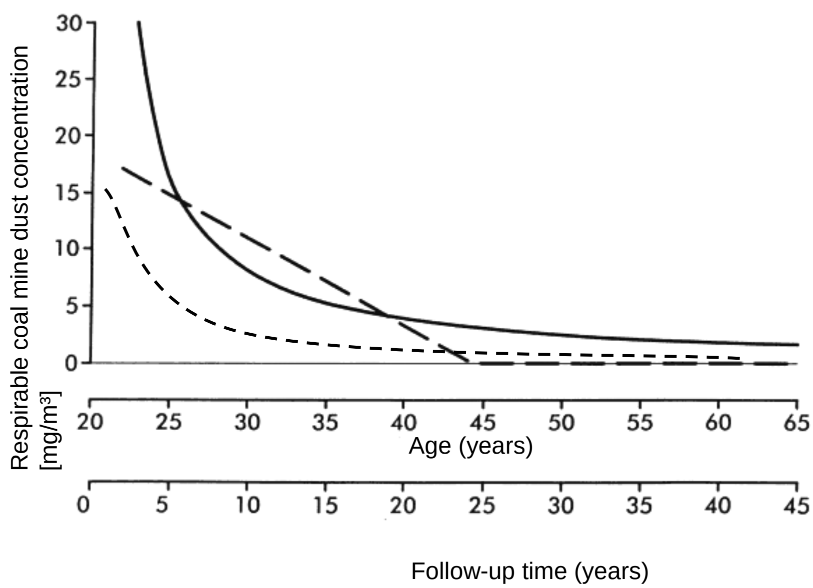

Figure 4. Respirable coal mine concentration by duration of exposure (follow-up time or age) causing in never smokers, doubling the risk (frequently used definition of occupational disease in Germany) of:

__________chronic bronchitis + FEV_1 < 80 %. Reference group: no dust exposure (Marine et al. 1988).

– – – – – COPD. Reference group: exposure duration 5 years by 2,5 mg/m^3 (Lange and Ulm 1983).

--------------Chronic bronchitis + FEV_1 < 80 % predicted Reference group: low exposure of 2.6 mg/m^3 (Seixas et al. 1992).

c) Comparison of Histopathologic Findings and Chest X-Ray Profusion Categories

Most coal miners after long-term underground employment have CWP on autopsy (Ruckley et al. 1984a, b). According to Vallyathan et al. 1996, macules were detected in 96 % and nodular-silicotic lesions in 70 %. This means that a chest X-ray does not reveal many of the CWP cases, especially those of a low degree (Vallyathan et al. 1997), as 22 % of callosities observed in tabula are not detected radiologically. Conversely, 25 % of cases with radiologically diagnosed CWP did not show a corresponding pathological correlation (Vallyathan et al. 1996, 1997).Very similar results were obtained in autopsies of South African gold miners (Hnizdo 1992). Attfield et al. (1994), Vallyathan et al. (1996) described a rough correlation between X-ray findings and micro- and macronodular pathological results (r (Pearson) c. to 0.5) in 430 autopsies of US coal miners. A good agreement was only established, however, with pathological findings of a higher degree or radiographic profusion categories of $\geq$ 0/1. Bauer et al. (1997) compared the histopathologic findings and ILO profusion categories in 126 German coal miners. Only the radiological subcategory 2/3 concurred with histopathologic findings (specifity 74 %, sensitivity 60 %), whereas PMF cases showed a good correlation between both investigations ($rs = 0.71$; $p < 0.001$).

These studies are evidence for the inability of chest X-rays to resolve low degree CWP that is demonstrable by histopathology. Thus, only advanced CWP/PMF can be reliably determined by chest X-ray.

d) Discrepancies between Lung Function Tests and Chest X-Ray Findings

Numerous studies have proven that long-term employment in coal mines leads to impaired lung function, regardless of the degree of radiological changes (pneumoconiosis profusion categories) (see 4b). The failure of a correlation with chest X-ray profusion categories may be associated with the pathological-anatomical findings that silicosis is frequently concomitant with emphysema (Bauer et al. 2001, Bauer et al. 2007, Bégin et al. 1995, Gevenois et al. 1998, Muysers et al. 1961, Wang et al. 1999a, Wang and Yano 1999b, Worth et al. 1961).

The radiologically detectable findings of nodule formation and fibrosis are obviously less responsible for lung function and performance restrictions than the consequences of these changes, namely lung emphysema, elasticity decrease and bronchial obstruction. Conversely, recent investigations do provide evidence for an acceptable correlation between pneumoconiosis profusion categories and/or emphysema scores as evaluated by computed tomography and lung function parameters (Yildiz et al. 2007, Bauer et al. 2007).

5. Mortality Studies

Recently, Sircar et al. (2007) found that the risk of death in US coal miners already increases with a decline of $FEV_1 > 0.060$ L/year and is significant with declines of ≥ 0.090 L/year, for smokers as well as for those who have never smoked.

Autopsy studies on coal miners indicate a substantial incidence of emphysema (Cockcroft et al. 1982, Lamb 1976, Ruckley et al. 1989). An association between the severity of histopathologically diagnosed emphysema and the duration of underground activities or inhaled dust quantity was described (Leigh et al. 1982, 1994; Ruckley et al. 1984a, b). About 50 % of the autopsied miners who had never had a pathological chest X-ray diagnosis or palpable nodules in their lifetime were reported to have emphysema.

In these studies, emphysema was most frequently associated with the fine p opacity type (92% of them showed emphysema) and these miners revealed dose-response relationships with respirable dust load.

Dependent on the dust load, coal miners have an increased relative risk of dying from COPD or emphysema which is not related to the presence or severity of pneumoconiosis (Coggon et al. 1995, Rockette 1977, Miller and Jacobsen 1985). Mortality and post-mortem studies on these workers frequently identified COPD as the cause of death (Atuhaire et al. 1985).

It should be reiterated that the sensitivity of a chest X-ray for detecting emphysema and COPD is inadequate (Fernie and Ruckley 1987; Hnizdo et al. 1993).

6. Diagnostics (See Table 1)

Diagnostics comprises a detailed clinical and occupational case history on the basis of the report from the industrial hygienist. The major symptoms are a dry or productive cough as well as exertional dyspnea. Patients with advanced disease may suffer from pulmonary failure including clubbing, cyanosis, cor pulmonale and right heart failure. Inspiratory crackles are frequently heard on physical examination.

The central diagnostic measures are comprehensive lung function analyses according to ATS/ERS recommendations (spirometry with flow volume curve, bronchodilator test in the case of bronchial obstruction, blood gas analysis, determination of CO diffusion capacity) (MacIntyre et al. 2005, Miller et al. 2005, Pellegrino et al. 2005). Where available, body plethysmography is an additional valuable method for verifying bronchial obstruction and lung emphysema. Frequently, a complex restrictive, obstructive and emphysematous ventilation pattern with impaired gas exchange is detected (see example in Figure 5). Ergospirometry with submaximal load should also be performed.

To interpret lung function values correctly, the individual course of the different parameters (mostly available in medical surveillance databases) as well as valid reference values have to be considered. Generally, spirometry does not appropriately assess pulmonary impairment, whereas CO diffusion capacity and ergospirometry parameters (see Table 2) are more sensitive and predict the degree of breathlessness better than spirometry in CWP subjects (Bauer et al. (2001, 2007). Therefore, the latter should be routinely included in the diagnostic work-up for symptomatic coal miners and those showing CWP on their chest X-ray film.

Table 1. Stepwise diagnostic examination and possible clinical findings in symptomatic coal workers

Diagnostic examination	Clinical findings (possible)
Questionnaire	Longtime working in a coal mine
Medical and occupational history	Exertional dyspnea
Physical examination	Crackles on auscultation of the lung
Lung function testing (spirometry, bodyplethysmography, diffusion capacity for CO, blood gases at rest and during exercise, bronchodilation test in case of obstructive ventilation pattern/ hyperinflation, if possible also ergospirometry)	Restrictive and/or obstructive ventilation pattern; impaired $D_{L,CO}$, $P_{a,02}$, and ergospirometric parameters (reduced $\dot{V}_E$, $\dot{V}_E/\dot{V}_{O2}$, $\dot{V}_E/\dot{V}_{CO2}$, $\dot{V}_{O2max}$, $\dot{V}_{O2AT}$, increased $P_{(A-a)O2}$, reduced exercise load)
Chest X-ray, in unclear situations HRCT	Pneumoconiosis profusion category ≥ 1
ECG	Signs of right ventricular hypertrophy
Echocardiography in case of signs of right ventricular hypertrophy	Dilated right atrium and ventricle, tricuspital valve insufficiency

$D_{L,CO}$ = diffusion capacity for carbon monoxide (CO)
$P_{a,02}$ =arterial oxygen tension
$\dot{V}_E$ =minute ventilation
$\dot{V}_E/\dot{V}_{O2}$=ventilatory equivalent for oxygen (O_2)
$\dot{V}_E/\dot{V}_{CO2}$=ventilatory equivalent for carbon dioxide (CO_2)
$\dot{V}_{O2max}$ =maximal aerobic power
$P_{(A-a)O2}$ =alveolar-arterial difference of oxygen tension
$\dot{V}_{O2AT}$ =oxygen uptake at anaerobic threshold

Table 2. Ergospirometric parameters of CWP patients compared with unexposed controls (from: Duvenkamp et al. 1998)

Parameter	Controls	Coal miners; ILO 1980 category 1 or 2
$(\dot{V}_E/\dot{V}_{O_2})$	25.71	32.90
$(\dot{V}_E/\dot{V}C_{O_2})$	30.98	39.40
P_{ET,O_2} (mmHg)	99.08	115.60
P_{ET,CO_2} (mmHg)	44.04	38.38

All of the following parameters showed significant differences ($p < 0.05$) between both groups:

$\dot{V}_E/\dot{V}_{O2}$= ventilatory equivalent for oxygen (O_2).

$\dot{V}_E/\dot{V}_{CO2}$ = ventilatory equivalent for carbon dioxide (C_{O2}).

$P_{ET,O2}$ = end-tidal oxygen (O_2) tension.
$P_{ET,CO2}$ = end-tidal carbon dioxide (CO_2) tension.

Figure 5. The results of an examination of a 70 year old coal miner who had worked for 20 years on the rockface up until 1995 and who was claiming compensation. Slowly progressive exertional dypnea and chronic bronchitis symptoms have existed for 10 years. The chest X-ray shows mainly r type opacities, profusion category 3 (ILO 2000).

Table for Figure 5. Results of lung function tests

Parameter	Percent of predicted
FVC (forced vital capacity)	79* percent of predicted
FEV_1 (forced expiratory volume in 1 second)	69* percent of predicted
PEF(peak exspiratory flow)	94 percent of predicted
FEF_{25} (forced exspiratory flow at 25 % of exspired vital capacity)	41* percent of predicted
FEF_{50} (forced exspiratory flow at 50 % of exspired vital capacity)	22* percent of predicted
FEF_{75} (forced exspiratory flow at 75 % of exspired vital capacity)	15* percent of predicted
R_{aw} (airway resistance)	160* percent of predicted
RV (residual volume)	105 percent of predicted
TLC (total lung capacity)	92 percent of predicted

Table for Figure 5. (Continued).

Parameter	Percent of predicted
TGV (thoracic gas volume)	102* percent of predicted
$D_{L,CO}$ (diffusion capacity for CO)	70* percent of predicted
$D_{L,NO}$(diffusion capacity for NO)	75* percent of predicted
$P_{a,02}$(arterial oxygen tension)	68 mmHg* (60 mm Hg)*
$\dot{V}_E$ (minute ventilation)	25 L/min (74 L/min)*
$\dot{V}_{O2}$ (oxygen uptake at rest)	0.18 L/min*
$\dot{V}_{O2AT}$ (oxygen uptake at anaerobic threshold)	1.1 L/min
$\dot{V}_{O2max}$ (maximal aerobic power)	1.5 L/min
$\dot{V}_E/\dot{V}_{02}$ (ventilatory equivalent for O_2)	30.2* (35.5)*
$\dot{V}_E/\dot{V}_{CO2}$ (ventilatory equivalent for CO_2)	35.9*(37.0)*
$\dot{V}_D/\dot{V}_T$ (physiological dead space/tidal volume ratio)	37 %*(33 %)
$P_{(A-a)O2}$ (alveolar-arterial difference of oxygen tension)	34.1 mmHg (45.8 mmHg)*

( )during exercise (maximum 120 Watt).
*abnormal value.

A further essential diagnostic tool is chest X-ray. However, due to its low sensitivity it is suggested that the first assessment of a symptomatic coal miner with unclear chest X-ray findings should involve the much more sensitive and specific high resolution computed tomography (HRCT) for a definitive pneumoconiosis diagnosis. HRCT is also the best method to visualize emphysema. HRCT shows a close correlation between nodule profusion and the extent of emphysema in silicosis but poor concordance with X-rays for lower pneumoconiosis categories (Talini et al. 1995, Bégin et al. 1991, 1995, Kinsella et al. 1990). ECG belongs to the basic examination repertoire and may indicate right ventricular hypertrophy, which should be further evaluated by echocardiography (Table 1).

7. Assessment of Causal Relation in a Compensation Claim

The precondition for recognizing CWP/PMF as an occupational disease is based on radiological and/or histopathologic evidence, i.e. the detection of rounded and/or irregular small opacities. In the case of an established functional impairment (restrictive and/or obstructive ventilation pattern, gas-exchange disorder), the cause should be evaluated by a medical expert and causally attributed.

Importantly, COPD and emphysema in the absence of radiologically determined CWP may also be caused by working in coal mines. Data and findings which have to be taken into consideration involve all kinds of previous noxious exposures, occupational case history, disease development, previous medical records, course of chest X-ray and HRCT findings, as well as further clinical examination results, confounders like smoking (packyears), respiratory allergies, systemic diseases, other occupational and non-occupational diseases. Differential diagnoses involve predominantly the other granulomatous lung disorders, such as tuberculosis, brucellosis, blastomycosis, coccidiomycosis, histoplasmosis, cryptococcosis, filiariosis, other pneumoconioses, hypersensitivity pneumonitis, drug-induced pneumonitis, pulmonary vasculitis, sarcoidosis, systemic lupus erythematosis, and the usual interstitial pneumonia.

In summary, there is a positive relation between the cumulative dust exposure in coal mines and the frequency of CWP/PMF, as well as COPD, and lung function impairment. Studies by Marine et al. (1988), the German Research Foundation (1971, 1975, 1984, 1998) and Seixas et al. (1992) as well as the publications by Collins et al. (1988), Rogan et al. (1973), Seixas et al. (1993) reflect this relationship without considering chest X-rays (review by Baur et al. 2005).

As shown in many studies, cigarette smoking also causes COPD and loss of lung function in a dose-dependent manner (Fletcher et al. (1976, 1977, Jaakkola et al. 1991). Jaakkola et al. (1991) reported an annual FEV_1 loss of – 0.084 L/packyear and so this is important for differential diagnosis.

The synergistic interaction between exposure to silicogenic dust in the mining industry and smoking has been consistently shown in many studies (Marine et al. 1988, the German Research Foundation 1971, 1975, 1984, 1998 and Seixas et al. 1992) and in the review by Oxman et al. (1993).

Overall, the appropriate literature reveals a consistent association between the dose of respirable coal mine dust and lung function impairments among non-smoking and smoking miners, as well as demonstrating the synergistic effects of dust exposure and smoking. Thus, the effects of cigarette smoking are important for differential diagnostics and should be differentiated from the known dose-effect relations of respirable coal mine dust. The comprehensive investigations by Collins et al. (1988) and Isidro Montes et al. (2004), in particular, assess lung function impairment in respect of the intensity of scarring (pneumoconiosis profusion categories) and smoking status.

Figures 5 shows the results of examining a 70 year old coal miner seeking compensation for CWP.

CONCLUSION

With regard to CWP, PMF, COPD and emphysema, the clinical and pathological studies on coal miners are consistent and plausible showing a typical time course and dose-response relationship. In addition to CWP and PMF, coal miners afflicted by COPD and/or emphysema should be considered for preventive measures, as well as for the recognition and compensation of these as occupational diseases even in the absence of pneumoconiosis. A report by a qualified industrial hygienist should be prepared on a regular basis, about every 5 years, with data on the qualitative and cumulative quantitative exposure in the coal mine.

The dust load in coal mines should be below the lowest observed adverse effect level of respirable inorganic dust which was shown to be 1 mg/m^3 (Morrow et al. 1991, German Research Foundation1971, 1998), Oxman et al. 1993). This necessitates the monitoring of dust in coal mines in line with the stipulated practice already adopted in many countries. Subjects who are exposed to respirable dust containing crystalline silica during their working activities should to be subjected to medical surveillance examinations. The findings should be archived in case of a future compensation claim.

The diagnosis of coal dust-induced disorders is generally based on a chest X-ray. Radiographic pneumoconiosis category 1 (International Labour Office 2000) is a minimal prerequisite for the diagnosis of CWP. However, the inherent low sensitivity of chest X-rays mean that any unclear findings should be resolved using HRCT for a definitive clinical diagnosis.

If there is a claim for compensation and an expert opinion has to be drawn up, a qualified and comprehensive diagnostic run-up is required. Furthermore, an expert report of the dust exposure during the whole working life of the individual should be prepared by an industrial hygienist.

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Chapter 10

POST-TRAUMATIC STRESS DISORDER AND ITS DETERMINANTS IN SURVIVORS AFTER COAL MINING DISASTER

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ABSTRACT

In the last 30 years in the Polish coal mines several serious disasters have occurred. In each of them up to 30 coal miners were killed. Altogether more than 150 people lost their life in coal mining disasters. Among those who experienced accidents in mines, many were injured and sustained damage to their health. As a consequence of disaster decline in mental health has been occurred too. One of the most specific disturbances in mental health in the aftermath of disaster is post-traumatic stress disorder. In our empirical study 52 coal miners, who took part in mining disaster and were injured, were taken into investigation. All of the subjects were men 23-54 years old (*M*=37.40, *SD*=7.41), they lived in the Silesian region (the region in which coal mining industry is the most widespread in Poland) and they experienced coal mining accident up to 25 months before the study. Several questionnaires were administered to the participants. Post-traumatic stress disorder symptoms were assessed as well as the range of their determinants, including emotional reactivity understood as a temperamental trait and sense of coherence. The findings show essential decline in mental health in survivors of coal mining disaster: about one third of the sample under study might be diagnosed as suffering from PTSD. In comparison with the findings in flood disaster survivors, the level of PTSD symptoms were higher, especially in the short period after accident. The range of determinants of PTSD symptoms, including temperamental trait emotional

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reactivity, seems to be comparable to the outcomes in flood survivors. In discussion the consequences of coal mining accident for mental health have been taken under consideration.

Keywords: PTSD, emotional reactivity, sense of coherence, coal mining disaster

INTRODUCTION

Poland has a long-lived tradition of coal mining industry. The records show that the first coal mining in Poland dates from the 12th century. On the large scale coal mining industry developed in the 19th century. In the year 2000 more than 50 different minerals were exploited in Poland. In order of the affluence of mineral deposits there were: hard bituminous coal, brown coal, copper, zinc and lead ore with accompanied silver, sulfur, salt and rock materials. Polish deposits of hard bituminous coal are characterized as difficult accessible. The most of this natural resource is placed on big depths and the geological system is adverse mainly. In the Silesian region – the main area of coal mining in Poland - coal is contaminated with sulfur and in coal mines deposits of gas and salinity of mine water leads to the higher risk of accidents. Nowadays coal mining industry is going through difficult period. Because of the geological conditions, productivity is on the low-level and a lot of coal mines are being closed down.

Unfortunately accidents in coal mines have also a long-lived tradition in Poland. The first historically proved disaster took place in the beginnings of this industry – in the 15th century in Zloty Stok where 59 miners lost their lives. After World War II several dozen fatal accidents took place in Polish coal mines. In each of them up to 30 coal miners were killed. Altogether more than 150 people lost their life in coal mining disasters. In the last most tragic disaster in "Halemba" Coal Mine 23 miners were killed in the aftermath of explosion of methane (see Wikipedia, Coalmine disasters in Poland, Polish edition).

All over the world coal mine accidents involves fatality and seriously injured survivors. The experience of being injured or being a witness of someone's death or being hurt involves emotions of fear, horror and helplessness. In psychological terms it may be treated as a traumatic experience.

The studies on trauma and its consequences has a long history and especially from 1980, when specific psychiatric sequel of such experience – Posttraumatic Stress Disorder (PTSD) - was formulated (APA, 1980), research has been conducted systematically. Posttraumatic Stress Disorder is a potential adverse consequence of experienced trauma. Although it is not the only adverse psychiatric disorder which may develop in the aftermath of traumatic experience, PTSD is specific to such experience and may be diagnosed only in people who passed through trauma.

At the moment, Posttraumatic Stress Disorder is a set of symptoms described in DSM IV-R (APA, 2006) and defined as a possible sequel of experience of traumatic event. Following the definition of traumatic event, the core feature of such an event is the threat of life or health (cf. APA, 2006). From this point of view coal mine accident meets the definition of traumatic event. The symptoms of PTSD are defined by means of three diagnostic criteria, each of them composed of similar kinds of symptoms. In short, the PTSD is manifesting as (1) symptoms of re-experiencing the event, such as intrusive thoughts or dreams, (2) symptoms of numbing, expressing emotional coldness or decreasing activity, and in symptoms of avoiding stimuli associated with the traumatic event, and (3) symptoms of the state of hyperarousal, e.g., expressed in difficulties to concentrate or fall asleep. To meet the diagnosis of PTSD, the level of intensity and duration of symptoms must reach a threshold as defined in DSM IV. Regardless of the clinical approach to PTSD, which is focused on identifying the occurrence of a psychiatric disease, the dimensional approach to intensity of PTSD symptoms may be applied. In this approach the full range of intensity of symptoms is taken into consideration (Ruscio, Ruscio & Keane, 2002).

The results from epidemiological studies show that much more people experience trauma as compared to these in whom PTSD has been developed (cf. Brunello, et al. 2001). In many studies results show, that only a part of survivors may be characterized as having a high level of PTSD symptoms, whereas the majority of victims finds a psychological balance after even horror experience. The worldwide studies show that about one third of the population is exposed to sever trauma experience during their lifetime, whereas the prevalence of PTSD ranges from 3 to 6%. It means that only 10-20% of trauma survivors develop Posttraumatic Stress Disorder. It leads to the conclusion that PTSD is not a normal reaction to abnormal experience – as it was emphasized in the previous literature (cf. Shalev, 1996). PTSD seems to be a rather abnormal reaction to very sever and rarely experience.

What do the symptoms of PTSD depend on? The mate-analytic studies show that there is a range of factors related to PTSD presence. They may be categorized as pre-, peri-, and posttraumatic factors (Brewin, Andrews & Valentine, 2000; Ozer, Best, Lipsey & Weiss, 2003). By definition, PTSD is related to the trauma and the more traumatic events occur, the more symptoms of PTSD are observed. Such phenomena is called dose-response effects. The dimensions of trauma are not only life and health threats, but also emotions aroused under the event, potential experience of dissociation and material losses if they are consequences of the event (*ibidem*).

Findings in meta-analysis carried out by Brewin and colleagues (2000) indicates on such factors like: gender (female), age (older), lower SES, lower education, low intellectual level, previous traumas and psychiatric history of the individual (and his/her family). Among peri- and posttraumatic factors, severity of the trauma, lack of social support and additional life stress are related to PTSD diagnosis. Also meta-analysis by Ozer and colleagues (2003) leads to the conclusion about similar complex of risk factors.

Relatively rarely individual personal features are included to the analyses. In review analyses by Norris, Friedman and Watson (2002), which is focused on the determinants of adjustment after mass disaster, personal features are considered as important resource for resilience and recovery after trauma. Basic optimistic view about the external world, other people and self seem to be positively related to adjustment after trauma. Such traits play a role as the factors protecting from developing adverse reactions as well as stimulating recovery after trauma. Obviously, a reciprocal relationship may be expected: people who feel higher sense of self-efficacy as well perceive the external word as being better organized and predictive, manifest higher level of adjustment and people who are better adjusted, have more positive basic views.

Besides cognitive characteristics, temperamental traits are worth studying in the context of trauma (Strelau & Zawadzki, 2006). Temperament is defined as such personality traits, which are present since early childhood, can be observed not only in human behavior but also in animals and refer rather to formal aspects of behavior (Strelau, 1998). Formal characteristics of behavior can be considered in terms of energetic and temporal patterns in behavior. Following the Regulative Theory of Temperament (RTT), formulated by Strelau and described in details in several publications (Strelau, 1996, 1998) temperament plays a regulative role, which consists in modifying (moderating) the stimulative and temporal value of situations and behavior, according to the individual-specific temperamental traits. This role is especially evident in difficult situations and extreme behaviors.

The “temperament – stress” phenomena constitute a system of complex and reciprocal relationships. Beside the role of temperament in moderating the intensity of the state of stress, studies indicate some further relationships inside the model. Temperament: (1) co-determines the intensity of stressors and, in case of stressors dependent on the individual, also its probability of occurrence, (2) moderates the coping efforts, and (3), contributes to the psychophysiological and/or psychological costs of the state of stress (Strelau, 1998).

In our previous studies on PTSD and temperamemental characteristics in natural disaster survivors, it was established that especially one of the temperamental traits – emotional reactivity – is consistently positively related to the intensity of symptoms of PTSD (Strelau, Kaczmarek & Zawadzki, 2006).

Hypotheses

PTSD is positively related to the severity of trauma experience. We expected that survivors of coal mining accident experience higher direct life and health threat as compared to natural disaster survivors, whereas the additional life stressors resulting from the aftermath of disaster, especially finical and housing problems are higher in natural disaster survivors. If so, it leads to different expectation towards dynamic of intensity PTSD symptoms. In survivors of the coal mining accident higher level of maladaptation should be expected in the short period after trauma and distinctly decline with time. The expected proportion of survivors who manifest high level of PTSD symptoms should be up to about 20%. Regarding the factors influencing PTSD, it was expected that:

- Emotional reactivity should be positively related to the intensity of PTSD symptoms in the coal mining accident sample as well as in other samples of survivors (in our study flood victims and residential fire survivors).
- Sense of coherence, which describes the level of perceiving the world and self as comprehensible, meaningful and manageable, should be positively related to the lower level of PTSD symptoms (resilience) and the higher decline in intensity of PTSD symptoms (recovery).

Table 1. Demographic characteristics of the investigated samples

Sample	Type of trauma and time of investigation after trauma	*Occasion of PTSD assessment*	N	Age *M (SD)*	Range of age
A (coal mining accident survivors)	Coal miners disaster survivors investigated in 1999, 3-25 months after accidents (*M* = 12.85) from Silesian region of Poland	Few weeks after (retrospective) & Few weeks before study	52M	37.40 (7.41)	23-54
B (flood survivors)	Flood disaster survivors investigated two years after disaster (1999) from Silesian region of Poland.	Few weeks after (retrospective) & Few weeks before study	88M	41.42 (9.39)	23-54
C (flood survivors)	Flood disaster survivors investigated 15 months after disaster (2002) from North part of Poland.	Few weeks before study	97M	43.27 (7.24)	23-54
D (fire survivors)	Residential firer disaster survivors investigated 3-12 months after disaster (2005-2007) from seven cities in Poland	Few weeks before study	94M	39.02 (8.56)	23-54

Note: Groups differed significantly with regard to age (F=6.87, p<0,01; post-hoc tests: A & D against B & C).; M – Males.

METHOD

Subjects

The group of coal mining accident survivors (sample A) consists of 52 coal miners (men only). All of them live and have been working in Silesian region of Poland. They experienced severe accident at work 3-25 month before being investigated (*M*=12.80; *SD*=6.55). Most of them – 81% of the sample – have been on the sick note. The coal miners sustained serious injuries, such as: 1) fractures and injuries of bones (legs, spine, skull) – 62%; 2) internal organs injures – 21%; 3) concussions – 6%; 4) serious burns – 1%. The average age of the sample was 37.40 years (*SD* = 7.41) with the range between 23 to 54 years old (Kowalczyk, 2000).

To compare the effect of trauma three other samples were included: flood survivors (sample B and C) and residential fire survivors (sample D). The samples consist of 23-54 years men only to be comparable with the group of coal miners.

The sample of flood survivors (sample B) is composed of subjects who experienced Great Polish Flood in 1997. They were investigated about 2 years after disaster. Participants came from three towns of suffered region in Silesia. As in the sample of coal mining accident survivors, the intensity of PTSD symptoms was assessed as the state in time of investigation and retrospectively – several weeks after experienced disaster.

The second flood survivors (sample C) were investigated 15 months after disaster. All of them were inhabitants of Gdansk – big city in the northern part of Poland which experienced flood in 2001. In sample C 53,7% of the subjects reported threat of life, 47,4% - injuries of the body and 79,2% high material losses.

The last sample (sample D) consists of residential fire accident survivors. They were recruited from several cities of Poland and experienced fire accident at their home (or – in case of 45 subjects – at their stalls, which was the main source of their income). Survivors of fire accidents were studied 3-12 months after the accident. All of them were appointed by fire brigades local departments. In sample D, 55,9% of subjects reported threat of life, 18,3% - injuries, while high material losses – 34,0%. The characteristics of the samples are shown in Table 1.

Measures

For measuring PTSD symptoms a self-assessed questionnaire - the PTSD–Clinical Version (PTSD-C) was developed by Zawadzki and colleagues (2002). It consists of 40 statements which depict the expression of Posttraumatic Stress Disorder symptoms according to DSM IV (APA, 1994). The subjects describe their behavior and feeling on a 4-point Likert scale. The PTSD-C is designed to measure the intensity of symptoms as a general dimension (cf. Bonnano, 2004) and was psychometrically constructed by the two-parameters model of Item Response Theory (Hambleton & Swaminathan, 1985). The range of scores is 0-120 points. However, more recently a procedure for calculation the data into typological diagnosis (PTSD-present or PTSD-not present), based on the criteria of PTSD in DSM IV, was developed (Izdebski, 2008). The psychometric properties of PTSD-C are acceptable with regards to both reliability (information function) and validity. The latter one was shown - among other things - by demonstrating its convergent and discriminant validity in analyses aimed to compare data based on the PTSD-C with data of the Revised Civilian Mississippi PTSD Scale (Norris, Perilla &Ibanez , 2001; Polish adaptation by Kaniasty, 2003) and the Mental Health Inventory (MHI; Veit & Ware, 1983; Polish adaptation by Cupas, 1997).

For measuring temperamental traits the Formal Characteristics of Behavior – Temperament Inventory (FCB-TI; Strelau & Zawadzki, 1993, 1995) was applied. The self-rating questionnaire is composed of six scales: Briskness, Perseveration, Sensory Sensitivity, Endurance, Emotional Reactivity, and Activity. All scales contain 20 items each scored in 'Yes-No' format (the scores range from 0 to 20 points). In further analyses we focused only one among these temperamental traits: emotional reactivity. It is defined as the tendency to react intensively to emotion-generating stimuli, expressed in high emotional sensitivity and in low emotional endurance. The FCB-TI is characterized by good psychometric properties.

Sense of Coherence was measured by the Orientation to Life Questionnaire (OLQ) developed by Antonovsky (1984) in Polish adaptation by Koniarek, Dudek and Makowska (1993). OLQ consists of 29 items in the form of questions about the view of the level of coherence in the perceived world. The questionnaire is composed of three scales: Comprehensibility (11 items), Manageability (10 items) and Meaningfulness (8 items). The scales highly correlate with each other and may be summed up to one total score. The subjects assess their behavior on a 7-point scale. The psychometric properties of OLQ both original version, and Polish adaptation are satisfying. Sense of coherence was measured only in the sample of coal mining accident survivors.

Procedure

All accident and disaster survivors were studied in their home place. The packets of self-report questionnaires, such as PTSD-F, the FCB-TI were administered to subjects of all three samples, whereas the OLQ only to the coal mining disaster sample. The contact with subjects was establish via official institution: the social welfare (flood survivors) , the fire brigades (fire survivors), and State Mining Authority (coal mining accident survivors). The study was conducted by professional psychologists in cooperation with MA's students. With the exception of coal miners, the subjects were paid for taking part in the study.

RESULTS

It was expected that the intensity of PTSD symptoms will be comparable high in all three samples and slightly higher level of symptoms in coal miners will be observed. In terms of syndrome we expected that higher percent of survivors will report PTSD symptoms when recorded retrospectively as compared to the acute state. The decline in symptoms will be more significant in case of coal mining accidents survivors with in comparison to natural disaster survivors.

In order to assess the PTSD syndrome, the 4-point format of answer was recoded to 0/1 format (0 – answer "never" or "seldom", 1 – "frequent" or "almost always"). At least one symptom from category B (intrusion symptoms), at least three symptoms from category C (avoidance symptoms), and at least two symptoms from category D (hyper-arousal symptoms) were taken as threshold for positive diagnosis of PTSD. Such procedure lead to ratings which are characterized by good validity (Izdebski, 2008).

In Table 2 demonstrates level of intensity of PTSD symptoms and estimation of positive diagnoses of PTSD in the sample of coal miners and in the remaining ones. On account of procedure, retrospective self-report assessment describing the state "just after" the trauma is included only in case of coal miners and in sample B of flood survivors.

Table 2. Characteristics of groups with regard to PTSD and ER scales

Variables	Sample			
	A	B	C	D
Emotional reactivity	9.40 (3.97)	10.22 (4.40)	9.63 (4.48)	9.70 (4.27)
Intensity of PTSD - just after	57.08 (33.58)	43.57 (23.20)	-	-
Intensity of PTSD - actual state	38.52 (20.92)	33.61 (23.91)	39.41 (26.19)	31.42 (26.28)
Diagnosis of PTSD - just after	55.8%	43.2%	-	-
Diagnosis of PTSD - actual state	26.9%	22.7%	29.9%	24.5%

Note: A – coal mining survivors, B – Silesian flood survivors, C- Gdańsk flood surviviors, D- fire accident survivors. Groups do not differ significantly with regard to emotional reactivity (F=0.49), but with regard to PTSD symptoms intensity assessed just after the traumatic event (F=10.94, p<0.01 - groups A & B) and not with regard to actual state of PTSD symptoms intensity (F=2.16 - all groups). See Figures 1 & 2.

The average level of PTSD symptoms as well as the proportion of positive diagnoses in all for all four samples are displayed on Figure 1 and Figure 2.

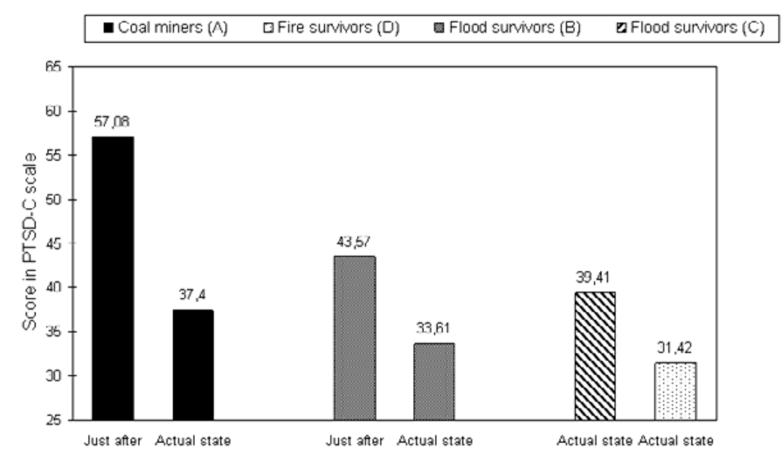

Figure 1. Intensity of PTSD symptoms, assessed by the PTSD-C.

The Figures show that average levels of PTSD symptoms are comparable among samples and slightly higher in coal mining accident survivors. These differences particularly occur in diagnosis when referring to time just after the accident. The second most suffering group are the Great Polish Flood survivors (sample B). It is comprehensible, having in mind the scale of this disaster. Although in the sample of coal miners the drop in PTSD symptoms and decline in PTSD diagnoses attendance is the highest. As it was expected, the specificity of accident in work place (coal miners) is that it does not involve material and financial losses for the individual. The consequences mainly refer to the decline in health status. The proportion of positive diagnoses is around 20%.

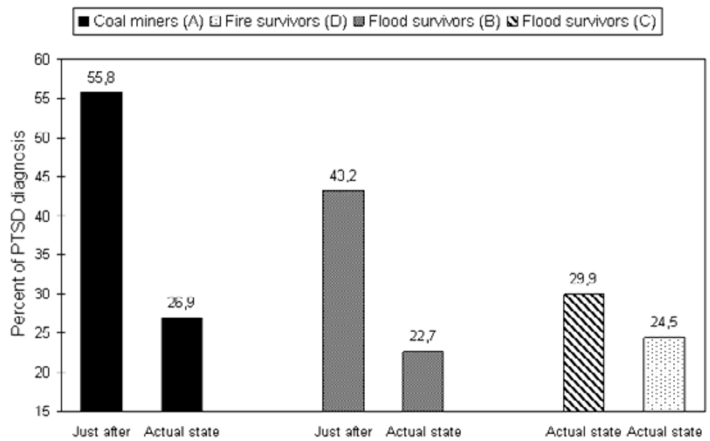

Figure 2. Percent of PTSD diagnosis.

Second, the roles of two types of predictors of intensity of PTSD symptoms and positive diagnoses of PTSD were analyzed. It was expected that emotional reactivity is positively related to PTSD symptoms of in the aftermath of trauma. The correlations are expected regardless of the period of time after trauma and regardless of the type of trauma. The findings are shown in Table 3.

Table 3. Coefficients of correlation between PTSD and emotional reactivity

Variables	Sample			
	A	B	C	D
Intensity of PTSD - just after	0.55*	0.55*	-	-
Intensity of PTSD - actual state	0.54*	0.48*	0.48*	0.25*
Diagnosis of PTSD - just after	0.30*	0.42*	-	-
Diagnosis of PTSD - actual state	0.47*	0.25*	0.33*	0.27*

Note: Coefficients of correlation significant at $p<0.05$ are marked by an asterisk. The only ER trait demonstated significant correlations with PTSD across all samples. For ‘diagnosis of PTSD’ the *Eta* coefficients were calculated. For description of symbols see Table 1.

The range of coefficients of correlation in the four samples under study is 0.25 - 0.55, and the median score is 0.44. The findings in the sample of coal mining accident survivors show that in three of four cases – correlation with intensity symptoms in both time points, and correlation with positive diagnoses – actual state – is above the median in the investigated samples. It means that emotional reactivity is positively related to PTSD symptoms, general strength of such relationships is moderate and the role of emotional reactivity is relatively higher in coal miners in comparison with the findings in the remaining samples.

In the next step regression analyses were done. With the use of Enter method two predictors were introduced to the models: emotional reactivity and level of PTSD intensity, 'just after' as a predictor of 'actual state' (bottom part of the table), and 'actual state' as a predictor of 'just after' PTSD level (top part of the table). The findings are presented in Table 4.

Table 4. Results of the regression analysis of PTSD symptoms intensity with emotional reactivity and symptoms, assessed at different time after the trauma as a predictors (sample A & B)

Variables	Coal mining survivors (PTSD - just after)	Silesian flood survivors (PTSD - just after)
R (R^2)	0.76* (0.58)	0.83* (0.69)
Emotional reactivity	0.18*	0.22*
PTSD intensity - actual state	0.52*	0.60*
Variable	Coal mining survivors (PTSD - actual state)	Silesian flood survivors (PTSD - actual state)
R (R^2)	0.75* (0.56)	0.80* (0.64)
Emotional reactivity	0.16	0.02
PTSD intensity - just after	0.53*	0.65*

Note: Coefficients of correlation significant at $p<0.05$ are marked by an asterisk. R – multiple correlation, R^2- proportion of explained variance. For independent variables the semipartial correlations are presented. Significant correlation between ER and PTSD – acute state may be also interpreted as the impact of PTSD on ER. However, the theoretical model assumed the only the one-way influence – ER on intensity PTSD symptoms.

In the sample of coal miners both factors – emotional reactivity and symptoms of PTSD measured in respect of time just after trauma - predict 56-58% of variance of intensity of PTSD symptoms. A little higher result was obtained in the sample of flood survivors (64-69%). In both analyses the most important predictor was the level of intensity of PTSD symptoms, what suggests the permanence of PTSD symptoms. Emotional reactivity significantly predicted only the symptoms assessed just after traumatic event – the effects of this trait were insignificant when PTSD actual state was controlled for PTSD symptoms 'just after'. These results indicate that emotional reactivity is responsible for arousing the PTSD symptoms – it influences the level of PTSD just after the trauma, and has no impact on changes in PTSD symptoms. So, the correlations between emotional reactivity and actual symptom PTSD intensity are due to the temporal stability of aroused PTSD symptoms in the period just after the traumatic event. The question arises, which factors are responsible for the decline of PTSD symptoms between both phases? It was expected that such individual features as comprehensibility, manageability, meaningfulness (as well as the general sense of coherence) are related to decline in PTSD symptoms as well as to the level of PTSD symptoms. Findings relating the PTSD to sense of coherence are shown Table 5.

The hypothesis was supported by the data: the general 'sense of coherence' score as well as the scores from the 'Comprehensibility' and 'Manageability' scales are positively related to the decline in PTSD symptoms and negatively - to the level of PTSD (the second time point). It means that subjects, who perceive world as more coherent, present lower level of symptoms and recover faster as well. While emotional reactivity is responsible for arousing PTSD symptoms, the sense of coherence seems to be a real ‘salutogenetic’ factor – it helps subjects to recover from posttraumatic disorders.

Table 5. Coefficients of correlation between change in PTSD intensity, PTSD actual state, and the sense of coherence (sample A)

Variables	Coal mining survivors (Reduction in PTSD symptoms intensity)	Coal mining survivors (PTSD - actual state)
Sense of coherence	0.31*	-0.58*
Comprehensibility	0.36*	-0.59*
Manageability	0.27*	-0.51*
Meaningfulness	0.19	-0.44*

Note. Coefficients of correlation significant at $p<0.05$ are marked by an asterisk. In the coal mining sample the reduction in PTSD symptoms intensity correlated with emotional reactivity 0.11 and 0.20 in the Silesian sample(n.s).

DISCUSSION

The findings show that more than 20% of studied coal miners accident survivors may suffer from the Posttraumatic Stress Disorders symptoms. In this sample the intensity of symptoms is elevated to the intensity of clinical level and suggests that professional support to these people should be addressed. The analyses based on self-reports and probably the proportion of positive diagnoses of PTSD is a little overstated. However, the problem has been serious still. The self-reported state just after the accident in comparison with natural disaster survivors seems to be more severe. Just findings are comprehensible in line with the fact that the proportion of death or injured victims in coal mining accidents is relatively high. This industrial accident is more dangerous than flood or fire accident at home. In this term, coal mining accident is a highly traumatic experience.

The symptoms of PTSD decline with time. These phenomenon is observed in coal mining accident survivors as well as in the remaining samples being studied. Decrease in the level of symptoms in coal miners is higher. The reason is the lower level of additional life stressors than in the situation of natural disaster. The coal miners after accident are on the sick note for a longer time and experience health problem. However, in comparison with natural disaster survivors, they do not experience to such extent as survivors of natural disaster financial and housing problems, which may be concerned as “secondary stressors”, leading to the permanence of PTSD symptoms.

Although the intensity of PTSD symptoms is high, there is a lot of survivors who sustain their well-being and mental health. Both considered factors – emotional reactivity and sense of coherence – were related to the intensity of PTSD symptoms and decline in symptoms. Emotional reactivity seems to be consistently related to the intensity of PTSD symptoms, but not to the decline in the level of symptoms. This suggests that emotional reactivity is related to the resilience phenomena, but not to the recovery after the state of maladaptation in the aftermath of trauma. Sense of coherence is related both to the lower intensity of symptoms of PTSD and to the higher decrease in PTSD symptoms intensity. It draws to the conclusion that sense of coherence is related both to resilience and recovery processes after trauma.

As mentioned in the Introduction posttraumatic stress disorder is not the only one adverse consequence. The studies on disaster show that also depression, anxiety and phobias may be observed in survivors (Norris at al, 2002). In trauma survivors occurs also higher risk of alcohol and drugs addiction and aggressive patterns of behaviors (Perkonigg, Kessler, Storz & Wittchen, 2000). The complex of pre- peri and posttrauma factors play a role in determining the consequences of accidents and disasters. However, psychological costs of such events should be taken into consideration. The solution is prevention and social support in case of such events, including professional psychological support addressed to all survivors of traumatic events, and – as our study has shown – especially to the coal mining accident survivors.

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INDEX

A

B

C

D

E

G

H

I

J

K

L

M

Q

R

S

U

V

W

X

Y

Z