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Sea Beaches Near Coal Mine Water: Emphasis on Selenium

Abstract

Groundwater and surface streams draining abandoned seleniferous coal mines and ash piles are among major causes of environmental exposure to selenium (Se). One such scenario is located on the eastern Adriatic coastline of the Istrian Peninsula (western Croatia), where the legacy of the former Raša coal industry is reflected in elevated levels of Se in key environmental media and biota. Selenium in animals and humans is an essential nutrient that has a quite narrow window between deficiency and toxicity. Geology exerts a fundamental control on the environmental Se concentrations, but aquatic contamination with Se has gained widespread concerns because Se is derived from the largest production activities, such as coal-fired power plants, oil refining, mining, and agriculture. Hence, Se was periodically found to be the cause of the devastating impacts to local ecosystems. Therefore, the objectives of this paper are as follows: 1) to provide a brief overview of coal-derived selenium in the environment, 2) to present basic principles of selenium geochemistry entailing environmental implications, and 3) to show variability of Se levels in ambient water samples collected by authorities of the coal-fired power plant Plomin during the period 2013-2023 for the monitoring purposes. This paper warrants further research of the Raša coal area which is close to beaches very popular among tourists and locals.

Keywords: Raša coal, selenium, leaching, the Adriatic Sea, mine water, contamination, monitoring.

1. Introduction

Marine coastal zones are affected by huge inflow of various pollutants, derived from natural as well as anthropogenic sources, carried by rivers and streams. Namely, eroded soils along untreated sewage and industrial chemicals are being discharged directly into the rivers. Afterwards, they can adversely impact marine coastal habitats that are particularly vulnerable to contamination by various organic and inorganic entities. The latter mostly refers to potentially toxic trace elements (PTEs), also known as heavy metals or metalloids. They are usually applied to the chemical elements such as As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn that commonly cause the environmental pollution and toxicity issues. Since they occur naturally in rock-forming and ore minerals, their normal background values in soils, sediments, waters and biota are highly variable. In case of the environmental pollution, anomalously high concentrations of PTEs relative to their background levels occur. A vast array of anthropogenic sources and natural geochemical processes contribute to the PTE cycling throughout the environment. The oldest cases of pollution related to PTEs are due to metal ore (e.g. Cu, Hg, Pb) as well as coal mining [5], smelting and utilization by ancient civilizations. This paper elaborates coal mining aspects.

Coal is a combustible sedimentary rock that has highly heterogeneous composition. Apart from the organic components (i.e. carbon), inorganic compounds can be found in the mineral matter, which contains virtually the whole periodic table [35]. Today, modes of occurrence or distribution of PTEs in coal have been generally well characterized, thereby allowing for assessments of PTE behavior during coal utilization, and for their potential environmental impact [13, 1, 32]. Coal PTE quantities and geochemical aspects depend on a number of factors, including: a) their levels in parent vegetation, b) their enrichment during the decay of plant material, c) sedimentation and diagenetic transformations, d) burial and concomitant coalification, and e) subsequent mineralization. It should be emphasized that PTE concentrations show an enormous variability among coal varieties from different sources and even among coal samples from the same layers (seams). It is important to consider that PTE levels vary depending on the rank of coal and its associated geology [9].

Selenium (Se) is a PTE often mentioned in the context of environmental aspects of coal use. It is because crops, including animal forages, can be very sensitive to the addition of small amounts of Se in soil that can induce toxic effects [2]. Interpretation of the environmental chemistry of Se is complex due to its various interactions with other compounds. Nevertheless, research has shown that Se emitted by coal-fired power stations induce toxic responses in test systems and in humans, such as gastrointestinal disturbance, liver and spleen damage, anemia, a possible carcinogenicity, and a suspected teratogenicity [9]. Selenium is an essential micronutrient for mammals, birds, fishes, algae, and bacteria, but only slightly excessive Se is toxic. This depends on chemical forms, or species (i.e. oxidation states) that affect the Se solubility and mobility throughout the environment. Since the toxicity of Se takes place at only approximately 50 times the dose required as an essential element, it is necessary to monitor water Se levels and examine biogeochemical processes involved in Se aquatic cycling [24].

Coal mining operations cause toxic waterways contamination with PTEs due to their leaching by runoff water or groundwater [33, 6]. Hence, by weathering of coal and coal waste material, exposed toxic substances can create a hostile environment for wildlife species [18]. Such dangerous contaminants become more concentrated in animals as they move up the food chain. Therefore, the impacts to the ecosystem go beyond just aquatic animals – PTEs can hurt or kill any animals that eat the contaminated fish — including humans. Many publications have reported selenium contamination of soil [37], drinking water supplies, lakes, rivers, streams, and seawater [25, 31, 17], which are heavily impacted by coal mines and power plants, particularly when national standards for wastewater discharges from mines are violated [39]. According to the World Economic Forum, a shortage of clean fresh water presents the greatest global, societal, and economic risk over the next decade. By 2030, the global population is expected to reach 8.5 billion, possibly facing a water shortage up to 40%. Little time is left to spare, and the mining industry must take the necessary steps to ensure that water is conserved as much as possible, beginning now, in order to protect available water resources. Sustainability must be a core focus of the mining industry due to the fact that more than 50% of mining operations are located in high water-risk regions; hence, we recognize the need to conserve water wherever possible.

2. Coal-derived selenium in the environment

Coals are mostly distinguished on the basis of their sulfur (S) content into low-S (<1% S) and high-S (>3% S) varieties. While low-S coals were deposited in freshwater environments, the high-S ones are commonly associated with marine strata, and most of their S comes from seawater sulfate. Coal is not usually preserved within marine carbonate successions. Quite contrarily, coal is most commonly preserved in nonmarine siliciclastic successions or paralic, interbedded siliciclastic–carbonate successions [8]. In coal research community, selenium is considered to be a high-coalphile element, i.e. it has a very high affinity for coal [16]. Generally, high-S coals are enriched in selenium as well as U, Mo, and V. More precisely, the brackish conditions are favorable for the highest Se enrichment in coal [40]. Given that so much coal can be found in proximities of marine environments, either naturally as coal layers in host rocks or anthropogenically in the form of coal terminals and coal waste dumps, the associated seawater sediments are frequently impacted by coal-derived PTEs. In such settings, leaching of toxic components from coal had been demonstrated, but researchers have suggested that environmental effects of coal should be coupled with unraveling the mechanisms controlling bioavailability of PTEs [3].

Coal combustion produces environmentally harmful by-product known as ash [33].

It can amount up to 30% of original coal mass or even much higher (~40%) as in case of some high-ash Indian Lower Gondwana coals. Hence, its enormous quantities entail difficulties in its safe disposal [29]. Physico-chemical composition of ash and release of its PTEs into the environment depend on various factors, such as coal geology, mode of occurrence of a given PTE, pH of combustion by-products, type of a combustion process, emission control technology, disposal techniques and relevant geographical conditions. Many studies have confirmed that selenium is among PTEs (e.g. As, Cd, Fe, Mn, etc.) which leach considerably from ash dumps on land surface and the ash utilized in the construction industry [7]. The study [36] found that selenium release increased above pH 4. When pH reached 12, nearly 50-70% of the total ash selenium was leached. This implies that the coal industry may release staggering amounts of Se to the environment, especially if the alkaline karstic environments (pH above 8) are considered in this regard.

By rain-driven leaching of coal piles and ash ponds, leachate enriched in Se can reach waterways. Herewith, Se usually gets bioaccumulated in aquatic food chains, thus contaminating the diet of fish, wildlife, and sometimes humans [20]. In southwest China (Enshi County, Hubei Province), a locality was investigated [38], and it was found out that the morbidity up to 50% (based on the total of 250 inhabitants) was a consequence of selenium intoxication between 1961 and 1964. The Se source was local coal exceptionally enriched in selenium. Upon its weathering, Se gets leached out and pervades soils and crops. Moreover, the use of lime fertilizer and smoking practices contributed additionally to the elevated Se intake by the villagers [38]. Typical adverse health effects in subjects exposed to high levels of environmental Se included higher prevalence of nausea and vomiting, bad breath, worm infestation, breathlessness exert, chest pain, hair and nail abnormalities and loss, garlic odor, edema, spontaneous abortion, and overall selenosis.

3. Selenium environmental geochemistry

Today, a growing number of interdisciplinary studies are examining selenium [14, 15], low levels of which are essential for humans and animals, but at slightly higher concentrations it becomes quite toxic, e.g. causing reproductive impacts in bird embryos and hatchlings [31]. The paper [21] emphasizes that leaching of selenium and resultant biological impacts are an undisputed fact of coal mining operations, and no effective treatment of leachate wastewater to render it safe to aquatic life in receiving waters at the scale and flows emanating from coal mines has been demonstrated so far. Under oxidative and alkaline conditions, such as the ones prevailing in karst, selenium is highly mobile and potentially bioavailable [10, 37]. Elevated selenium impairment of aquatic ecosystems is an international issue most commonly resulting from natural geochemical processes as well as anthropogenic activities related to agriculture and mining industry [4, 11, 12]. The mining operations are substantially causing increased mobility of Se from concentrated mineral deposits (including coal) and metal-sulfide ores.

Estimates reported that coal combustion accounted for 60% of the total Se, followed by losses of Se in nonferrous mining, smelting, and refining operations, which accounted for 25% of the total [9]. Natural concentrations of Se appear to be much more important than man-made concentrations, and any industrial Se pollution would probably be restricted to the immediate vicinity of refineries emitting Se. No data were available to show whether industrial emissions of selenium or selenium compounds to the atmosphere were recycled to the land and sea by normal atmospheric processes [30]. Reduction of industrial emissions of Se mostly happened due to an implementation of other pollution-control actions. The close association of selenium with sulfur in its occurrence and their similar chemical properties could explain a corresponding reduction in the emission of selenium following the effective sulfur control and associated removal of particulates.

According to the study [23], selenium is above all a reproductive toxicant (a gonadotoxicant and a teratogen). The authors note that adverse effects on reproduction takes place at lower levels of exposure than acute mortality. They give grim predictions that Se issues will worsen in the coming years due to the ongoing exploitation of coal and similar fossil fuels, irrigation in semiarid regions, and mining of phosphate ore. Their recommendation in terms of management of Se contamination is that food web relationships need to be identified in order to understand, predict, and manage ecological risks from Se.

4. Water selenium levels related to Raša coal and ash

Croatian Raša coal is a rarely unique type of coal that is also known as superhigh-organic-sulfur (SHOS) coal; similar varieties can be found in southwest China, for example the abovementioned Enshi County [8]. It is anomalously enriched in organically bound S (up to 11%), and Se (80-150 mg/kg), while world coal Se levels are less than 10 mg/kg [40]. The study [22] found leachable concentrations of Se, Cr, and Mo in local soil contaminated by Raša coal ash. As a consequence of weathering of Raša coal by various karstic hydrological processes, increased levels of Se have bioaccumulated in local flora [28], and fauna [34].

In Croatia, water quality is protected by law, so additional measures must be taken to ensure that no contamination leaks from the mine workings. A study locality presented in this paper is the Plomin Bay (the northern Adriatic Sea, Fig. 1). Decades ago, the Plomin coal-fired power plant's authorities put lots of efforts and significant funds into protective measures in relation to the storage of huge quantities of Raša coal ash. However, approximately 4.4 Mt. of local Raša coal, intercalated within marine carbonate rocks, remain underground. Hence, several coal mine water discharges are constantly inflowing into local waterways and finally in the Raša and Plomin Bays for decades. Previous papers [25-28] reported increased environmental Se, U, S, Mo, and V levels, derived from Raša coal leaching by groundwater. Compared to world stream water Se levels of 0.2 μg/L, total Se values in Raša coal mine water and local streams were mostly 10-15 μg/L, thus exceeding the Croatian regulatory limit value for Se in surface water of 10 μg/L. World studies have shown that much lower Se levels (2-5 μg/L) pose health concerns, and certain toxicological and reproductive effects are related to Se >5 μg/L in ambient water [20]. The local groundwater, resulting from freshwater and seawater mixing, is important in actively and continuously leaching, transporting, and redepositing Se [26, 27]. The large volumes of water could have transported rather large amounts of Se and deposited it in bottom sea sediments of the Raša Bay [19]. On one hand, Se is the rarest micronutrient on Earth, and its scarce resources are largely lost. On the other hand, selenium has attracted much of scientific interest recently [15], what has resulted in molecular, genetic, biochemical, and health applications. Hereby, this paper should add up a needful knowledge on the uniquely elevated Raša coal-derived selenium in an Adriatic environment (Fig. 1).

Figure 1: Map of the study area (a) Regional map showing geographical location of Croatia, the Adriatic Sea and the Istria Peninsula; (b) The coal-powered thermal plant Plomin (red rectangle) and the sampling points of the seven piezometers (PZ1-PZ7) and (c) The Plomin Power Plant with position of PZ6 and PZ7.

Measurements taken under the auspices of the 10-year environmental monitoring of groundwater throughout the Plomin Bay area (Fig. 1), found selenium levels (presented as mean values of respective seasons) well above 10 μg/L (Fig. 2).

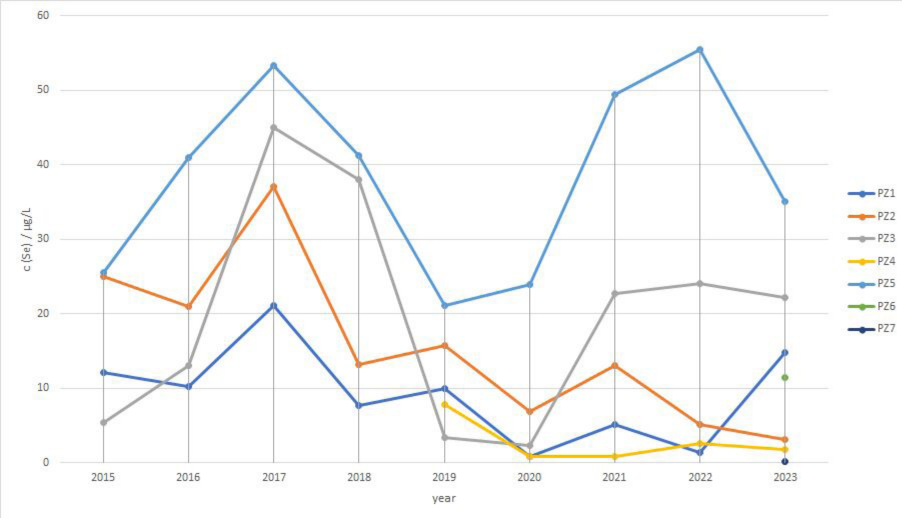

Figure 2: Selenium levels in seven piezometers PZ1 to PZ7 across the Plomin Bay study area from 2015 to 2023.

Nevertheless, Fig. 2 shows that some piezometers (PZ1, PZ2, PZ3 and PZ4) had Se levels below10 µg/L. The most interesting was PZ 5, which is in a direct contact with Raša coal beds. The Se averages for position of PZ5 were above 20 µg/l. Therefore, its PTE values were analyzed and the results (basic statistical parameters) are presented in Table 1.

Table 1: levels of PTEs in piezometer PZ 5 (Raša coal beds)

µg/L	Se	Cd	V	Mo	Hg
n	36	36	36	36	36
Min	0.5	0.01	0.25	0.5	0.002
Max	129	0.5	7.3	25	0.15
Mean	38.5	0.09	1.64	3.2	0.06
SD	28	0.12	1.83	4.3	0.06
Median	34.5	0.05	0.7	2.5	0.03
Q_1	19.2	0.01	0.5	2.5	0.01
Q_3	56.7	0.1	1.9	2.5	0.12
RSD (%)	74	136	111	134	95

The values of RSD (Table 1) reflect a substantial variability of all analyzed PTEs, mostly due to seasonal factors (e.g. quantity of water discharge, physico-chemical conditions, etc.). The paper [27] reported Se, Cd, V, and Mo values (in µg/L) in the Raša coal mine water (Rabac and Krapan sites) as follows: 5-10; 0.2; 4.6; and 29, respectively. By their mutual comparison, it is generally evident that the values in [27] and Table 1 (this paper) are fairly similar in terms of Cd, V, and Mo, while Se found in PZ 5 greatly exceeds levels previously found at the Raša Bay area. This is probably due to the fact that PZ 5 more realistically (i.e. a lesser dilution factor) reflects the local selenium groundwater hydrogeochemistry. Minimum values (in µg/L) of Se, Cd, V, and Mo (Table 1) were lower than respective levels in [27] reported for the natural spring water Fonte Gaja as follows: 1.1, 0.03, 1.4, and 2.04, respectively. Considering the values of Se (Table 1) along the fact that selenium is highly mobile and potentially bioavailable under oxidative and alkaline conditions, such as the ones at the study locality, this paper warrants further geochemical research of the Raša coal locality.

5. Conclusion

Many scientific publications reported that waters draining from abandoned as well as active coal/metal mines are a major cause of freshwater degradation. Therefore, this paper is summarizing data related to PTE values (Se, Cd, V, and Mo) in the groundwater from the coal fired power plant Plomin, for the purpose of evaluation of the impacts of abandoned Raša coal mines and their ash on the local environment. The Raša coal mining and combustion activities ended more than two decades ago, with a total of 40 million tons of coal excavated. An estimated 4.4 Mt. of Raša coal still remains underground, and its leaching by groundwater contributes to the constant release of PTE contaminants from abandoned mine water discharges. Given the fact that the local karstic environment is highly susceptible to contamination, it is important to determine processes governing the cycling of PTEs, selenium in particular, driven by local hydrogeochemical conditions.

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