Chapter 1
Heavy Metals in the Post-catastrophic Soils

Vesna Stankov Jovanović, Violeta Mitić, Snežana Nikolić Mandić, Marija Ilić, and Strahinja Simonović

1.1 Effect of Accidents Caused by Metal Mining on Heavy Metal Content in Soil

Under normal circumstances and in the geologically short periods, metal mines do not disturb significantly the content of heavy metals into the surrounding soil. However, if for some reason any incident occurs that is caused by meteorological conditions (collapsing tailings dam due to the enormous precipitation and outpouring of nearby rivers in the excavation or tailings) or human error (fault on plants for waste water treatment and mine raw sewage spill), it leads to a significant increase in the content of heavy metals in the surrounding soil and river sediments.

The content of heavy metals around the mine varies depending on atmospheric conditions and geochemical characteristics of the tailings and the surrounding area. Metals/metalloids can be transported into the surrounding soil due atmospheric conditions or erosion of the tailings. The ways of pollution can be air and water (waste water discharged into the river recipients or through groundwater by direct transport). Also, the soil can become contaminated with heavy metals when water from the river, into which mine wastewater is discharged, is used for irrigation. Major threat to the environment is represented by abandoned mines and unsecured tailings.

V.S. Jovanović (✉) • V. Mitić • M. Ilić
Faculty of Science and Mathematics, Department of Chemistry, University of Niš, Visegradska 33, 18 000 Niš, Serbia
e-mail: sjvesna@pmf.ni.ac.rs

S.N. Mandić
Faculty of Chemistry, Universty of Belgrade, Studentski trg14-16, 11 000 Belgrade, Serbia

S. Simonović
Faculty of Science and Mathematics, Department of Chemistry, University of Priština (Kosovska Mitrovica), Ive Lole Ribara 29, 38220 Kosovska Mitrovica, Serbia

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In the case of the active mine Panasqueira in Portugal, where wolframite, cassiterite, and chalcopyrite were exploited, as a by-product of the ore treatment process, the waste products rich in arsenic are produced, which are stored in open reservoirs. Determination of heavy metals in rhizosphere soils collected in S. Francisco de Assis village, downstream of the Barroca Grande tailings deposit, showed a high content of As 223.6, Ba 192.8, Cd 1.3, Co 10.7, Cr 37.8, Cu 163.7, Mn 531.3, Mo 0.6, Ni 24.9, Pb 58.6, Sb 0.6, and Zn 323.2 (average concentrations in ppm), which are in the case of As, Cu, and Mn several times higher than those prescribed by Ontario Soils Quality Guidelines (Candeias et al. 2014).

Nearby the two mines, the northern part of Jequetepeque River Basin, Peru, was investigated for the contents of As 20.55, Cd 3.17, Cu 68.93, Cr 5.50, Hg 0.34, Ni 7.90, Pb 12.33, Sb 1.10, and Zn 70.53 ppm. A comparative study of metal content in the sediments showed that the highest concentrations are present in the points that are closest to the mine in both cases and are substantially higher than in unpolluted areas (Yacoub et al. 2012).

In the vicinity of Dabaoshan Mine (China), research was conducted in order to determine the degree of contamination by heavy metals using the sequential indicator simulation, in order to distinguish between the spatial patterns derived from data on land; adjustment of multiple linear regression models for the intake of heavy metals by crops; and interpretation of land use with the images obtained by remote sensing and integrating spatial pattern, models of input, and land use in the dose–response model for the risk of heavy metals to human health. Areas with higher concentrations of heavy metals in soil are mainly in areas of Dabaoshan Mine in the river basin of Hengshi, Tielong, and Chuandu. Average concentrations of Cu, Zn, Cd, and Pb in the soil from the studied area are above natural background levels in soils. Of the various land uses in the studied areas, agricultural and residential land uses have the greatest health risk, because food intake is the main route of exposure to heavy metals. Spatial patterns of heavy metal concentrations and soil pH indicate that areas with the highest risk for people's health are directly matched with the areas with the highest concentrations of heavy metals but coincide with areas of low pH soils. Pollution with high concentrations of heavy metals is a potential source of risk, but the combination of high concentrations of heavy metals, low pH, and agricultural or residential land use is necessary for the existence of real threats to human health. The spatial distribution risk coefficient indicates that the Cd is the most important pollutant that contributes to human health risks (Zhao et al. 2012).

The central region of Minas Gerais (Brazil) is rich in important mineral reserves; Fe, Mn, Cu, Sb, As, Au, Al, and U are intensively exploited, emitting tons of waste into the air, water, sediment, and soil. A significant amount of these metals and toxic elements penetrate into the soil, groundwater, rivers, and lakes, affecting even distant farm regions by contaminated water and sediments due to the frequent flooding of the river Das Velhas. The contents of Al, As, Au, Ba, Br, Ca, Cl, Co, Cr, Cs, Cu, Fe, Hg, K, La, Mg, Mn, Na, Nd, Rb, Sb, Sc, Sm, Th, and Zn were determined in samples of water, sediment, animal feed, and fish in unpolluted areas, mining areas, and agricultural lands surrounding the river Das Velhas. Farming areas of the Das Velhas river basin, though hundreds of miles away from the mine, at the time of floods, showed the high level of contamination, mainly in the sediments (As 650, Co 15, Cr 260, Cu 60, and Mn 1,030 ppm) (Veado et al. 2006).

In the area which is located in Agra and Guadiamar river valleys and associated with tailings impoundment of mine Aznalcóllar, the samples of soils were analyzed after spill from the pyrite's mine in 1998 (after removing tailings), 1999 (after cleaning very contaminated areas), and 2004 (after plowing the upper soil layers 20–25 cm). It was found that the removal of mineral waste has led to mixed forms of metals distribution, where heavily polluted soils interchanged with less polluted soils. In relation to that in 1998, average pollutant concentrations in the upper soil layers were 918 ppm for Zn, 2.7 ppm for Cd, 156 ppm for As, and 440 ppm for Pb and decreased from 19 to 30 % in 1999 amounting to 675 ppm, 2.1 ppm, 126 ppm, and 305 ppm, respectively, for Zn, Cd, As, and Pb, while they fell in 2004 from 24 to 30 % to 487 ppm, 1.6 ppm, 89 ppm, and 224 ppm, respectively, for Zn, Cd, As, and Pb. Remedial actions did not significantly change the concentration of pollutants in the upper 50 cm of land, but subsequent measures of cleansing in 1999 considerably reduced the concentration of pollutants in heavily polluted areas. Considering the high concentration of pollutants in the fields (especially As), plowing the upper 20–25 cm, despite the decrease in the mean concentration of pollutants in the upper layers, did not significantly reduce the percentage of soils that exceed a concentration of 40 ppm As and nearly doubled the percentage of soils that exceed this concentration at a depth of 10–30 cm. How remediation measures are mainly affecting the upper layers of soil, the concentrations of Zn, Cd, As, and Pb in the deeper layers have hardly changed over the years. Very moving elements Zn and Cd, by their movement through the soil accumulate in the depth, lead to a reduction in the concentration of contaminants in the surface layer (10 cm) and lower percentage of soils that excess the reference concentrations of these elements (900 ppm Zn and 2 ppm Cd), while do not increase the percentage of soils that exceed the concentration at a depth of 10–50 cm (Simóna et al. 2008).

Samples of soil and corresponding vegetation, which originated from Monchegorsk, Northwest Russia, and Naruska, North Finland, were analyzed on heavy metal content (Ag, As, Co, Cs, Fe, Ir, Ni, Rb, Sb, and Sc), since they are located in the vicinity of a Cu–Ni smelter in which emitted species were mostly accumulated in the topsoil. The metal concentrations in soil and vegetation samples waned with distance from the smelter, except Cs and Rb, whose concentrations increase (Haugland et al. 2002).

The total concentrations of heavy metals in the soil in the drainage system of the mine (comprised of the river Atrai, Little Jamuna, Karatoa, Bandai) and surrounding agricultural fields located in Barapukuria (Bangladesh) coal basin and neighboring agricultural fields were investigated. For the irrigation of agricultural fields, the water from the main drainage system of the mine is used, despite that it contains high levels of potentially toxic elements. Average concentrations of Ti, Mn, Zn, Pb, As, Fe, Rb, Sr, Nb, and Zr exceeded the world average values, and in some cases, Mn, Zn, As, and Pb exceeded the limit of toxicity for the given metals. The coefficients of enrichment (EF) of 0.05–1.5 show that metal comes from materials of the earth's crust or natural processes, while EF values greater than 1.5 indicate anthropogenic sources. The soils showed a significant enrichment in Ti, Mn, Zn, Pb, As, Fe, Sr, and Nb, as consequences of mining activities (Zhang and Liu 2002).

The influence and extent of heavy metal contamination of rice fields affected by metal mining activities were examined, involving the soil of rice fields at different depths, rice plants, and irrigation water along six traverse lines in the vicinity of the mine and the surrounding checkpoint. The analysis of 25 elements including Cd, Cu, Pb, and Zn was performed. The concentrations of Cd, Cu, Pb, and Zn in the soil (0.9–1.7 ppm, 16–31 ppm, 25–90 ppm, 188–465 ppm), plants (0.1–0.5, 1.2–5.8, 0.1–0.6, and 19.0–37.0), and water for irrigation (1.0–50.0, 1.0–53.0, 1.0–67.0, 1.0–49,100) in the immediate vicinity of the mine were relatively high due to the leakage of metals from mining waste dumps. Increased concentrations of the metals in all parts of the rice plants are the result of increased metal content in the soil surface (Jung and Thornton 1997).

Watering with water from rivers in which wastewater of the mine is released can significantly increase the amount of heavy metals in soils. That situation is in the area around Dabaoshan Mine in Guangdong province in China, and therefore soil contamination (land with rice fields and garden soil) with heavy metals (Cu, Zn, Pb, and Cd) was investigated, which is located in the immediate vicinity of the mine Dabaoshan, irrigated with water from the river Hengshi and Chuandu, in which waste from the mine was discharged. Concentrations of Cu, Zn, Pb, and Cd in soils with rice fields (502 ppm, 498 ppm, 278 ppm, 3.92 ppm) and garden soil (271 ppm, 349 ppm, 190 ppm, 3.13 ppm) exceed the maximum permitted value of Chinese agricultural fields (50 ppm, 200 ppm, 250 ppm, 0.3 ppm). In addition, content of heavy metals in rice and vegetables from the gardens was investigated. It was found that rice can accumulate unexpectedly high concentrations of Pb and Cd (1.44 and 0.82 ppm), which exceed the maximum allowable limit for grains in China (0.2 ppm) (Zhuang et al. 2009).

In the soils of Les Malines mining district, 40 km from the city of Montpellier (France), the contents of Zn, Pb, and Cd were determined. Sampling was conducted at three sites of Petra Alba mine, which is located at the beginning of Crenze valley upstream from the village of Saint-Laurent-le-Minier; Les Avenieres, 1 km downstream from Saint-Laurent-le-Minier and 3.5 km from the Ganges; and Les Malines Mine, 2.5 km upstream of Saint-Laurent-le-Minier and 6 km from the Ganges. The highest concentration of heavy metals was found in the tailings pond from Les Avenieres (Zn 161,000 ppm, Pb 92,700 ppm, Cd 1,382 ppm) (Escarré et al. 2011).

Tailings from abandoned mines due to the effects of water and/or wind erosion can be an important source of heavy metal pollution, years after the end of economic exploitation of the mine. Results of the analysis of abandoned mine Fedj Lahdoum in Tunisia show that the total concentrations of metals in the accumulation were 10,460 ppm of zinc, 2,100 ppm of lead, and 62.08 ppm of cadmium, while by geochemical analysis of soil obtained, contents of Pb, Zn, and Cd were 3,646 ppm, 3,236 ppm, and 17 ppm, respectively. These high contents registered in the land surpassed both Tunisian and Canadian standards (Babbou-Abdelmalek et al. 2011).

In the soil in the vicinity of the abandoned iron mine of Daduk in Korea, increased contents of Cd, Cu, Pb, and Zn, with average values of 8.57 ppm, 481 ppm, 4,450 ppm, and 753 ppm, respectively, were recorded (Lee et al. 2001).

In the waste material of the abandoned chalcopyrite mine of San Finx in the Galicia (NW Spain), Fe with a total concentration of 4,315–31,578 ppm is the most abundant, then Cu from 273 to 5,241 ppm, Mn from 294 to 2,105 ppm, Zn from 73 to 894 ppm, and Cr from 0.01 to 30 ppm. The concentration of Fe in the bioavailable form ranged from 40 to 1,550 ppm, while Zn is present at least in this form of 2–100 ppm. Copper was the most abundant heavy metal in the exchange complex and in the aqueous extracts, followed by Zn, Mn, and Fe. Cu in exchangeable form ranged between 17.7 and 1,866 ppm, whereas the maximum concentrations of exchangeable Zn, Mn, and Fe did not exceed 140 ppm. The concentration of heavy metals in plants that grow on the studied area was determined, and significant increase in the content of heavy metals in some tested plants was recorded, which contributes to the natural detoxification of contaminated waste materials (Alvarez et al. 2003).

In the areas near the mine and tailings, flood can lead in a large extent to more prominent mobilization of heavy metals and their transfer to agricultural land, enabling in that way their further spreading into the plants, animals, and finally humans.

In Gyongyosoroszi in Hungary, analysis of the content of heavy metals in vegetable gardens to evaluate the effects of floods was performed, since they are located near the abandoned lead and zinc mine. There was a significant increase in the concentration of heavy metals in the flooded vegetable gardens in relation to non-flooded. The greatest differences were registered in the content of cadmium and lead, and concentrations in the flooded vegetable gardens were 0.33–13.6 ppm for cadmium and 29.2–694 ppm for lead. These concentrations of cadmium and lead were 19 and 17 times higher than the non-flooded vegetable garden. However, such a high concentration of heavy metals in the soil did not represent an unacceptable risk to human health because the plants grown in the soil absorb quantities of heavy metals that are not posing a threat. This indicates that the risk of soil contamination is not necessarily an unacceptable risk to human health, and influence of heavy metals greatly depends on human health on the plant barriers (Sipter et al. 2008).

Los Frailes mines in Aznalcóllar are polymetallic deposits of the Iberian pyrite belt. They are generally consisting of pyrite with a small part of sphalerite, chalcopyrite, galenite, arsenopyrite, and some sulfate salts. After the collapse of the embankment dam at the tailings impoundment (1998), which consists mainly of pyrite and other minor parts of sulfide tailings, pond spilled approximately 4,286 ha of alluvial soils in the valleys of the rivers Agrio and Guadiamar. The area is flooded with about 60,00,000 m^3 of barren land that is mainly composed of acidic water, full of traces of metals, metal sulfides, and materials used in the flotation process. Soil analysis of a few selected areas along the river valley Guadiamar after toxic flood and removing deposited sludge showed serious contamination with metals in the surface soil layer. Overall mean concentrations of nine elements

(As, Au, Bi, Cd, Cu, Pb, Sb, Tl, and Zn) of 23 elements analyzed were higher in soil-covered mud (2,878, 0.55, 61.8, 25.1, 1,552, 7,888, 669, 51.6, and 7,096 ppm) than in soils that have not been affected by the floods. The overall mean of these elements in the soil were higher than the upper limit of normal soils worldwide (0.1–40, 0.01–0.02, 0.1–13, 0.01–2, 2–250, 2–300, 0.2–10, 0.1–0.8, 1–900). In all areas that are analyzed, serious heavy metal contamination in the surface layer (0–20 cm) is observed for the most soils (Cabrera et al. 1999).

After a spill of acidic water from the Los Frailes mine in Aznalcóllar (Spain) containing trace elements, metal sulfides, and materials used in the process of refining/flotation, soil analysis before and after remediation (removal of sludge treatment and afforestation) showed a serious contamination of the surface layers by microelements (mostly As, Cd, Cu, Pb, Tl, and Zn). The aim of this study was to determine the influence of tailings spill and remedial measures on the contents of Hg in the soil. The soil was sampled at several locations along the valley of the river Guadiamar. The amount of Hg immediately after the spill (0.512 ppm) was eight times higher than the background (0.061 ppm) on the surface (0–5 cm) and about 3–4 times higher in the deeper layers (0–20 cm, 0172 ppm, and 0–50 cm, 0253 ppm). After the applied measures of rehabilitation (2002), mean values of Hg (0.404 ppm) and other elements (As, Cd, Cu, Pb, and Zn) were still higher than background values and sometimes greater than the value before rehabilitation. This is a consequence of the rest of the sludge on the surface or sludge that is buried in the depths during the remedial measures. The total concentration of trace elements was very changeable, indicating a very irregular distribution of these elements on the surface along the Guadiamar river basin. The highest values of less mobile elements were observed within 5 km from the tailings dam (up to 176 ppm As, 2.36 ppm Hg, and 1,556 ppm Pb) (Cabrera et al. 2008).

The Dawu river that flows through the Dexing copper mine (DCM) and the Jishui river that runs near the Yinshan mine (YLM) (lead and zinc mine) and several smelters, which are located in the basin of the Lean river, flooded a large area. A survey was conducted in order to determine the content of heavy metals (Cd, Ni, Cu, Pb, and Zn) and total sulfur in surficial sediments and neighboring flooded fields, in order to understand the consequences of flooding on heavy metals in soil, sediment quality evolution, and transfer of metals in sediments. Moderate concentrations of metals in tailings from the DCM were Cu (5,957 ppm), Pb (67.7 ppm), Zn (55.9 ppm), Ni (27.9 ppm), and Cd (0.11 ppm). In tailings from YLM, most abundant metals are Zn (1,836 ppm) and Pb (1,604 ppm). The sediments of the Lean river contained mean concentrations of Cu, Pb, Zn, Ni, and Cd of 271.9 ppm, 241.8 ppm, 119.4 ppm, 18.7 ppm, and 0.31 ppm, respectively. In the soil, mean concentrations of Cu, Pb, Zn, Ni, and Cd were 190.2 ppm, 45.5 ppm, 64.4 ppm, 15.4 ppm, 0.08 ppm respectively. At the most upstream and downstream locations, the concentration of metals in sediments is similar to the content of metals in the soil. In places near the Dexing copper mine, flooding brought in the floodplain system clay poor in copper, while in places that are located along the Yinshan lead–zinc mine, suspended solids contained high concentrations of iron and magnesium oxides that absorb large amount of dissolved Cd, Pb, and Zn and are deposited on the floodplain during floods. In spite of the increased production of the Dexing copper mine, there is a significant reduction in the concentration of Cu in the sediment compared to that of 10 years ago. The location in the vicinity of the Yinshan lead–zinc mine contained increased amounts of Pb and Zn in the sediments (Xiao et al. 2011).

The impact of accidental spills and accompanying floods of pyrite fluids and sludge from the flotation facility in Aznalcóllar mine (Spain) on the soil was examined, and the degree of contamination of soil at various depths was studied also, at various depths and over time. The analysis was carried out 15 days and 3 months after the flood. Total metal content was analyzed after aqua regia extraction from six different locations at various distances from the source of spills along the rivers Agrio and Guadiamar. Land affected by flooding is polluted with Zn, Cu, Pb, As, and Cd in different degrees and at various depths. The soil samples that were tested 15 days after a flood showed that level of contamination varies and have elevated concentrations values in comparison to the unpolluted soil—Zn (73.8–986.2 ppm at 300 m from the river Guadiamar, 49.7–4,045 ppm near the dam, 820.4 ppm nearby agricultural fields), Cu (21.3–193.9 ppm at 300 m from the river Guadiamar, 29.4–626.2 ppm near the dam, 154.5 ppm surrounding agricultural fields), Pb (42.3–835.1 ppm at 300 m from the river Guadiamar, 10.2–2,320 ppm near the dam, 104.7 ppm surrounding agricultural fields), As (27.2–452.8 ppm at 300 m from the river Guadiamar, 14.2–1,266 ppm near the dam, 39.1 ppm surrounding agricultural fields), and Cd (0.25–3.71 ppm at 300 m from the river Guadiamar, 0.18–16.35 ppm near the dam, 2.88 ppm surrounding agricultural fields). In soil samples after 3 months of flooding, it can be seen that the degree of contamination is the same or even higher than in the first case (Sierra et al. 2000).

The area around the mine Aznalcóllar was affected by accidental spill of acid water and sludge from pyrite flotation plant. Potentially toxic elements (PTE) were extracted with aqua regia and analyzed by ICP to determine the level of residual contamination at selected spots along the Agrio and Guadiamar river. Analysis was performed 1 year after the removal of the sludge. The analysis showed that the soil is still contaminated with several PTE in various degrees and at different depths. The degree of contamination of soil with Zn, Cu, Pb, and As is high at a depth of up to 30 cm (1,452–1,543 ppm, 222.2–310.3 ppm, 815.9–1,721 ppm, 488.2–720.1 ppm respectively). In deeper layers of soil (up to 300 cm), the degree of contamination is moderate (Sierra et al. 2003).

The zinc content in the bottom sediment mud and the suspended particulate matter along the river Guadalquivir, main tributary of the river Guadiamar, was also determined. The analysis was carried out 1 month after the spill and was recorded a high zinc content, with the mean value of 780.71 ppm in bottom sediment and 996.1 ppm in suspended particulate matter (Palanques et al. 1999).

Heavy rainfall has led to severe erosion and malfunction of the tailings impoundment of Abaroa antimony mines in Bolivia, when about 5,500 m^3 of contaminated waste dump in Rio Chilco–Rio Tupiza drainage system was released. Of primary importance are contaminated floodplain soils that are downstream from the Rio Tupiza, which have been found to contain mean concentrations of metals Pb, Zn, and Sb that exceed Canadian (200 ppm, 400 ppm, 20 ppm), German (500 ppm, 300 ppm, –), and Dutch (530 ppm, 720 ppm, –) regulations for agricultural land use. The sampling spot located 50 m from the river, at different depths, contained the concentration of Pb, Zn, and Sb ranging from 20.7 to 326.2 ppm, 52.6 to 750.7, and 6.3 to 111.3 ppm, respectively (Villarroel et al. 2006).

The contamination of soil with heavy metals (Cd, Cu, Pb, and Zn) in the vicinity of the gold and silver mine in Imcheon, Korea, was investigated. After the closing of the mine in 1978, a large amount of waste, including tailings rested as they were. This material has been spread by surface erosion, wind, and effluents into the deeper soil layers, which are used as rice fields and domestic gardens. Increased concentrations of metals (Cd, Cu, Pb, and Zn) were found in the soil (extracted by 0.1 N HCl), which is located in the center of the tailing (1.35 ppm, 26.4 ppm, 70.3 ppm, and 410 ppm, respectively), still remaining below the allowable limit of concentrations for metals in soil in Korea (30 ppm for Cd, 500 ppm for Cu, and 1,000 ppm for Pb). High concentrations of heavy metals were found in the soil (aqua regia extraction) in the center of the tailing (9.4 ppm, 229 ppm, 6,160 ppm, and 1,640 ppm for Cd, Cu, Pb, and Zn, respectively). As a result of the spreading of metals from this soil, samples from locations around the tailing have a higher metal content (0.8–2.6, 9.8–57.2, 100–225, and 104–465 ppm for Cd, Cu, Pb, and Zn, respectively) compared to the control land (0.8 ppm, 33.4 ppm, 51 ppm, and 108 ppm for Cd, Cu, Pb, and Zn respectively) (Jung 2001).

During January and March 2000, a dam collapse occurred in two tailings in Maramures County, northwestern Romania, which released about 2,00,000 m^3 of contaminated water and about 40,000 t of waste material to the tributaries of the Tisza River, which is a large tributary of the Danube. High concentrations of cyanide and metals, due to these accidents, contaminated and caused poisoning of fish, not only in Romania but also in Hungary, Serbia, and Bulgaria. The research program was conducted in northwestern Romania, to determine the metal content in the rivers affected by the leakage of water and solid tailings caused by the dam collapse, and the values obtained were compared with samples originated from mining and industrial regions, which were not affected by this disaster. In July 2000, from the region affected by these accidents, 65 samples of surface water and river sediments and 45 sediment samples from agricultural areas on the metal content were analyzed. Pb, Zn, Cu, and Cd pollution was drastically reduced downstream from the current active mines and tailings dumps. Concentrations of the heavy metals in river water and sediments on the borders of Hungary and Ukraine are mostly below the legal standards of the European Union, although the contents of Zn, Cu, and Cd in river sediments are approaching or exceeding these limits on Romanian territory. Therefore, there is a necessity for the long-term monitoring of heavy metals in this area, in order to facilitate content, fate, and environmental impacts of heavy metals, released by these accidents (Macklina et al. 2003).

In Chenzhou lead and zinc mine in Hunan province in southern China, the tailings dam collapsed and tailings waste speeded to the agricultural fields in the coastal area of the river Dong. In some places immediately after the accident, emergency cleanup was conducted. Seventeen years later, analysis of heavy metals was carried out in some types of cereals, pulses, and vegetable crops as well as land on which they grow, at four sites in the area of mining, land that is still covered by the flood tailings deposits, and land that was covered by flood tailings coat and later cleaned (which served as control). This study was conducted to comprehend the long-term consequences of spill of large amounts of heavy metals in agricultural crops and the potential risks to human health. The results showed that the physicochemical properties of the agricultural land changed depending upon the application of different processing techniques from various farmers. The effect of leaching and extraction of heavy metals from the some soils were very weak. Some lands were still heavily contaminated with As, Cd, Zn, Pb, and Cu. The concentration of heavy metals was lower in soils, where the cleaning procedure was carried out, although the maximum allowed concentrations of heavy metals by Chinese standards are still very high, especially for As and Cd (followed by Zn, Pb, and Cu), with mean concentrations of 709 and 7.6 ppm, exceeding prescribed amount 24 times for As and 13 times for Cd. Generally, the heavy metal content in all tested plants exceeds the standards for RDA (recommended dietary allowance), which indicates that the crops grown in the vicinity of the mine in Chenzhou, affected by the spill of tailings, are not safe for human health, and it is necessary to apply additional measures for cleaning of As, Cd, Pb, Zn, and Cu to the land (Liu et al. 2005).

1.2 Effect of Floods on Heavy Metal Content in Soil

Due to frequent flooding in the river Niger Delta in Nigeria Ubeji region, the growing contamination of arable soils with heavy metals is registered, especially for mercury, whose concentration in parts of studied area reaches a value up to 14,200 ppm, and iron, whose concentration approximates to 4,300 ppm. Increased content of heavy metals originated from petrochemical companies, from where the floods distribute heavy metals through arable land (Achudume 2007).

The total amount and available forms of metals (Cd, Cr, Cu, Ni, Pb, and Zn) in the fluvial sediments were determined in surface soil samples (0–30 cm), which were collected before (in 2009) and after a flood of the Odra river in western Poland (in 2010). The soil samples after the flood were changed in regard to physicochemical properties, as well as the content of the tested metals. In the samples from 2009, total concentrations of the following metals were determined as follows: Zn (1,270 ppm), Pb (340 ppm), Cu (243 ppm), Ni (96.8 ppm), Cr (83.5 ppm), and Cd (20.2 ppm). After flooding in 2010, these concentrations are increased (with the exception of Ni and Cu), and their amounts were 1,544 ppm of Zn, 404 ppm of Pb, 234 pm for Cu, 80.2 ppm for Ni, 133 ppm of Cr, and 86.7 ppm of Cd, showing a statistically insignificant increase in the total content of Cd, Cr, Cu, and Pb. However, the total concentrations of Cu, Cd, Cr, Pb, and Zn in sediments before and after the flooding exceed the allowable values in Poland. The content of available metal is strongly correlated with the total metal content, and the only significant increase in the concentration was recorded for Cr in available fraction after the flood (Ibragimow et al. 2013).

Apart from the significance of determining the total amount of metals present in the soil, it is also important to determine the forms in which they exist, because their availability depends on the way they are bound, and it can help to better understand the impact on the environment and human health. A study conducted by Khaokaew et al. aimed to determine not only the total amount of metals present in the soil that is periodically flooded (the four periods of flooding were 1, 7, 30, and 150 days) but also the speciation of Cd. Metal content in the analyzed soil was 142 for Cd, 3,050 for Zn, 18,328 for Fe, 34,360 for Ca, 25 for Cu, 878 for Mn, and 5,793 for Mg. For most of the samples, it was found that Cd is less bound to Zn than to Ca and thus is more likely to find Cd and Ca present together in the same mineral phase than Zn and Cd, which are found together along the sediment in the vicinity of zinc mine in Mae Sot district, Tak province, Thailand (Khaokaew et al. 2011).

The prediction of the distribution of heavy metals on the border of solid–liquid for flooded lowland soils is very important. The mechanic geochemical modeling was compared to a statistical approach. In order to characterize heavy metal pollution of land protected by dikes in the Netherlands, 194 soil samples from 133 sites distributed in the Dutch part of the Rhine and Meuse river systems were analyzed. Total amounts of As, Cd, Cr, Cu, Ni, Pb, and Zn in soil samples were determined in soil fraction extracted with 2.5 mM $CaCl_2$. The high correlation in the content of heavy metals and organic matter content was found, which was almost identical for both systems (Schröder et al. 2005).

1.3 Effect of the Hurricanes on Heavy Metal Content in Soil

Hurricanes and tropical storms are formed over warm tropical seas and may be defined as a storm system, with low pressure in the center and stormy weather around it, which causes extremely strong winds and torrential rains. Cyclone denotes a characteristic of the system when the air turns around the center. In different parts of the world, the same phenomenon has different names (hurricane, over the Atlantic; typhoons, over the Pacific Ocean; or cyclone, over the Indian Ocean). Hurricanes besides strong winds and heavy rainfalls cause also high waves, storm, and tornado, threatening primarily coastal areas. The US government appoints each tropical storm over the Atlantic.

In 2005 Catherine hurricane struck New Orleans, inflicting great damage in southeastern Louisiana, where there are 21 oil refineries that have been damaged or completely damaged and it came to spill more than 70,00,000 gallons of oil. The content of heavy metals in the soil after the hurricane in the Greater New Orleans Region was determined. Study results showed significant contamination with As and V whose maximum concentrations were 49.07 ppm and 92.06 ppm respectively. The highest concentration of vanadium was found near the oil refinery, which can be explained by its use in refining industry (Su et al. 2008).

The leaching of pollutants (As, Cd, Cr, Cu, Hg, Pb, and V) from the soil under simulated acid rain conditions was determined in sediments and associated soils in New Orleans and the Louisiana Peninsula. The maximum amounts of leachable metals observed for As and Pb were 293 pg/L and 72 pg/L, respectively. Thus, these levels could potentially pose a health threat, if significant exposure occurred (Adams et al. 2007).

In January 2006, from 75 sites in the New Orleans (LA, USA), area soil and sediment samples were collected and analyzed on metals. The study design was intended to provide a spatial pattern of metal concentrations within the city, following hurricanes Katrina and Rita. Throughout the city, concentrations of Pb and As exceeded the criteria unequivocally. Nineteen percent of all analyzed samples exceeded the soil screening criteria for Pb, while 97 % exceeded the criteria for As. Fifty-seven percent of samples coincided with a previous sampling event in October 2005. Metal concentrations were evaluated for temporal comparisons, and it was found that As concentrations are significantly different over time, but Pb concentrations are not (Abel et al. 2007).

It is expected for urban areas to have elevated concentrations of heavy metals, and New Orleans is no exception. Generally, samples of street mud and suspended sediment and samples from the 17th Street Canal area had higher heavy metals concentrations, in comparison to samples in other media or from other different locations. As a control, mid-lake reference site (MID) served. Some of the samples had elevated concentrations of Ag, Cu, Pb, and Zn, which all of them (except Ag) are elevated in street dust and have vehicular sources. Elevated Ag might originate from wastewater contamination. The bottom-sediment samples, collected near the 17th Street contained elevated levels of trace elements (Cd, Cu, Pb, Zn, and Hg). Levels of analyzed metals varied among the sampling sites in a short time, indicating sediment redistribution by Hurricane Rita. In the case of samples farthest from the coast and most of the lake sediment samples, relatively low heavy metal concentrations were registered. Earlier studies of Lake Pontchartrain revealed similar distributions of heavy metals in the bottom sediments. In the early 1980s decrease in Pb content, within 5–10 km from New Orleans, was recorded. Elevated Cu and Pb values were recorded in bottom sediments from the 17th Street Canal in September 1996 but not in August 1997, characterizing the contamination as temporary. In the same time, elevated Ba, Cu, and Zn off the mouth of the Industrial Canal were also reported. In surface and deeper samples, following Hurricane Rita, most elemental concentrations decreased, indicating that a large amount of sediment deposited by Rita obviously did not come from contaminated sources (Van Metre et al. 2006). After the tsunami in 2004 that hit most of the countries around the Indian Ocean, the analysis of the content of heavy metals in sediments occurring due to the impact of the tsunami in the coastal areas of Thailand was carried out. The most noticeable difference in the concentrations of bioavailable heavy metals between sediments that were affected by the tsunami and the reference sample was recorded for Cd, Cu, Zn, and Pb, especially for Zn and Pb whose maximum concentrations are several times higher in sediments (49.1 ppm and 46.3 ppm for Zn and Pb) in comparison to the reference sample (2.7 ppm for Zn and 1.1 ppm for Pb) (Szczuciński et al. 2005).

And along the southeast coast of India, the content of heavy metals in sediments brought on by the tsunami in 2004 was determined, where an increase in the concentration of some heavy metals was recorded. High concentrations of heavy metals can be explained by the relocation of pollutants of anthropogenic origin. The data also suggested that increased pollution by heavy metals was also controlled by the sediment source (Srinivasalu et al. 2008).

Tsunami does not necessarily cause contamination by heavy metals in soils of stricken regions. The analysis of sediments on Upolu, Samoa, after a South Pacific tsunami as well as sediments in Sendai Plain, Japan, after the Tohoku–Oki tsunami in 2011 revealed that there are no significant changes in the concentrations of heavy metals. This can be explained by the lack of sources of pollution in areas affected by the tsunamis, as well as with the nature of the source from which sediments came (Chagué-Goff et al. 2011).

Large areas of farmland in the Sendai Plain, Japan, were inundated by the 11 March 2011 Tohoku–Oki tsunami and covered by a discontinuous 0.2–30 cm thick sediment layer consisting of sand and/or mud. Two months after the tsunami, numerous rice paddy fields and depressions remained ponded with brackish or saline water. Field analysis in May, August, and October 2011 was performed, with an aim to estimate the environmental impact of the tsunami. Tsunami sediments, underlying soil, and soil beyond the tsunami inundation limit were collected at 43 sites along and near a transect extending over 5 km inland and analyzed for grain size, organic content, water leachable ions, acid leachable metals, and exchangeable metalloids. Anion and cation concentrations in water leachable fraction were elevated in sandy and muddy tsunami deposits and soils, particularly in areas where seawater had stagnated for a longer period of time after the tsunami. Vertical variations were also recorded, with higher concentrations often measured in the surface samples. A similar trend could be observed for some of the metalloids (As) and metals (Zn, Cu, and Ni), although, in general, maximum concentrations of metals and metalloids were not much higher than in soils not inundated by the tsunami and were within background levels for uncontaminated Japanese soils (Chagué-Goff et al. 2012).

1.4 Effect of Volcano Eruptions on Heavy Metal Content in Soil

The soils in Kanagawa prefecture, which had previously been affected by the eruption of Mt. Fuji, was analyzed in order to determine heavy metal content. Mean values of heavy metals in soil were Ni 36.3, Cu 128, Zn 119, Cd 0.59, and Pb 19.8 ppm of dry soil (Okamoto et al. 1997).

The effect of clouds of gas emissions, due to activities of Masaya volcano (Nicaragua) on metal deposition in surrounding soils, was investigated. Preliminary studies showed that rapid deposition of metals occurs in the soils, which are located close to the source, while the metals concentration decreases with distancing from the emission source. Cr and As follow this trend, with maximum concentrations of 20.71 ppm and 7.61 ppm, respectively, near the volcano crater. The concentrations of Mn, Co, Ni, Cu, and Zn (959.30, 21.57, 13.44, 152.85, and 72.73 ppm) were registered at some distance from the crater, indicating that these metals are transferred further. It was also found that the concentrations of Cr, Co, Al, Mn, and Ni increase with increasing depth, while the concentration of Zn decreases. Metal concentrations in control soils were lower than metal concentrations in soils in the vicinity of the volcano, which confirms that volcano smoke contributes to increasing concentrations of metals in the soil (Hinrichs et al. 2011).

Evidence from volcanic plumes and fumarolic sublimates indicates that certain elements are fractionated into the vapor phase during eruption and shallow degassing of magmas. Especially important are high concentrations of metals (As, Sb, Hg, Bi, Cd, Cu, In, Ag, Au, Re, MO, Sn, W, and Pb) in vapor associated with some intermediate-to-silicic systems. Understanding the timing of release and natural fluxes of these elements in volcanic systems is important, both because of their potentially negative impact on human health and because of the significant economic importance of some of these metals. The possible release and redistribution of volatile metals (particularly Pb) during the eruption process and during subsequent post-emplacement degassing, crystallization, and cooling of the Bandelier Tuff (Stimac et al. 1996) were studied.

1.5 Effect of Wildfire on Heavy Metal Content in Soil

Fires are a frequent cause of changes in environmental (soil, air, waters) characteristics and vegetation area coverage and are classified as prescribed (controlled) fires and wildfires. The consequences of fires are mostly estimated by intensity and duration (Certini 2005).

The direct effects of fire on soil characteristics appear to be observable several decades after the accident, and it is very important to monitor changes of soil characteristics, especially concerning heavy metal content (Belanger et al. 2004).

There is limited number of studies dealing with influence of fire on micronutrients fate such as Fe, Mn, Cu, Zn, B, and Mo. In the after-fire area, on the habitat of *P. pinaster*, there was a significant increase in Mn content in the fraction of total and easily reducible fractions, while in the soil exchangeable fraction, Mn content remained the same. It is assumed that the Fe, Cu, and Zn also follow this pattern (Gonzalez et al. 1994).

Fire on the Vidlic Mountain in eastern Serbia, which occurred in summer 2007, lasted for 10 days, and it was caused by human factor. The study was focused on four metals, i.e., Cd, Cu, Pb, and Zn. Intake of metals generally depends both on soil and plants characteristics. It was shown that total heavy metal concentrations in soils after fire were increased for all analyzed metals, except for Cd, which can be explained by its presence in the soil, rather than consequence of fire. For both areas, not affected and affected by wildfire, metal content did not exceed average Earth values for each metal, indicating that both of them are still unpolluted by heavy metals (Stankov Jovanovic et al. 2011).

After the fire that completely destroyed the Brazilian research base in Antarctica, the concentration of potentially toxic elements (Cd, Cr, Cu, Mn, Ni, Pb, V, and Zn) in soil samples that were collected before 2008 and after 2012 fire was examined. The total of 34 samples after the fire at locations within the Comandante Ferraz's ruins around the research station was analyzed. For Ni it was found that its concentration did not differ significantly between the three groups of samples: samples collected before the fire (8 ppm), samples collected after the fire and outside the station (7 ppm), and samples collected after the fire, inside the station (15 ppm). The highest concentrations within the ruins of research base were observed for Cu, Pb, and Zn (34,000, 13,700 and 42,200 ppm), which are 85, 46, and 42 times higher than the values for residential areas proposed by the Brazilian National Environment Council (Guerra et al. 2013).

The municipal landfill of Tagarades which is located about 20 km from Thessaloniki has already suffered from several small fires, but in 2006, large-scale fire occurred, involving about 50,000 t of waste, and more than a week, a thick cloud of smoke covered the area of about 10 km^2 around the landfill. The effect of atmospheric pollution on the concentration of metals in the surrounding soils was investigated. Soil samples were collected at a depth of 0–5 cm from the fields in the vicinity of the landfill and contained similar concentrations of metals and reference soils and soils from other locations, not affected by fire. Surprisingly, the soil of the landfill was particularly enriched by Zn, Cu, Sn, Sb, and Pb (Chrysikou et al. 2008).

To determine the concentrations of heavy metals in the soils from four locations after the wildfire in forest (1986 and 1992) and meadows (2006 and 2008) in Lower Silesia (Poland), soil samples were collected from two sites in the woods and two in the meadows, at different depths. It was found that there is an increase of some heavy metals, mainly in upper layers. Maximal concentrations of Zn, Cu, Pb, Ni, and Cr in the soil of the forest areas were 2.77 g m^{-2}, 1.06 g m^{-2}, 4.82 g m^{-2}, 1.40 g m^{-2}, and 0.40 g m^{-2} and of the meadows area 5.58 g m^{-2}, 3.70 g m^{-2}, 5.34 g m^{-2}, 2.65 g m^{-2}, and 2.24 g m^{-2}, respectively (Bogacz et al. 2011).

The concentrations of Hg in soil after the fire were determined, in samples collected from several locations that have been exposed to fire in CA (USA). Total Hg concentrations in soil samples from the Malibu Creek watershed ranged from 1 to 37 ppb Hg, with a mean concentration of 17 ppb of Hg; in soil samples from the Arroyo Seco watershed (2006 Pines Fire, ASB1-4) ranged from 14 to 349 ppb of Hg, with a mean concentration of 134 ppb of Hg; and in soil samples from the Piru Creek watershed (2006 Day Fire, PCB1-6) ranged from 2 to 44 ppb of Hg, with a mean concentration of 18.5 ppb of Hg (Burke et al. 2010).

Tsagan–Daban crest (Tarbagatayskiy rayon, Republic of Buryatia) in Siberia (Russian federation) was subject to constant fire, and soddy-podbur soil samples were analyzed on heavy metals. It was observed that the fires of intermediate and high intensities result in a considerable increase in the content of chemical elements in the horizon of the siero humic soils which consequently leads to the increase in Zn, Co, Cd, and Pb, while the amount of Cu and Ni is decreased. In the pine forest belt, the content of Pb and Cd in the litter ash is slightly increased. One year after the fire, the total content of Mn, Zn, Cu, Ni, Cr, Pb, and Cd was increased 1.2–2-fold in the upper soil layer, and the total content of Cr and Cd was decreased. Five years after the fire, the content of Mn, Zn, and Cu is still relatively high in the 0–1 cm-deep soil layer (Sosorova et al. 2013).

1.6 Conclusion

Metals can be relatively easily transferred from one area to another by means of water and air, depending on the form in which they are bound in the soil. These processes were studied a lot and allow creation of distribution matrices and transfer models, taking into account known environmental conditions. Processes of metal transfer are becoming more dynamic and more intense in case of catastrophic events, where they can largely deviate from the previously created models and predictions.

The most prominent effect on metal content in soil has, as expected, vicinity of metal mines. This influence may be observed over the possibility of spreading metals from the tailings, where the metal content is uneconomic but is significantly higher than the average presence of metals in the Earth's crust. Unsecured tailings, tailings dam collapse accidents, spills, and floods by water located nearby, as well as the production process either due to outdated and obsolete equipment, or due to human error, cause the mobilization of large amounts of metals and their transfer to broad areas. In general, the content of heavy metals in soil is inversely related to the distance of the source (the mine or tailings), but the factors that can further affect and possibly change this rule, e.g., the nature of the metal, a form in which it is bound in soil as well as the nature of the soil receiver, should also be taken into account.

In flooding areas, where excess of heavy metals is not present (i.e., which are not near the mines, smelters, or industries that produce waste, are burdened with heavy metals) changes in distribution of heavy metals in soil also may be expected, although to a lesser extent than in case of metal mines and smelters, regardless of the fact that floods as a phenomenon are potentially much more represented in almost all regions of the Earth. Also, in the coastal river areas, agricultural lands are generally found, and through the crops, heavy metals can enter the food chain, posing a serious threat to the health of humans and domestic animals. On the other hand, applying measures of flood management, these accidents becoming controllable, and their influence is in most cases reduced to acceptable limits.

Atmospheric phenomena, in particular in the tropic ocean coastal areas, may also cause disturbances in the distribution of heavy metals in soil. Hurricanes and tsunamis are natural disasters that usually can lead to an increase of heavy metals in soil, and the degree of the impact depends on the distance to which the ocean flood wave penetrates into the land, the composition of the local soil, and the existence of potential natural and anthropogenic sources of heavy metals in the endangered area.

The influence of volcanoes on the content of heavy metals in soil is relatively little studied, since there are a small number of active volcanoes in the world. In contrast to the above-discussed disasters, in which the transport of heavy metals predominantly took place through water, in the case of the volcano, the main medium for transport of heavy metals is air, thus enabling very rapid spread of polluting matter and covering much larger surfaces.

Fires, whether caused by natural or human factor, change the distribution of heavy metals in soil, and their effects can be recorded for a long time after the accident. Dominant role in the content of heavy metals after the fire has their representation in the affected area prior to the accidents. In some cases fires may cause a reduction of heavy metals in soil affected by fire, because they are converted during the fire in a water-soluble form, which is transmitted via water flows further to the environment.

All the disasters provoke modified distribution of heavy metals in soil. Whether it will significantly affect the environment and human health depends on their primary presence in a particular area. It is essential knowing their contents, the form in which they are bound in soil and sediments, as well as their nature, and the surrounding soil characteristics as potential receptors in order to be able to control and keep within limits that represent the acceptable risks to the environment and human population.

It has been shown that the measures of remediation of land contaminated with heavy metals as a result of any of the aforementioned catastrophes provide encouraging results in the reduction of heavy metal pollution, although there is an imperative for their further study and improvement in order to protect the land from contamination in the most effective way and preserved as a resource for the future.

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