

Arsenic in the environment: enrichments in the Slovenian soils

Arzen v okolju: vsebnosti v tleh na nekaterih območjih Slovenije

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Abstract

Arsenic, a toxic element with metalloid properties, is found in detectable concentrations in environmental samples. In nature it is enriched in metal (sulphide) ore deposits, mainly as arsenides of Cu, Ni and Fe. Arsenic compounds are used mainly in agriculture and forestry as pesticides and herbicides. The ecosystem can be contaminated with arsenic via both natural and anthropogenic sources. Uses of arsenic contaminated water present so far the greatest health hazard. Occurrences of mining related arsenic problems have also been recorded in many parts of the world.

The impact of mining and metallurgic industry with regard to arsenic contents in soils in some potentially contaminated areas in Slovenia is discussed. Enriched contents of arsenic were found in Mežica. Arsenic correlates very well with lead, zinc and other heavy metals which are enriched as a result of long lasting lead production in the area. Also in Celje and Jesenice arsenic has the same distribution pattern as other anthropogenically introduced pollutants. In Idrija there are some slightly arsenic enriched areas, but there is no correlation with mercury, so the origin of arsenic is not clear yet.

Povzetek

Arzen, strupen element s kovinskimi lastnostmi, je splošno razširjen in prisoten v naravnih materialih v zaznavnih koncentracijah. Najdemo ga predvsem v kovinskih (sulfidnih) rudnih nahajališčih, kjer nastopa najpogosteje kot arzenid Cu, Ni in Fe. Spojine arzena se uporabljajo pretežno v kmetijstvu in gozdarstvu kot pesticidi in herbicidi. Naravni ekosistemi so lahko obremenjeni z arzenom tako zaradi naravnih kot zaradi antropogenih virov. Največjo nevarnost za zdravje predstavlja v današnjem času uporaba z arzenom onesnažene vode. Problemi z arzenom pa se v raznih delih sveta pojavljajo tudi zaradi rudarske dejavnosti.

Obravnavan je vpliv rudarjenja in metalurške industrije na vsebnosti arzena v tleh na nekaterih onesnaženih območjih Slovenije. Povišane vsebnosti arzena so bile ugotovljene v Mežici, kjer kaže arzen zelo dobro korelacijo s svincom, cinkom ter ostalimi težkimi kovinami, ki so na tem območju povišane zaradi dolgotrajne proizvodnje svinca. Tudi v Celju in na Jesenicah so tla obremenjena z arzenom in njegova prostorska porazdelitev se dobro ujema s porazdelitvijo drugih antropogeno vnesenih prvin. Nekoliko povišane vsebnosti arzena so tudi na nekaterih območjih v Idriji, kjer izvor arzena še ni pojasnjen, saj ne kaže povezave z vsebnostmi živega srebra.

Introduction

Arsenic, a naturally occurring chemical element in rocks and soil, is present in trace amounts also in groundwater. Arsenic and its compounds are poisonous. It is one of the most toxic elements that can be found. Inorganic arsenic compounds occur on Earth because of human activities and also naturally in small amounts and can have toxic effects. Humans may be exposed to arsenic through food, water and air. Exposure may also occur through skin contact with soil or water that contains arsenic.

In the present work, natural and anthropogenic sources of arsenic in the environment, its concentrations in rocks, soils and sediments and health problems related to consumption of high arsenic contaminated groundwater in Bengal delta plain are presented. With regard to the world's well known mining related arsenic problems, the situation in mining and some industrial areas in Slovenia is presented.

Arsenic - chemical element

Arsenic is a chemical element in the periodic table that has the symbol **As** and atomic number 33. This is a notorious poisonous metalloid that has three allotropic forms: yellow, black and grey (Adriano, 1986).

Chemically, arsenic is very similar to its predecessor phosphorus, so that it partly substitutes it in biochemical reactions. When heated it rapidly oxidizes to arsenic trioxide, which has a garlic odor. Arsenic and some arsenic compounds can also sublime upon heating, converting directly to a gaseous form. Elemental arsenic is found in two solid forms: yellow and grey/metallic, with specific gravities of 1.97 and 5.73, respectively (<http://en.wikipedia.org/wiki/Arsenic>). The more common oxidation states available to As are -III, 0, III, and IV (Adriano, 1986).

Sources of arsenic in natural environment

Minerals

Arsenic is widely distributed throughout the earth crust. It occurs as a major consti-

tuent in more than 200 minerals including elemental arsenic, arsenides, sulphides, oxides, arsenates, and arsenites (Smedley & Kinniburgh, 2005). Most are ore minerals or their alteration products. Among the most common occurrences in ore zones are arsenopyrite (FeAsS), realgar (AsS), orpiment (As₂S₃), cobalite (CoAsS), niccolite (NiAs), and scorodite (FeAsO₄·2H₂O). Arsenopyrite is probably the most important source of arsenic in ore zones (Nordstrom, 2000 in Smedley & Kinniburgh, 2005). Arsenic is often present in varying concentrations in other rock-forming minerals. As the chemistry of arsenic follows sulphur closely, the greatest concentration tend to occur in sulphide minerals, of which pyrite (FeS₂) is the most abundant. Pyrite is an important component of ore bodies and is also formed in low temperature sedimentary environments under reducing conditions. Such authigenic pyrite plays a very important role in present-day geochemical cycles. It is present in sediments of many rivers, lakes and the oceans as well as in many aquifers.

Rocks, Sediments, and Soils

The occurrence of As in the continental crust is often given as 1.5 - 2 mg/kg (NAS, 1977 in Adriano, 1986). In igneous rocks these contents are generally low (1.5 mg/kg, Ure & Berrow, 1982 in Smedley & Kinniburgh, 2005). Arsenic contents in metamorphic rocks tend to reflect the concentrations in their igneous and sedimentary precursors (average 5 mg/kg). Concentrations in sedimentary rocks are typically in the range of 5-10 mg/kg (Webster, 1999 in Smedley & Kinniburgh, 2005). Average sediments are enriched in arsenic relative to igneous and metamorphic rocks because they contain quantities of minerals with high adsorbed arsenic loads. Arsenic concentrations in coals are often high (0.3 - 35,000 mg/kg), in part because they are closely associated with sulphide minerals (Smedley & Kinniburgh, 2005).

There is often a significant positive correlation between the iron and arsenic in sediments (Smedley & Kinniburgh, 2005).

Concentrations of arsenic in uncontaminated soils are generally in the order of 5-15 mg/kg (Smedley & Kinniburgh, 2005).

The median of soils presented in Geochemical Atlas of Europe is 6.02 mg/kg for subsoils and 7.03 mg/kg for topsoils (Salminen et al., 2005).

Acid sulphate soils from the weathering of pyrite-rich shales in Canada have As concentrations of up to 45 mg/kg (Dudas, 1984 in Smedley & Kinniburgh, 2005).

Mining, smelting of non-ferrous metals and burning of fossil fuels are the major industrial processes that contribute to anthropogenic arsenic contamination of air, water and soil. Historically, the use of arsenic-containing pesticides has left large tracts of agricultural land contaminated. The use of arsenic in the preservation of timber has also led to contamination of the environment (WHO, 2001).

Concentrations of arsenic in sediments and soil contaminated by the products of mining activity, including tailings and effluent, can be orders of magnitude higher than under natural conditions (Smedley & Kinniburgh, 2005).

Naturally elevated levels of arsenic in soils may be associated with geological substrata such as sulphide ores.

Arsenic in groundwaters

Redox potential (Eh) and pH are the most important factors controlling arsenic speciation in aqueous systems. Compared to many other toxic elements, arsenic is relatively mobile at pH values typically found in natural waters (pH 6.5-8.5) and under both oxidizing and reducing conditions. Under natural conditions it is mostly found in inorganic form as trivalent arsenite or as oxyanions of pentavalent arsenate (Smedley & Kinniburgh, 2005).

Arsenic may be found in water which has flown through arsenic-rich rocks. Severe health effects have been observed in populations drinking arsenic-rich water over long periods of time in countries world-wide.

Drinking water from unpolluted sources normally contains only small amounts of arsenic. Drinking water from underground wells can become heavily contaminated in certain areas where the groundwater is in contact with natural arsenic from minerals. Investigations worldwide have revealed a number of aquifers with significant ground-

water arsenic problems (exceeding 50 µg/l). It was found out that geologically young (Quaternary) aquifers are particularly prone to developing and preserving high-arsenic groundwater (Smedley & Kinniburgh, 2005). This can be a serious problem in countries like Bangladesh, West Bengal in India, and Taiwan. In Bangladesh, large numbers of people regularly drink water containing more than 5 times and up to more than 100 times the usual concentration of arsenic. Adverse effects on health, such as skin changes and cancer have been experienced by people living in these regions.

In Bangladesh, West Bengal (India) and some other areas, most drinking-water used to be collected from open dug wells and ponds with little or no arsenic, but with contaminated water transmitting diseases such as diarrhoea, dysentery, typhoid, cholera and hepatitis. Programmes to provide "safe" drinking water over the past 30 years have helped to control these diseases, but in some areas they have had the unexpected side-effect of exposing the population to another health problem - arsenic.

Arsenic in drinking-water in Bangladesh is attracting much attention for a number of reasons. It is a new, unfamiliar problem to the population, including concerned professionals. There are millions of people who may be affected by drinking arsenic-rich water. There is fear for future adverse health effects as a result of water already consumed.

Arsenic occurrences in groundwater of the Bengal delta plain is one of the largest environmental health disasters of the last 20 years, where at least 50 million people are at risk of cancer and other arsenic related diseases due to consumption of high arsenic contaminated groundwater and foods (Patel et al., 2005).

International bodies have previously evaluated arsenic: the World Health Organization (WHO) has set a provisional guideline value of 10 µg/l for arsenic in drinking-water and according to the International Agency for Research on Cancer (IARC) there is enough evidence to conclude that "arsenic and arsenic compounds" can cause cancer in humans (WHO, 2001).

Uses

Lead arsenate has been used as an herbicide on fruit trees and copper arsenate has been recorded (in the 19th century) as a colouring agent in sweets (Adriano, 1986). In the last half century, monosodium methyl arsenate (MSMA), a less toxic organic form of arsenic, has replaced lead arsenate role in agriculture (<http://en.wikipedia.org/wiki/Arsenic>).

The application of most concern is probably that of wood which has been treated with copper arsenate (Adriano, 1986; <http://en.wikipedia.org/wiki/Arsenic>).

In past centuries a number of arsenic compounds have been used as medicines (Adriano, 1986).

Other uses are various agricultural insecticides, pesticides, herbicides and poisons. Gallium arsenide is an important semiconductor material, used in integrated circuits, arsenic trioxide is used in Australia for treating termite infestations in houses and arsenic is used in various alloys, bronzing and pyrotechny (<http://en.wikipedia.org/wiki/Arsenic>).

Effects on human health

Soluble inorganic arsenic is acutely toxic, and ingestion of large doses leads to gastrointestinal symptoms, disturbances of cardiovascular and nervous system functions, and eventually death. In survivors, bone marrow depression, haemolysis, melanosis, polyneuropathy and encephalopathy may be observed (WHO, 2001).

Long-term exposure to arsenic in drinking-water is causally related to increased risks of cancer in the skin, lungs, bladder and kidney, as well as other skin disorders, notably pigmentation changes (melanosis) and keratosis (WHO, 2001).

Even with some negative findings, the overall weight of evidence indicates that arsenic can cause clastogenic damage in different cell types with different end-points in exposed individuals and in cancer patients. For point mutations, the results are largely negative (WHO, 2001).

Conclusions on the causality of the relationship between arsenic exposure and other health effects are less clear-cut. The evi-

dence is strongest for hypertension and cardiovascular disease, suggestive for diabetes and reproductive effects and weak for cerebrovascular disease, long-term neurological effects, and cancer at sites other than lung, bladder, kidney and skin (WHO, 2001).

Sulphide mineralization and mining-related arsenic problems

Arsenic problems have long been recognized in association with zones of ore mineralization as a result of high concentration of arsenic in sulphide minerals (Smedley & Kinniburgh, 2005). Oxidation of sulphide minerals may lead to the release of substantial quantities of arsenic and heavy metals. Many documented cases of mining contamination report very high concentrations of arsenic and other trace elements in soils, stream sediments, and mine tailings (Oyarzun et al., 2004; Razo et al., 2004; Wilson et al., 2004; Reis et al., 2005; Lu & Zhang, 2005; Chatain et al., 2005; Yi et al., 2005; Lengke & Tempel, 2005; Chang et al., 2005; Ahn et al., 2005; Kim et al., 2005). It is expected that arsenic problems exist in many other undocumented areas.

Arsenic enrichments in Slovenian soils

Mining, smelting of non-ferrous metals and burning of fossil fuels are the major industrial processes that contribute to anthropogenic arsenic contamination of air, water and soil. Mining is one of the oldest economic branches in Slovenia; it is more than 2000 years old. This has been proven by findings of mining tools from pre-Roman times. Mining and metallurgy have been continually present in Slovenia since then.

Potential enrichments of arsenic in Slovenia were expected in the areas of sulphide ore mining. Although all metal mines in Slovenia are closed now, we investigated the impact of past mining in the areas around the Mežica lead-zinc mine, Idrija and Podljubelj mercury mines and Litija Pb-Zn-Hg-Ag-Sb mine. Industrial areas like Celje and Jesenice were also examined (Figure 1, Table 1).

Soil was sampled from the surface to a depth of 5 to 10 cm and in some localities also from 20 to 30 cm. One soil sample represents a composite material sampled in five sub-sampling points. The samples were



Figure 1. Studied areas in Slovenia
Slika 1. Raziskana območja v Sloveniji

air-dried and then gently crushed in a ceramic mortar and passed through a sieve with 2 mm openings. Fraction smaller than 2 mm was pulverized before chemical analysis. The analysis of arsenic was performed by inductively coupled plasma mass spectrometry method (ICP-MS) after four-acid digestion (mixture of HClO_4 , HNO_3 , HCl and HF at 200°C).

Quality assurance was carried out by shipment of samples to the laboratory in a random succession to distribute any errors due to laboratory performance. Objectivity was assured through the use of neutral laboratory numbers. Accuracy was estimated by blind determinations of geological standards. Reliability of determinations was assessed as very satisfactory.

In the Mežica area, 300 years of lead and zinc ore mining and smelting had a very negative impact on the environment (Šajn

Table 1. Averages and ranges of arsenic concentrations in soils of studied areas and in Europe
Tabela 1. Mediane in razponi vsebnosti arzena v tleh na raziskanih območjih in v Evropi

| Location | Md | Min | Max |
|---|----|------|-----|
| Europe subsoil (Salminen et al., 2005) | 6 | 0.22 | 593 |
| Europe topsoil (Salminen et al., 2005) | 7 | 0.32 | 282 |
| Slovenia, soil 0-5 cm, n=59 (Šajn, 2003) | 15 | 6 | 37 |
| Slovenia, soil 20-30 cm, n=59, Šajn, unpublished data | 16 | 6 | 41 |
| Slovenia, attic dust, n=59 (Šajn, 2003) | 13 | 4 | 237 |
| Celje-urban area, soil 0-5cm, n=35 (Šajn, 2005) | 22 | 9 | 91 |
| Celje-environs, soil 0-5cm, n=64 (Šajn, 2005) | 14 | 4 | 41 |
| Celje-urban area, attic dust, n=35 (Šajn, 2005) | 63 | 19 | 482 |
| Celje-environs, attic dust, n=64 (Šajn, 2005) | 28 | 6 | 222 |
| Idrija, soil, 0-10cm, n=68, Gosar & Šajn, unpublished data | 19 | 7 | 57 |
| Idrija, attic dust, n=64, Gosar & Šajn, unpublished data | 9 | <2 | 141 |
| Jesenice, topsoil, n=44 (Šajn et al., 1998) | 18 | <4 | 76 |
| Jesenice, bottom soil n=78 (Šajn et al., 1998) | 16 | <4 | 61 |
| Podljubelj, soil 0-5 cm, n=26, Šajn & Gosar, unpublished data | 16 | 8 | 24 |
| Podljubelj, soil 20-30 cm, n=23, Šajn & Gosar, unpublished data | 21 | 15 | 53 |
| Litija, soil 0-5 cm, n=120, Šajn & Gosar, unpublished data | 14 | 5 | 78 |
| Litija, soil 20-30 cm, n=120, Šajn & Gosar, unpublished data | 14 | 7 | 41 |
| Meža valey-upper part, soil 0-5 cm, n=62 (Šajn, 2002) | 16 | 7 | 387 |
| Meža valey-lower part, soil 0-5 cm, n=53 (Šajn, 2002) | 16 | 8 | 45 |
| Meža valey-upper part, attic dust, n=62 (Šajn, 2002) | 34 | 6 | 369 |
| Meža valey-lower part, attic dust, n=53 (Šajn, 2002) | 25 | 9 | 65 |

et al., 2000; Šajn & Gosar, 2004). The area is strongly polluted with lead, zinc, cadmium, molybdenum and also with arsenic. The average content of arsenic in soil is 16

mg/kg (from 7 to 387 mg/kg, Table 1). Spatial distribution of arsenic is presented in Figure 2. The multivariate cluster analysis and R-mode factor analysis (Davis, 1986;

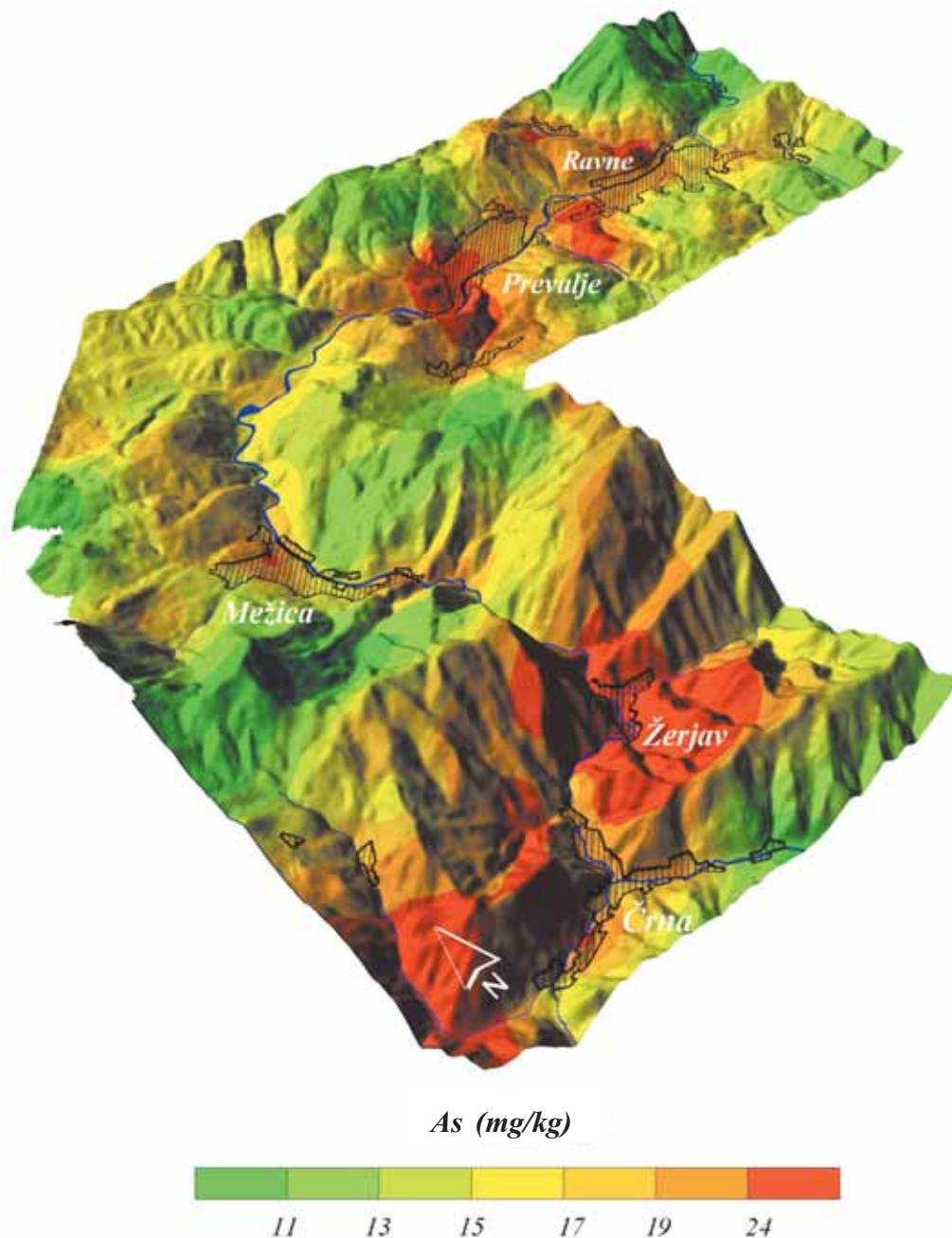


Figure 2. Spatial distribution of As in topsoil (0–5 cm) in Meža valley
Slika 2. Porazdelitev As v tleh (0–5 cm) na območju doline Meže

Reimann et al., 2002) based on 41 determined elements were used to reveal the associations of chemical elements. It was established that the strong association of Pb-Zn-Cd-Mo-As-Ag-S-Sb-Sn is a consequence of long lasting lead production in the area.

In the area of Celje, very high contents of cadmium, zinc, lead and arsenic were determined as a result of zinc and sulphuric acid production in the past (Šajn, 2005). The following association of elements Ag-As-Cd-Cu-Hg-Mo-Pb-S-Sb-Zn is enriched in the narrow town centre passing from the western margin of the urban zone to Štore in the east. The areal distribution patterns of individual elements of this association do not differ much. In Figure 3 the distribution of arsenic is presented. The average arsenic content in the urban area of Celje is 22 mg/kg (from 9 to 91 mg/kg) and in the Celje

environs 14 mg/kg (from 4 to 41 mg/kg, Table 1).

In the area of Jesenice the impact of centuries long lasting ironworks activities in a narrow alpine valley was investigated (Šajn et al., 1998). We identified anthropogenic enrichment of Cd, Cu, Hg, Mn, Pb and Zn in the upper horizon of soil. The average content of arsenic in topsoil is 18 mg/kg (from 4 to 76 mg/kg, table 1). Spatial distribution of arsenic is presented in Figure 4.

In Idrija and its close surroundings, the influences of natural dispersion of mercury combined with half millennium of mining on the environment have been studied. An area of 90 km² around the Idrija mercury mine was investigated (Gosar & Šajn, 2001). Arsenic enrichments were found in some areas. There is no correlation with mercury, so the origin of arsenic is not yet clear. The average arsenic concentration in the re-

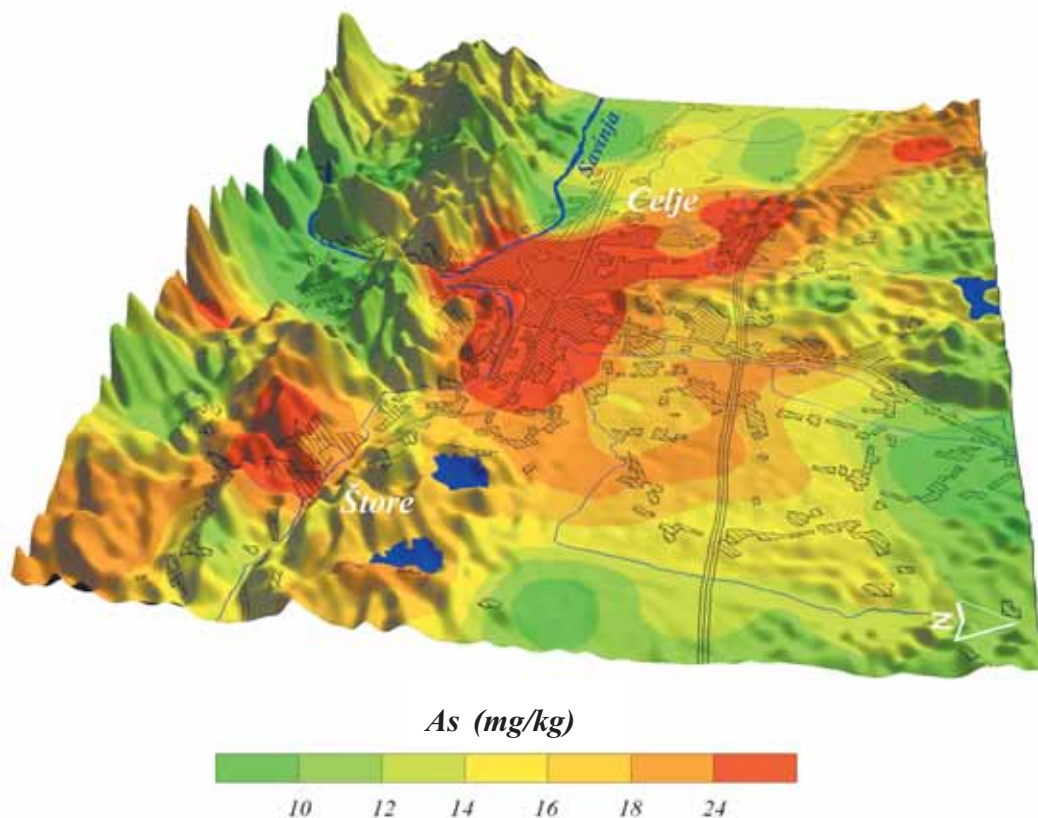


Figure 3. Spatial distribution of As in topsoil (0–5 cm) in Celje area

Slika 3. Porazdelitev As v tleh (0–5 cm) na območju Celja

searched area is 19 mg/kg (from 7 to 57 mg/kg, Table 1).

In the vicinity of the abandoned mercury mine in Podljubelj the soil sampling was conducted in the years 2003–2004. 26 samples of topsoil (0–5 cm) and 23 samples of bottom soil (20–30 cm) were taken in a grid 100 x 100 m in the narrow area of the mine and smelter (88 ha) (Teršič et al., 2005).

Beside the enriched mercury, higher contents of arsenic were found in some locations of the researched area. The average arsenic concentration for topsoil in the area is 16 and for bottom soil 21 mg/kg, maximum in top soil is 24 mg/kg and in bottom soil 53 mg/kg (Table 1) The results of cluster and factor analyses did not show positive correlation with mercury.

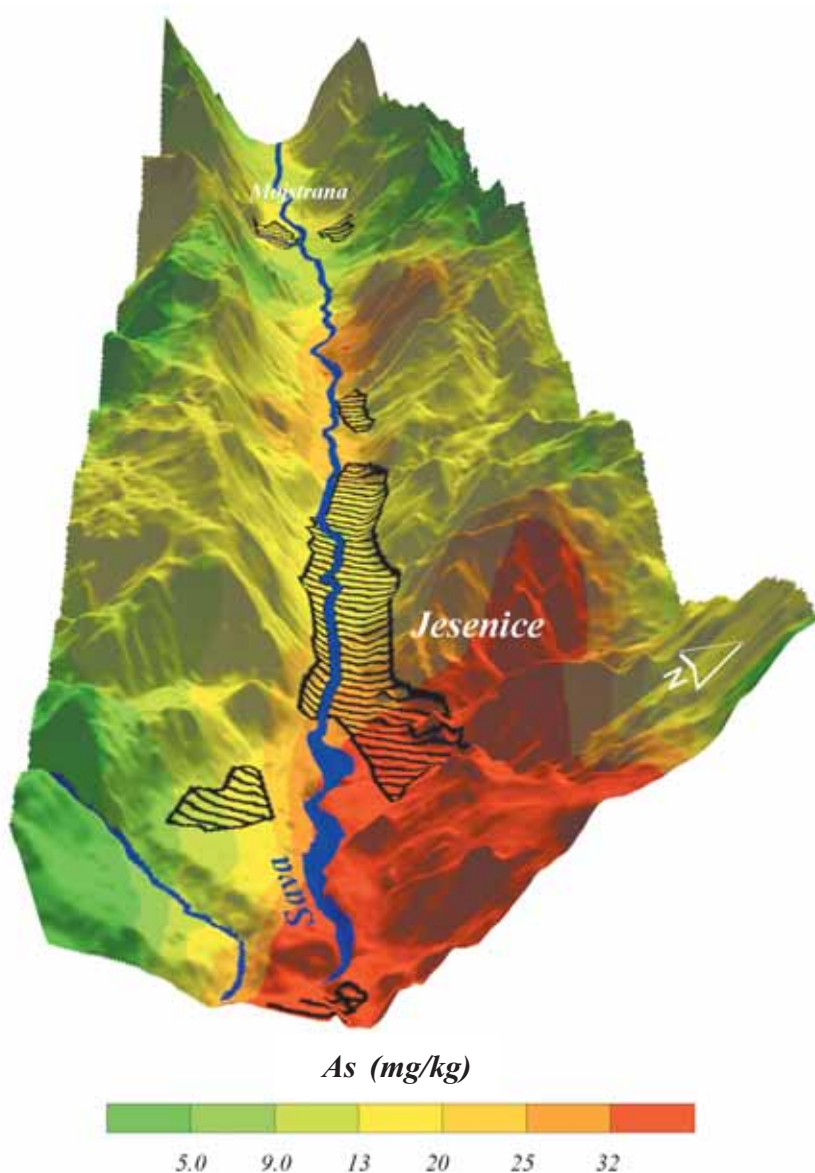


Figure 4. Spatial distribution of As in topsoil in Jesenice area
Slika 4. Porazdelitev As v tleh na območju Jesenic

First results of our ongoing research in the area influenced by the abandoned poly-metallic mine and smelter in Litija show enriched contents of Pb-Zn-Ag-Sb-Hg-Sn-As in the past mining area. Arsenic contents vary from 5 to 78 mg/kg with an average value of 14 mg/kg (Figure 5, Table 1).

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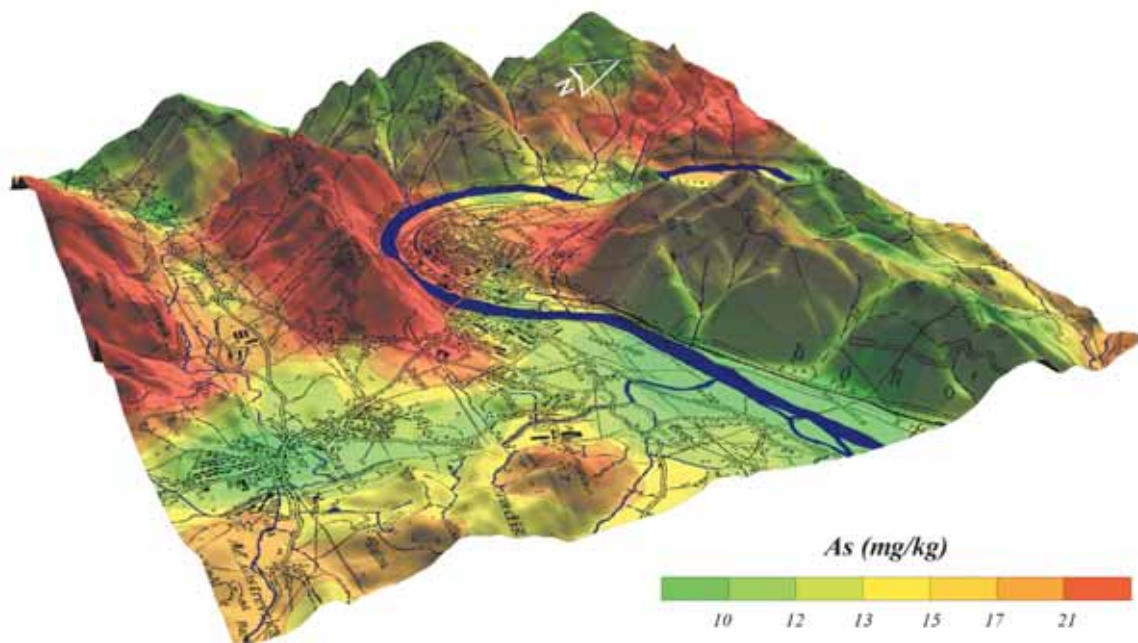


Figure 5. Spatial distribution of As in topsoil (0-5 cm) in Litija area
Slika 5. Porazdelitev As v tleh (0-5 cm) na območju Litije

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