

## **AN OVERVIEW OF ARSENIC POLLUTION OVER FOUR NORTH-EAST COUNTRIES OF EUROPE INFLUENCED BY NATURAL AND ANTHROPOGENIC SOURCES**

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**Abstract.** Arsenic (As) is one of the most important elements found in the environment. It is a toxic metalloid that is responsible for the contamination of soil/sediments and water courses due to various natural and anthropogenic processes. This may lead to adverse effects on human health, therefore it is important to monitor and control. The objective of this paper is to summarize the literature on arsenic anomalies in soil/sediments and water of four North-East European countries; the measurements are reported for Finland, Sweden, Lithuania and Poland. The origin of most of the arsenic pollution is determined to be natural and mostly anthropogenic for these countries. The data reveal that As is present in matrices such as soil, sediments and water. This review highlights that the As concentration in drinking water or soil/sediments of the four countries exceeds the international standard limits. As at higher concentrations are associated with the mining region of Adak in the Västerbotten district of northern Sweden (e.g. groundwater upto 2900 µg/L; sediments upto 900 mg/kg).

**Keywords:** arsenic, sediments, soil, water.

### **Introduction**

People are exposed to different kinds of threats as the quality of our environment is becoming worse over time. Soils are critical environments that are interfaces between air and water. They are inevitably exposed to direct and indirect effects of natural and anthropogenic activities. Higher concentrations of As in the terrestrial environment may be caused both by natural enrichment and anthropogenic pollution. Pollution in soil and water by metals has become widespread and serious due to the non-biodegradable nature and long-biological half-lives of these metals (Radha et al., 1997).

Metals and metalloids, including As, are present in marine, estuarine, and fresh water environments; marine and continental sediments; and rocks and soils at different concentration levels; they are also present in the biota of such environments. As is mainly derived from two sources: (1) natural processes such as weathering, biological activity, and volcanic emissions; and (2) human activities such as mining, industrial processes, smelting of metals,

production of pesticides and wood preservatives, as well as the use of fossil fuels. Relatively high concentrations of naturally occurring As may also be present in some areas as a result of input from geothermal sources (Osuna-Martínez et al., 2021).

As has been widely used as a pesticide (calcium arsenite and copper acetoarsenite-Paris Green) and herbicide (methylarsenic acid and dimethylarsenic acid). It is also used in the pharmaceutical and glass industries, and in the manufacturing of leather preservatives and poisonous baits. Some organic arsenicals, and derivatives, are used as feed additives for poultry and pigs to increase weight gain and to treat and prevent diseases (Osuna-Martínez et al., 2021).

The concentration of heavy metals in soil and their impact upon ecosystems can be influenced by many factors, such as parent material, climate and anthropogenic activities (Facchinelli et al., 2001). Mine tailing, ore processing and other human activities have continuously added to the pool of contaminants in the environment. As is a toxic element among those heavy metals which causes

health hazards when in a high concentration in soil, sediments, water and to some extent, in air (Sarkar & Paul, 2016).

As contaminated groundwater has been reported globally including in Asia, America and Europe (Achene et al., 2010; Pazand & Javanshir, 2013; Parrone et al., 2020). European countries have a considerable amount of data on As concentrations in soil, surface waters and/or groundwaters, often collected by the national Geological Survey organizations (Tarvainen & Hatakka, 2017).

Several investigations carried out in four North-East European countries such as Finland, Sweden, Lithuania and Poland. As pollution has been discovered in the soil/sediments and waters of different parts of these countries. This review aims to focus on As anomalies these four countries and outlines the sources of As contamination in these areas from references.

### Study areas and concentration of As over four North-East European countries

The investigations were divided into four North-East countries of Europe – Finland, Sweden, Lithuania and Poland.

#### Finland

The Tampere region of southern Finland (Figure 1) is severely affected by As contamination. The Tampere region is located approximately 160 km northwest of the capital area of Helsinki, Finland. It covers around 14 500 km<sup>2</sup>, with about 500 000 people living in 22 municipalities. Two European projects RAMAS (Risk Assessment and risk Management procedure for Arsenic in the Tampere region) and ASROCKS (Guidelines for sustainable exploitation of aggregate resources in areas with elevated arsenic concentrations), focused on this region to investigate As anomalies as this area contains more As in bedrock and soil than in other parts of Finland (Parviainen et al., 2015). The Tampere region is divided into two distinct geological units which are given as follows:

- (1) The Tampere Belt (TB) located at the centre, is predominantly composed of turbiditic metasedimentary rocks and felsic-intermediate arc-type metavolcanic rocks, and plutonic intrusions (Parviainen et al., 2015).
- (2) The Pirkanmaa Belt (PB) situated in the south, mainly composed by mafic and ultramafic plutons and granitoids cutting magmatic metasedimentary rocks, containing graphite-bearing

gneiss interlayers found scattered (Parviainen et al., 2015).

In Finland, the groundwater, from drilled bedrock wells, may contain As concentrations higher than 10 µg/L (the European Union quality guideline for As in drinking water). The median As concentrations in the drilled bedrock wells are 5.5 µg/L and 1.6 µg/L in TB and PB respectively. Dug wells contains 0.32 µg/L and 0.22 µg/L, in TB and PB respectively. In case of soil, median As concentrations are 5.9 mg/kg and 12 mg/kg in TB and PB, respectively. The As concentrations in soil and rock samples were preliminarily measured using portable X-ray fluorescence (XRF), and aqua regia soluble arsenic concentrations were analyzed by inductively coupled plasma mass spectrometry and inductively coupled plasma atomic emission spectrometry (ICP-MS/AES) (Parviainen et al., 2015).

#### Sweden

The Adak mine site (Figure 1) of Västerbotten district of northern Sweden which is affected by As and other elements around the tailing piles associated with the Adak mine. The mine tailings at this site were derived from a plant, which processed ores from the Adak mines. Mining ceased in 1975, and the influx of tailings to the ore-processing plant declined.



Figure 1. Study areas of four North-East countries of Europe

Before the site was finally abandoned, the metal-rich tailings (extending over 1500×1000×5 m) were covered

with a 1–2 m thick layer of glacial till to anticipate weathering; however, the airborne degree of the tailings has expanded due to weathering (Bhattacharya et al., 2006).

Investigations at the Adak mine site shows up to 2900 µg/L and 900 mg/kg of As detected in ground water, and sediments, around the site which is far beyond the limit of international standard (Bhattacharya et al., 2006, 2007). Major and trace elements in the water and sediment sample extracts were analyzed on a Varian Vista Pro Ax ICP-OES (Bhattacharya et al., 2007).

### Lithuania

Elevated amount of arsenic was detected in the wellfields of Ražaitėliai and Šienlaukis of Raseiniai district (Figure 1) in Lithuania in 2017. The investigators conducted research on this area in order to find the source of the As pollution in the groundwater. The most frequent prevalence of arsenic anomalies was detected in the Quaternary intermorainic aquifers. In deeper layers, elevated concentrations are rare. The Upper Nemunas–Medininkai aquifer (at a depth of approximately 30–40 m), stands out for arsenic anomalies. Since there are few Palaeozoic faults in the Raseiniai District area, deeper aquifers cannot be the source of arsenic anomalies there. Due to lack of paleozoic fault and as there is no trace of Sulfidic ore, the natural origin of high arsenic concentration is doubtful. The wells with high arsenic concentrations have been installed by different companies at different times. Therefore, the thesis that pollution from incorrect installation of the wells is doubtful too. In order to confirm or reject the hypothesis on high arsenic origin, the LGT organized the groundwater research in the different wells of Raseiniai district in 2018 and investigators did not find any evidence relating to the installation of wells. The anomalies are anthropogenic and related to slow migration of pesticide metabolites to a certain depth (Radienė & Pūtys, 2018).

Median concentrations of As in groundwater are 28.5 µg/L and 39 µg/L in Ražaitėliai and Šienlaukis, respectively which exceed the standard limit for safe potable water (Radienė & Pūtys, 2018). Concentration of As in groundwater analyzed by Atomic mass spectroscopy.

### Poland

High concentration of As identified in Wiśniówka acid mine drainage (AMD) area, south-central Poland (Figure 1). The Wiśniówka study area lies about 5 km

northeast of Kielce, the capital of the Holy Cross Mountains region, Poland. This takes up a massif which is an east-west trending ridge with approximately a 100 m of vertical relief. Land at the site has been owned by different mining companies that have quarried quartzites for more than a century. The Wiśniówka massif consists predominantly of alternating beds of Upper Cambrian (Furongian)-age quartzites, quartzitic sandstones and clayey-silty shales, locally with thin bentonite and tuff layers. These rock series are assigned to the regional lithostratigraphic unit termed informally Wiśniówka Formation. The uniqueness of this site, compared to other regional Cambrian formations, is highlighted by the presence of at least two different pyrite mineralization zones assigned to lowermost and middle Upper Cambrian rock series. The oxidation of the prevailing micro-grained pyrite (gel-pyrite) effectively generates acid mine drainage waters. The water sources of Podwiśniówka and Wiśniówka Duża acid pit lakes, historic tailings pile ponds, and acid seeps/pools occurring at different sites of the mining area showed concentration ranges for As 7.02–22.2 mg/L and 0.006–0.040 mg/L respectively. It is noteworthy that Wiśniówka Duża acid pit lake revealed far lower contents of As due to their localization within bedrock showing a decreased amount of As-rich pyrite. All the samples were analyzed for As using an ICP-QMS; model ELAN DRC II, Perkin Elmer (Migaszewski et al., 2018).

### The sources of As contamination in the investigated areas

Numerous research work has been made in soil sciences, as soils are considered the most important environmental element that act as a sink for trace elements released by human activities. Agrochemicals, especially pesticides, including herbicides, fungicides, insecticides, etc. are widely used in intensive agriculture for the control of weeds, insects and diseases in various crops. The amount of trace elements introduced into the soil vary according to the type of pesticide used (Senesi et al., 1999). Various As containing fertilizers have been used in agricultural lands for better harvest which ultimately responsible for the As contamination is soil. Range of As contents (mg/kg) in investigated fertilizers, limestone fertilizers and pesticides are given in Table 1 and Table 2.

The main anthropogenic sources of contamination of water with As are mining, burning of fossil fuels, use of arsenical fungicides, herbicides and insecticides in agriculture and wood preservatives. Burning of coal has a profound effect on contamination of As in the environment.

Emission of As takes place in the environment by volatilization of  $As_4O_6$  due to burning of coal, which condenses in the flue system and ultimately transferred into water reservoirs (Shankar et al., 2014).

Table 1. Range (first line, minimum or unique value; second line, maximum value) of As contents (mg/kg) of investigated fertilizers (Senesi et al., 1999)

	Principal element	Trace element (As)
Ammonium sulphate	N	4.2 29.0
Ammonium nitrate	N	2.7 119.7
Calcium nitrate	N	2.2 10.1
Urea	N	5.6 33.4
Calcium cyanamide	N	2.2
Super phosphate	P	2.4 28.5
Triple super-phosphate	P	321.5
Potassium sulphate	K	2.4 8.0
Soil, usual range	–	1.0 50.0
Soil, extreme range	–	< 0.1 1000.0

Table 2. Range of contents of As in agricultural limestone and pesticides (Senesi et al., 1999)

Trace element	Limestone (mg/kg)	Pesticides (%)
As	0.1–24.0	0.8–60

Study says that the bedrock is the ultimate source of As in Tampere-Häme region in southern Finland. Weathering and erosion of the bedrock, glacial transport and settling are responsible for the movement of As into the soil. As a consequence, the groundwater of Finland is affected by the lithological source. Moreover, according to RAMAS (Risk Assessment and risk Management procedure for Arsenic in the Tampere region) project, the anthropogenic sources of contamination in target areas such as plants using CCA (chromated copper arsenate) impregnation, old landfills, wood preservation and shooting ranges. Naturally occurring As in bedrock and soil may also cause the mobilization of As during rock aggregate production and construction activities, potentially impacting on groundwater aquifers, surface waters, and biota (Pärviainen et al., 2015).

Investigation in Adak mine site, which is an extension of the Skellefteå ore deposit located at Västerbotten district of Sweden said that the Adak is a Cu–Zn–Pb–Au–Ag sulfide deposit intercalated with basic volcanic, and redeposited volcano-clastic rocks. The massive sulfidic ore bodies (volcanic-hosted) are composed of pyrite, sphalerite, arsenopyrite, chalcopyrite, and pyrrhotite (Bhattacharya et al., 2006). Anthropogenic activities such as mining and ore processing in northern Sweden have resulted in more than 600 000 tons of As in mine tailings exposed to weathering. Weathering of mine tailings have resulted in high As concentrations in water and sediment samples around the Adak mine (Bhattacharya et al., 2007).

During investigation in Raseiniai district, Lithuania, it has been assumed that deep aquifers cannot be the reason for arsenic anomalies there. Moreover, the sulfidic ore has not been found in Lithuania, and there is no evidence of Palaeozoic faults in the Raseiniai District area. Therefore, the natural origin of high arsenic concentration is doubtful. The increase of arsenic concentrations also can be related to the various industrial and agricultural pollutants: medicines, dyes, supplements, pesticides, insecticides, etc. However, usage of pesticides has been quite widespread for some time (Radienė & Pūtyš, 2018).

The basic source of metalloid in AMD (acid mine drainage) water bodies is micro-grained pyrite that forms two different mineralized zones within the Upper Cambrian rock formation. Due to specific textural and geochemical characteristics, these minerals undergo rapid oxidation on exposed quarry walls and unvegetated tailings piles, thus contributing to elevated arsenic concentrations in acid pit lakes and ponds, and locally intermittent pools (Migaszewski et al., 2018).

## Conclusions

Arsenic is already an identified problem in many countries and is likely to cause problems in many others, although not yet recognized. This is due to the abundance of arsenic in geologic materials and its relatively common use in industry and agriculture. Presently, the industrial use of arsenic is restricted in many countries, but the historical consumption has left behind sites that require remediation. Since the soil is interlinked with air and water in such a way that it regulates their quality. In the case of larger contaminated areas, such as historical mining areas, risk assessment and management should be based on larger drainage areas (Ruskeeniemi et al., 2011).

It is noted that, except Sweden the studies in Finland, Lithuania and Poland were performed with total or elemental As analysis; thus, it is necessary to perform future studies determining the As speciation in order to evaluate the most toxic forms of this element. This will also be important to predict As mobility since As(III) and As(V) differ in the specific physico-chemical and hydrogeological settings of polluted waters.

1. This review study provides insight into the distribution of arsenic over four north east European countries regarding accomplished researches. The natural and anthropogenic sources of As in soil and water of four different locations of four aforementioned countries are highlighted. The areas with elevated or high arsenic concentrations in bedrock, soil and groundwater were mentioned properly.

2. Extremely high concentrations of As were found in As mining and processing areas (Karczewska & Krysiak, 2007). There is a possible visual connection between highly polluted areas and anthropogenic factors, although other factors like some other factors such as pH, SI (saturation index), TDS (total dissolved solids), EC (electric conductivity) and depth of sampling wells may play important roles in the mobility and presence of arsenic that should be taken into account (Hamidian et al., 2019).

The government and local authorities must pay special attention to limit the human activities that leads to As pollution in soil and water. The social awareness of the population is equally important in maintaining and choosing methods to mitigate As pollution. However, even for well-aware populations, there is sometimes a dilemma regarding prohibitive costs versus the wish to improve their situation.

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## TARŠOS ARSENU IŠ NATŪRALIŲ IR ANTROPOGENINIŲ ŠALTINIŲ KETURIOSE ŠIAURĖS RYTŲ EUROPOS ŠALYSE APŽVALGA

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Santrauka

Arsenas (As) – vienas svarbiausių elementų, randamų aplinkoje. Tai toksiškas metalas. Jis teršia dirvožemį / nuosėdas ir vandenį iš įvairių natūralių ir antropogeninių šaltinių, o tai daro neigiamą poveikį žmonių sveikatai ir ekosistamai. Dėl to kyla būtinybė stebėti ir kontroliuoti šį elementą aplinkoje. Šio straipsnio tikslas – apibendrinti literatūros šaltinius apie fiksuojamas arseno anomalijas keturių šiaurės rytų Europos šalių dirvožemyje, nuosėdose ir vandenyje. Pateikti matavimai, atlikti Suomijoje, Švedijoje, Lietuvoje ir Lenkijoje. Arseno natūralioje gamtoje yra aptinkama, tačiau analizuojamose šalyse daugiausia jo susidaro iš antropogeninių taršos šaltinių. Duomenys rodo, kad As aptinkama dirvožemyje, nuosėdose ir vandenyje. Šiame apžvalginiame straipsnyje aptariama keturių minėtų šalių As koncentracija geriamajame vandenyje, dirvožemyje, nuosėdose, viršijanti tarptautinius standartinius apribojimus. Didesnės koncentracijos yra susijusios su Adako kasyklomis, esančiomis Västerbotten rajone, Švedijos šiaurėje (pvz., požeminiame vandenyje – iki 2900 µg/l; nuosėdose – iki 900 mg/kg).

**Reikšminiai žodžiai:** arsenas, nuosėdos, dirvožemis, vanduo.