

Many faces of arsenic

by

Barbara Radke*, Grażyna Dembska,
Grażyna Pazikowska-Sapota,
Katarzyna Galer-Tatarowicz

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*Department of Environmental Protection,
Maritime Institute in Gdańsk,
Długi Targ 41/42 St., 80-830 Gdańsk,
Poland*

Abstract

Arsenic (As) is a natural component of the Earth's crust. Due to its specific properties, arsenic became e.g. the favorite poison in the 19th century in Europe, a component of an effective insecticide and herbicide in agriculture, a specific chemical weapon during World War II and a medication used to treat various diseases. The bad reputation of this element was confirmed after World War II, when arsenic-based chemical weapons were dumped on the seabed and became a potential threat to the marine ecosystem. The wide distribution of arsenic compounds in the environment necessitated the development of technologies aimed at removing arsenic from the aquatic ecosystem. This study provides a detailed overview of the occurrence, distribution and transformation of arsenic species in the aquatic environment.

Key words: arsenic species, aquatic environment, toxicity, removal technology, chemical weapon

* Corresponding author: bradke@im.gda.pl

Introduction

Arsenic (As) is a natural component of the Earth's crust. This element may be released into the environment from both natural (e.g. volcanic activity, biomethylation and microbial reduction) and anthropogenic (e.g. coal-fired power generation, smelting and vegetation burning) sources (Litynska et al. 2017).

Arsenic compounds were well-recognized in ancient time (Subramanian et al. 2002; Akhtar et al. 2017). The controversial history of arsenic began in the 19th century, when As was a preferred poison used by homicidal practitioners (Frith 2013). The bad reputation of arsenic increased even more when the toxic properties of this element were used to develop chemical weapons during World War I and World War II. Despite its bad reputation, this element was also employed in therapeutic treatments (Izdebska et al. 2008; Akhtar et al. 2017). Later on, arsenic proved to be useful in the production of pesticides and insecticides sold to farmers and fruit growers. The majority of arsenic-based pesticides has now been banned. However, approximately 75% of the total arsenic consumption is still used in the agriculture in the form of monosodium methylarsonate (MSMA), disodium methylarsonate (DSMA), dimethylarsinic acid (cacodylic acid) and arsenic acid (Subramanian et al. 2002). This means that arsenic still affects millions of people through contaminated groundwater and drinking water.

This study presents a summary of the current state of knowledge about the production and use of arsenic in basic branches of industry, agriculture and medicine. We have focused in particular on the occurrence and distribution of arsenic compounds in individual components of the aquatic ecosystem. We have also made an effort to present the latest information on arsenic chemical weapons dumped in the Baltic Sea. Some attention is also paid to the toxicity of arsenic compounds. Additionally, this paper presents some aspects of the technology for arsenic removal from the water and soil/sediments.

Application of arsenic and its compounds

The word "arsenic" evokes a reaction of fear in most people. This is because arsenic has a long history of being a potential threat to humans (Hughes et al. 2011). Nevertheless, the history of the world is associated with the development of technology, in which arsenic played a particularly important role. Some aspects of

the usage of arsenic compounds in the history of the world are presented in Table 1.

Poison

For centuries, arsenic has gained a negative reputation as "the poison of kings" or "king of poisons" because it is colorless, odorless, tasteless and difficult to detect even after death (Antman 2000; Frith 2013; Akhtar et al. 2017). The first medical reports on the effects of arsenicals were written by Hippocrates (460–357 BC), Aristotle (384–322 BC) and Pliny the Elder (23–79 AD). One of the earliest documented cases of arsenic poisoning was that of Britannicus who was poisoned by the psychopathic murderer, emperor Nero, to secure his Roman throne in 55 AD (Nriagu 2002). Later, Rodrigo Borgia better known as Pope Alexander VI (1492–1503) and his son, Caesar Borgia, became truly legendary in the history of the world when they assassinated a number of wealthy cardinals and accrued in this way a great fortune (Frith 2013). The next infamous poisoner was Catherine Deshayes (1640–1680), who was sentenced to death by a judicial commission (established by Louis XIV) for the murder of more than 2000 infant victims (Klimczak 2016). Famous victims of arsenic poisoning are King George III of Great Britain and the American explorer Charles Francis Hall. Even Napoleon was rumored to have died of arsenic poisoning on St. Helena Island, although the debate is contentious and continues to this day (Antman 2001; Klimczak 2016).

Arsenic was the favorite poison in the 19th century France and Great Britain, becoming part of the social and political life. Until 1851, there were no legal restrictions on the sale of arsenic (Bartrip 1992; Frith 2013). Nearly everyone could buy and sell any poison including arsenic, which was also readily available and very cheap. The official statistics in the United Kingdom (1839–1849) indicate that 239 people were tried for murder or attempted murder by poison (Bartrip 1992). Fortunately, the popularity of arsenic poisoning rapidly decreased in 1830, since the development of a chemical test for detecting arsenic in human tissues by the British chemist James Marsh (Magdalan 2007).

Medicine

Arsenic has been used in medicine as a therapeutic agent. Ancient Indians, Greeks, Romans, Arabs and Chinese employed arsenic in their medicinal treatments for more than 2400 years (Akhtar et al. 2017). Hippocrates used arsenic sulfides, realgar and orpiment to treat ulcers, while Dioscorides used

Table 1

Selected information on the use of arsenic compounds in human history (Bartrip 1992; Antman 2001; Hughes et al. 2011; Frith 2013; Radke et al. 2014; Wu et al. 2016; Akhtar et al. 2017; Beldowski et al. 2018)

Age/year	Application/Use
B.C.	The first application of arsenic compounds in ancient times for the therapeutic treatment as well as in combat (by Chinese, Egyptian, Indian, Rome)
406–357 B.C.	Hippocrates presented the first medical reports on arsenic
384–322 B.C.	Aristotle published a report on negative effects of arsenic
82 B.C.	Consul Lucius Cornelius Sulla issued the Lex Cornelia outlawing arsenic poisoning
A.D.	The first in the history documented cases of arsenic poisoning involving Britannicus, Caesar Claudius
55 A.D.	A documented report stating Britannicus' death by arsenic poisoning (by the psychopathic murderer, emperor Nero, to secure his Roman throne)
23-79 A.D.	First medical reports (by Pliny the Elder) in AD
1250 A.D.	The official date of discovery (by Albertus Magnus) of arsenic
8th	Jabir ibn Hayyan invented white arsenic
15th	William Withering performed pharmacological experiments using arsenic
1492–1503	The Borgia pope (Alexander VI) murdered numerous cardinals by arsenic compounds
17th–19th	An increase in the popularity of arsenical poisons (the apogee was reached in the 19th century)
1640–1680	Catherine Deshayes was sentenced to death for murdering (using arsenic) more than 2 000 infant victims
17th	Teofania di Admo developed Aqua Tofana (one of the most famous arsenic poisons in world history)
18–19th	Development of pigments based on As (Scheele's Green, King's yellow, Paris, or emerald green) for wallpapers
1786	Dr. Thomas Fowler invented arsenic solution for medical treatment
1820	The documented case of the murder of King George III of Great Britain
1836	The first test to detect arsenic in human body, developed by British chemist James Marsh
1845	Invention and application of Fowler's solution for the treatment of leukemia
1881	Preparation (by LaCoste) of the first modern arsenical chemical weapon (called Dick)
1871	American explorer Charles Francis Hall became a victim of arsenic poisoning
1880	Pharmacological texts promoted arsenic compounds for treating skin and breast cancers
1910	The use of organoarsenic compounds in the treatment of pellagra, malaria and sleeping sickness
1913–1939	Synthesis and development of chemical weapons, including arsenic compounds: Adamsite, Lewisite, Clark I and Clark II
1940	Worldwide production of arsenic trioxide chromated copper arsenate (CCA)
1942	The U.S. Government established a limit standard for arsenic in drinking water at 50 $\mu\text{g l}^{-1}$
1970	Application of arsenic trioxide (As_2O_3) for the treatment of acute promyelocytic leukemia; major production of arsenic chemical agents for wood protection
1975	EPA ¹ adopted a standard for arsenic in drinking water at 50 $\mu\text{g l}^{-1}$
1993	WHO ² recommends drinking water standard of 10 $\mu\text{g l}^{-1}$
1995	Dimethylarsinic acid, a tumor promoter in four rat organs
2000	U.S. FDA ³ approves arsenic trioxide for leukemia chemotherapy
2001	EPA lowers the U.S. arsenic drinking water standard to 10 $\mu\text{g l}^{-1}$
2002	Arsenic (+3 oxidation state) methyltransferase isolated in rat liver cytosol
Present	Application of As in veterinary and occasionally in human medicine; the use of organoarsenicals in the production of pesticides, herbicides and insecticides; production of an arsenic by-product from smelting of copper, lead, cobalt, and gold ores; replacement of CCA by alternative reagents; a chemical weapons destruction program

¹EPA – Environmental Protection Agency; ²WHO – World Health Organization; ³FDA, U.S. – Food and Drug Administration

orpiment as a depilatory agent. In Latin culture, the first pharmacological experiment was initiated in the 15th century by William Withering, who became a strong proponent of arsenic-based therapies. In 1786, Fowler's solution (As_2O_3 in potassium bicarbonate solution; 1% wt/vol.) was discovered and later used for treating various diseases, including malaria, syphilis, asthma, chorea, eczema and psoriasis (Antman 2001). Since the 1880s, pharmacological texts have described

the use of arsenical pastes and arsenous acid, the former for treating skin and breast cancers, and the latter for the treatment of hypertension, bleeding gastric ulcers, heartburn, chronic rheumatism and promyelocytic leukemia (APL) (Antman 2001; Akhtar et al. 2017). In the 1990s, scientists from China presented the results of clinical studies on the use of trioxide arsenic (ATO) in the treatment of acute promyelocytic leukemia and myelodysplastic syndromes (Akhtar et

al. 2017). As a result, ATO has become a more effective treatment of APL than other, newer medications and has less severe adverse reactions and greater safety.

Research aimed at locating tumors using arsenic-74, a positron emitter, has recently been reported. Arsenic trioxide has demonstrated efficacy and safety in patients with first and subsequent relapses or refractory promyelocytic leukemia (APL), regardless of the disease-free interval. The research results showed the complete remission in 87% of patients, and molecular remission in 83% (Douer et al. 2003). Clinical trials are currently underway, using arsenic-based medicines for the treatment of hematopoietic and lymphocytic proliferative diseases, not only as monotherapy, but also in combination with other compounds, including retinoic acid, ascorbic acid, and GM-CSF – a growth factor (Izdebska et al. 2008; Wu et al. 2016).

Industry

Arsenic is obtained as a by-product of the smelting of copper, lead, cobalt, and gold ores (Brininstool 2017; Li et al. 2018). In 2016, the world's leading producers exported the following approximate amounts of arsenic compounds (in metric tons): 25 000 to China, 7000 to Morocco, 1500 to Russia, 1000 to Belgium, 50 to Bolivia and 45 to Japan. This means that the estimated global production of As was 36 500 metric tons (t) (Brininstool 2017). Currently, China and Morocco are the world's leading producers of arsenic trioxide, accounting for 87% of the estimated world production. In China, in addition to reclaiming arsenic as a by-product of nonferrous smelting, arsenic is recovered as a by-product of gold mining from orpiment (As_2S_3) and realgar (AsS), which are more common ore minerals of arsenic. In 2010, the price of arsenic reached \$3.20 per kg (Walker 2010). The price is expected to rise in the future. This means that arsenic production is still a profitable business.

Since the 1970s, the demand for arsenic has been growing, mainly in response to its increased use in the grids of lead-acid batteries. In 1974, the price peaked at nearly \$2.00 per pound (Brooks 2013). However, its major production (about 70% of the global arsenic production) was intended for the preparation of arsenical pesticides. As a result, organic arsenical pesticides such as: monosodium methane arsenate (MSMA) – $HAsO_3CH_3Na$, disodium methane arsenate (DSMA) – $Na_2AsO_3CH_3$, dimethylarsinic acid (cacodylic acid) – $(CH_3)_2AsO_2H$, arsenic acid – H_3AsO_4 have been released into the marine environment and some of them are transported, modified or even absorbed on sediments/organic matter (Panagiotaras

& Nikolopoulos 2015). These organic compounds are resistant to environmental degradation through chemical, biological and photolytic processes. Moreover, due to their persistence and ability to accumulate in living organisms, they constitute a dangerous group of chemical waste (ATSDR 2007).

Currently, the most recognized arsenical pesticide is chromated copper arsenate (CCA). This compound was widely used for many years as a wood preservative. However, exposure to arsenic leached from CCA-treated wood caused the serious health problems. In 2003, CCA was replaced in industrial applications by new alternative wood preservatives, including alkaline copper quaternary, ammoniacal copper quaternary, ammoniacal copper zinc arsenate, copper azole and copper citrate (Brininstool 2017). Presently, the production of some arsenic agents is prohibited or strictly limited; the range of restrictions depends on the requirements of a given country and the usage of arsenic compounds for domestic consumption.

Chemical weapon

Arsenic warfare agents (CWA) belong mostly to the arseno-organic group and are characterized by high affinity for the sulfhydryl groups and high toxicity (Firth 2013). The CWA irritate the mucous membranes of the eyes, nose and throat. They cause tearing, coughing, sneezing, pain in lungs and breathing difficulties.

The following popular warfare agents based on arsenic compounds exist: Clark I (diphenylchloroarsine), Clark II (diphenylcyanoarsine), Adamite (diphenylaminechloroarsine), Lewisite (Dichloro (2-chlorovinyl)-arsane) and Dick (ethylchloroarsine) (Radke et al. 2014; Bełdowski et al. 2016a). The first modern arsenic-based chemical agent, i.e. Dick, was invented in 1881 by LaCoste. In 1918, two organic arsenical compounds, Lewisite and Adamsite, vesicant and respiratory irritant agents, were developed by the U.S. Army (Firth 2013). Clark I and Clark II were developed in German laboratories in 1917.

Although arsenic-based agents were produced on a large scale, generally they have never been used much in combat. The Chemical Weapons Convention (CWC) on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on their Destruction was established on 29 April 1997. The Convention has been ratified by 192 countries (Arms Control Association 2018). The global campaign of chemical weapons destruction is still in process.

At present, arsenic-based munitions dumped on the seabed is a serious problem. Shortly before

the end of War World II (WWII), the Nazis started the process of dumping weapons on the seafloor, mostly in the southern part of the Baltic Sea. Based on the agreement signed in Potsdam on 17 July 1945, the Allies continued the dumping of stockpiles collected during WWII. Consequently, dangerous conventional as well as unconventional weapons were dumped on the seafloor at 300 dumpsites all over the world, including the Atlantic, the Pacific and the Indian Ocean, the east and west Canadian and U.S. coasts, the Gulf of Mexico, the coasts of Australia, New Zealand, India, the Philippines, Japan, Great Britain and Ireland, as well as the Caribbean Sea, the Black Sea, the Red Sea, the Baltic, the Mediterranean and the North Sea (Radke et al. 2014; Beldowski et al. 2018). The issue of corroded chemical munitions on the seabed has attracted public attention and appears not to be completely resolved.

Occurrence of arsenic in aquatic environment

Transformation of arsenic in water and sediment

The water system is enriched with arsenic from anthropogenic (e.g. runoff contamination) as well as natural sources (e.g. geological contribution). The transport and partitioning of arsenic in water depend on its chemical form as well as interactions with other materials present. All soluble forms move with water and can be transported over long distances via rivers. However, arsenic can also be adsorbed from water onto sediments and soils, particularly clay, iron oxides, aluminum hydroxides, manganese compounds and organic material (ATSDR 2007).

The form in which this element exists in the marine ecosystem depends on biotic and abiotic processes, where pH values and redox potential play an essential role. Arsenic in the water system (i.e. freshwater, groundwater and seawater) is mainly represented by two inorganic species, i.e. arsenite – As(III) and arsenate – As(V). Inorganic As(V) is a predominant form under oxic conditions and dominates over arsenite As(III). As a result, the ratio of As(V) to As(III) ranges from 10 to 100 $\mu\text{g l}^{-1}$. At pH values of 7.5–8.2, arsenate is an anion and occurs as HAsO_4^{-2} and $\text{H}_2\text{AsO}_4^{-}$, while arsenite is present as a neutral species (H_3AsO_3) (ATSDR 2007; Flora 2015). Under reducing conditions at pH below 9.2, the uncharged arsenite species H_3AsO_3^0 (Smedley & Kinniburgh 2002) predominates, but when pH exceeds the value of 12, the form of HAsO_3^{2-} occurs in water. As reported by Li et al. (2018), the percentage contribution of As(III) reduced from As(V) can reach > 80% of total

As(III) in most hypoxic zones. This applies in particular to seawater from the seabed of the Baltic Sea, the Black Sea and the Changjiang Estuary.

The oxidation of As(III) by O_2 is a long and slow process. The organic species (i.e. monomethylarsonic acid MMA and dimethylarsinic acid DMA) naturally occur in seawater, however, they are presented at lower concentration levels (Panagiotaras & Nikolopoulos 2015). In seasonally anoxic estuarine water, variations in the relative proportions of As(III) and As(V) can be large. In marine and estuarine waters, organic forms are usually less abundant, but are often detected and depend on temperature and variations in aquatic biota (Flora 2015).

As(V) predominates also in aerobic sediment, while As(III) dominates in anaerobic conditions. Arsenic(III) partitions into the aqueous phase in anoxic environments. Unlike As(III), As(V) usually remains bound to minerals, such as ferrihydrite and alumina, which reduces its mobility and bioavailability (ATSDR 2007). Clay minerals (kaolinite, montmorillonite and illite) have greater affinities for As(V) than As(III) (Panagiotaras & Nikolopoulos 2015).

At the maximum range of adsorption (from 5.5 to 7.5), a higher adsorption occurs for As(V) than As(III), because the positively charged particle edges have more propensity for adsorbing H_3AsO_4^0 ($\text{pK}_1 = 2.20$) and H_2AsO_4^- ($\text{pK}_2 = 6.97$) than H_3AsO_3^0 ($\text{pK}_1 = 9.22$) (Lin & Puls 2000). However, illite shows slightly greater adsorption of As(III) compared to kaolinite. At $\text{pH} < 9$, goethite hydroxide and iron hydroxide have higher adsorptive capacity for arsenite compared to arsenate. Moreover, carbonate species (e.g. bicarbonates) present in the aqueous environment may affect some sorption processes and lead to a decrease in arsenic adsorption onto clay minerals (Lenoble et al. 2002). Furthermore, arsenic in sediments can be released back into the water through chemical and biological interconversions of arsenic species. In this way, arsenic in the marine environment becomes again available for living organisms. Therefore, it should be considered as a potential threat.

Concentrations of arsenic in the aquatic ecosystem

Due to the fact that arsenic occurs in over 200 minerals, arsenic-rich minerals can be one of the main natural sources of this element in the marine environment. Other natural sources responsible for the release of arsenic into the marine environment include: volcanic eruption, rock erosion and forest fires (Smedley & Kinniburgh 2002; Flora 2015; Li et al. 2018).

Air is one of the main media for chemical and biological reactions, transport and circulation through

soil to the marine environment. The concentration of As measured in remote or rural areas ranges from 0.02 to 4 ng m⁻³, whereas in urban areas varies from 3 to 200 ng m⁻³ (Chappell et al. 2001; Panagiotaras & Nikolopoulos 2015). Higher concentrations (> 1000 ng m⁻³) occur in the vicinity of industrial sources (WHO 2011).

Arsenic concentrations in uncontaminated soil are generally in the range of 0.1 to 40 µg g⁻¹. However, higher levels, i.e. 100–2500 µg g⁻¹, were observed in the vicinity of copper smelters and in soil contaminated with pesticides (WHO 2000; Litynska et al. 2017).

Ocean water contains arsenic at a concentration level up to 2 µg l⁻¹, while open seawater – from 1 to 3 µg l⁻¹ (Panagiotaras & Nikolopoulos 2015). However, in the case of a semi-closed area such as the Baltic Sea, the arsenic concentrations may depend on the distance from a shore, the location of point sources of pollution, atmospheric distribution and specific activities at sea (e.g. shipping, dredging, dumping). For example, Truus et al. (2007) reported total arsenic concentrations between < 0.1 and 1.75 µg l⁻¹ in seawater samples from the highly industrial area of Tallin (Estonia). Values between 0.49 and 1.10 µg l⁻¹ of As(V) + As(III) were found in samples collected from the region between Kiel Bight and the northern Gotland Sea, where hypoxia in deep water contributed to the increase in As(III) concentrations. Furthermore, the near-bottom seawater from the chemical weapon dumpsite in the Bornholm Basin contained about 1.04 µg l⁻¹ of As(V) + As(III) (Li et al. 2018). Another report from the Bornholm chemical weapon dumpsite showed that the total concentration of As was between 0.55 (off the dumping site) and 0.76 (the central part of the dumping site) (µg l⁻¹) (Khalikov & Savin 2011).

More variable conditions occur in marine estuaries, where the level of As is assessed at less than 4 µg l⁻¹. This is due to varying river inputs, changes in salinity and redox gradients or some anthropogenic discharges from terrestrial sources (Smedley & Kinniburgh 2002; Flora 2015). However, the concentration of arsenic in the estuarine water can be even higher (from 12.7 to 17.0 mg l⁻¹), when it is strongly affected by soil enriched with acid sulfate (AS). This applies in particular to water samples from the estuary of the Vörå River (Nystrand et al. 2016). The lower concentration of As (between < 2 and 4.9 µg l⁻¹) was found in water samples from the estuary of the Tinto River (southern part of Spain), though this region is highly polluted with acid lixiviates from old sulfide mines (Hierro et al. 2014). In the Mahanadi estuary (India), As (8.0 µg l⁻¹) comes from both natural and anthropogenic sources. In addition, arsenic was

partially removed from water in the mixing zone (Mandal et al. 2016). In water of the Taehwa River estuary (South Korea), As was found mainly near urban and industrial areas and it occurred primarily in the As(V) form (94 µg l⁻¹) (Hong et al. 2016) (Table 2).

Panagiotaras & Nikolopoulos (2015) reported that the concentration below 10 µg l⁻¹ is mainly addressed towards natural waters of rivers and lakes. However, several studies addressing natural and anthropogenic sources have shown higher levels of arsenic (µg l⁻¹) in freshwater, e.g. up to 20.0 (Po River, Italy), 13.31–41.53 (Karnaphuli River, Bangladesh), 26.70–68.30 (Carmo River, Brazil), 35–157 (Manchar Lake, Pakistan), 58–413 (Chasicó Lake, Argentina) (Arain et al. 2009; Chetia et al. 2011; Varejão et al. 2011; Marchina et al. 2015; Ali et al. 2016; Puntoriero et al. 2014) (Table 3). These levels often exceed the tolerance limits for drinkable water defined by the European Council Directive (Council Directive 98/83/EC 1998) and by the World Health Organization as well as the Environmental Protection Agency (10 µg l⁻¹) (U.S. EPA 2002; WHO 2011). Considering that symptoms of arsenic poisoning may occur at the ppb (µg l⁻¹) level (Panagiotaras & Nikolopoulos 2015), the presented concentrations may be dangerous for terrestrial and aquatic organisms. Fortunately, there are still some places where arsenic is at the background level (< 1.0 µg l⁻¹, e.g. Red and Anllóns rivers) or close to the limit established by WHO (< 10 µg l⁻¹, e.g. Caohai and Waihai lakes) (McArthur et al. 2012; Wei & Zhang 2012; Pietro et al. 2016).

The highest arsenic concentrations are found mainly in natural hydrothermal systems (from 900 to 3560 µg l⁻¹) (Ning 2002; Litynska et al. 2017) and in samples from the most contaminated areas of the world, including West Bengal, Bangladesh, Taiwan, Mexico, Chile and India (from 100 to more than 4700 µg l⁻¹) (Saint-Jacques et al. 2014; Litynska et al. 2017).

Examples of As concentrations in sediment samples from different parts of the world are presented in Table 2. In this case, arsenic concentrations reported for rivers, lakes and seas range from 0.004 to 342 µg g⁻¹ d.w. (Table 2). According to ATSDR (2007), the concentration below 10 µg As g⁻¹ d.w. is considered as a standard background level, whereas higher values can be attributed to anthropogenic activities such as fertilization, application of pesticides, industrial pollution, tanning and copper smelters (Ali et al. 2016). However, the occurrence of some natural rocks and minerals may also contribute to an increase in the arsenic content in sediments. The best example is authigenic pyrite, which appears in sediments of many rivers, lakes and oceans. As reported by Litynska et al. (2017), the content of arsenic in rocks of contemporary or recent volcanic activity can be up to

Table 2

Total arsenic concentration values in environmental samples from selected worldwide localities

Country	Area	Concentration	Units	References
Water				
Spain	Tinto River estuary	< 2.00–4.90	$\mu\text{g l}^{-1}$	Hierro et al. 2014
Finland	Vörå River estuary	12.10–17.00	mg l^{-1}	Nystrand et al. 2016
India	Mahanadi estuary	8.0 ± 3.7	$\mu\text{g l}^{-1}$	Mandal et al. 2016
South Korea	Taehwa estuary	2.3 (AsIII), 94 (AsV)	$\mu\text{g l}^{-1}$	Hong et al. 2016
France	Gironde estuary	5.3	$\mu\text{g l}^{-1}$	Deycard et al. 2014
Italy (Alps – Adriatic Sea)	Po River	n.d.–20.0	$\mu\text{g l}^{-1}$	Marchina et al. 2015
Bangladesh	Karnaphuli River	13.31–41.53	$\mu\text{g l}^{-1}$	Ali et al. 2016
Vietnam	Red River Basin	< 1.00	$\mu\text{g l}^{-1}$	McArthur et al. 2012
Brazil	Carmo River	36.70–68.30	$\mu\text{g l}^{-1}$	Varejão et al. 2011
Poland	Wieprza River	< 2.00	$\mu\text{g l}^{-1}$	Bojanowska et al. 2010
India	Ganga–Brahmaputra river system	up to 128	$\mu\text{g l}^{-1}$	Chetia et al. 2011
Spain	Anllóns River	0.98	$\mu\text{g l}^{-1}$	Pietro et al. 2016
China	Caohai Lake	9.45 \pm 1.93 surface 9.84 \pm 2.37 bottom	$\mu\text{g l}^{-1}$	Wei & Zhang 2012
China	Waihai Lake	6.68 \pm 1.72 surface 6.72 \pm 1.64 bottom	$\mu\text{g l}^{-1}$	Wei & Zhang 2012
Argentina	Chasicó Lake	0.195–0.315 (wet period) 0.058–0.413 (dry period)	mg l^{-1}	Puntoriero et al. 2014
Pakistan	Manchar Lake	35–157	$\mu\text{g l}^{-1}$	Arain et al. 2009
Baltic Sea	Coastal waters around Tallin Kakumäe region	< 0.1–1.75 2.12 \pm 0.03	$\mu\text{g l}^{-1}$	Truus et al. 2007
Baltic Sea	Arkona Basin	0.05–0.19 (As(III)) 0.49–1.10 (As(III) + As(V))	$\mu\text{g l}^{-1}$	Li et al. 2018
Baltic Sea	Bornholm Basin	< 0.001–0.28 (As(III)) 0.58–1.04 As(III) + As(V))	$\mu\text{g l}^{-1}$	Li et al. 2018
Baltic Sea	Eastern Gotland Basin	< 0.001–0.54 (As(III)) 0.52–1.10 As(III) + As(V))	$\mu\text{g l}^{-1}$	Li et al. 2018
Baltic Sea	Western Gotland Basin	0.02–0.61 (As(III)) 0.49–0.99 As(III) + As(V))	$\mu\text{g l}^{-1}$	Li et al. 2018
Baltic Sea*	Bornholm	0.59 ^A 0.76 ^B 0.63 ^C 0.55 ^D	$\mu\text{g l}^{-1}$	Khalikov & Savin 2011
Sediments				
Bangladesh	Karnaphuli River	11.56–35.48	$\mu\text{g g}^{-1}$ d.w.	Ali et al. 2016
China	Yangtze estuary	7.86 \pm 2.63	$\mu\text{g g}^{-1}$	Han et al. 2017
Spain	Anllóns River	106	$\mu\text{g g}^{-1}$	Pietro et al. 2016
India	Mahanadi estuary	2.1	$\mu\text{g g}^{-1}$	Mandal et al. 2016
Slovenia	Valenjsko Lake	9.69 \pm 3.68	$\mu\text{g g}^{-1}$ d.w.	Petkovšek et al. 2011
Slovenia	Družmirsko Lake	8.12 \pm 2.55	$\mu\text{g g}^{-1}$ d.w.	Petkovšek et al. 2011
Slovenia	Škalsko Lake	7.51 \pm 2.30	$\mu\text{g g}^{-1}$ d.w.	Petkovšek et al. 2011
Baltic Sea	Bothnian Sea	167–216	$\mu\text{g g}^{-1}$	Uścinowicz 2011
Baltic Sea	Gdańsk Deep	15.5	$\mu\text{g g}^{-1}$	Bełdowski et al. 2016a
Baltic Sea	Gulf of Gdańsk	9.8	$\mu\text{g g}^{-1}$	Bełdowski et al. 2016a
Baltic Sea	Lithuanian EEZ	6.2	$\mu\text{g g}^{-1}$	Bełdowski et al. 2016a
Baltic Sea	Gulf of Finland (Estonia)	15.80–27.70	$\mu\text{g g}^{-1}$ d.w.	Vallius 2014
Baltic Sea*	Bornholm Deep	17.0	$\mu\text{g g}^{-1}$	Bełdowski et al. 2016a
Baltic Sea*	Gotland Deep	13.3	$\mu\text{g g}^{-1}$	Bełdowski et al. 2016a
Baltic Sea	Southern Baltic Sea	< 5–29	$\mu\text{g g}^{-1}$	Uścinowicz 2011
Tunisia	Mediterranean Sea	13.11–36.00	$\mu\text{g g}^{-1}$ d.w.	Zohra & Habib 2016
Croatia	West Istria Sea	8.12–23.44	$\mu\text{g g}^{-1}$ d.w.	Duran et al. 2015
Iran	Southern Caspian Sea	8–17	$\mu\text{g g}^{-1}$ d.w.	Bastami et al. 2015

* – area of dumped chemical munitions; A – sampling area: the southern part of the circle; B – sampling area: the central part of the circle; C – sampling area: circular area of dumped chemical weapon; D – sampling area: the area beyond the circle

20 $\mu\text{g g}^{-1}$. During diagenesis or autogenesis processes, the concentration of arsenic in sedimentary rocks may reach 60 $\mu\text{g As g}^{-1}$. According to the current research on stream sediments from Europe, the concentration of arsenic ranges from 1 to 241 $\mu\text{g g}^{-1}$. The distribution of As in sediments from Northern Europe (Norway, Finland, southern Sweden, north-west Scotland, northern Poland and the Baltic States) and from south and south-east Spain shows a low total value of As, i.e. $< 4.0 \mu\text{g g}^{-1}$, while higher values ($> 11.0 \mu\text{g g}^{-1}$) occur in the Skellefte mineralized belt in northern Sweden, Portugal and western Spain, the eastern Pyrenees, a zone from the Massif Central to southern Brittany in France, most of England, Wales, Northern Ireland and northern Bohemia and point anomalies in southern Hungary, south-eastern Switzerland and south-eastern Spain. The most enriched stream sediment sample occurs in Brittany, with 241 $\mu\text{g g}^{-1}$ of As and 1.7% of S. This was associated with the major shear zone of known mineralization (high content of Sn, Li, Sb and Cs), indicating a leucogranitic hydrothermal change. A similar pattern was found for floodplain sediments collected from the same regions. However, the values were slightly different, i.e. total As was between < 1 and 390 $\mu\text{g g}^{-1}$, while low values were $< 3.0 \mu\text{g g}^{-1}$, and high values of As were $> 13.0 \mu\text{g g}^{-1}$ (Salminen 2005).

Finally, it is worth mentioning the sediment affected by substances originating from chemical weapons. Recently, this problem has been again investigated by researchers, which additionally has provided new information. For example, Emelyanov (2007) studied sediment samples from the Gotland Basin (a potential region of dumped chemical weapons). Surprisingly, he found no chemical munitions there. The high content of arsenic (77 $\mu\text{g g}^{-1}$) resulted from a natural (diagenetic) process and the presence of iron sulfides.

The potential leakage of arsenical chemical weapons was also examined by Beldowski et al. (2016a). Sediment samples from the Gulf of Gdansk and the Słupsk Furrow, as well as from Gotland and Bornholm dumpsites contained arsenic in the range of 0.3 to 23 $\mu\text{g As g}^{-1}$ (mean values of arsenic from dumping sites: 13.0 $\mu\text{g g}^{-1}$ – Gotland Deep, 17.0 – Bornholm Deep $\mu\text{g g}^{-1}$). Only some samples from the Bornholm Deep contained arsenic derived from chemical weapons. However, the elevated concentrations of mercury (Hg) (130–135 ng g^{-1}) were found in three samples from the Gotland dumpsite area. Moreover, four samples from the Gdansk Deep, which contained elevated concentrations of Hg, showed some influence on CWA. Elevated levels of zinc were found in approximately 115 sediment samples (179 in total), though only 17 samples contained

detectable amounts of CWA. Degradation products of CWA are widespread in sediments from the Bornholm Deep area and some places of the Gotland Deep and the Gdansk Deep. Furthermore, the obtained results suggest that munitions containing CWAs are more scattered on the seafloor than previously suspected. Beldowski et al. (2016a) concluded that there is still some leakage of CWA around dumpsites. Therefore, it is recommended that the environment close to chemical and conventional weapons should be further investigated.

Toxicity of arsenic to aquatic organisms

Arsenic is highly toxic to living organisms (Flora 2015; Akhtar et al. 2017; Li et al. 2018). The toxicity of arsenic depends on the dose, the time of exposure, the route of penetration into the body and As forms penetrating the organisms. In general, the inorganic As forms proved to be more toxic than its organic species. As reported by Panagiotaras & Nikolopoulos (2015), typical arsenic residues in marine organisms range from 1 $\mu\text{g g}^{-1}$ to about 100 $\mu\text{g g}^{-1}$. This means that aquatic organisms can be exposed to arsenic from contaminated water and/or sediments. These organisms accumulate, store and transform arsenic species inside their body. As a result, arsenic can be biomagnified within the aquatic food web (Khan et al. 2014). Due to this fact, a value of 25 $\mu\text{g l}^{-1}$ was proposed to establish Environmental Quality Standards (EQS) for the protection of all marine organisms (expressed as annual average dissolved concentration). It is currently being adopted in UK legislation (HMSO 1989; UKMPA 2001).

Phytoplankton in the aquatic environment may be exposed to acute and chronic arsenic poisoning (Table 3). The ability of marine phytoplankton to accumulate high concentrations of inorganic arsenicals is a well-recognized phenomenon (Eisler 1988). Moreover, phytoplankton, along with some bacteria, is responsible for arsenic cycling in the marine ecosystem. On the other hand, phytoplankton and bacteria may reduce the toxic effects of arsenic. This phenomenon takes place during the process of methylation, when harmful inorganic arsenic compounds are converted enzymatically to less toxic forms (i.e. MMAs and DMAs) (Wurl et al. 2015). The scheme of the transformation process is presented below (Singh et al. 2007; Jaishankar et al. 2014):

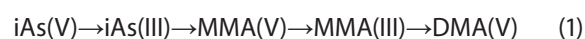


Table 3

Selected symptoms of arsenic poisoning (Das et al. 1980; Sanders 1986; Eisler 1988; Gomez-Camirero et al. 2001; UKMPA 2001; Kumari et al. 2016)

Living organisms	Standard measure of toxicity	Poisoning symptoms
Fish	LC50 varies from 5.5 to 91 mg As l ⁻¹ and depends on individual species. Chronic poisoning may occur at 1 µg l ⁻¹	Acute exposure: It may cause behavioral and hematological changes, lethal effects, internal damage of organs (liver and kidney, gills, gonads, brain), skin problem, shock, breathing problem, decrease in orientation. Chronic poisoning triggers problems with reproduction and development of young fish, changes in enzymes and DNA structure, death, permanent degradation of the gastrointestinal tract and circulatory system.
Marine mammals, seabirds and sea turtles	Symptoms occur within a few hours and deaths within 1 to 6 days. Death or malformations have been documented after single oral doses of 2.5 to 33 mg As kg ⁻¹ body weight, chronic doses of 1 to 10 mg As kg ⁻¹ body weight, and at dietary levels > 5 and < 50 mg As kg ⁻¹ diet.	Acute exposure creates gastroenteritis, shock, breathing problems, decrease in orientation, degenerative changes in liver, and kidney, gills, gonads and brain, muscular incoordination, debility, slowness, jerkiness, hyperactivity, drooping eyelid, huddled position, unkempt appearance, loss of righting reflex, immobility, seizures, loss of hearing, dermatitis, blindness Chronic poisoning is responsible for effects on reproduction, changes in the immune system, destruction of enzymes (e.g. glutathione-S-transferase), changes in cellular detoxification, receptor damage, cancer, chromosomal damage, birth defects, death
Bottom organisms (e.g. mussels, snails, cephalopods)	48 h LC/EC50 values range from 0.68 to 73.5 mg l ⁻¹ for trivalent arsenic and from 3.6 to 49.6 mg As l ⁻¹ for pentavalent arsenic.	Acute exposure: It can cause dermal effects, decrease in orientation, lethal effects and destruction of organs Chronic poisoning causes mutations, population decline, increase in mortality
Zooplankton (e.g. rotifers, copepods and cladocerans, diatoms)	Concentration of 4 mg As(III) l ⁻¹ reduction in population. 48 h EC50 is 326 µg l ⁻¹ (<i>E. affinis</i>), No significant survivals among copepods when exposed to < 4 and 10 mg As(V) l ⁻¹	Acute exposure: lethal effects, shock, degradation Chronic poisoning: Population decline (4 mg As l ⁻¹), reduction in the number of young individuals, intraspecific mutations, increased mortality, reduced immunity
Phytoplankton (e.g. algae, blue-green algae)	EC50 from 0.007 to > 2.0 mg l ⁻¹ . EQS was established at 25 µg l ⁻¹ . Low value (< 7 µg l ⁻¹) is suggested for particular sensitive species	Acute exposure is associated with dermal effects, population decline, lethal effects Chronic poisoning is responsible for inhibition of the growth as well as blocking of phosphate uptake, inhibition of cell multiplication (at 3.5 mg As(V) l ⁻¹), change in species composition, population decline and increase in mortality

LC50 – Lethal concentration 50. The standard measure of toxicity of a certain medium (water, air etc.) that may kill 50% of the test animals during the observation period;

EC50 – Median effective concentration. It is a concentration of a test substance, which results in 50% reduction in certain species;

EQS – Environmental Quality Standards. It is a concentration level below which the ecological functions and the environmental safety level remain unchanged

This biomethylation is a detoxification process. The end products of the reaction are removed from the body of living organisms (e.g. excreted through urine). However, MMA(III) is not excreted and remains inside the cell as an intermediate product. MMA(III), an intermediate product, is found to be highly toxic compared to other arsenicals, potentially accountable

for arsenic-induced carcinogenesis (Singh et al. 2007; Jaishankar et al. 2014).

Algae belong to this sensitive group of marine living organisms that can be highly exposed to arsenic pollution. Algae, especially macroalgae, show high accumulation rates and affinity for metals. Furthermore, they are also considered to be important

producers in seawater. In general, there are some data suggesting that the arsenic concentration varied depending on algae classes: red macroalgae may accumulate the highest concentration of arsenic (4.3–24.7 $\mu\text{g g}^{-1}$ d.w.), followed by blue green algae (10.4–18.4 $\mu\text{g g}^{-1}$ d.w.) and green macroalgae (8.0–11.0 $\mu\text{g g}^{-1}$ d.w.) (Thomson et al. 2007; Khan et al. 2014). Although the EQS of 25 $\mu\text{g l}^{-1}$ was adopted to protect all saltwater life in seawater (HMSO 1989; UKMPA 2001), nonetheless Smith & Edwards (1992) suggested reducing the established value for some sensitive algal species ($< 7 \mu\text{g l}^{-1}$). This was due to the significant inhibition of the growth of the alga *Fucus vesiculosus*. However, the data were considered insufficiently reliable to influence the EQS. Moreover, further research performed by Grimwood & Dixon (1997) showed no significant evidence for higher sensitivity of saltwater organisms. As a result, they recommended the use of EQS of 25 $\mu\text{g l}^{-1}$ as an appropriate value for the protection of all saltwater life.

Bottom marine organisms (e.g. mollusks: mussels, snails, cephalopods) may accumulate arsenic from contaminated sediments. Moreover, they can be more sensitive than vertebrates. According to Canadian interim marine sediment quality guidelines, arsenic bound by sediment can pose a hazard to bottom organisms at concentrations above 7.24 $\mu\text{g g}^{-1}$ (UKMPA 2001).

Both fish and marine mammals can be exposed in the aquatic environment to acute and chronic poisoning of arsenic. Acute exposure may occur within a few hours and is mostly associated with behavioral and hematological changes. This type of poisoning may also cause lethal effects. Chronic toxicity can damage gonads and cause problems with the development of young specimens (Khan et al. 2014; Kumari et al. 2016). More information about acute as well as chronic poisoning is presented in Table 3. The estimated toxicity of inorganic arsenic (lethal concentration 50, LC50) depends on the species and individual abilities. In the case of fish, LC50 may range from 5.5 to 91 mg As l^{-1} (Kumari et al. 2016), while the chronic poisoning may appear at a systematic supply of 1 $\mu\text{g l}^{-1}$ concentrations (Das et al. 1980).

Technology of arsenic removal from water and soil/sediment

The main technologies for removing arsenic from water, groundwater, mine drainage etc. are presented in Table 4. In the past, the arsenic removal technology required the final drinking water quality between 0.050 and 0.010 mg l^{-1} . Current methods, which are

very effective and efficient, make it possible to obtain the required concentration in raw water. The total capital cost of treating water depends on the use of advanced technology. When the technology is based on a simple mechanism, the remediation system is inexpensive and does not require specialists to operate it. The best example of using the simplest technology at a cost of \$1 is Bangladesh, where about 10 l of water is treated per day (10 l needed per person) (National Driller 2010). However, the application of more advanced technology may cost even up to \$2 million (including the construction, design, consultation and advanced equipment). A cost-effective approach for arsenic removal from water is coagulation and precipitation (chemical processes). Precipitation may reduce a high concentration of arsenic (e.g. hundreds of mg l^{-1}) to a moderate level (e.g. 1 to 5 mg l^{-1}), while coagulation – from 400 to 10 $\mu\text{g l}^{-1}$ (Sancha 2006; Reinsel 2015). The ion exchange treatment may reduce the content of As in solution from 200 mg l^{-1} to less than 2 $\mu\text{g l}^{-1}$. However, the most effective method for removing arsenic is reverse osmosis, the efficiency of which is more than 95 percent (Rowe 2013).

The alternative approaches are phytoremediation and rhizofiltration. These important green methods are cost-effective and environmentally friendly strategies for the remediation of soil and groundwater contaminated with toxic compounds (Souri et al. 2017). The methods use plants with a certain capacity to accumulate high levels of heavy metals in their bodies (i.e. over 100–1000 mg kg^{-1}) (Ghori et al. 2016; Souri et al. 2017). Some of the tested plants may remove from the environment more than 93% of arsenite and 95% of arsenate within 60 min of exposure to arsenic (Rmalli et al. 2005).

Soil/sediment contaminated with arsenic compounds represents another problem. However, the treatment of contaminated soil/sediment can reduce large amounts of arsenical waste, e.g. from 0.19 to 0.017 $\mu\text{g l}^{-1}$ in wastewater, from 100 to $< 2 \mu\text{g l}^{-1}$ in waste from metal ore mining and smelting, from 28.0 to 6.5 mg l^{-1} in waste from pesticides (U.S. EPA 2002). The total costs of treating soil containing arsenic depend on the contaminated surface, arsenic concentration, soil condition and the technology used. For example, the capital cost of applying the ion exchange is \$9000, electrokinetics – from \$1.2000 to \$70 per ton for 325 cubic yards, vitrification – \$375–200 000 for 3000 cubic yards, phytoremediation – \$200 000 per 12 acres, biological treatment – from \$0.50 to \$2 per 1000 gallons, and solidification/stabilization – from \$60 to \$290 per ton (U.S. EPA 2002). The main soil/sediment and waste treatment technologies are presented in Table 4.

Table 4

Selected examples of treatment technologies for arsenic compounds (Johnston & Heijnen 2001; U.S. EPA 2002; Nicomel et al. 2015; Reinsel 2015)

Technology used	Description of the technology used
Technology for arsenic removal from water, wastewater and groundwater	
Oxidation	This method [e.g. air oxidation by ozone; chemical oxidation by gaseous chlorine, hypochlorite, permanganate, hydrogen peroxide, or potassium permanganate, and Fe(II), Mn(II)] is very effective in removing the pentavalent form of arsenic (arsenate) via arsenite to arsenate conversion. Oxidation must be coupled with a removal process such as coagulation, adsorption or ion exchange. Oxidation is a very slow process, which can take hours or weeks to complete. An atmospheric oxygen, hypochlorite, and permanganate is the most commonly used technology in developing country.
Precipitation/Coprecipitation	This system is frequently used for the treatment of arsenic-contaminated drinking water and groundwater as well as wastewater originating from the metallurgical industry. This technology uses chemicals to transform dissolved contaminants into an insoluble solid or form another insoluble solid onto which dissolved contaminants are adsorbed. The solid is removed from the liquid phase by clarification or filtration. The method is associated with a simple operation system and the availability of sorbents, which in this case are ammonium sulfate, manganese sulfate, copper sulfate, sulfide, ferric salts (e.g. ferric chloride, sulfate and hydroxide), alum (aluminum hydroxide) and calcium hydroxide. The sulfide precipitation is the most widely used technology.
Coagulation-Flocculation and filtration	It is based on the addition of a proper coagulant (alum, ferric chloride or ferric sulfate) to contaminated water. After that, the water is stirred, allowed to settle, and filtered for best results. Coagulation with ferric salts works best at pH below 8, while with alum – at a pH range of 6–7. The production of high amounts of arsenic-concentrated sludge is disadvantage of coagulation-flocculation, which requires a costly treatment of waste. Therefore, this process is not so common as the other methods.
Ion-Exchange Resins	The synthetic materials (ion exchange resins) are applied to remove some compounds from water as well as for water softening. These resins mostly remove arsenate, therefore the raw water with arsenite should be oxidized first. The amount of water that can be treated is largely independent of arsenic concentration and pH.
Activated Alumina	This commercially available method is based on the use of activated alumina, which works better in slightly acidic environment (pH 5.5 to 6). For best results, raw water with arsenite should be oxidized before treatment.
Membrane methods	This method is based on the reverse osmosis and nanofiltration. For this purpose, synthetic membranes are used, which are water permeable but reject larger molecules, including arsenic, chloride, sulfate, nitrate and heavy metals. Reverse osmosis also effectively removes other constituents from water (e.g. organic carbon, salts, dissolved minerals, and color). This treatment process is relatively insensitive to pH.
Other technologies	They are less documented. Some of the technologies are still under development, e.g. low-tech iron-coated sand and greensand, novel iron-based sorbents, aeration and sedimentation, and specially engineered synthetic resins.
Technology for arsenic removal from soil/sediments and other waste	
Solidification/Stabilization	It physically binds or encloses contaminants within a stabilized mass and chemically reduces the hazard potential of waste by converting the contaminants into less soluble, mobile or toxic forms.
Vitrification	High temperature treatment that reduces the mobility of metals by incorporating them into a chemically durable, leach-resistant, vitreous mass. The process reduces the concentration of compounds in soil and waste.
Soil Washing/Acid Extraction	The ex situ technology that uses the behavior of some contaminants to preferentially adsorb onto fine soil/sediment fractions. The soil/sediment is suspended in a wash solution and the fines are separated from the suspension, thereby reducing the contaminant concentration in the remaining soil.
Biological treatment	It involves the use of microorganisms that act directly on contaminant species or create ambient conditions that cause the contaminant to leach from soil/sediment or precipitate/co-precipitate from water.
Electrokinetic treatment	The usage of current and electrodes for soil/sediment. The current is applied to soil to mobilize contaminants in the form of charged species. Contaminants arriving at the electrodes can be removed by electroplating or electrodeposition, precipitation or co-precipitation, adsorption, complexing with ion-exchange resins, or by pumping water (or other fluid) near the electrode.
Phytoremediation	It involves the use of plants to degrade, extract, contain, or immobilize contaminants in soil, sediment and groundwater.
In situ soil flushing	It extracts organic and inorganic contaminants from soil/sediment by using water, a solution of chemicals in water, or an organic extractant, without excavating the contaminated material itself. The solution is injected into or sprayed onto the area of contamination, causing the contaminants to become mobilized by dissolution or emulsification. After passing through the contamination zone, the contaminant-bearing flushing solution is collected and pumped to the surface for treatment, discharge or reinjection.

Conclusions

Arsenic (As) is a natural component of the Earth's crust. It can be released into the environment from both natural and anthropogenic sources.

Geological processes (e.g. erosion, weathering and geothermal activity, volcanic emissions) are responsible for the natural presence and distribution of arsenic in the environment. The anthropogenic emission of As is mostly associated with mining/smelting of copper, gold, lead and zinc ores as well as agricultural activities.

The arsenic compounds were well recognized by ancient Chinese, Egyptian and Greek. From ancient times to the present day, arsenic compounds have been employed in therapeutic treatments. The positive use of arsenic has been strongly promoted since the 18th century, when it was used as a reagent for treating a number of dangerous diseases (e.g. leukemia, malaria and syphilis). It is interesting that in modern medicine this toxic element is still used in the treatment of humans and animals.

On the other hand, arsenic has for centuries got a negative reputation as "the poison of poisons". Additionally, it has become one of the most efficient pesticides in the 20th century. Recently, the use of arsenicals for domestic purposes has been strictly limited or even banned altogether. Furthermore, some of the arsenicals (e.g. CCA) have been replaced by substitutes (e.g. pentachlorophenol and creosote).

The bad reputation of arsenic was confirmed by the production of chemical warfare agents during War World II. Over the years, it has become clear that arsenic warfare agents are one of the most effective and dangerous chemicals ever created by humans. The problem of chemical weapons was not solved with the end of World War II. Shortly before the end of War World II, the process of dumping of chemical weapons on the seafloor started on a large scale. At present, the dumped munitions attract public attention due to the threat of an imminent ecological disaster. The recent investigations have shown that there are still some problems with the dumped munitions on the seabed and further monitoring of dangerous areas is necessary. Moreover, researchers discovered the undocumented dumpsite of chemical weapons in the Gdansk Deep.

Arsenic occurs in the marine environment in several oxidation states (-3, 0, +3 and +5), but it is mostly found in inorganic forms as oxyanions of trivalent arsenite As(III) or pentavalent arsenate As(V). The natural concentration of arsenic in the aquatic environment is low (from 1 to 4 $\mu\text{g l}^{-1}$). The highest arsenic concentrations are mainly found in the natural

hydrothermal system or in soil/sediments enriched with arsenical minerals. Although the concentration $< 10 \mu\text{g As g}^{-1}$ d.w. is considered as the standard background level for sediments (ATSDR 2007), many considered as researchers obtained higher values of arsenic in sediment samples. Similar results were found for water samples collected from various parts of the world. This alarming phenomenon is a result of arsenic contamination. Due to the fact that arsenic is toxic, additional doses of arsenic in the marine environment are a potential threat to living organisms.

Marine organisms can be exposed to acute and chronic arsenic poisoning. The former is a single but strong exposure to arsenic in a short period of time. The latter is an exposure to a low level of arsenic over a long period of time. Both exposures bring many negative symptoms. Algae, bivalves, mollusks and fish are particularly vulnerable to toxic effects of arsenic. However, macroalgae due to their high affinity for trace metals, may accumulate the highest content of As. On the other hand, fish and marine mammals are continuously exposed to food contaminated with As.

Finally, there is some good news. The intensive development of technology has brought a number of methods for treating arsenic-contaminated soil/sediment and water. It seems that the present-day arsenic removal technology is very efficient. These facts let us believe that there is a good chance for the proper protection of living organisms against arsenic.

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