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REVIEW: ARSENIC CONTAMINATION IN THE WORLD AND THE SPECIFIC CASE OF ARSENIC POLLUTED AREA OF TARNIȚA, NORTHEASTERN ROMANIA

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Abstract: Arsenic occurrence in the world affects both public health and the living organisms. This review is focused on the literature in recent years about arsenic contamination in the world, keeping in mind the large sterile dumps, which are highly contaminated with arsenic and heavy metals. Arsenic toxicity and bioavailability, chemical decontamination methods, glutathione effect, and other key influencing factors are also being summarized. Tailings dumps around the closed barite mine of Tarnița, Suceava County affect much the environment. The effect of various concentrations of arsenite and arsenate on wheat seeds and seedling growth within several germination experiments was also investigated in order to assess potential individual toxicity of arsenic released from the sterile dumps.

***Keywords*:** Arsenic toxicity; Tarniţa polluted area; Cancer; Biotests; Germination test

Introduction

Arsenic in the environment has become a global concern due to its toxicity and adverse effects on human health.[1-3] Arsenic is a toxic metalloid and therefore areas of forest highly contaminated with its salts are a matter

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of considerable concern.[4] Arsenic exposure represents one of the devastating setbacks of environmental pollution in the history.[5] Recently, the As contamination in soils worldwide has been reviewed, and the influence of pH, clay mineral, organic matter, texture of soil as well as the environmental conditions such as ionic strength, anions, bacteria was evaluated to show how these parameters affect the adsorption of As species on soils.[6,7] It is well accepted that arsenic concentrations in agricultural topsoil are both geogenic and anthropogenic.[8] It was also reported that arsenic is mainly enriched in fly ash during high-arsenic coal combustion.[9] However, groundwater and rivers may become contaminated naturally from mining or agriculture.[10]

On the other hand, an intense mining activity in Tarnița area, Suceava county, northeastern Romania, induced severe environment pollution.[11,12] Arsenic speciation in Tarniţa area and its risk assessment was therefore highlighted.[13] Although many toxic heavy metals, such as Cu, Pb, Cd, Zn, Fe, etc. are present as major factors that promote the environmental pollution, As present in sterile dumps and soils can be highly reactive and mobile, resulting in the formation of metal arsenates.[14] Tarniţa area is a particular case of arsenic pollution due to the existing sterile dumps containing both noxious metals and As.

Therefore, this paper aims to review some information about the contamination, toxicity and biochemistry of arsenic, in close connection with our research conducted on the contaminated area Tarnița, Suceava County, Romania. We also highlight the worldwide spread of arsenic and possible decontamination measures. We started from the assumption that humans and animals should avoid contamination of As and where this is not possible, decontamination measures should be taken.

Arsenic toxicity

Although the underlying precise mechanisms of arsenic-induced neurotoxicity have not yet been determined, the changes caused by As exposure coincide with the pathological progression, clinical symptoms, and biochemical features of AD. Arsenic extends its toxic effects to a number of vital organs, and it causes neurodevelopmental abnormalities in childhood and cognitive deficits in adults.[5] The long term consumption of As contaminated water may lead to arsenicosis, which causes several skin lesions, such as skin pigmentation (hyperpigmentation), and hard patches that develop on the skin (hyperkeratosis), palms, and soles.[15,16] Arsenic also causes chronic effects, such as anemia, vascular illnesses, nervous system disorders, liver disorders, diabetes mellitus, skin cancers, and internal cancers.[17-19] Therefore, the threshold concentration of As is only 10 $\mu g\ L^{-1}$ in groundwater for their domestic water supply, because of its high toxicity.[20] Arsenic in waters and soils around some closed mines is present as arsenate ions (aerobic environment) and arsenite in certain anaerobic conditions.[21] These ions inactivate about 200 enzymes, including those involved in cellular energy pathways and DNA synthesis and repair.[10] Inorganic arsenic, administered orally or parenterally, is rapidly distributed throughout the body.[22] Arsenic poisoning is generally associated with nausea, vomiting, abdominal pain as well as severe diarrhea. Arsenic toxicity depends on the oxidation state, intake rate, frequency and route of intake, exposure time and bioavailability.[3] Among the adverse health effects, skin diseases, carcinogenesis, and neurological diseases have been reported due to arsenic exposure.[23] Furthermore, arsenic uptake can lead to the development of risk factors for diabetes mellitus and hypertension. Free radical-mediated oxidative damage is a common denominator of arsenic pathogenesis.[24] Arsenic causes hypertension by increasing oxidative stress, upregulating proinflammatory cytokines and inflammatory mediators, disrupting NO signaling, altering vascular response to neurotransmitters, impairing vascular muscle Ca^{2+} signaling, interfering with the renin-angiotensin system, and phosphorylating MLCK.[25-29] Indeed, chronic arsenic exposure has been shown to elicit a wide range of clinical complications, including skin disorders, diabetes mellitus, and cardiovascular disease.[30-34] Risk of neurodegenerative disease due to tau phosphorylation alteration was also highlighted.[35] Nevertheless, the mechanisms by which long-term exposure to low levels of arsenic causes health effects such as non-communicable diseases is not yet fully understood.[36] However, As is both a carcinogen as also a mutagen and toxicity of arsenic depends on its oxidation states.[37]

As for the arsenic-induced diabetes, they include decreased PPAR- γ expression, interference with ATP-dependent insulin secretion, and altered *glucocorticoid* receptor-mediated transcription.[38] Therefore, chronic exposure to inorganic As may cause various illnesses, from cognitive impairment, mental health and skin disorders to different types of cancer.[30,39,40]

Arsenic toxicity therapy

Whereas acute As toxicity needs the use of specific antidotes, existing therapies for chronic As exposure are limited to supportive only.[41] When it is impossible to avoid arsenic exposure by people of arsenic-endemic areas, arsenic toxicity can be reduced through proper treatment or diet.[42] Natural dietary bioactive compounds or nutraceuticals are considered a cost-effective management option.[43]

Chelation therapy is the well-known treatment options for arsenic toxicity, but it has many side effects, and it also is not economically feasible for poor people.[44,45] However, some authors showed that a daily balanced diet with proper nutrient supplements (vitamins, micronutrients, natural antioxidants) may be effective to reduce the damages caused by arsenic exposure.[23] Safe drinking water, nutritious meals, and adequate physical activity may prevent chronic arsenic toxicity.[24]

The liver is involved in arsenic metabolism, and, therefore, it is considered as a primary site of arsenic toxicity.[46] Mitochondria are highly abundant in hepatocytes that make them key players in hepatotoxicity. As is highly toxic to mitochondria and causes oxidative stress and alters an array of signaling pathways and functions. Therefore, mechanistic aspects of mitochondrial dysfunction in As-induced hepatotoxicity as well as various ameliorative measures should be undertaken concerning mitochondrial functions.[46]

Arsenic contamination in the world

Geochemical mapping of As with a variety of sample materials shows that variation is high at all scales and that different processes govern the As distribution.[47] Arsenic contamination in water and soil is a serious environmental concern in many countries, which have led to a myriad of research on risk assessment and remediation of arsenic.[48,49] Nearly 300 million people are at risk of arsenicosis, a pathology caused due to arsenic exposure due to groundwater arsenic contamination across the world.[23] Anthropogenic sources of arsenic are related to the use of arsenic compounds in a large number of applications, including wood preservatives, agricultural chemicals, glass, nonferrous alloys, electronics, chemical munitions etc.[50] Burning high-arsenic coals releases toxic fumes and ashes, which can be rich in arsenic.[51,52]

In addition, mining tailings dams pose a high risk to the environment because they contain mining by-products such as metals, metalloids and, in particular, arsenic compounds.[53] Temporal and spatial changes in the contaminant concentrations have been measured and waters, sediments and biota were deeply affected after a dam failure in Brazil.

The soils in the vicinity of the mining area in Hunan Province, China have been severely polluted by As and other heavy metal.[54,55] Soil remediation has been performed through replacement with clean soils and phytoremediation by hyperaccumulator plants since 2012 in the contaminated area.[56,57] However, migration and transformation of As were observed in the soils and terrestrial plants.[58]

The largest population at risk is found in Bangladesh, followed by West Bengal state in India along the Indo-Gangetic plains.[37] Large scale natural As contamination of groundwater is found in Bangladesh, India, China and Hungary, and inland basins in arid or semi-arid areas, like Argentina and Mexico. Higher arsenic concentration in groundwater is reported at several places in the Ganga basin, India.[59] Arsenic contamination and the link between arsenic release and clay abundance was investigated in the groundwater resources of Sirjan Plain, Iran.[60] Arsenic uptake from water and soil to maize may represent an important exposure route for humans, in particular in Latin America, Africa and Asia.[61]

Tarniţa case

Arsenic concentrations lower than those estimated in the tailings dumps, in Tarniţa area, have been found to have devastating effects on plant development and growth.[62,63]

A higher toxicity of the sterile of the Tarniţa tailings dumps was reported as well as the possibility to decontaminate using water in order to dissolve and remove soluble contaminants (Figure 1).[64] The authors showed that the remaining residue was not harmful.

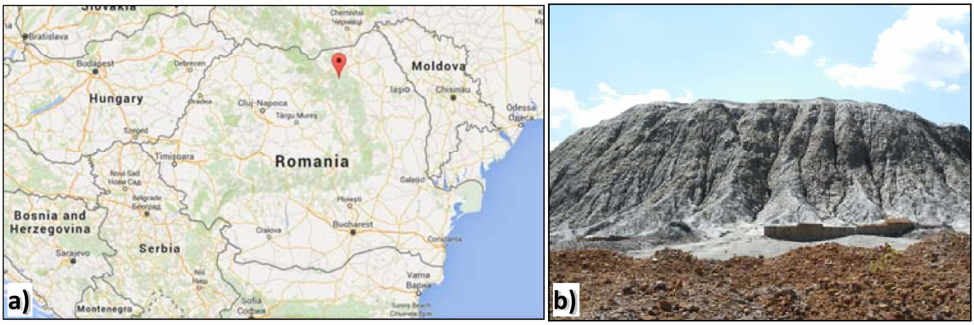

Figure 1. Tarnita mining complex (a) located in the North-East of Romania, Eastern Carpathians (N 47°21'36" E 25°42'42") and one of the tailings dumps (b).[62]

In another experiment, the authors collected the sterile material from one of the tailings dumps, which was used without any treatment or was washed many times with distilled water to remove the toxic contaminants.[63] Thus, seeds grown in Petri dishes containing 1 g of waste produced seedlings with an average height of 1.6 cm, which means 85.8% less than the control with distilled water (Figure 2). The tailings extracted two or three times with 10 mL of distilled recovered the seeds germination or growth of wheat seedlings.

However, the concentrations of all contaminants in the sterile of the dumps should be measured.[65] Indeed, high concentrations of copper, iron, lead, aluminum, and other harmful elements have been found along with arsenic compounds.[66,67] It was hypothesized that arsenic present in the tailings as arsenate or arsenite may have additive toxicity to that of other toxic elements such as copper, lead, iron, aluminum. Therefore, in order to study the contribution of arsenic to the overall toxicity of the tailings on plants, it was necessary to determine the toxic effect of some arsenite- or arsenate-containing solutions at various concentrations.

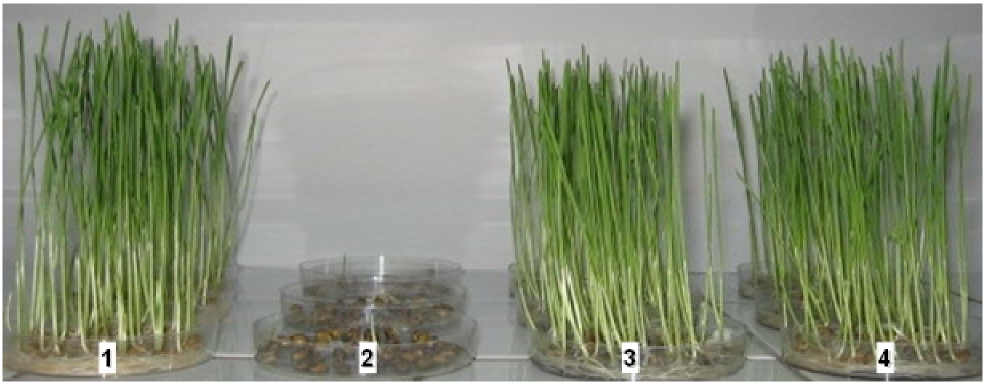

Figure 2. Effect of waste material (WM) collected from Tarniţa tailings dumps on wheat germination: 1) 5 mL of H_2O; 2) 1 g of WM; 3) 1 g of WM washed two times with 10 mL of water before germination test; 4) 1 g of WM washed three times with 10 mL of water.[63]

Germination tests were considered as reliable methods in the investigation of plant responses to toxicity of various substances.[68]

Arsenic speciation

Among the four oxidation states of As, namely +V (arsenate), +III (arsenite), 0 (arsenic), and −III (arsine),[69] the species As(III) and As(V) are the most commonly found in environmental systems.[70] The As toxicity, fate, and bioavailability are intrinsically related to its chemical species. The species As(III), As(V), monomethylarsonic and dimethylarsinic acids are likely to occur in natural water, and the inorganic arsenic oxyanions, such as arsenite and arsenate, are the major arsenic species found in most waters, soils, and sediments.[71] Arsenic speciation is highly dependent on pH, electrical conductivity, and organic matter content.[69] In addition, different inorganic and organic arsenic compounds may be further combined with Fe and Mn oxides or organic ligands containing thiol groups or with humic substances to give coordination complexes.[71]

Arsenic uptake by plants

Plants are generally well protected against As uptake. However, some plant species can accumulate unusually high As concentrations.[72] The marine environment is generally enriched in As. The bioaccumulation and uptake of arsenic in plants is very little known.[73] However, the process of bioaccumulation of arsenic in plants is one of the major aspects of arsenic toxicity. Therefore, further research must be devoted in this direction to understand fully the role of arsenic uptake and bioaccumulation in different plants. Thus, because the plants have different genetic systems, there is a large variation of arsenic uptake by plants.

Both arsenite and arsenate ions from the contaminated environment may penetrate the plants, either by absorption from soil (through roots) or by the aerial parts of the plant as a result of the deposition of particulate contaminants.[63] Generally, As is mainly taken up by root adsorption, depending on both the plant species and the chemical speciation of As in soil.[74] An exception makes As immobilized by iron oxides.[75] However, As accumulation generally decreases from roots to seeds.[76] As accumulation varies between different plants, so that rice accumulates more than eggplant.[77] Arsenic interferes with a variety of metabolic processes in plants.[2] Arsenic uptake in crop plants from the arsenic-contaminated irrigation water was also investigated.[78] Arsenic induces oxidative stress in plants and reduces the nutritive value of the harvesting products.[79]

Arsenite seems to be more toxic and mobile than arsenate to plants. Yet, arsenate uncouples phosphorylation and inhibits the uptake of phosphates.[80] In fact, arsenate ions are up taken by high-affinity phosphate transporter in plants and about 95% of it is reduced to more toxic arsenite by cytoplasmic or nucleus arsenate reductase.[81,82]

Wheat seeds are sensitive to toxic metal and metalloid ions as well and, therefore, shoot heights and root lengths recorded after wheat germination can be indicators of choice for arsenic toxicity.[83] Both arsenite and arsenate ions have been shown to be very harmful to wheat.[62,63] Consequently, the germination performance of wheat seeds under arsenic pollution was evaluated through a facile incubation method in Petri dishes with a seven-day incubation period.

Some nanoparticles might be a potent tool for mitigating As-induced phytotoxicity.[84] Thus, nanoparticles promote plant growth under As-stress by stimulating various alterations at physiological, biochemical, and molecular levels. An increase in phytochelatin synthesis and the activity of glutathione S-transferase, respectively, was observed in the tomato seedlings treated with arsenic.[85,86] Thus, As reduces the biomass yield and pigment content, alongside with increases in the oxidative stress. However, NaHS and silicon (Si) improves As tolerance in tomato plants as well as the phytochelatins, glutathione and key antioxidant biomolecules. Arsenic stress caused the high levels of H_2O_2 in maize leaves and induced antioxidant enzyme activities.[87] Hesperidin and chlorogenic acid preserves cellular redox status with the AsA-GSH cycle. These phenolic compounds improve the capacity of superoxide dismutase (SOD), catalase (CAT), peroxidase (POX), glutathione S-transferase (GST) and glutathione peroxidase (GPX) and then ROS accumulation (H_2O_2) and lipid peroxidation (TBARS) are effectively removed.

Estimation of ecological risks

Worldwide arsenic contamination is a global public health issue.[88-90] Therefore, we believe that there is both acute and potential toxicity of arsenic-containing mining waste.[91] Therefore, the measurement of the total content of arsenic or heavy metals in the environment does not express the actual toxicity of contaminants on humans, animals and plants living around tailings dumps. Thus, the samples collected from the mining waste have a high content of arsenic and heavy metals, elements that greatly influence the germination of the common wheat species *Triticum aestivum* L. used in our experiments as an indicator of toxicity. However, only soluble As and metal ions have been shown to be toxic to plants (acute toxicity); the material resulting from washing the soluble compounds with water was not harmful to the wheat. The quantification of arsenic and heavy metal concentrations by ICP-OES may evidence the potential ecological risks and contamination status of the tailings dumps.[62] In fact, one can measure both acute and potential toxicity. On the other hand, wheat germination tests can be reliable and inexpensive biological methods to demonstrate the harmful effect of arsenic on plants. Generally, the biological tests using the treatment solutions are performed in triplicate. Lots of 50 wheat seeds are placed in sufficiently large test tubes (180 x 18 mm) to allow mixing and then the treatment solution is added to each test tube. After one hour, the seeds together with the treatment solutions were placed as evenly as possible in Petri dishes with a diameter of 9 cm, on double filter paper. The germination process in the presence of treatment solutions takes 7 days. Therefore, the measurements are made after the 7^{th} day of germination and the results are expressed as energy and rate of germination as well as the average weight and height of the seedlings.[63]

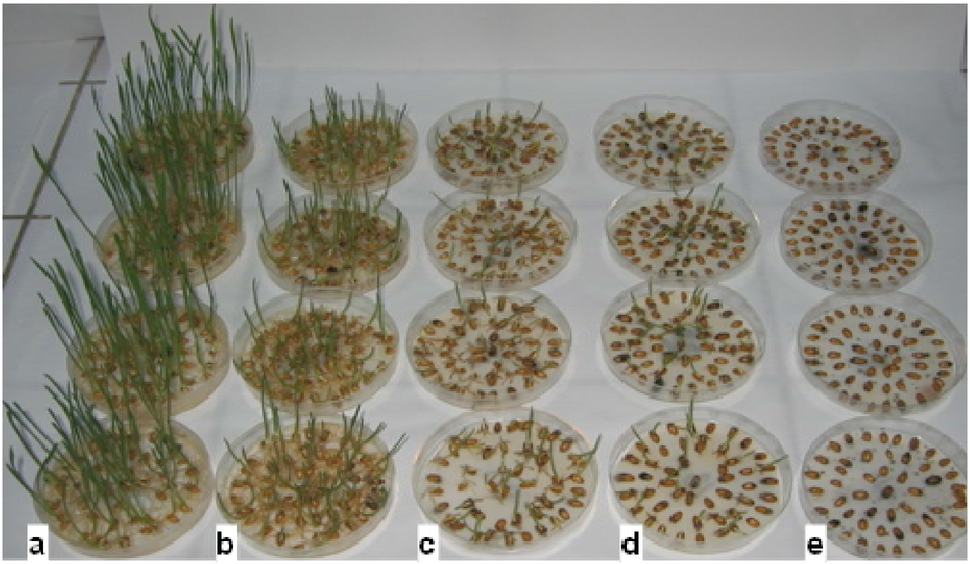

Figure 3. Effect of arsenite ions on wheat seed germination. Sodium arsenite concentrations: a, 0 mM; b, 0.25 mM; c, 0.826 mM; d, 1.8 mM; and e, 5 mM.[63]

Arsenite at concentrations lower than those in the sterile materials of Tarniţa (up to 90 mM) are highly toxic to wheat seeds and almost completely inhibited both germination and growth of seedlings of wheat caryopses.[63] Under the action of arsenite, the size of the radicles reduced significantly, until disappearing (Figure 3).

Conclusions

The available literature on the occurrence, toxicity, behavior, and removal technologies of arsenic present in environmental media and especially in Tarniţa polluted area was reviewed. A large volume of literature raises concerns about arsenic pollution worldwide. We also discussed here on both acute and potential toxicity of arsenic-containing mining waste.

The process of bioaccumulation of arsenic in plants and some aspects of arsenic toxicity were also highlighted. In fact, wheat germination tests can be reliable and inexpensive biological methods to demonstrate the harmful effect of arsenic on plants.

Glutathione exhibits protection against the arsenic toxicity in experiments with wheat seeds. The germination test may be trustworthy biomarker for arsenic toxicity. More research efforts are necessary to study the interaction of all factors under relevant environmental conditions to determine the toxicity and mobility of arsenic in the environment.

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