

## THE NEGATIVE EFFECT OF ARSENIC IN AGRICULTURE: IRRIGATION WATER, SOIL AND CROPS, STATE OF THE ART

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**Abstract.** The existence of high content of arsenic exceeding international regulations established for irrigation water can be the main factor for the relationship of arsenic content found in soil and crops of many countries around the world such as Bangladesh, Mexico and Spain. The drinking water is not the only source of consumption of arsenic in human diet. Irrigating agricultural fields with arsenic contaminated water produces accumulation of arsenic in soil and subsequently an increases of arsenic concentration in crops. Concentration of arsenic in crops depends of many factors, for example, type of crop, arsenic concentration of soil and water, soil type, among others. In this paper, data from several studies are presented to show that arsenic in irrigation water tends to accumulate in agricultural soil and through several mechanisms is absorbed by crops. The problem of arsenic in agriculture requires more research that allows to know the actual situation and to propose solutions in order to solve some cases and avoid others.

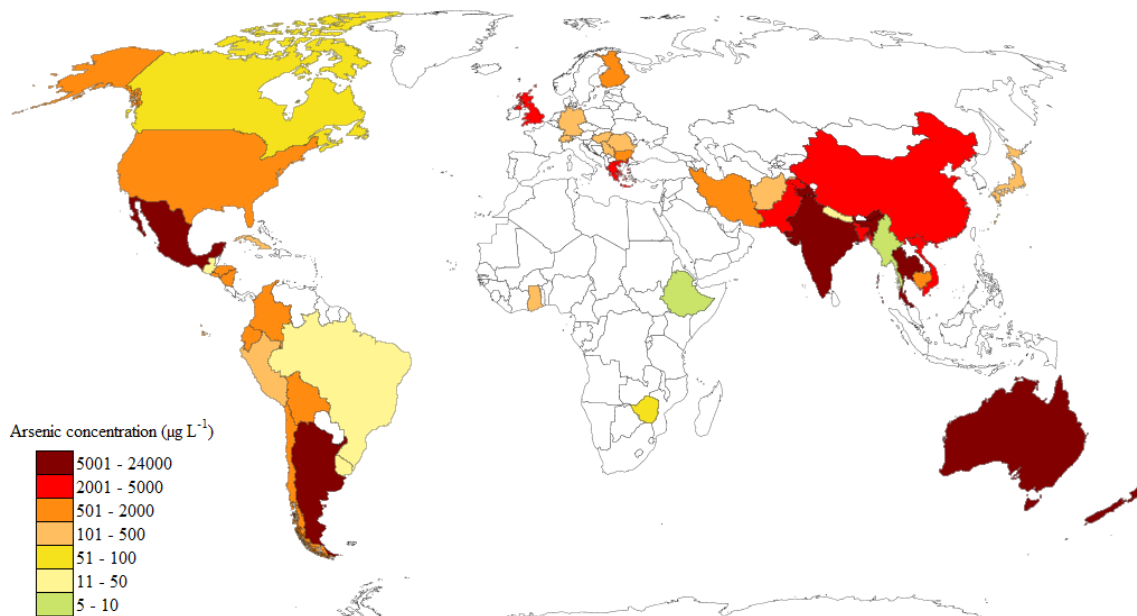
**Keywords:** *accumulation, concentration, absorption, agriculture, impact*

### Introduction

Arsenic excess present in groundwater may be a natural contaminant and it is currently a problem that impacts many sites around the world, for example India, Spain, Nicaragua, Peru, Argentina, Mexico and Chile are among the countries where have detected concentration above of 10 µg L<sup>-1</sup> of this pollutant (*Figure 1*), this concentration exceeds the permissible limit according to World Health Organization (WHO, 2003). In India, natural sources of arsenic from aquifer rocks has been reported to add arsenic to underground water (Ranhman et al., 2007), the same for Argentina (Hopenhayn et al., 1996), while in Mexico a large part comes from mining (Ongley et al., 2007). The problem of arsenic of natural origin, added to that generated by copper mining, is also critical in northern Chile (Arica), at communities that are facing water shortages at the same time (Carbonell et al., 1995).

Irrigation water is not an exception to the above described and is compromised by contamination of arsenic in surface water bodies at many countries (Azcue and Nriagu, 1994; Chen et al., 1994; Das et al., 1995; Nickson et al., 2000; Schreiber et al., 2000; Smedley et al., 2002; Mishra and Mahato, 2016; Yazdani et al., 2016; Rosas et al., 2016; Núñez et al., 2016). Concentration of arsenic in irrigation water is accumulated in

soil, showing greater accumulation at top layers of soil and it is found in soluble form. Finally, arsenic in soil and water reaches plants (Pandey and Singh, 2015; Kramar et al., 2015; Dixit et al., 2016; Dousova et al., 2016; Ma et al., 2016).



**Figure 1.** Arsenic concentration in groundwater around the world (elaborated with data from Rasheed et al., 2016)

Accumulated arsenic in plants affect the growing mechanisms and hence the yield of crops, as well as the accumulation of arsenic in crops may impact on health of living beings (Rosas et al., 2016). A specific case of the arsenic effect, is the 50% yield reduction when having an arsenic concentration of  $43.8 \text{ mg L}^{-1}$  in radish and  $4.5 \text{ mg L}^{-1}$  in tomato (Carbonell et al., 1995). Due to the high toxicity and bioavailability of arsenic, it is necessary to conduct research in various subjects to help tackle the problem comprehensively, for example, knowing the mechanisms by which this element moves through the system water-soil-plant, concentrations affecting yield of crops and health of living beings, geographical distribution of an index for bioavailability and propose solutions economically and technically viable.

Therefore, this article presents the state of the art about the effect of arsenic contamination in agricultural soil and water, absorption of the most common arsenic species in some parts of crops, effects on productivity of some crops and solutions proposed to the problem.

## Fundamentals

### *Arsenic in water*

Arsenic contamination of drinking water is a serious and widespread problem that threatens human health and the environment. The World Health Organization (WHO) recommends a maximum quantity of arsenic of  $10 \mu\text{g L}^{-1}$  in drinking water.

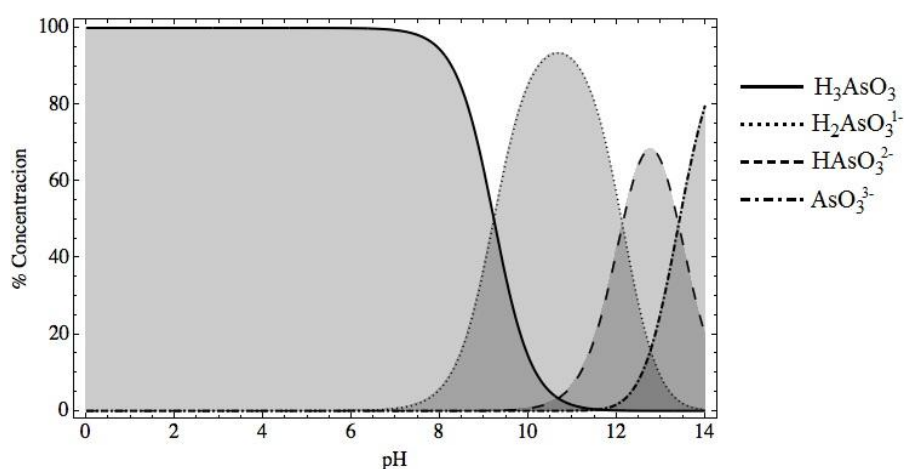
In water with dissolved oxygen concentrations below  $0.8 \text{ mg L}^{-1}$  is more common to find arsenic (III) than arsenic (V).  $\text{H}_2\text{As}_4^-$  and  $\text{H}_2\text{AsO}_4^{2-}$  species may dominate under oxidizing conditions, however, the oxidation of arsenic (III) is often slow and persists under conditions of oxygenation, the *Table 1* shows some properties of Arsenic III and V. On the other hand, greater sorption of arsenic (V) of the form  $\text{H}_3\text{AsO}_3$  could increase the rate of dissolution of arsenic (III) / arsenic (V) in surface water bodies (Boyle et al., 1998).

**Table 1.** Properties of Arsenic III and V

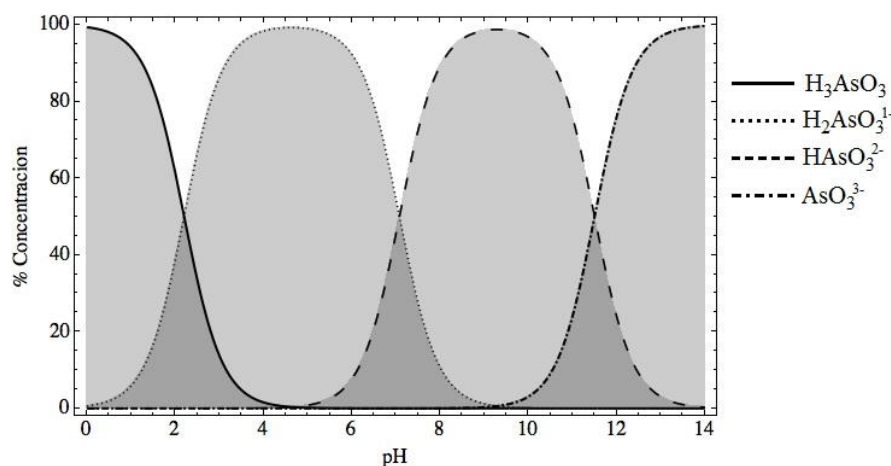
Properties	Valence state		Reference
	As III	As V	
Coordination number	Sixfold	Fourfold	Klein, 2002
Radius (Å)	0.58	0.34	Klein, 2002
Density ( $\text{g cm}^{-3}$ ), 25 °C and 1 bar	5.75 (rhombohedral form)	5.75 (rhombohedral form)	Lide, 2007
Electronegativity	2.0	2.2	Langmuir, 1997
First ionization potential (eV)	9.7886	9.7886	Lide, 2007

The adsorption of arsenic depends on the species in which it is located, and represents the dominant mechanism that controls the transport of arsenic in many water systems. Hydroxides of iron, aluminum, magnesium and clay minerals are commonly associated with solid aquifers, which show that these species are important absorbents of arsenic. The amount of arsenic absorbed is influenced by the chemistry of the aqueous phase, including arsenic speciation, the presence and concentration of different ions of competition for arsenic and pH.

Chemical and physical conditions of the aqueous phase of water affect arsenic chemical behavior in the water-soil-plant system, i.e. in a water system with neutral pH conditions, inorganic arsenic (III) is an uncharged molecule  $\text{H}_3\text{AsO}_3$ , which improves mobility, as it does not adsorb strongly enough to the surface of minerals. In contrast to the anions of arsenic (V) that are strongly adsorbed by minerals under conditions of neutral pH (Smedley et al., 2005), i.e. in moderate reduction, trivalent arsenite is stable and increases adsorption with increasing pH, on the other hand under oxidizing conditions, arsenate is stable and the absorption decreases with increasing pH. A pH diagram of aqueous arsenic species is shown in *Figure 2*.



(A)



(B)

**Figure 2.** pH diagram of aqueous arsenic species: (A) III. (B) V.

Another factor that influences the transport of arsenic in water, like adsorption, is organic matter. Organic matter is composed of a wide variety of organic compounds, some of the most important due to interaction with arsenic are the humic substances. Humic substances affect mobility and balance of the sorption of arsenic (Grafe et al., 2002; Redman et al., 2002; Lin et al., 2003; Ko et al., 2004; Sjöblom et al., 2004; Warwick et al., 2005; Buschmann et al., 2006), since this can be absorbed by organic material and compete for adsorption sites on mineral surfaces (Haw et al., 2004). Due to the arsenic concentration in water, the agricultural soils are contaminated, and even accumulating more arsenic after each crop cycle, which is a topic explored in more detail in the next section.

### **Arsenic in soil**

The soil is an important natural resource, but also an important media of accumulation, transformation and migration of arsenic. The main factors influencing the concentration of arsenic in soil are the parent rocks (Tanaka, 1988) and human activities, which may come from industrial waste and/or agricultural use of arsenical pesticides. The average range of the natural content of arsenic in soils around the world is from 0.1 to 40 mg kg<sup>-1</sup> with an average of 6 mg kg<sup>-1</sup> (Vinogradov, 1959; Backer and Chesnin, 1975, Bowen, 1979, Zou, 1986; Boyle et al., 1998). Little quantities of arsenic are also accumulated in soil by fertilizers, irrigation, emissions from burning fossil fuels, industrial waste and sludge with high concentration of arsenic (Nasier et al., 1977).

Agricultural practices with chemicals, historically used, contributes to the accumulation of arsenic. Some combinations of pesticides and chemical fertilizers were widely applied over long periods of time in the past (Carbonell, 1995).

Arsenic in soil is mainly found as inorganic species although the organic arsenic is also found in organic matter of some soils, since some reducing bacteria catalyze and improve the rate of oxidation of certain arsenious minerals (Mihaljevic et al., 2004), thus converting inorganic arsenic into organophosphorus compounds. Typically, arsenic (V) is dominant with values of electric potential (Eh) around 200 mV and pH conditions of 5-8 (Henke, 2009).

Togashi et al. (2000) argue that climate, erosion and sedimentation are responsible for the enrichment of arsenic in soil. The temperature, humidity, precipitation and evaporation

are important as they contribute to the oxidation of arsenic sulfide minerals. In particular, for warm and humid climates, excessive rainfall causes intensive biological activity, thus creating reduction conditions on the surface and underground, which prevents the oxidation of sulfur. The soil surface under high temperatures and moisture can promote the oxidation of arsenic sulfide minerals, releasing arsenic into the environment (Williams, 2001).

Soil texture is another important characteristic that affects the chemistry of arsenic. Fine clay minerals tend to adsorb and trap arsenic more effectively than sandy soils (Scazzola et al., 2004). In many soils and sediments, the mobility of arsenic (V) is limited by adsorption to clay minerals, organic matter or iron oxides (Inskeep et al., 2002).

Soil organic matter is generally composed of a wide variety of compounds, that including, carboxylic acids, carbohydrates, phenols, amino acids and humic substances (Drever, 1997; Wang and Mulligan, 2006; Fakour and Lin 2014). Organic matter affects the mobility and bioavailability of arsenic in soils and sediments by the same mechanisms that water sorption (Sjöblom et al., 2004; Warwick et al., 2005; Buschmann et al., 2006). Most of the components of organic matter are found in an oxidation state under conditions of alkaline and neutral pH, which implies that compete with oxy-anions of arsenic to be adsorbed by hydroxides or oxy-hydroxides on the surface of minerals (Wilkin and Ford, 2006). Then the effect of arsenic contamination in agricultural soil and water, affects crops, decreasing the crop yield and in this way enters to the food chain.

## **Arsenic in agriculture**

### ***Soil and plant***

There are many studies about the mobilization and accumulation of arsenic in soil, as well as the effect of oxalic, citric and malic acids on this mobilization. These acids were tested in terms of mobilizing arsenic that was bound to iron components. The results showed that the arsenic mobility increases as dose of oxalic acid increases. In other hand, it was observed that there was a close relationship between the mobilized iron and the mobilized arsenic, in fact the iron plays an important role for arsenic mobilization (Onireti and Lin, 2016), while the results of Dousova et al. (2016) showed that chemical composition (Fe, OM content) played a minor role, being important just in the kinetics of surface processes.

In the West of England, retention of arsenic was examined for forest soils rich in organic matter and spatial and temporal patterns of arsenic dissolved concentrations were analyzed. Concentration of arsenic was found to change as a function of soil depth, and the results revealed the highest arsenic concentration of 28.3 mg kg<sup>-1</sup> at the topsoil layer (0.07 m), and below 0.13 m, concentration fluctuated around 9 mg kg<sup>-1</sup>. On the other hand, the study demonstrated that those soils were contaminated with anthropogenic arsenic derivatives and that organic matter plays an important role in the dynamics of arsenic (Rothwell et al., 2009). Arsenic reported, in previous publications, that major contamination of soil occurs in the upper layer of soil, which is at 0.50 m depth, where contamination occurs due to irrigation with contaminated water.

A study in Portugal (Marques et al., 2009) found that the soil on the slopes of a river presented a higher concentration of arsenic, at the closest points to a sewage canal. In addition, the highest concentrations of arsenic were found at the top layers of soil, similar to the results reported by Rothwell et al. (2009). Marques et al. (2009) found that the closer the ground to channel water, the higher concentration of arsenic. Moreover, these authors

reported that in Blackberry (*R. ulmifolius*), arsenic concentration ranged between 277 and 1721 mg kg<sup>-1</sup> at the root, from 30 to 110 mg kg<sup>-1</sup> at the stem from 60 to 265 mg kg<sup>-1</sup> at the leaf. Also they found that extractable percentage of arsenic per plant is 0.7% with respect to the total concentration of metalloid in the soil. On the other hand, arsenic concentration in Blackberry plants are higher compared with results of other studies (Ma et al., 2001). However, the absorption of arsenic in the system of plant-soil is also related by the presence of different metals and anions that compete for adsorption sites with arsenic. Several authors (Azcue and Nriagu, 1994; Cardwell et al., 2002; Marques et al., 2007) have found a clear pattern of increased concentration of arsenic present in aquatic macrophytes as Zinc concentration increases, indicating an interaction between different metals or anions.

Stoltz and Greger (2002) found that some tests showed a high correlation between the concentration of arsenic among varieties of cotton (*Eriophorum angustifolium* and *E. scheuchzeri Honckenya Hoppe*) and arsenic concentration in agricultural soil, and reported maximum concentrations of 8.4 mg kg<sup>-1</sup> in soil and 276 mg kg<sup>-1</sup> in root, like Marques et al. (2009). Also, Stoltz and Greger (2002) found that concentrations of arsenic in root is higher than the arsenic content in the aerial part. The correlation of the concentration of arsenic in plant root and the concentration of arsenic in soil was positive and significant, while for leaf and stem was generally not significant.

Studies have demonstrated that Arsenic (V) uses the same pathway than phosphate to be absorbed by the root of rice from soil, it is due to the chemical analogy of phosphate (Abedin et al., 2002; Lee et al., 2016), in Table 2, a summary plant species and the main uptake mechanism is presented. The main form of arsenic in aerobic soils is arsenic (V), this form presents many chemical similarities of phosphate and get in to plant root tissue through the mechanism of phosphate transporters. Some studies reported that the high affinity phosphate transporters AtPht1;1 and AtPht1;4 facilitate the acquisition of phosphate and arsenic (V) (Shin et al., 2004; Remy et al., 2012; Ye et al., 2015; Punshon et al., 2017). Absorption of arsenic/phosphate take place through the same plasma membrane in plants of *Holcus lanatus* and *Hordeum vulgare*, these mechanism presents a higher affinity for phosphate than arsenic (V).

**Table 2.** Transport mechanism in selected plant species. For a more complete review of uptake mechanism, see Farok et al., 2016

Plant species	Arsenic species	Uptake and transporter name	Reference
Xenopus Laevis oocyte	MMA	OsNIP2;1 gene	Li et al., 2009.
Rice and Castor Bean	DMA	Translocated from roots to shoots, takes place via both the xylem and the phloem	Carey et al., 2011; Ye et al., 2010.
Rice	DMAA and MMAA	Glycerol transport pathway	Rahman et al. 2011.
Rice	As <sup>V</sup>	Uptake and translocation root to shoot	Kamiya et al. 2013.
Arabidopsis thaliana	As <sup>V</sup>	Phosphate transporters	Shin et al., 2004.
Pteris vittata	As <sup>V</sup>	Transport	DiTusa et al., 2016.
Arabidopsis	As <sup>III</sup>	PC complex transport	Song et al., 2010.
Arabidopsis	As <sup>III</sup>	Phloem translocation	Duan et al., 2016.
Barley	As <sup>III</sup>	Transport	Katsuhara et al., 2014.
Pteris vittata	As <sup>III</sup>	Uptake	He et al., 2016.

Due to high concentrations of arsenic that crops are capable to accumulate and as a consequence entering into the food chain, several remediation/removal methods of arsenic from water and soil have been proposed.

### **Removal of arsenic in soil**

There are several options to eliminate or reduce arsenic concentration of agricultural soil; the principals can be suggested such as adsorption, precipitation, inverse osmosis and phytoremediation. The phytoremediation of contaminated soils with arsenic has been considered feasible and environmentally friendly technique (Ma et al., 2001; Azizur and Hasegawa 2011; Ye et al., 2011). The effectiveness of phytoremediation is determined by two factors: first, identification of hyperaccumulators of arsenic, and second, by the knowledge of factors that maximize the accumulation of it.

Another study, in southeastern France (Chaney et al., 2007) found that it is possible to clean the agricultural land used for growing rice, from inorganic compounds by combining a high intake and translocation of contaminants to the harvestable biomass. In addition, phytoremediation showed that the root of plants such as amaranth (*Amaranthus blitoides*), bermuda grass (*Cynodon dactylon*), chicory (*Cichorium intybus*) and milk thistle (*Sylibum marianum*) can absorb metals especially plumb and copper (Marmiroli et al., 2005; Del Río Celestino et al., 2006; Vazquez et al., 2006; Yoon et al., 2006), so the root exudative may cause precipitation or mobilization of the metal. For example, the mobility of arsenic in soils and sediments of northern Argentina is highly controlled by precipitation processes, dilution and/or sorption of the surface of metal particles (Smedley and Kinniburgh, 2002), and the final arsenic disposition is affected by organic matter (Bauer and Blodau, 2006; Buschmann et al., 2006). By the study of these mechanisms, it becomes technically feasible to devise methods to control the mobility of arsenic in soils and then propose an effective remediation for soils contaminated with arsenic.

Shrivastava et al. (2006) reported that *P. Biaurita*, *L. P. quadriaurita* Retz and *P. ryukyuensis* Tagawa are hyperaccumulators fern of arsenic and all these may be used in phytoremediation of sites contaminated by arsenic. Other arsenic hyperaccumulators as *Pteris viatta* and *Ptyrogramma calomelanos* (Francesconi et al., 2002), also *P. Longifolia* and *P. Umbrosa* (Zhao et al., 2002) were already validated.

A decade ago, biomass resulting from plants accumulating As by phytoremediation process was thought as a drawback for its application, because the biomass was usually either disposed at regulated landfills or incinerated (Chaney et al., 2007). Current research is working to find new recovery methods of As from hyperaccumulator plants. In fact, *Pteris vittata* is a good example of phytoremediation, since it takes up As and rapidly translocates it into the fronds (Danh et al., 2014). Thus, recent research is testing As removal from *P. vittata* by different methods (da Silva et al., 2018). After extracting As, next step is to use it in the industry of wood preservation chemicals, insecticides and poison for pests.

Arsenic contamination in agricultural irrigation water produces an accumulative effect on soils and crop, so many studies have been developed on these topics and the next section explores it.

### **Water and plant**

The arsenic in soil and water is taken by crop plants up and that is how this arsenic is present in food (Punshon et al., 2017). The relationship between arsenic concentration of water and arsenic concentration absorbed by plants is influenced by parameters such

as pH, temperature, soil type and kind of plant, so Carbonell et al. (1995) remarked the need to study the interactions of arsenic through water-plant.

Dahal et al. (2008) monitored the influence of arsenic in irrigation water and alkaline soils on onion, cauliflower, rice and potato, directly in field. They found arsenic concentrations to range from 0.005 to 1.014 mg L<sup>-1</sup> for irrigation water, from 6.1 to 16.7 mg kg<sup>-1</sup> for soil; and for crops mentioned above it was found that arsenic concentration changed from high to low accumulation in different parts of plants as follows: roots > shoots > leaves > edible.

Arsenic concentration in soil is determined by its mineralogical and chemical properties as well as the amount of arsenic contained in the irrigation water. In particular, an increment of arsenic in grain is more sensible to the arsenic concentration in soil than in water (Mukherjee et al., 2017).

In cases of sprinkler irrigation Soybean as affected by high concentrations of arsenic and fluoride in irrigation water under controlled conditions, arsenic and fluoride are accumulated in soil. Moreover, as the concentration increases over 0.6 mg L<sup>-1</sup> of arsenic and 25 mg L<sup>-1</sup> of fluoride, it is observed a bioaccumulation and a biomass reduction of plant (Bustingorri and Lavado, 2014).

The arsenic contained in the irrigation water, is bioaccumulated in crops, which form part of the diet in some countries, and in this way reaches humans beings. As a consequence, this bioaccumulation of arsenic has affected negatively the human health (Mayorga et al., 2013).

Hu et al. (2015) found that by minimizing the amount of arsenic in irrigation water diminishes the amount of arsenic in rice. In fact, Newbigging et al. (2015) proposed that this is the best option, since the arsenic intake by rice is difficult to control.

The main source of arsenic in agriculture is contaminated irrigation water, thus irrigation technologies with high efficient use of water may help to solve the problem in the best sustainable way by reestablishing the levels of water in aquifers, since arsenic comes from deep groundwaters. In the meantime, studies about the removal of arsenic from water are being done due to the significant effect that arsenic in water have on crops and soil, which is the subject of next subsection.

### ***Removal of arsenic in water***

In Latin America, some people have severe health problems caused by consuming water with high content of arsenic, because of this; different arsenic removal methods have been applied to drinking water (Camacho et al., 2011). Conventional technologies such as oxidation, coagulation/co-precipitation, adsorption, reverse osmosis, ion exchange, are used to remove arsenic from water but they are expensive techniques. For this reason, more economical and decentralized methods have emerged such as natural adsorbents, sunlight or biological treatments as essential methods to reduce contamination of arsenic for low-income areas and remote regions of Latin America (Litte et al., 2010). Several adsorbents have been used to remove arsenic from water. In general, the adsorbents can be grouped into two types, namely, adsorbents with iron content (IC) and adsorbents without iron content (WIC). The adsorbents without Fe content include, Chitosan/Cu(OH)<sub>2</sub> and Chitosan/CuO, which were used for arsenic (V) removal from aqueous solution. A recent research results showed that sorption uptake was highly dependent on pH, temperature, initial arsenic (V) concentration and sorbent dosage (Elwakeel and Guibal, 2015). Seawater neutralized red mud (Bauxsol<sup>TM</sup> technology) was used for arsenic (V) removal. Bauxsol has the potential for removing



arsenic (V) (Genc et al., 2003). The Zirconium loaded activated carbon (Zr-AC) was used for arsenic removal and it allows high flows with a remarkable adsorption capacity (Daus et al., 2004). Manna et al. (2010) investigated removal of arsenic from contaminated groundwater using a new method that works with distillation membranes in direct contact with solar membrane. This system produces almost 100% water free from arsenic. The solar distillation membrane has a high potential to remove arsenic in contaminated groundwater.

The aluminum sulfate was used to remove the arsenic from water by precipitation – co-precipitation (Meltem and Pala, 2010). In this study, a statistical design of experiments Bahnken box was done and also response surface methodology to investigate the effects of the most significant operating variables. Aluminum sulfate was found to be an effective and safe coagulant for drinking water due to the dose required of it. The optimal pH range for maximum removal of arsenate was from 6 to 8. At low concentration of arsenate, removal efficiency obtained was high using elevated doses of aluminum sulphate, whereas under high initial concentrations of arsenate, a high removal efficiency was performed with low doses of the coagulant.

Another solution is the use of adsorbent media. Adsorbents with Fe content includes, Green synthesis of  $\alpha\text{Fe}_2\text{O}_3$  nanoparticles, this adsorbent shown that is affected by temperature and pH and its adsorption capacity was  $38.48 \text{ mg g}^{-1}$  indicating a good potential for the adsorption of arsenic (V) (Mukherjee et al., 2016). Alginate beds impregnated of hydrous iron oxide presented an effective removal, the adsorption efficiency for both arsenic species increased as iron loading is augmented (Sigdel et al., 2016). Moreover, Sánchez et al. (2016) studied the adsorption capacity of arsenic on a mixed oxides produced from thermal treatment of hydrotalcite-like compound's, these authors report more than 98% removal for initial concentrations below  $250 \mu\text{g L}^{-1}$ . The iron-aluminum hydroxide coated onto macroporous supports was proved for arsenic removal and it was compared with Granular Ferric Hydroxide (GEH), Kumar et al. (2016) show that the iron-aluminum hydroxide coated onto macroporous supports is capable to treat seven times more volume of water than GEH. The adsorption capacity of different adsorbents is related to other ions present in water, such as, phosphate, sulfate, carbonate, fluorides and humic and fulvic acids. Saldaña-Robles et al. (2017) evaluated GEH in presence of humic substances to study the adsorption capacity of arsenic (V) onto GEH. The results showed that humics and fulvic acids enhance the mobilization of arsenic (V), reducing the removal efficiency of adsorbent.

Other synthesized materials with iron such as diatom- $\text{FeO}_x$  (Thakkar et al., 2015) and Zr- $\beta$ - $\text{FeOOH}$  (Sun et al., 2012) showed adsorption capacities for arsenite and arsenate. While, the first adsorbed  $10 \text{ mg g}^{-1}$  of arsenite and  $12.5 \text{ mg g}^{-1}$  of arsenate, the second adsorbed  $60 \text{ mg g}^{-1}$  and  $120 \text{ mg g}^{-1}$ , respectively. On the other hand,  $\delta$ - $\text{FeOOH}$  showed an adsorption capacity for arsenate of  $37.3 \text{ mg g}^{-1}$  (Faria et al., 2014). The iron coated sand (Thirunavukkarasu et al., 2002), the CFe (Gutiérrez et al., 2013), CarFe (Gutiérrez et al., 2013), NADMCF (Malana et al., 2011), BNNT (Chen et al., 2011), IOCS-2 (Thirunavukkarasu et al., 2002), kaolinite (Ladeira and Ciminelli, 2004), GAC-Fe (0.05 M) (Gu et al., 2005) and nanostructures akaganeite (Deliyanni et al., 2003) have shown potential capacity for arsenic adsorption. In the case of IC adsorbents, the adsorption is compatible with a multilayer adsorption for CFe, CarFe, NADMCF and BNNT in agreement with the Freundlich model for adsorption capacity ranging from 0.99 to  $2.59 \text{ mg g}^{-1}$ . IOCS-2, Kaolinite, GAC-Fe, GAC-Fe- $\text{O}_2$  and Nanostructures akaganeite show an adsorption mainly monolayer with adsorption capacity ranging  $0.008$  to  $2.96 \text{ mg g}^{-1}$ .

The accumulative effect caused by arsenic in agricultural soil and water on crops has been studied by several authors. This is mainly due to the environmental importance and the negative effects in the food chain and so for human health. Some arsenic effects on human health could be related by the type (inorganic or organic) and concentration of trivalent ( $\text{As}^{+3}$ ,  $\text{MMA}^{+3}$  and  $\text{DMA}^{+3}$ ) or pentavalent arsenic forms ( $\text{As}^{+5}$ ,  $\text{MMA}^{+5}$  and  $\text{DMA}^{+5}$ ). In this sense,  $\text{As}^{+3}$  and  $\text{As}^{+5}$  are considered more toxic than methylated organic ( $\text{MMA}^{+5}$  and  $\text{DMA}^{+5}$ ) forms (Rasheed et al., 2016). Different organs in the human body can be affected by long term arsenic exposure provoking skin lesions, different types of cancer, diabetes, lung disease, neurotoxicity, among others (Carlin et al., 2014). According to Abdul et al. (2015), the effects of arsenic exposure may be classified into four stages: preclinical, clinical, internal complications and malignancy stages. There are many examples of arsenic human exposure. In Taiwan, residents were chronically exposed to high levels of arsenic due to drinking water and presented Black Foot Disease (Chen et al., 1985; Tseng, 1977). Hindmarsh et al. (1977) reported Peripheral neuropathy after long-term exposure to inorganic arsenic in drinking water. A recent case occurred in West Bengal, a state of India, a large population is still exposed to arsenic contamination which is acquired from drinking water, and which results in consequent escalation in the number of chronic arenicolids (Pal et al., 2015).

### ***Arsenic in crops***

The ratio of the concentration of arsenic and crops is a topic of general interest, as the plant is the media by which the arsenic reaches living beings. Furthermore, the effect that arsenic has on crop yield impacts the economy of the agricultural sector.

Several authors have studied the arsenic accumulation in wheat. The results showed that arsenic in wheat grains mainly exist as inorganic form (Shi et al., 2013; Brackhage et al., 2014). On the other hand, the results obtained by Shi et al. (2015) showed that the accumulation of arsenic and translocation were a significant difference among wheat cultivars studied.

Rice consumption is the main source of exposure to organic arsenic for people in Asia. Therefore, recent studies have been conducted on the accumulation and speciation of arsenic in different rice varieties. Lu et al. (2010) studied Indica and a hybrid of Indica and found that arsenic content in different parts of plants increased in the next order: grain <shell <stem <roots. The concentration of arsenic in the grain of both varieties was significantly different and correlated with concentration of phosphorus being higher for Indica than the hybrid of Indica. Also, inorganic arsenic was found to be the dominant specie present in grains of rice for all of analyzed species.

In Poland, studies were conducted comparing the concentration and speciation of arsenic incorporated into plants of white mustard (*Sinapis alba*), which took place in the presence of various arsenic compounds and found that mustard has the capacity to absorb different arsenic forms. The samples of mustard were grown in different solutions containing arsenic (III), arsenic (V), methylarsonic acid (MMA) or dimethylarsonic acid (DMA). The translocation factor reported by authors was high (0.70) when DMA was added to the nutrient solution (Lukasz et al., 2010).

Vamerali et al. (2009) found that the concentration of trace elements (As, Co, Cu, Pb and Zn) is higher in roots of poplar (*Populus*) and willow (*Salix*) than in the aerial shoot. Moreover, this accumulation is more pronounced in thin roots. In different species used for this study, a pronounced aging of thick roots was found.

Ruiz et al. (2008) found a concentration of  $1750 \text{ mg kg}^{-1}$  of arsenic in plant samples at sites with arsenic contaminated soil that presented a concentration range of arsenic from 1.14 to  $98.5 \text{ mg kg}^{-1}$  (dry weight), while in other plants that grow in sites with the same geological characteristics presented a concentration range from 0.06 to  $0.58 \text{ mg kg}^{-1}$ . On the other hand, the arsenite and arsenate were found in all plant samples and in some plant species was found organic arsenic as MMA, DMA and trimethylarsine oxide. The importance of know the arsenic present in water produce diferent effects in human healths

## Conclusions

The presence of high concentrations of arsenic in the agricultural system of water-soil-crop has led to a serious problem. Therefore, to dimension and solve this problem, considerable research is being done around the world. In general terms, there are two sources of arsenic in agriculture, namely, arsenic coming from deep wells from sites that due to its geological characteristics contain heavy metals and arsenic coming from agrochemicals and industrial wastes. The contaminated water used in agriculture for irrigation is moving arsenic to soil and crops, which is currently the major source of this element in agriculture.

The arsenic adsorbed by crops from contaminated water depends on several factors such as pH, temperature, oxidation state of arsenic, type of soil and crop. However, it is required to study the interaction among arsenic, organic matter, metals, pH and its relationship with the mobility and adsorption in plant. It is known that bioaccumulation of arsenic in some crops leads to biomass and yield reduction. Usually, in crop plants, it is found that arsenic concentration is the highest at the root, followed by stem, leaf and the lowest concentration is found in grain or fruit. It is lacking in the technical literature a differentiation of the arsenic effects on plant depending on the way it is exposed to arsenic, either by soil or water. In the other hand, the interaction of arsenic and nutrients intake by plant and the intake mechanisms as well as the transport of arsenic in several plant structures is up to day not completely understood.

Additionally, the agricultural soil is accumulating arsenic from contaminated irrigation water. The bioaccumulation and adsorption of arsenic in soil is affected by its properties such as the content of oxalic, citric and malic acids. In the other hand, organic matter plays an important role in the dynamics of arsenic in soil, since the greater arsenic concentrations are found in surface layers (about 0.50 m deep) in cases where the arsenic contamination is due to irrigation. In addition, the adsorption of arsenic is related to the presence of ions and metals that competes by the adsorption sites of arsenic in soil.

Since cutting off the main source of arsenic may be the solution to the problem of arsenic in agriculture, reestablishing the water levels of groundwater and aquifers by good irrigation practices and efficient irrigation technologies can be considered the best sustainable solution. In the meantime, removal technologies of arsenic from water and soil may help. Thus, removal technologies of arsenic in soil such as inverse osmosis, precipitation, adsorption and phytoremediation are proposed. Among of them, phytoremediation is more environmental friendly and is easier to implement than its counterparts. However its effectivity relies in characteristics of the arsenic hyperaccumulator plant. Therefore, finding better hyperaccumulators is still an active area of research. Remediation technologies including oxidation, coagulation/

coprecipitation, adsorption, reverse osmosis and ion exchange are proposed for cleaning drinking water. However, these technologies are either too expensive to be incorporated in agricultural daily practices due to the huge water volumes required in agriculture. To the best acknowledge of the authors, it is still required to propose a remediation technology cheaper than existing ones and able to remove arsenic from water volumes required in the agriculture.

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