

# Arsenic in Eastern Croatia - problems and solutions

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## ARSENIC IN EASTERN CROATIA – PROBLEMS AND SOLUTIONS

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review

### Summary

Groundwater in Eastern Croatia contains elevated concentrations of inorganic arsenic. The biggest well field in the area has an average arsenic concentration of 200 µg/L and it supplies the population of around 200,000 people with drinking water. Croatian Regulation has adopted guidelines from the European Council Directive for the maximum concentration limit (MCL) of 10 µg/L of As in drinking water. However, it has been estimated that almost 120,000 people drink water from that well field with a concentration of arsenic over 10 µg/L. To reduce the health risks associated with arsenic-contaminated water intake in Eastern Croatia it is important to develop proper strategies that will use one of the following technologies for arsenic removal: oxidation, coagulation-flocculation, adsorption, ion exchange or membrane technologies.

*Keywords:* drinking water, groundwater, arsenic removal, Eastern Croatia

### Introduction

The contamination of groundwater by arsenic has been reported all over the world and the largest poisoning of a population in history was in Bangladesh, where millions of people were exposed (Smith et al., 2000).

Some parts of Europe are affected by a high concentration of arsenic and it is estimated that around 600,000 people are exposed to the danger (Smedley and Kinniburgh, 2002). A summary of the recent research in the Pannonian basin can be found in Table 1. (Romić et al., 2011; Varsanyi and Kovacs, 2006; Lindberg et al., 2006; Papić et al., 2012).

**Table 1.** Maximum concentration of arsenic in countries of the Pannonian basin (Romić et al., 2011; Varsanyi and Kovacs, 2006; Lindberg et al., 2006; Papić et al., 2012)

Country/region	µg As/L
Croatia	610
Hungary	800
Romania/Transylvania and Western Plain	200
Serbia/Vojvodina	150

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The presence of arsenic in the groundwater of Eastern Croatia's was confirmed almost 20 years ago and since then many studies were conducted to understand the biogeochemical cycling of As in the groundwater of the affected areas (Ujević Bošnjak et al., 2012). Ujević Bošnjak et al. (2013) have reported that elevated concentrations of arsenic in Eastern Croatia's groundwater are due to the geological composition of the soil. The analysis of drinking water in that area showed that the population of 200,000 people daily consume water with arsenic concentrations between 10 and 610 µg/L (Habuda-Stanić et al., 2007).

The European guidelines for arsenic in drinking water are in accordance with the WHO guidelines for the maximum concentration limit (MCL) of 10 µg/L (WHO, 2008; CD 98/83/EC, 1998). Croatian Regulation has adopted those guidelines, but it has been estimated that almost 120,000 people from the city of Osijek drink water with a concentration of arsenic over 10 µg/L (MCL) (NN 125/17 2017; Romić et al., 2011).

Arsenic causes largescale health effects through drinking-water exposure, including beverages that are made from drinking water (WHO, 2008). Exposure to arsenic can result in a variety of health problems in humans, including various forms of cancer (e.g. skin, lung, and bladder), cardiovascular and peripheral vascular disease, and diabetes (Hughes, 2002).

This paper represents a short overview of arsenic concentrations found in groundwater in the region of Eastern Croatia. It also describes the treatment technologies that have been applied at a full-scale level for the treatment of drinking water in the affected areas. The technologies for arsenic removal usually include the following processes: flocculation with microfiltration, adsorption on natural or synthetic materials, ion exchange, microfiltration, ultrafiltration, nanofiltration, reverse osmosis, and electrodialysis, which are predominantly based on arsenic peroxidation (Habuda-Stanić et al., 2015).

### **Description of the study area**

The study area of this research is Eastern Croatia. It is situated between the Sava, Drava and Danube rivers and it belongs to the southern brim of the Pannonian basin. The area comprises three geotectonic units: the eastern part of the Drava depression in the north, a part of the Slavonia-Srijem depression in the south, and the central Đakovo-Vinkovci plateau together with the Vukovar plateau (Ujević Bošnjak et al., 2012).

The groundwater of the region is characterized by high water hardness and it contains high concentrations of iron, manganese, ammonia, organic substances and arsenic (Habuda-Stanić et al., 2015).

In the past decade, many studies were conducted to understand the presence of arsenic in the groundwater of Eastern Croatia. A recent review of the literature on this topic found that the distribution of arsenic in the groundwater of Eastern Croatia varies between <1 µg/L and >100 µg/L (Fig. 1) (Ujević et al., 2010).

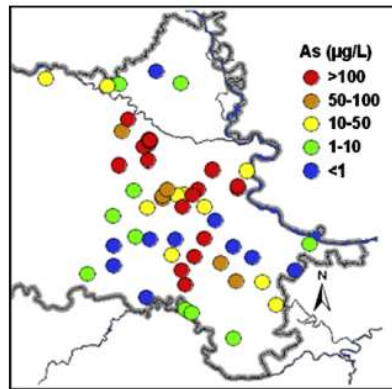


Fig. 1. Distribution of  $As_{tot}$  in the groundwater of Eastern Croatia (Ujević et al., 2010)

The biggest well field in the region is “Vinogradi” and it has an average arsenic concentration of 200 µg/L. The variations in the mean concentration of  $As_{tot}$  in the 18 water wells of the “Vinogradi” well field are shown in Fig. 2 (Habuda-Stanić et al., 2007; Romić et al., 2011).

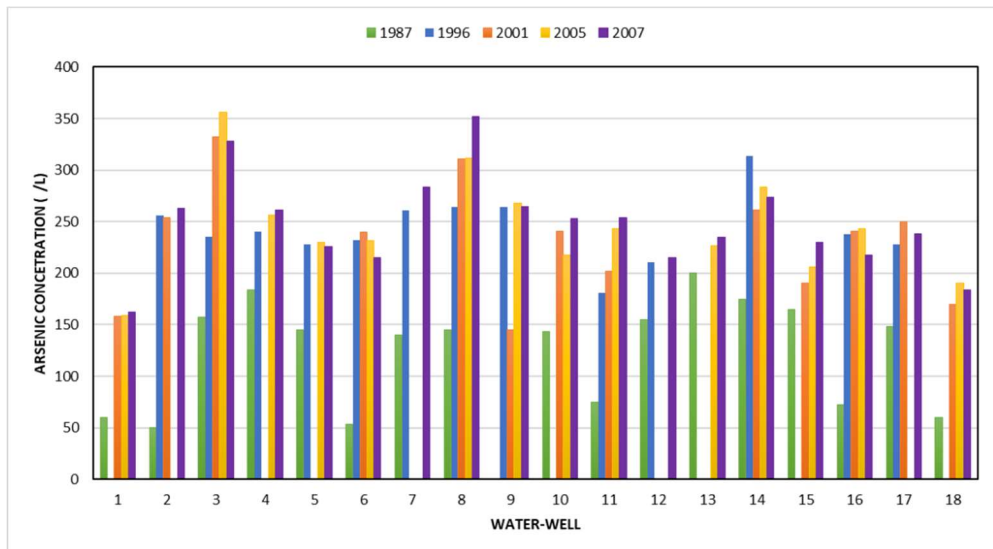
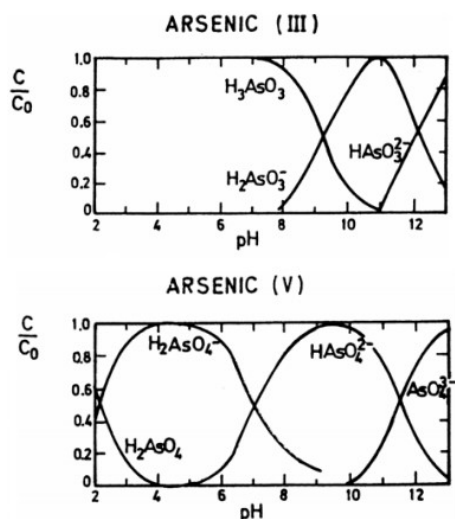


Fig. 2. Arsenic concentration (µg/L) in the groundwater resource of the “Vinogradi” well field

## Removal of arsenic

Arsenic is found widely in the earth's crust, in oxidation states of -3, 0, +3 and +5, often as sulphides or metal arsenides or arsenates (WHO, 2008). In natural waters, arsenic can be found in inorganic forms as oxidized trivalent arsenite [As(III)] or pentavalent arsenate [As(V)], mostly as  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ ,  $\text{H}_3\text{AsO}_3$  and  $\text{H}_2\text{AsO}_3^-$  (Habuda-Stanić et al., 2008). The pH value and redox potential are the most important factors in the determination of the form of arsenic in water. In moderately reducing anaerobic environments (e.g., subsurface waters, reduced sediments), arsenic primarily exists as As(III). On the other hand, arsenate is prevalent in aerobic oxidizing environments, such as surface waters (WHO, 2011). Moreover, at lower pH values (<6.9)  $\text{H}_2\text{AsO}_4^-$  is a dominant form, while at higher pH values the dominant form is  $\text{HAsO}_4^{2-}$  (Fig. 3) (Habuda-Stanić et al., 2008).



**Fig. 3.** The stability and predominance of arsenite and arsenate in the water as a function of pH (Gupta and Chen, 1978)

The chemistry and composition of arsenic-contaminated water are the major factors determining the removal of arsenic (Singh et al., 2015). By now many methods have been developed to manage arsenic pollution and other types of water pollution. The efficiency of arsenic removal depends on its valence. Arsenic is most effectively removed or stabilized when it is present as As(V), because As(III) is predominantly non-charged at the pH value below 9.2 (Fig. 3) (Jekel, 1994; Johnston and Heijnen, 2001).

Nicomel et al. (2015) reported several conventional technologies for arsenic removal from drinking water:

- oxidation (oxidation and filtration, photochemical oxidation, photocatalytic oxidation, biological oxidation, in situ oxidation etc.),
- coagulation-flocculation,
- adsorption (activated alumina, iron-based sorbents, zero-valent iron, indigenous filters, miscellaneous sorbents, metal organic frameworks etc.),
- ion exchange and
- membrane technologies (microfiltration, ultrafiltration, nanofiltration, reverse osmosis).

### *Oxidation*

Oxidation is a reaction that reduces or oxidizes chemicals, thus changing their chemical form. In the case of arsenic removal, oxidation involves the conversion of soluble As(III) to insoluble As(V). However, oxidation alone does not remove arsenic from a solution, and it must be coupled with a removal process such as coagulation, adsorption or ion exchange (Johnston and Heijnen, 2001). Various oxidants are used in this process, such as atmospheric oxygen, chlorine, hydrogen peroxide, potassium permanganate and many other chemicals, as well as bacteria. Ahmed (2001) specified that the oxidation of As(III) with oxygen is a very slow process, which can take hours or weeks to complete. On the other hand, chemicals, such as chlorine, ozone, and permanganate, can rapidly oxidize As(III) to As(V) (Nicomel et al., 2015). Singh et al. (2015) emphasised that interfering substances present in water need to be considered before selecting the proper oxidant, as these substances can greatly affect and dictate the kinetics of As(III) oxidation.

### *Coagulation-flocculation*

Coagulation and flocculation are among the most employed and documented techniques for arsenic removal from water (Johnston and Heijnen, 2001; Choong et al., 2007). The principle of this technology is that dissolved arsenic is transformed by the chemicals (coagulants) into an insoluble solid, which undergoes precipitation later (Habuda-Stanić and Kuleš, 2002). Solids are then removed from water by sedimentation and/or filtration. The most used coagulants are  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{FeCl}_3$ . They are equally effective in removing arsenic from water but their efficiency depends on the pH value.

One of the biggest problems of the coagulation-flocculation technology is the production of high amounts of arsenic-concentrated sludge and it is necessary to properly dispose of that sludge to prevent secondary pollution of the environment. Habuda-Stanić and Kuleš (2002) reported that these limitations make this process less feasible, especially in field conditions. Moreover, in Eastern Croatia, water supply systems of two towns, Vinkovci and Osijek, use groundwater processed by the coagulation–filtration method. The continuous optimization of key parameters during the water treatment in the Osijek Waterworks Company resulted

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in the removal of up to 85% of total arsenic (from average 250 µg/L to average 40 µg/L) (Habuda-Stanić et al., 2007).

*Adsorption and ion exchange*

Adsorption is a process that uses solids as a medium for the removal of substances from gaseous or liquid solutions (Singh et al., 2015). The principle of adsorption is a separation of substances from one phase followed by their accumulation at the surface of the adsorbent. They are characterized by the use of natural and synthetic exchangers whose polymeric structures are saturated by various adsorbents, in order to increase efficiency (Habuda-Stanić et al., 2008). Recent studies reported a wide range of adsorbents, including activated carbon, minerals and biomaterials; although granular ferric hydroxide, as well as several Fe(III) oxides, such as amorphous hydrous ferric oxide, goethite and poorly crystalline hydrous ferric oxide, proved to be promising adsorptive materials (Habuda-Stanić et al., 2008; Hossain et al., 2005; Huang and Fu, 1984; Singh et al., 2002). This can be explained by the fact that there is a high affinity between inorganic arsenic species and iron (Gupta et al., 2012). Several advantages of adsorption are: relatively high arsenic removal efficiency (Singh and Pant, 2004; Mohan and Pittman, 2007), easy operation, and handling (Jang et al., 2008), cost-effectiveness (Anjum et al., 2011), and no sludge production (Singh et al., 2015). Moreover, ion exchange can be considered as a special form of adsorption and it involves the reversible displacement of an ion adsorbed onto a solid surface (ion exchange material) by a dissolved ion in solutions (Johnston and Heijnen, 2001). Ion exchange materials or ion exchange resins are commercially produced synthetic materials that can remove some compounds from water, most commonly those that cause hardness of water (Johnston and Heijnen, 2001). Ion exchange is also used for arsenic removal and its efficiency depends on the pH value of water, valence and the concentration of arsenic in water and the selectivity of ion exchange resins. Various strong-base anion exchange resins are commercially available (sulfate-selective resins, nitrate-selective resins and the most common are strongly basic resins in Cl<sup>-</sup> form) and those can effectively remove arsenate from a solution, producing effluent with less than 1 µg/L of arsenic, while arsenite, being uncharged, is not removed from solutions (Johnston and Heijnen, 2001). The disadvantages of ion exchange technologies are: low efficiency in the removal of As(III), a high concentration of SO<sub>4</sub><sup>2-</sup>, Fe ions and other soluble substances can decrease the affinity of the exchanger for arsenic compounds (AWWA, 1999).

*Membrane technologies*

Membrane technologies are based on the preferential permeation or rejection of various solute molecules in a semi-permeable polymer or inorganic membranes (Maroulis and Saravacos, 2003). The driving force in this process is the difference in mechanical pressure between the feed and the permeate sides. Membrane filtration has the advantage of removing

many contaminants from water, including bacteria, salts, and various heavy metals (Johnston and Heijnen, 2001). Two types of membrane separation processes can be distinguished: low-pressure membranes (microfiltration – MF and ultrafiltration – UF) and high-pressure membranes (nanofiltration – NF and reverse osmosis – RO). RO and NF are used for arsenic removal due to appropriate pore size. Dissolved arsenic is in the ‘metal ion’ size range (Fig. 4). Moreover, RO can remove >99% of arsenic, while MF and UF in combination with coagulation-flocculation can remove 95% of arsenic.

Johnston and Heijnen (2001) reported several disadvantages of membrane technologies:

- high investment costs;
- membranes can be fouled by colloidal matter in the raw water, particularly organic matter, including iron and manganese;
- low water recovery rates (typically only 10-20% of the raw water passes through the membrane);
- treated water has very low levels of dissolved solids, and can be very corrosive, and deficient in minerals, which can include important micronutrients for humans.

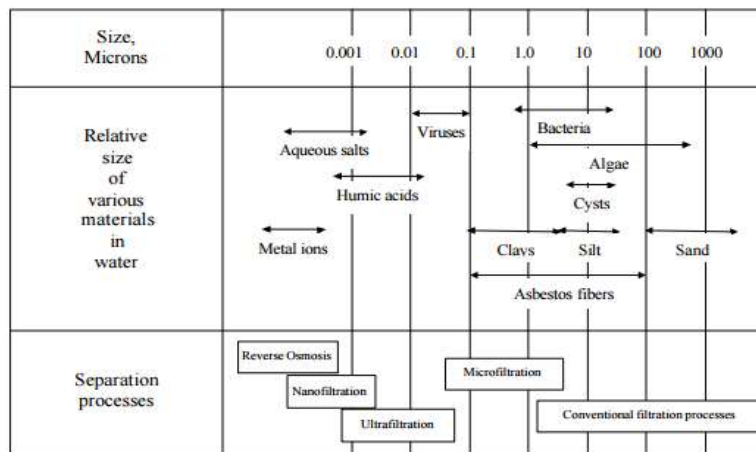


Fig. 4. The membrane separation spectrum (Johnston and Heijnen, 2001)

## Conclusions

This paper has summarized the major arsenic-affected areas of groundwater in the region of Eastern Croatia. Several studies have shown that the occurrence of arsenic in natural groundwater is due to the geological composition of soil and that it is not the result of anthropogenic influence.

The analysis of drinking water in the area showed that the population of 200,000 people daily consume water with arsenic concentrations between 10 and 610 µg/L. Long-term



intake of drinking water with elevated arsenic concentrations can cause the development of arsenicosis, the collective term for diseases caused by chronic exposure to arsenic. Moreover, this review has explained the technologies that have been applied on a full-scale level for the treatment of drinking water in the affected areas. In Eastern Croatia, the water supply systems of two towns, Vinkovci and Osijek, are using groundwater that is processed by the coagulation–filtration method. However, all other water supply systems in Eastern Croatia are using rapid sand filtration for drinking water treatment, which has also resulted in high arsenic residuum.

In order to reduce the health risks associated with the intake of arsenic-contaminated water in the region of Eastern Croatia, it will be necessary to develop proper strategies that will use the technologies for arsenic removal which are described in this paper.

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