Science of the Total Environment 543 (2016) 147–154

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Toxicological and chemical assessment of arsenic-contaminated groundwater after electrochemical and advanced oxidation treatments

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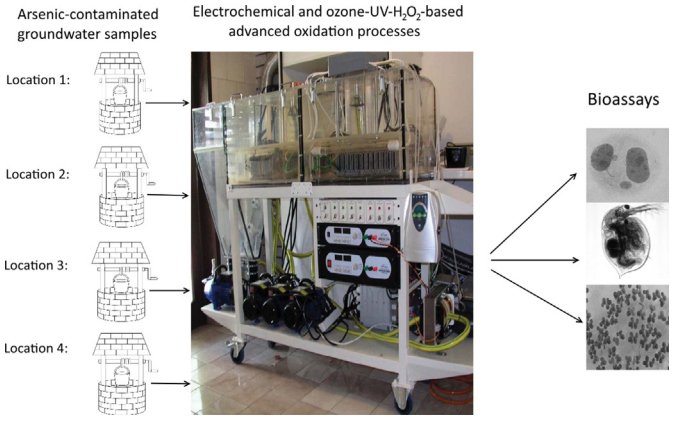
HIGHLIGHTS

- Toxicity of treated and untreated arsenic-contaminated groundwater was assessed.
- Chemical analysis and bioassays on human cells, plants and *Daphnia* were conducted.
- Genotoxic and toxic compounds induced oxidative stress.
- Toxicity and genotoxicity were removed following the treatment.
- Chronic toxicity test more suitable in evaluation of arsenic-polluted groundwater

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 May 2015
Received in revised form 30 October 2015
Accepted 30 October 2015
Available online xxxx

Editor: D. Barcelo

Keywords:
Arsenic
Toxicity
Human lymphocytes

ABSTRACT

Owing to its proven toxicity and mutagenicity, arsenic is regarded a principal pollutant in water used for drinking. The objective of this study was the toxicological and chemical evaluation of groundwater samples obtained from arsenic enriched drinking water wells before and after electrochemical and ozone–UV–H_2O_2-based advanced oxidation processes (EAOP). For this purpose, acute toxicity test with *Daphnia magna* and chronic toxicity test with *Lemna minor* L. were employed as well as in vitro bioassays using human peripheral blood lymphocytes (HPBLs). Several oxidative stress parameters were estimated in *L. minor*. Physicochemical analysis showed that EAOP treatment was highly efficient in arsenic but also in ammonia and organic compound removal from contaminated groundwater. Untreated groundwater caused only slight toxicity to HPBLs and *D. magna* in acute experiments. However, 7-day exposure of *L. minor* to raw groundwater elicited genotoxicity, a significant growth inhibition and oxidative stress injury. The observed genotoxicity and toxicity of raw groundwater samples was almost

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http://dx.doi.org/10.1016/j.scitotenv.2015.10.158

Lemna minor
Daphnia magna
Advanced treatment

completely eliminated by EAOP treatment. Generally, the results obtained with *L. minor* were in agreement with those obtained in the chemical analysis suggesting the sensitivity of the model organism in monitoring of arsenic-contaminated groundwater. In parallel to chemical analysis, the implementation of chronic toxicity bioassays in a battery is recommended in the assessment of the toxic and genotoxic potential of such complex mixtures.

1. Introduction

Inorganic arsenic species are able to cause cancer in humans though it is harmful to other biota as well (Ng et al., 2003). In many nations, more than half of the withdrawn groundwater is used for domestic water supplies providing 25 to 40% of the world's drinking water (WWAP, 2006). The main environmental exposure to elevated concentrations of arsenic for humans is through contaminated groundwater, imposing a health risk for millions of people worldwide (Ng et al., 2003). Uncontaminated freshwaters seldom contain more than 10 μg L^{-1} of arsenic; this concentration has been determined as a threshold for arsenic in drinking water by the World Health Organization (WHO) (Sharma and Sohn, 2009). Although in most European countries this standard is rarely exceeded, elevated concentrations of naturally-occurring arsenic in groundwater are found in the Pannonian Basin (Eastern Europe). This incident may cause serious health problems upon prolonged exposure for more than half a million people in several countries of Eastern Europe (Van Halem et al., 2009). Approximately 200,000 inhabitants of Eastern Croatia are exposed to arsenic at levels ranging from 10 to 610 μg L^{-1} since the groundwater from water wells is used as a principal drinking-water source (Habuda-Stanić et al., 2007). Various purification methods have been developed for the treatment of arsenic contaminated water (Choong et al., 2007). Besides arsenic, the groundwater in Eastern Croatia is often loaded with high concentrations of iron, manganese, ammonia and organic substances (Ujević et al., 2010). In the present study, arsenic-contaminated groundwater samples collected from four drinking water-wells in Vinkovci County (Eastern Croatia) were subjected to simultaneous electrocoagulation (using iron- and aluminum-electrodes) and ozonation and subsequent advanced oxidation processes (AOP) comprising simultaneous ozone and UV light and/or hydrogen peroxide treatment (Oreščanin et al., 2013; Oreščanin et al., 2014).

The aim of this research was to evaluate the acute and chronic toxicological effects of groundwater samples obtained from drinking water wells prior to and after the treatment. For this purpose, two standardized toxicity tests (ISO 6341, 2012; ISO 20079, 2005) with freshwater organisms *L. minor* and *D. magna* were applied. Since the contaminated groundwater is still commonly used for human consumption, human cells were also employed as target organisms. Bioassays (cell viability and comet assays) with peripheral blood lymphocytes (HPBLs) used as sensitive in vitro models have previously proven their suitability in the evaluation of cytotoxic and genotoxic potential of arsenic and carcinogenic metals (Gajski et al., 2015). The use of a battery of bioassays with model systems covering different trophic levels is recommended in water quality testing as toxic substances have different modes of action and target receptors and thus do not produce the same effects in divergent test organisms (Hernández Leal et al., 2012; Kungolos et al., 2015). Since *L. minor* showed high sensitivity to raw groundwater in our preliminary experiments, additional analysis (comet assay and indicators of oxidative stress) was performed with this model organism. Oxidative stress parameters were analyzed as the number of contaminants, including arsenic and metals, have been found to act as potent elicitors of reactive oxygen species (ROS) formation (Fodor, 2004; Radić et al., 2013).

2. Material and methods

2.1. Collection and handling of water samples

Drinking wells from four locations – Andrijaševci (46°1′27″ N, 6°48′35″ E), Antin (44°43′51″ N, 6°59′29″ E), Komletinci (47°5′50″ N, 6°25′33″ E) and Vrbanja (47°14′5″ N, 6°31′17″ E) – situated in the Vukovar-Srijem County, Eastern Croatia were used as sampling sites. As much as 300 L of groundwater was collected per well and stored at +4 °C. Water was pumped into acid cleaned polyethylene containers using a handheld electric deep water sampler, model ZYC-2A (EJER TECH, Zhejiang, China). Homogenization of water samples was performed for 10 min before the treatments and analysis using mixer model SJBQ-2.2 (Siehe Industry, Shanghai, China).

2.2. Purification experiments

2.2.1. Removal of arsenic and metals

All purification experiments were conducted at room temperature (22 °C). The method was described in detail in Oreščanin et al. (2014). In short, a certain volume of groundwater from each of the four drinking water wells (each water sample was taken in triplicate) was treated with ozone (OzoneMax 1668, Ozonemax Water Technologies, Kochi, Kerala, India) for 10 min to convert arsenite to arsenate as the latter shows the highest adsorption capacity for both iron- and aluminum-electrodes. Electrocoagulation was first performed with an iron- and then with an aluminum-electrode set, in each case with parallel arrangement — 12 cathodes and 12 anodes (dimension of individual electrode 200 × 500 × 2 mm, separation among electrodes 5 mm, reaction time 5 min). The following steps included mixing the solution with ozone (10 min), passing through an electromagnet and collection of the suspension in sedimentation tank where solids were separated from liquid (60 min). The treatment unit was a patented product (WO2013144664A9) of Advanced energy Ltd., Zagreb, Croatia. The unit and treatment method were also described in detail in our previous work (Oreščanin et al., 2013).

2.2.2. Ammonia and organic matter removal

Further treatment of partially treated groundwater samples included UV light (60 W) and ozone. In the case of AS and KO groundwater samples, 0.15 mL L^{-1} of 30% hydrogen peroxide was also added to the solution and treated for 30 min while the other two samples (AT and V) were treated for 30 min with UV and ozone only.

2.3. Physicochemical and toxicological analysis

Water samples for physicochemical and toxicological evaluation were collected from the production wells (raw groundwater samples: AS, AT, KO, V) and from the treatment plant after the completion of the purification process (AST, ATT, KOT, VT).

2.3.1. Physicochemical analysis

Assessment of water quality is done in accordance with international standards (ISO) by authorized laboratories. pH and conductivity (mS cm^{-1}) of raw (untreated) groundwater samples were determined on site whereas both parameters of all of the treated groundwater samples were measured in a laboratory.

Chemical analyses included color, turbidity, suspended solids (SS, mg L^{-1}), chemical oxygen demand (COD, mg of O_2 per liter), total organic carbon (TOC), nitrate (mg L^{-1}), nitrite (mg L^{-1}), total ammonia (mg L^{-1}), soluble phosphate (PO_4^{3-}, mg L^{-1}), cloride (Cl^-) and fluoride (F^-) contents (EN 1484, 1997; ISO 7888, 1985; ISO 6060, 1989; ISO 10523, 1994; ISO 11923, 1997; ISO 14911, 1998; ISO 7027, 1999; ISO 10304, 2007; ISO 7887, 2011; ISO/TR 11905, 1997). Mercury was determined by atomic fluorescent spectrometry (QuickTrace M-8000