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Boron in groundwaters of Nicosia (Cyprus) and its treatment by reverse osmosis

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Abstract

Boron levels in groundwaters of Nicosia have been determined, compared to previous concentration data and correlated to the concentration of other chemical species contained in the groundwaters under investigation. According to data evaluation boron levels measured at different time do not differ statistically significant from each other, indicating that basically the geological background governs the boron content and origin in these systems. However, analytical data point out that boron levels in Nicosia groundwaters are toxic for boron sensitive crops and hence these have to be appropriately treated prior usage for irrigation purposes. Treatment of those groundwaters by reverse osmosis has shown that boron removal by this technique can be used effectively for the reduction of boron in groundwaters, particularly at pH > 9.5.

Keywords: Boron; Groundwaters; Geological background; Reverse osmosis; pH

1. Introduction

Present and future availability of drinking and irrigation water has become of cardinal importance for the economic and social development of Cyprus. The problem is more serious because Cyprus is a semi-arid region and groundwater is (besides desalination) of primary importance for drinking and irrigation purposes.

In arid and semi-arid areas groundwater used for irrigation contains high levels of boron related to the origin and composition of the background lithology [1]. Boron enters into the surface and groundwater systems by leaching of rocks and soils, as well as by geothermal releases [2,3]. On the other hand anthropogenic sources of boron are related to release of boron containing products into water through municipal sewage systems and mining and processing of boron minerals [4].

Boron concentration in irrigation water is of particular interest because of its beneficial and toxic effects in plants. The range between deficiency and toxicity symptoms is narrow, necessitating accurate quantification of solution

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boron concentrations and pre-treatment of irrigation water, that contains elevated amounts of boron, prior application. Generally, boron levels above 0.3 mg/L in irrigation waters for sensitive crops (e.g. citrus trees) and levels above 1.0 mg/L for most plants are considered to be toxic [5,6].

Among several technologies that have been proposed for the removal of boron from waters and wastewaters, reverse osmosis represents a widely applied water purification technique [7,8]. Regular reverse osmosis membranes reject boron to a level of about 40–80%, while the rejection of certain salts (e.g. NaCl) is almost 100%. The low rejection efficiency of boric acid is ascribed to the ability of this neutral species to diffuse through the membranes [9].

The present paper reports about seasonal variation of boron levels in groundwaters of Nicosia, the comparison of these data with previous concentration data and the correlation of boron levels with concentration of other chemical species contained in the corresponding groundwaters. Furthermore, the purification of a selected groundwater by reverse osmosis as a function of pH is presented and discussed.

2. Materials and methods

Groundwater samples were collected in 1-L plastic bottles from 20 different sites of Nicosia and surroundings. Groundwater sampling was carried out at three different time periods (Summer 2002, Winter 2002/2003 and Spring 2003) and overall 60 groundwater samples had been collected and immediately analysed for pH, electrical conductivity (EC) and cation (Na^+, K^+, Ca^{2+} and Mg^{2+}) and anion (Cl^-, NO_3^-, HCO_3^- and SO_4^{2-}) concentration.

pH was measured potentiometrically by means of a glass electrode (WTW-Model pH537), which was calibrated against pH 4, 7 and 10 standard buffer solutions and the electrical conductivity using a commercially available conductivity meter and electrode (Jenway-Model 4020). Before chemical analysis, the groundwater samples were filtered through a 450 nm cellulose acetate filter. Concentration of the cations was determined spectroscopically by means of ICP-OES (Shimadzu ICP-7500). Additionally, determination of sodium and potassium concentration was carried out by flame photometry (Gallenkamp Flamme Analyser) and calcium and magnesium concentration was analysed by complexometric titrations using EDTA. Determination of anion concentrations was carried out as follows: sulfate by ICP-OES and gravimetry, chloride by means of argentometry (Mohr Method), nitrate by colorimetry (Lovibond 550) and HCO_3^- by acid/base titration. The concentration of boron in solution was determined by ICP-OES or by photometry using the azomethine-H method [10]. The precision of the classical methods of chemical analysis was 1%, whereas overall precision of instrumental methods of analysis was estimated to be 5%.

Reverse osmosis experiments were carried out by means of a commercially available system (Nimbus Co.) designed for a flow of 18 L min^{-1}. The pre-filtered (by safety microfilters) groundwater was stored in plastic tanks (2 tons) and prior processing the pH was adjusted to the desired pH by addition of a base (1 M NaOH) or acid (1 M HCl). The pH of the samples has been varied between 6.5 and 11. Every hour samples of purified water were taken and analyzed for their chemical composition.

Data regarding boron imports were adopted from the annual imports and exports statistics of the Statistical Service of the Republic of Cyprus (1974–2001) and data concerning previous measurements of boron concentration in the corresponding groundwaters were obtained from old reports of the Geological Survey Department (1982–1984). Statistical analysis of the experimental data such as comparison of group means and multivariate analysis was performed using the JMP statistical software package (version 4).

3. Results and discussion

3.1. Long-term and seasonal variation of boron levels

Fig. 1 shows boron concentration data measured in groundwaters of Nicosia at different time periods. The data denoted as “1982–1984” correspond to boron levels measured in groundwaters from different boreholes in the time period between 1982 and 1984, and the data denoted as “summer2002”, “winter2002” and “spring2003” correspond to boron levels measured in groundwaters obtained from the same boreholes within this study. In Fig. 1 the different groups are represented by a “means diamond” and a quantile box plot. The “means diamond” provide the mean, as a horizontal diagonal line and the span of boron concentration values corresponding to the 95% confidence interval for each group, as top and down corners. The quantile box plot shows the median as an inside horizontal line, while the ends of the box indicate the 25th and 75th percentiles. The (comparison) circles at the right of the plot provide a graphical presentation of whether the mean values of the concentration measured in the groundwaters at different time are statistically different or not. The mean values of the different groups of data are 0.6 ± 0.5, 0.77 ± 0.4, 0.70 ± 0.3 and 0.72 ± 0.4 mg/L, respectively. These values statistically don’t differ from one another at a confidence level of 95%.

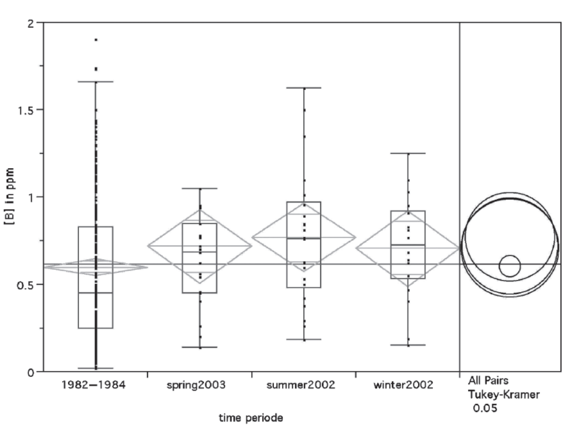

Fig. 1. Comparison of boron levels determined in groundwaters of Nicosia at different time period.

However, there are small differences between the data obtained at different time periods. The mean and in particular the median value of the previous data are lower than the corresponding values of the recent data. This relative increase of boron concentration in Nicosia groundwaters is not strictly anthropogenic. The boron content of the groundwaters originates basically from the geological background hosting the groundwater and the observed increase of boron levels is attributed to the exhaustive utilization of the groundwater reservoirs, particularly during the recent decades, which has lead to deeper boreholes and the disturbance of the respective aquifer systems. This is corroborated by the fact that import and use of boron products e.g. washing powders have been restricted in Cyprus since 1974 and hence recent increase of boron levels in Nicosia groundwaters cannot be attributed to anthropogenic sources. Nevertheless, although of natural origin the increased boron levels in Nicosia groundwaters are toxic for boron sensitive crops and have to be processed prior application. Furthermore, the slight increase of boron levels in summer period is attributed to the exhaustive groundwater use and the lack of rainwater intrusion in the groundwater reservoirs during the hot summer-period.

In addition to boron, the concentration of other main constituents (e.g. anions and cations) and physical parameters such as pH and electrical conductivity (EC) of the groundwaters have been determined. The mean values and the related standard deviations as well as corresponding mean values given in literature for groundwater and seawater are summarized in Table 1 [11] and presented graphically in Fig. 2. Comparison of the composition of the different water systems with one another reveals a relatively increased concentration of ions, which are found predominantly

Table 1
Chemical analysis of groundwater (mean values), seawater and Nicosia groundwaters

Chemical species	Groundwater (average values), mg/L	Groundwater (Nicosia), mg/L	Seawater mg/L
Cl^-	20	490 ± 325	19,000
SO_4^{2-}	30	260 ± 235	2700
HCO_3^-	200	408 ± 155	142
Na^+	30	355 ± 250	10,500
Mg^{2+}	7	75 ± 40	1350
Ca^{2+}	50	105 ± 85	410
K^+	3	10 ± 8	390
Boron	0.3	0.6 ± 0.5	4.7
pH	7	7–8	8.2
EC (μS/cm)	1500	1000–5700	55,000

in seawater, in the Nicosia groundwaters and points out the predominance of marine remains in these waters. This phenomenon is related to the geological evolution and formation of the island. During geological evolution of the island, seawater enclosed within the area under investigation was gradually evaporated leaving behind its salt and boron content [12]. Furthermore, the slope of the linear correlation between chloride and sodium ion concentration in Nicosia groundwaters, which is close to unity (0.7), and the relatively strong correlation between boron levels and the concentration of ions found predominantly in seawater e.g. Cl^- and Na^+ (Table 2), indicate that the increased boron levels in Nicosia groundwaters are related to seawater remains.

3.2. Boron removal by reverse osmosis

To investigate the effect of reverse osmosis on boron removal, a groundwater has been selected and treated by this technique. Specifically, the impact of pH of the feed water on the removal efficiency has been investigated in the pH range between 6.5 and 11. The physico-chemical

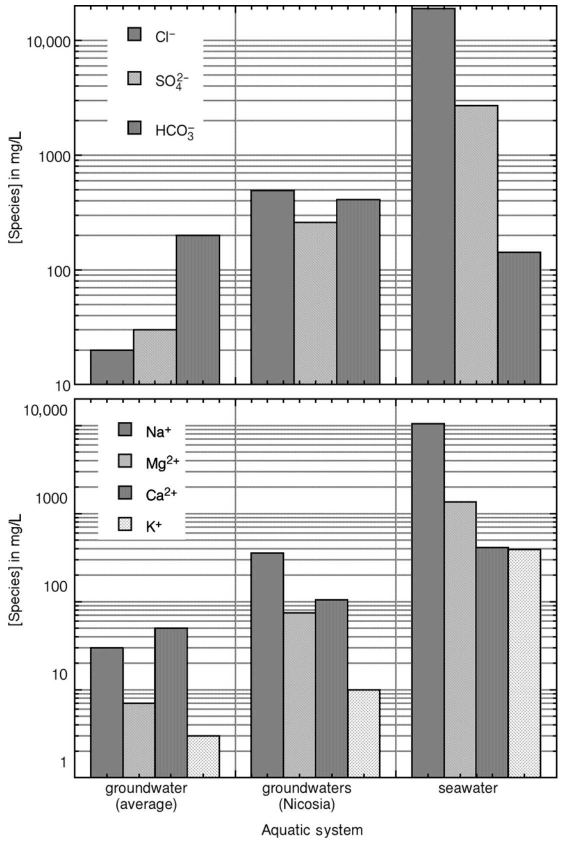

Fig. 2. Comparison of the composition (main constituents) of groundwaters (mean values), Nicosia groundwaters and seawater.

parameters of the groundwater under investigation are summarized in Table 3.

Fig. 3 shows on a logarithmic scale the concentration of the chemical species in the purified

Table 2
Regression coefficients (*R*) corresponding to linear regression analysis between boron and other main ionic constituents determined in Nicosia groundwaters

Anion	*R* value	Cation	*R* value
Na^+	0.7	Cl^-	0.7
Ca^{2+}	0.2	SO_4^{2-}	0.4
Mg^{2+}	0.4	HCO_3^-	0.6
K^+	0.4	NO_3^-	0.3

Table 3
Physico-chemical parameters of the groundwater sample treated by reverse osmosis

Anion	Concentration in mg/L	Cation	Concentration in mg/L
Na^+	1350	Cl^-	1900
Ca^{2+}	550	SO_4^{2-}	3070
Mg^{2+}	450	HCO_3^-	360
K^+	20	NO_3^-	31
	Value	Boron	2.3
pH	7.85		
EC	12,000 mS		

water after single treatment. Both, anions (e.g. Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-) and cations (e.g. Na^+, K^+, Mg^{2+}, Ca^{2+}) are almost quantitatively rejected by the reverse osmosis membrane and their concentration in the purified water decreases by factor 10 (for most species) or even 100 for calcium anions. Among the groundwater constituents, boron shows the smallest separation efficiency. The concentration of boron decreases due to reverse osmosis of the untreated groundwater (pH 7.8) from 2.3 to 1.6 ppm, which corresponds to about 30% separation efficiency. This value is comparable to corresponding values given in literature [13]. The lower separation efficiency of boron by reverse osmosis is attributed to the acid/base properties of boric acid, which is the dominating species of boron in natural aquatic systems. The value of the dissociation constant of boric acid is equal to $pK_a = 9.24$, which means that boron exists in aqueous solutions at pH < 9, and hence in the groundwater under investigation, predominantly as boric acid [11]. This neutral species permeates easily the reverse osmosis membrane, leading to lower purification efficiencies for boron in comparison to the ionic species. Boric acid is able to form hydrogen bridges with the active groups of the membrane and can diffuse in a similar way to that of water [9].

Fig. 4 shows the relative amount of boron in the purified water as a function of the pH of the feed water, as well as curves corresponding to the ratio of boron species e.g. boric acid (line) and borate (dotted line), which were calculated using the dissociation constant of boric acid. The relative amount of boron in the purified water is

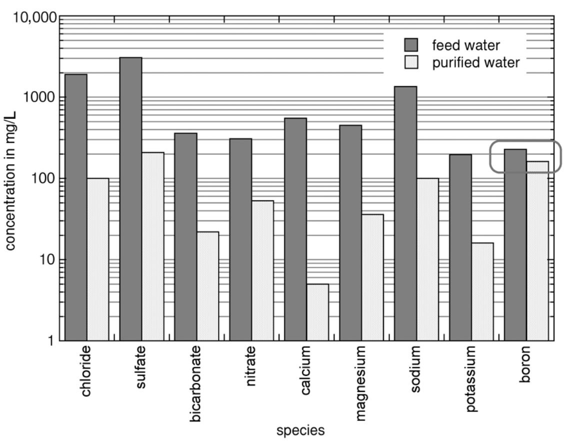

Fig. 3. The concentration of chemical species in the purified water after single treatment by reverse osmosis of a groundwater solution.

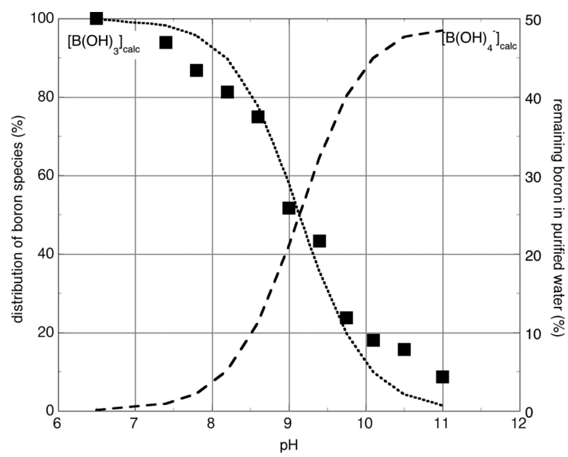

Fig. 4. Distribution of boron species as a function of pH (lines) and remaining boron in the purified water after single treatment of a groundwater sample by reverse osmosis (squares). The lines represent the calculated distribution of boron species based on the acidity constant of boric acid.

given as the percentage of boron permeated and is calculated according to Eq. (1):

$$\text{relative amount of B in purified water} \; (\%) = 100 \cdot \frac{[B]_{permeate}}{[B]_{feed}} \qquad (1)$$

where $[B]_{permeate}$ is the concentration of boron in the permeate (mg/L) and $[B]_{feed}$ is the concentration of boron in the feed (mg/L).

According to Fig. 4 the experimental data for the relative amount of boric acid in the purified water follow exactly the ratio of boric acid calculated based on the acid/base equilibrium. This occurs because borate anions are rejected, similar to other ionic species, whereas boric acid molecules permeate the membrane. Since the ratio of the boron species in solution is determined by pH, this physico-chemical parameter governs unambiguously the efficiency of reverse osmosis with respect to boron removal. The effect of pH can be better illustrated by the acid/base equilibrium given by Eq. (2):

$$B(OH)_3 + H_2O \xleftrightarrow{pH=9.24} B(OH)_4^- + H^+ \qquad (2)$$

Boric acid ($B(OH)_3$), which is a Lewis acid reacts with water resulting in the production of borate anions and protons. Reaction (2) is favoured with increasing pH. At pH 9.5 over 50% and at pH 11 almost 100% of the boric acid reacts to borate. The effect of pH is enormous because in contrast to the neutral boric acid, which permeates easily the pores of the reverse osmosis membrane, the anionic borate is held back. Similar effects have been observed also in the treatment of seawater by reverse osmosis [9,13].

4. Conclusions

In conclusion, it may be stated that generally, groundwaters of Nicosia contain boron in levels, which are toxic for boron sensitive crops. Furthermore, mean boron concentration in the groundwaters of Nicosia has slightly increased during the last three decades. This can be most probably attributed to exhaustive utilization of groundwater reservoirs during the recent decades and not to release of boron containing products through municipal sewage systems. Moreover, analysis of the groundwater composition indicates that boron in groundwaters of Nicosia is basically governed by the geological background and is of marine origin.

The pH of the groundwater is a critical parameter with respect to boron removal. Increased pH favours the formation of borate anions and hence the removal efficiency of boron by reverse osmosis. Regarding boron removal from Nicosia groundwaters it could be shown that at inherent pH the removal efficiency lies between 30 and 40% and can be increased up to 100% by increasing the alkalinity of the groundwater to values above pH > 9.5.

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