



Article

Survey of Heavy Metal Contamination in Water Sources in the Municipality of Torola, El Salvador, through In Situ Sorbent Extraction

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Abstract: The presence of heavy metals in water resources directly affects consumer health. The quality of surface water resources in Central America is usually low due to the presence of metals and other pollutants. The lack of analytical instrumentation to perform routine monitoring of water has encouraged the development of easy tools to facilitate the determination of heavy metals in waters in remote sites. In this study, we evaluated the use of different sorbents, such as Adsorbsia As600 (titanium dioxide), Iontosorb Oxin, 8-hydroxyquinoline bearing functional groups, and Duolite GT-73, with thiol functionality, for Cd, Ni, Cu, Zn, and Al extraction. It was found that both Adsorbsia As600 and Iontosorb Oxin allowed the adsorption of all metals, and the recovery was achieved using either HCl or ethylenediaminetetraacetic sodium salt (EDTA) solutions. Hence, Adsorbsia As600 was employed for in situ sampling in the metal contamination evaluation of water samples (from 15 wells and nine storage tanks) from the municipality of Torola, Mozarán, El Salvador. The developed procedure allowed all the metals in the samples to be detected, and Ni and Al were found to be above Salvadoran guidelines for drinking water quality.

Keywords: water resources; heavy metals; Adsorbsia As600; titanium dioxide; solid-phase extraction; in situ extraction; El Salvador

1. Introduction

Heavy metals are natural constituents of the Earth's crust and since they cannot be degraded or destroyed, they are considered persistent environmental pollutants. Generally, heavy metal pollution originates from anthropogenic sources, such as untreated domestic and industrial wastewater discharges, accidental chemical spills, direct soil waste dumping, and residues from some agricultural inputs [1,2] and are present in air, sediments, and water. These elements have been associated with environmental degradation, poor water quality [3], and different human diseases [2] due to their toxicity at very low doses. They can enter the body through food, air, and water, and bio-accumulate over a period of time [4]. Toxicity effects can be divided into two categories: acute and chronic effects. Acute effects appear immediately or shortly after exposure, while chronic effects may be manifested many years later and their etiological origins are often difficult to trace [5,6].

El Salvador is a small country located on the Pacific coast of Central America. It borders with Honduras in the north and east, and with Guatemala in the west. It has rough mountainous areas with

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several active volcanoes and steep mountain ranges on its northern border. It has a total area of only 21,000 km², but it has the largest population density in continental America (304 inhabitants/km²) [7]. The environment has been heavily damaged by deforestation related to farming activities and unregulated urban development. Several studies have reported high concentrations of arsenic and pesticides in surface waters [6,8–11]. The rural population in El Salvador lives in poverty with only partial access to basic services. In rural areas, most housing is not connected to the national water grid and water is obtained from traditional hand-dug wells or local water networks. These water sources do not have regular quality control from health authorities. Previous studies carried out in Salvadoran rural communities identified a high prevalence of the so-called chronic kidney disease of non-traditional causes (CKDnt) [12,13] mainly affecting male farmers, but also women and children not involved in agricultural work [14]. The disease cannot be explained by traditional causes, such as diabetes mellitus or hypertension [15] and it has also been identified in other Central American countries, as well as in Asian countries, such as Sri Lanka and Vietnam. This type of disease is described as chronic interstitial nephritis related to both environmental conditions and to the farmers' hard labour conditions [16,17]. However, in Sri Lanka researchers have identified risk factors, such as exposure to pesticides and heavy metals together with the intake of hard water [18].

The quality of drinking water is an issue of paramount importance to ensure the health of the population around the world. To this end, analytical techniques devoted to the determination of inorganic and organic pollutants are continuously being improved. Focusing on the determination of heavy metals in water at low concentration levels, separation and preconcentration steps are usually needed, despite the evolution in the instrumentation and optimization of analytical conditions. Hence, solid-phase extraction (SPE) techniques are widely applied. SPE enables the limit of detection to be lowered and/or the elimination or reduction of interferences, and it has become the most popular preconcentration technique in atomic spectrometric methods used for metal quantification. Moreover, when sampling sites are located far from the laboratory, in situ application of solid sorbents affords the possibility of analyte preconcentration and preservation before analysis is feasible. Solid phases used for this purpose include organic sorbents, both natural and synthetic materials, as well as inorganic sorbents. Review documents have been published in the literature dealing with the characteristics and applications of different materials for the preconcentration of heavy metals [19–22]. According to our experience [23–25], and the information given by suppliers, the sorbents Adsorbsia As600 (Dow Chemical Company, Midland, MI, USA), Iontosorb oxin (Lachema, Ústí nad Labem, Czech Republic), and Duolite GT-73 (Supelco, Bellefonte, PA, USA) could be used as solid phases with multi-elemental capacity and high affinity for toxic heavy metals, such as Cu, Cd, and Pb.

The aim of this study was to evaluate the quality of water intended for drinking purposes with special emphasis on the detection of Cu, Zn, Ni, Cd, and Al in the municipality of Torola (Morazán, El Salvador). Different sorbents were evaluated for in situ metal preconcentration and preservation of water from remote regions before analysis could be performed in an analytical laboratory. This approach could then be exploited to evaluate the sanitary conditions of water in different sites around the world.

2. Material and Methods

2.1. Reagents and Solutions

The sorbents tested in this study were: Adsorbsia As600 (Dow Chemical Company, Midland, MI, USA), Iontosorb oxin 100 (Lachema, Ústí nad Labem, Czech Republic) and Duolite GT-73 (Supelco, Bellefonte, PA, USA). Adsorbsia As600 consists of a granulated titanium dioxide media with a particle size ranging from 250 to 1180 μ m and, according to the manufacturer, Adsorbsia As600 is designed as a single-use adsorbent for the treatment of drinking water. To perform these experiments, the solid was cleaned with high purity water and air-dried before being used, and only particles with sizes ranging from 500 to 900 μ m were selected. Iontosorb oxin and Duolite GT-73 consist of an organic

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matrix with 8-hydroxiquinoline and thiol functional groups, respectively. They were used as received. The main characteristics of the sorbents are depicted in Table 1.

| Sorbent | Matrix | Functional Group | Particle Size | Specific Surface Area | Swelling | Exchange Capacity |
|-----------------------|-------------------------------|-------------------------------|---------------|----------------------------------|---|---------------------------------|
| Adsorbsia As600 | Titanium dioxide (anatase) | Titanium dioxide (anatase) | 250–1180 μm | $250 \text{ m}^2 \text{ g}^{-1}$ | a | a |
| Iontosorb Oxin 100 | Cellulose | 8-hydroxiquinoline | 30–50 μm | b | 1.4558 g H ₂ O/ g dry sorbent | 0.77 mmol Cu/g dry |
| Duolite GT-73 | Polystyrene | Thiol | 300–1180 μm | b | ь | 0.25 mmol Cu/g dry ^c |

Table 1. Physicochemical characteristics of the sorbents used in this study.

Notes: ^a not applicable; ^b not available; ^c according to Iglesias et al. [23].

ICP-stock standard solutions (1000 mg L^{-1} , Sigma-Aldrich, Madrid, Spain) of Cu, Zn, Cd, Ni, Al, and Y were used to prepare spiked water samples. The calibration curves for ICP-OES measurements were also prepared using ICP-stock standard solutions (in ultrapure water or in 0.1 M NaCl, depending on the samples), using Y as an internal standard.

Other reagents (HCl, NaEDTA, and NaSCN) were purchased from Panreac (Spain) and were of analytical grade.

Ultrapure water was obtained from a MilliQ water purification system (Millipore Iberica S.A., Madrid, Spain).

2.2. Instruments and Apparatus

A micropH 2001 (Crison, Barcelona, Spain) pH meter and an Ecoscan conductimeter (Entech Instruments, Simi Valley, CA, USA) were used for pH and conductivity measurements, respectively, in the laboratory.

Metal concentrations in the samples were determined by an Agilent 5100 Synchronous Vertical Dual View inductively-coupled plasma optical emission spectroscope (ICP-OES) (Agilent Technologies, Santa Clara, CA, USA), or an Agilent 7500c Inductivity Coupled Plasma Mass Spectrometer (ICP-MS) (Agilent Technologies, Tokyo, Japan) .

A rotary mixer (Labinco, Dinko instruments, Barcelona, Spain) was used to facilitate the contact of the water sample with the sorbent.

Aquafast colorimeter (Thermo Scientific Orion AQ3700) was used for the in situ measurement of chloride (AC2017,), sulphate (AC208), nitrate (AC2007), ammonium (AC2012), phosphorous (AC2095), fluoride (AC2009), and hardness (AC3032C), using the reagents provided by the manufacturer. Aquafast colorimeter and all the reagents kits were supplied by Thermo Scientific, Beverly, MA, USA.

2.3. Evaluation of the Different Sorbents

Both the extraction and the elution efficiency of the sorbents were studied by means of batch experiments in the laboratories of the University of Girona (Spain). A test solution containing all the metals was prepared in a synthetic water sample (2 mM NaHCO₃, 1 mM CaCl₂, 0.5 mM NaSO₄) and the corresponding volume of the metal ICP-stock standard solution was added to achieve the desired heavy metal concentration, i.e., 200 μ g L⁻¹ Al, 50 μ g L⁻¹ Cd, 1 mg L⁻¹ Ni, 1 mg L⁻¹ Cu, and 1 mg L⁻¹ Zn. The resulting pH and conductivity of this water sample were 8.3 and 238 μ S cm⁻¹, respectively.

The amount of sorbent needed for metal extraction was selected based on the theoretical capacity of the sorbents (reported in Table 1), and on results from some preliminary tests. Thus, 200 mg of both Iontosorb oxin 100 and Duolite GT-73 were used, while in the case of Adsorbsia As600, 400 mg was employed. Extraction experiments were done by contacting each sorbent with 40 mL of the test sample in a stoppered plastic tube for a predetermined time under rotary agitation (35 rpm). Afterwards, the solution was filtered using cellulose paper and the metal remaining in the solution was measured with the ICP-OES instrument

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Extraction efficiency was calculated according to the following equation:

$$Extraction(\%) = \frac{\left(C_0 - C_f\right)}{C_0} \times 100 \tag{1}$$

where C_o is the initial concentration of the metal in the water sample and C_f is the final concentration after the predetermined contact time.

After filtration, the loaded solid was rinsed with ultrapure water and elution was performed in a plastic tube with 5 mL of the different elutants (3 M HCl, 0.1 M EDTA, and 0.5 M NaSCN prepared in 0.01 M HCl).

Elution efficiency was calculated as:

$$Elution(\%) = \frac{(C_e \times V_e)}{m} \times 100$$
 (2)

where C_e is the concentration of the metal recovered in the elution solution, V_e is the volume employed for elution (5 mL), and m is the amount of metal loaded in the sorbent.

To determine the equilibrium time, a kinetic study was also performed for Adsorbsia As600 using the test solution. The measurement of the metal remaining in the sample was carried out with an ICP-MS instrument.

Final conditions for extraction and elution experiments were 24 h and 5 h contact time, respectively.

2.4. Field Study

2.4.1. Description of the Studied Area and Sampling Sites

Torola is a remote municipality located in the northern mountain ranges of El Salvador, in the Morazán Department (see Figure 1). Torola is divided demographically into four neighbourhoods called *cantones*, where about thirty *caseríos* (rural hamlets) are spread, some of them very isolated. The municipality is located in the Torola river valley, a tributary of the Lempa River, the longest river in Central America and the country's main water source. The northern mountain ranges of El Salvador have a tropical climate with a dry season (November–April) and a wet season (May–October) with temperatures ranging from 19 °C to 28 °C [18]. Torola municipality is spread over volcanic rocks dating from the Miocene to the Pleistocene [19]. The economic sectors of Torola are agriculture and livestock production. Traditional agriculture (grains and horticulture) coexists with extensive coffee production.

Different sites of the municipality area were sampled to determine water quality and possible metal contamination, since studies on the presence of heavy metals in this area of the country were non-existent. Water sources to supply drinking water to the inhabitants of the municipality are wells and tanks, and can be found in almost every rural hamlet. Thus, water samples were taken from both sources whenever possible and only a small number of rural hamlets had no wells or tanks in operation, or they had dried up and could not be analysed. In the end, 15 wells and nine tanks were sampled (see Figure 1).

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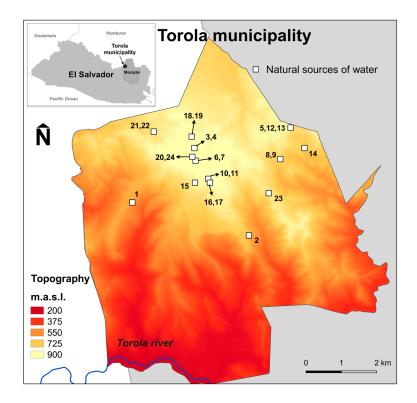


Figure 1. Map of El Salvador highlighting the municipality of Torola, the Department of Morazán, and the Torola River. Sampling sites. Code, 1: T. La Caída; 2: W. Cerritos; 3: T. El Picacho; 4: W. El Picacho; 5: W. Peña Hueca; 6: T. Maragua; 7: W. Maragua; 8: T. Ojos Agua Amates; 9: W. Ojos Agua Amates; 10: T. El Calvario; 11: W. El Calvario; 12: T. Aguazarca; 13: W. Aguazarca; 14: W. La Ceiba; 15: W. Joya del Chongue; 16: W. Barrio Ctro. Nuevo; 17: T. Barrio Ctro. Nuevo; 18: W. El Portillo; 19: T. El Portillo; 20: W. Sicahuites; 21: W. La Joya de Tijeretas; 22: T. La Joya de Tijeretas; 23: W. El Pedrero; and 24: W. El Borbollón.

2.4.2. In Situ Metal Extraction Procedure

A simple methodology was used to determine the possible presence of metals in water sources based on the use of the sorbent Adsorbsia As600. Thus, previous to the field study, plastic stoppered tubes containing 400 mg of the sorbent to be used in situ were prepared in the laboratory. Water samples were collected at the points described in Figure 1 between April and June 2015. Immediately after the water sample was taken, a volume of 40 mL was introduced in the corresponding stoppered tube and agitated using a home-made rotary mixer for 24 h. Then, the sorbent was filtered and kept refrigerated at 4 $^{\circ}$ C until it was sent to the laboratory of the University of Girona (Spain) for elution and measurement.

To obtain more information about water characteristics, some chemical parameters were measured in situ with an Aquafast colorimeter. Conductivity and pH were also determined in the sampling sites using portable instruments kindly supplied by INS (National Institute of Health) officials of El Salvador.

2.4.3. Data Treatment

In laboratory experiments, metal concentration was reported as the mean \pm standard deviation (SD). For field studies, data analysis and graphical plots were performed with IBM SPSS statistics 23 (SPSS Inc., Chicago, IL, USA).

3. Results and Discussion

3.1. Evaluation of the Sorbents

Different sorbents were tested with the aim of finding an appropriate material to interact with heavy metals and a suitable way of preserving the sample from a remote site until it could be analysed in the laboratory.

Accordingly, the kinetics of the adsorption process of different metals using Adsorbsia As600 in batch experiments was evaluated in a first stage. This inorganic sorbent exhibits a high affinity towards As(V) and As(III) [25] and, in this case, we studied its multi-elemental capacity with respect to the adsorption of Cu, Zn, Ni, and Cd contained in a mixture solution at the tested level (see experimental part).

In Figure 2, the extraction efficiency, calculated with Equation (1) was plotted against time. As shown, all metals were extracted with this sorbent, the adsorption process being fast and reaching equilibrium in less than 30 min. It is worth mentioning that complete extraction of Zn, Cu, and Cd was achieved under these experimental conditions. For Ni, an equilibrium value of 42–50% extraction was found, which did not increase even after 24 h contact time.

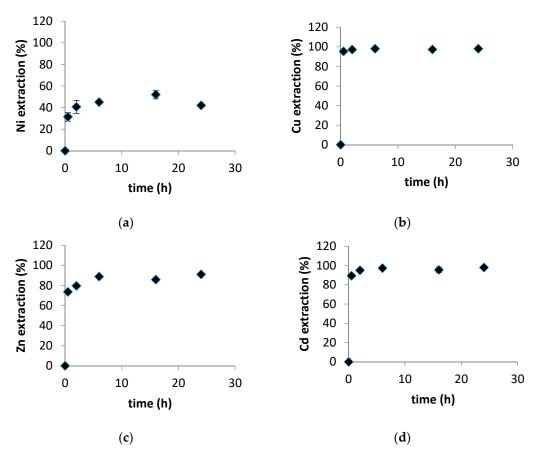


Figure 2. Kinetics of (a) Ni, (b) Cu, (c) Zn and (d) Cd adsorption with Adsorbsia As600 sorbent (n = 2).

Based on these results, contact time was set at 24 h to ensure optimal conditions for the extraction process when evaluating the other sorbents.

Extraction experiments were performed with the three sorbents and Al was included in the study. Figure 3 shows the extraction efficiency for each metal, and as expected from the characteristics of the materials, Iontosorb oxin and Adsorbsia As600 presented the highest metal extraction efficiency. For Iontosorb oxin, metal extraction was higher than 90% for all elements, as was the case of Adsorbsia As600, except for Ni, as seen in the previous section. The ability of TiO₂ to bind cations is due to the

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 OH^- on the surface at $pH > pH_{pzc}$, which was found to be around 5.8–6 for this material [25]. Metal extraction with Iontosorb oxin is explained by the formation of metal quelates with the 8-hydroxiquinoline group of the sorbent [24]. On the contrary, Duolite GT-73 was only efficient for Cu extraction [23].

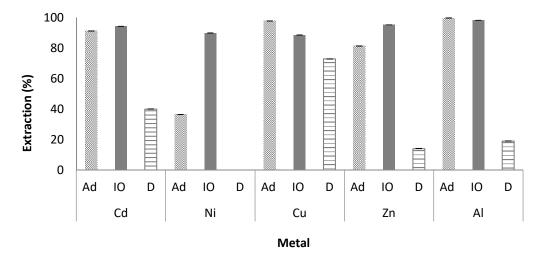


Figure 3. Metal extraction efficiency depending on sorbents used (n = 5); Solid sorbents: Ad, Adsorbsia As 600; IO, Iontosorb Oxin; and D, Duolite GT-73

From these results, Duolite GT-73 was discarded for further experiments, and the possibility of recovering the extracted metals was investigated for both loaded Adsorbsia As600 and Iontosorb oxin sorbents.

Different reagents or mixtures of reagents were tested for this purpose and were selected considering the different chemical reactions, acid-base or complex formation, involved in the recovery process. The results obtained are shown in Table 2 in terms of elution efficiency (calculated with Equation (2)) for each tested metal and eluent solution.

Table 2. Elution efficiency (%) and (SD) for metals loaded in Adsorbsia As600 (Ad) and Iontosorb oxin (IO).

| Eluent | Cd | | Ni | | Cu | | Zn | | Al | |
|-------------|--------|----|---------|----|--------|----|---------|----|---------|----|
| Liuciit | Ad | Ю | Ad | IO | Ad | Ю | Ad | Ю | Ad | Ю |
| 3 M HCl | 41 (1) | 69 | 31 (8) | 86 | 62 (5) | 74 | 62 (15) | 78 | 58 (19) | 55 |
| 0.1 M EDTA | 67 (5) | 36 | 47 (13) | 45 | 71 (5) | 43 | 61 (10) | 52 | 12(1) | 12 |
| 0.5 M NaSCN | 52 (2) | 53 | 23 (2) | 12 | 60 (8) | 13 | 38 (2) | 20 | 44 (2) | 25 |

Note: n = 2 for Ad and n = 1 for IO.

As shown in Table 2, even though the quantitative recovery of the metals was not possible in any case, all of them could be eluted. This was of special interest in the case of Adsorbsia As600, since the manufacturer had pointed out that it was not possible to regenerate the sorbent. Moreover, taking into account that the volume of the eluent solution was only 5 mL, these recovery values were suitable to allow metal determination by ICP spectroscopy.

As shown in Table 2, the three tested eluents provided similar elution efficiency in the case of Adsorbsia As600, while for Iontosorb, HCl solution gave higher elution efficiency. Thus, elution with HCl may be explained by the protonation of the 8-hydroxiquinoline moiety in the case of Iontosorb oxin, and the neutralization of surface charge in the case of Adsorbsia As600 [25]. With EDTA, elution of Cd, Ni, and Cu from Adsorbsia As600 was even better, and slightly worse for Al. Taking into account that filtration with Adsorbsia As600 is easy due to the larger size of the granules, and that

EDTA is a less toxic reagent compared to HCl or thiocyanate, the final conditions chosen for the field study were the use of Adsorbsia As600 sorbent and elution with 0.1 M EDTA.

Hence, the overall efficiency (extraction plus recovery) of the process was 61% for Cd, 17% for Ni, 69% for Cu, 50% for Zn, and 12% for Al. These overall efficiency percentages were taken into account for the determination of heavy metal concentration in water samples from Torola, Morazán.

3.2. Results Obtained in the Field Study

3.2.1. General Physicochemical Parameters

Physicochemical parameters such as T, pH, conductivity, hardness, major anions, and nutrients were measured in situ and the results are plotted in Table 3.

pH, hardness, and sulphate were below the limits set by legislation in El Salvador [26], where the maximum allowed levels are 8.5, 500 mg $\rm L^{-1}$, and 400 mg $\rm L^{-1}$, respectively. High levels of phosphate and ammonium were found. Rainfall can cause phosphates to wash from farm soils into nearby waterways. Phosphates are not toxic to people or animals unless they are present in very high levels, and only digestive problems may occur from extremely high levels of phosphate [27]. However, it has been recognized that phosphate levels found in the waters studied could affect aquatic life because they may cause eutrophication [28]. Ammonia (NH $_3$ and NH $_4$) is not of direct importance to health in the expected concentrations in drinking water, nor can the levels of ammonia obtained endanger aquatic life, although high levels of this substance give water a bad taste [29]. Finally, both chloride and nitrate concentrations determined in the sampling sites cannot be considered significant enough to affect either water quality or taste.

Table 3. Physicochemical parameters of the water samples (T: tank: W: well).

| Code | Sampling Point (W = Wells) (T = Tanks) | pН | T (°C) | Conductivity (µS cm ⁻¹) | Chloride (mg L ⁻¹) | Sulphate (mg L ⁻¹ SO ₄) | Hardness (mg L ⁻¹ CaCO ₃) | Nitrate (mg L^{-1} N-NO ₃) | Ammonium (mg ${ m L}^{-1}$ N-NH ₄) | Phosphate (mg L ⁻¹ PO ₄) | Fluoride (mg L ⁻¹) |
|------|--|-----|-----------|--|-----------------------------------|---|---|--|--|--|-----------------------------------|
| 1 | T. La Caída | 7.2 | - | 179 | >25 | <5 | <50 | 0.61 | 0.26 | 0.98 | < 0.05 |
| 2 | W. Cerritos | 8.2 | 26 | 195 | 3.4 | 10 | < 50 | 1.53 | 0.14 | 0.55 | 0.55 |
| 3 | T. El Picacho | 6.8 | 26.6 | 37.9 | 1.7 | 21 | < 50 | 0.11 | 0.12 | 0.36 | < 0.05 |
| 4 | W. El Picacho | 6.8 | 24.7 | 40.5 | 4.2 | <5 | < 50 | - | 0.27 | 0.38 | 0.13 |
| 5 | W. Peña Hueca | 6.6 | 24.4 | 112.9 | 13.7 | <5 | < 50 | 0.17 | 0.8 | 1.06 | < 0.05 |
| 6 | T. Maragua | 8.2 | 26 | 110 | 11.6 | <5 | < 50 | < 0.3 | 0.36 | 1.62 | < 0.05 |
| 7 | W. Maragua | 7.6 | 25 | 96.7 | 22.5 | <5 | < 50 | < 0.3 | 0.51 | 0.83 | < 0.05 |
| 8 | T. Ojos Agua Amates | 7.6 | 26.2 | 170 | 9.2 | 12 | < 50 | | >1 | 0.62 | < 0.05 |
| 9 | W. Ojos Agua Amates | 7.6 | 24.5 | 175 | 9 | <5 | < 50 | 0.1 | 0.28 | 0.08 | 0.29 |
| 10 | Ť. El Čalvario | 7.2 | 26 | 136 | 19.2 | <5 | < 50 | 0.15 | 0.09 | 0.8 | 0.18 |
| 11 | W. El Calvario | 6.8 | 25.9 | 94 | 11.7 | 29 | < 50 | < 0.3 | 0.14 | 1.11 | 0.07 |
| 12 | T. Aguazarca | 8.3 | 26.3 | 102.3 | >25 | 13 | < 50 | 0.18 | >1 | 0.65 | < 0.05 |
| 13 | W. Aguazarca | 6.8 | 25.8 | 110.8 | 5.1 | 23 | < 50 | 0.54 | 0.27 | >4 | < 0.05 |
| 14 | W. La Ceiba | 7.2 | 26.5 | 208 | 5.9 | <5 | < 50 | 0.1 | 0.61 | >4 | 0.96 |
| 15 | W. Joya del Chongue | 6.8 | 28 | 106 | - | - | - | < 0.3 | 0.36 | 1.02 | 0.06 |
| 16 | W. Barrio Ctro. Nuevo | 6.8 | - | 132.8 | 9.6 | <5 | 117 | < 0.3 | 0.37 | 0.6 | < 0.05 |
| 17 | T. Barrio Ctro. Nuevo | 7.2 | 26.5 | 135.2 | 4 | <5 | < 50 | < 0.3 | 0.03 | 0.97 | < 0.05 |
| 18 | W. El Portillo | 6.8 | 24.8 | 143.3 | 4.6 | <5 | < 50 | < 0.3 | 0.38 | 1.84 | 0.11 |
| 19 | T. El Portillo | 7.6 | 36 | 90.5 | 3.8 | 43 | < 50 | < 0.3 | >1 | 1.34 | 0.15 |
| 20 | W. Sicahuites | 6.5 | - | 75.2 | < 0.5 | <5 | < 50 | < 0.3 | 0.21 | 0.39 | 0.12 |
| 21 | W. La Joya de Tijeretas | 6.8 | 28 | 110 | - | - | - | - | - | - | - |
| 22 | T. La Joya de Tijeretas | 6.8 | 32 | 106 | 5.9 | <5 | < 50 | < 0.3 | 0.18 | 1.16 | 0.15 |
| 23 | W. El Pedrero | 7.6 | 25.2 | 106 | 24.8 | <5 | <50 | < 0.3 | 0.18 | 1.9 | < 0.05 |
| 24 | W. El Borbollón | 7.6 | - | 146 | >25 | <5 | < 50 | 0.41 | 0.17 | >4 | 0.17 |

3.2.2. Heavy Metals

The results obtained after elution of the loaded Adsorbsia As600 samples have shown that all the metals included in this study were found in the 15 wells and nine tanks from Torola municipality. Table 4 shows the median and quartiles of metal concentration in the water samples.

Table 4. Median and quartiles (25% and 75%) of metal concentration in well or tank waters. Concentrations are expressed in $\mu g L^{-1}$.

| Metal | Well $(n = 15)$ | Tank $(n = 9)$ | | | |
|-------|----------------------|----------------------|--|--|--|
| Al | 215.2 (191.0, 284.6) | 225.2 (166.5, 317.5) | | | |
| Cd | 1.04 (1.00, 1.12) | 1.2 (1.05, 1.16) | | | |
| Cu | 39.1 (33.1, 48.4) | 60.7 (32.2, 96.3) | | | |
| Zn | 87.3 (54.9, 126.8) | 147.7 (98.0, 316.2) | | | |
| Ni | 56.5 (46.2, 84.6) | 86.1 (45.0, 196.6) | | | |

In Figure 4, the corresponding box plots are presented for each metal and water source, and the median metal concentration in tanks is seen to be higher than in wells. Moreover, the 1.5 interquartile ranges of Zn, Cu, and Ni are large, pointing to variability in the data in the different tanks. Both higher median concentration and variability in metal content can be related to water evaporation in tanks. Regarding well sources, even though metal amounts were lower, in the case of Al and Ni, concentrations reached levels above the standards proposed by the Salvadoran Guidelines for Drinking Water Quality (Al 200 μ g L⁻¹ and Ni 20 μ g L⁻¹, respectively) [27]. Ni may cause an allergic reaction and is a suspected carcinogen. The presence of nickel in groundwater is usually related to the presence of industrial activities and landfill leachates, which are not observed in the municipality, where mainly agricultural activities take place. In this case, Ni is thought to be present in water due to laterite dissolution, known to be present in Central America, and in particular in the Morazán area [30,31]. Considering the identified high levels of phosphate related to farming activities, Ni impurities in phosphate fertilizers should also be considered as a possible contribution to nickel pollution [32]. Al can be mobilized from laterites, clays, and other alumino-silicate minerals found in soils, sediments, and rocks. In general, Al dissolution is favoured in the presence of fluoride [33], and Table 3 shows that this anion is present in ground waters in the municipality of Torola.

Cu, Zn, and Cd concentrations were below the standards proposed by the Salvadoran Guidelines for Drinking Water Quality in both tanks and wells. In the case of Cd, concentrations were similar to other studies undertaken in the region [7].

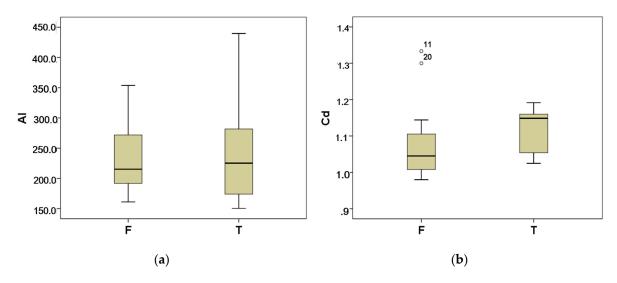


Figure 4. Cont.

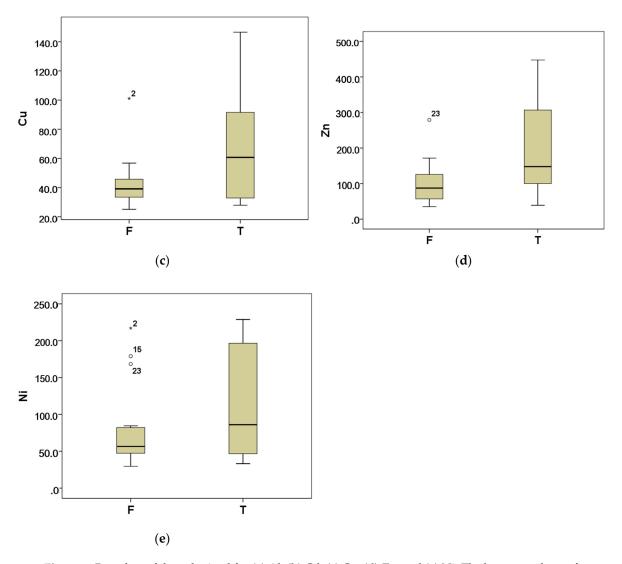


Figure 4. Box plots of data obtained for (a) Al, (b) Cd, (c) Cu, (d) Zn, and (e) Ni. The bottom and top of the box are the 25th and 75th percentiles; the line inside the box is the median (50th percentile), and the whiskers indicate the lowest and highest data within the 1.5 interquartile range. Concentration given in μ g L⁻¹.

4. Conclusions

This study has shown that Adsorbsia As600 (titanium dioxide) was a suitable material to extract Cu, Zn, Cd, Ni, and Al, with an efficiency >80%, except for Ni extraction, which was around 40%. Elution with 0.1 M EDTA allowed preconcentration of Cd, Cu, and Zn, whereas the overall efficiency of the process was suitable to permit the detection of Ni and Al. In situ application of this sorbent in a field study of waters in Torola municipality has shown that, among the studied metals, Al and Ni are of major concern. It seems that the contribution of the geological background is mainly responsible for water pollution in this area. Thus, these results point to the need to extend survey programs to rural areas without access to treated water networks. Point-of-use water treatment should be implemented to avoid toxicity effects associated with the presence of heavy metals in drinking water.

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