Graphite furnace and hydride generation atomic absorption spectrometric determination of cadmium, lead, and tin traces in natural surface waters: Study of preconcentration technique performance

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ABSTRACT

In this study three major types of preconcentration methods based upon different principles (cation exchange, physical absorption and hydrophobic extraction) were evaluated and optimized for the extraction and determination of three highly toxic heavy metals namely Cd, Pb and Sn by graphite furnace and hybrid generation atomic absorption spectrometry in real samples. The optimum analytical conditions were examined and the analytical features of each method were revealed and compared. Detection limits as low as 0.003–0.025 μg L^{-1} for Cd^{2+}, 0.05–0.10 μg L^{-1} for Pb^{2+} and 0.1–0.25 μg L^{-1} for Sn^{4+} depending on the extraction method were obtained with RSD values between 3.08% and 6.11%. A preliminary assessment of the pollution status of three important natural ecosystems in Epirus region (NW Greece) was performed and some early conclusions were drawn and discussed.

1. Introduction

The determination and monitoring of metallic contaminants in the natural environment is a continual task due to their release from a plethora of anthropogenic activities. For this reason, a large number of articles have been devoted to the development, modification or optimization of analytical methodologies able to accomplish the determination of multiple metallic contaminants in the natural environment.

From an analytical standpoint, the selection of the appropriate method is not always a facile-undertaking since it depends on many factors related to the available detection device, the required detection limits, the reproducibility and recovery of the method as well as the potential interferences stemming from the sample matrix composition. As a result of the synergistic effect of all these factors a compromise should be pursued when multi-analyte determinations are of concern [1,2]. Although highly sophisticated techniques like ICP offer the necessary versatility to resolve most of these issues [3,4], their application to monitoring surveys is rather limited by the high operational and maintenance cost involved with their use, especially when a large number of samples must be analyzed. Therefore, the provision of analytical protocols that combines

optimum analytical features with low analysis cost is a continuous challenge for the analytical community [5–9].

Up to date, AAS has been the most popular analytical technique for the determination of metallic contaminants in environmental matrices since it combines several analytical advantages along with low operational cost. However, the trace quantities of most metallic ions in environmental samples in combination with the complex matrix composition necessitate the application of an appropriate extraction or preconcentration protocol either to lower the detection limits within the measuring range of the AAS detector or to remove co-existing species that interfere with the detection or even both. The versatility of AAS enables its application with a large a variety of methodologies, including co-precipitation [10], chelates solvent extraction with conventional or novel (ionic liquid) solvents [11,12], absorption [13–15], ion exchange [16–18], solid phase extraction [19–22] and cloud point extraction [23–26] to achieve ultra trace determination. The high variety of commercially available sorbents, chelating agents and extraction reagents creates possibilities for modifying the existing methods and achieving high metal recoveries depending on the required application. Nevertheless, sample matrix composition may exert different effects on the extraction [27], therefore it is not always clear how well the methods perform at realistic conditions [2].

Motivated by a monitoring survey of three important water ecosystems in Epirus region (NW Greece) this study examines the

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optimum analytical conditions for the extraction and preconcentration of Cd^{2+}, Pb^{2+} and Sn^{4+} using three analytical methodologies based on different principles. Absorption onto activated carbon, ion exchange and hydrophobic isolation of chelate metal complexes using SPE were assessed. The selection of methods was based on the accuracy, simplicity and cost of analysis as well as its applicability in conjunction with AAS detector device. To this effect, all methods were separately optimized and are discussed in terms of analytical performance. Their practical application to the determination of the target elements in real samples is also demonstrated. Preliminary results regarding the pollution status of the examined ecosystems are also discussed.

2. Experimental

2.1. Reagents and solutions

All reagents were of analytical-grade unless otherwise stated. Standard metal ion solutions of Sn (IV), Pb (II) and Cd (II), $1000 \, mg \, L^{-1}$ were prepared by appropriate dilution of AAS grade metal solutions (BDH, Poole, Dorset, UK). Working solutions were prepared by appropriate dilution of the stock standard solutions with doubly distilled water.

The $NaBH_4$ acid solution was provided by BDH and used for the hydride generation. A 0.4% NaBH4 solution and a 0.5-M HCl reagent streams in a merging mode were used in a FI manifold system for the determination of tin.

Real samples were filtrated through Whatman no. 40 filters (pore size, $0.45 \, \mu m$). Amberlite IR-120 PLUS Resin (Sigma–Aldrich Ltd. Greece), powdered activated carbon (Merck, Darmstadt, Germany) and Chromabond C18-end capped cartridges (500 mg) (Machereu Nagel Gmd H & Co.) were used for metal extraction. A 12-port SPE vacuum apparatus (Supelco Preppy) purchased from Supelco (Bellefonte, USA) was used for solid phase extraction.

Ammonium pyrrolidineditiocarbamate (Sigma–Aldrich Ltd.) 10% (w/v) was prepared weekly in doubly distilled water. Nitric acid (HNO_3) 1 M was used for the elution of metal complexes from the resin and the activated carbon, while spectroscopic-grade methanol (Carlo Elba, Italy) was used for the elution of the metal complexes from the C_{18} cartridges.

2.2. Instrumentation

A Shimandzu AA-6800 atomic absorption spectrophotometer with hollow cathode lamps (Hamamatsu Photonics K.K., Japan) operating at 8 mA, 10 mA and 20 mA for Cd^{2+}, Pb^{2+} and Sn^{4+}, respectively, were used throughout measurements, which were made at 228.80 nm, 217.00 nm and 224.61 nm, respectively. An adjustable capillary nebulizer and supplies of argon with flow rate of $1.8 \, L \, min^{-1}$ for Cd^{2+}, $2.0 \, L \, min^{-1}$ for Pb^{2+} and $2.0 \, L \, min^{-1}$ for Sn^{4+} was used as carrier gas. The output signals were collected and processed with peak-height mode. The non-flame procedures were performed in a Shimadzu GFA-6500 and the optimum temperatures and atomization times are presented in Table 1.

The pH of the working solutions and real samples was monitored with a WTW 552 Model glass-electrode and maintained to the desired pH values by drop-wise addition of dilute HCl or NaOH.

2.3. Preconcentration methods

2.3.1. Resin

For conditioning, the Amberlite IR-120 PLUS Resin was washed sequentially with: doubly distilled water, 1 M HCl, 1 M NaOH and doubly distilled water to remove eventual chemicals residues (solvents, functionalizing agents) trapped in the resin matrix and

Table 1
Temperature and flow rate programmed atomization protocol for cadmium determination by GFAAS

Temperature (°C)	Cd^{2+}		Pb^{2+}	
	Time (s)	Gas ($L \, min^{-1}$)	Time (s)	Gas ($L \, min^{-1}$)
120	10	0.1	20	0.1
250	10	0.1	10	0.1
500	–	–	10	1
500	–	–	10	1
500	–	–	3	0
600	10	1	–	–
600	7	1	–	–
600	3	0	–	–
2200	–	–	3	0
2300	3	0	–	–
2400	–	–	2	1
2500	2	1	–	–

converted in hydrogen form by 1 M HNO_3. Three grams of the resin were added in 300 mL of water sample (pH 5.0) and the mixture was stirred for 5 h. The water was removed with a filter using a peristaltic pump and the target elements were eluted by stirring the resin with 30 mL HNO_3 of 1 M for 2 h.

2.3.2. Activated carbon

Activated carbon was used after pre-treatment with hydrochloric acid. A suitable portion of AC was boiled two times with 3 M of hydrochloric acid of GR grade for 10 min, filtered and washed with deionized water. 150 mg of activated carbon were added in 500 mL of each sample, adjusted at pH 6 and the mixture was steered at room temperature for 2 h. The dispersion was filtered with the aid of a peristaltic pump and the activated carbon was washed with 25 mL of 2.0 M HNO_3 for 2 h to recover metal ions quantitatively.

2.3.3. Solid phase extraction

Prior to analysis, C18-ec cartridges were conditioned with spectroscopic-grade methanol followed by doubly distilled water. Subsequently, water samples containing $4 \, g \, L^{-1}$ of APDC/100 mL of sample (pH 4) were percolated throughout the cartridge at a flow rate of $5 \, mL \, min^{-1}$ with the aid of a vacuum pump. Metal complexes were desorbed with 10 mL of spectroscopic-grade methanol.

2.4. Real samples

2.4.1. Sampling areas

River and lake water samples were collected from three important water ecosystems of Epirus region (NW Greece); Louros river, Acheron river and lake Pamvotis.

Louros river is 75 km long with a catchment area of $780 \, km^2$ of which $332 \, km^2$ belong to the highlands and $448 \, km^2$ to the lowlands. The river drains with a mean annual discharge of $19–28.6 \, m^3 \, s^{-1}$ from 1400 m over the sea level to Amvrakikos Gulf which is a RAMSAR protected ecosystem. The underlying geology in the wider area is dominated by alluvial geological formations, calcitic and silicate tertiary deposits as well as hard limestones. Louros river receives treated domestic effluent and effluent from light industrial activities including meat processing, abattoirs, pig farms and a small quantity of olive mill wastewater mostly during the autumn and early winter months. Its water is the main source of irrigation for a cultivated land of $133.6 \, km^2$ dominated by horticultural species, citrus trees/fruits, maize, cotton plants and olive trees. It is also used for aquaculture activities (mainly of trout, salmon and eel) while its tributaries cover the water supply demands of small settlements located around the river. Three sampling points were decided along the route (from the springs to the outfall) to monitor
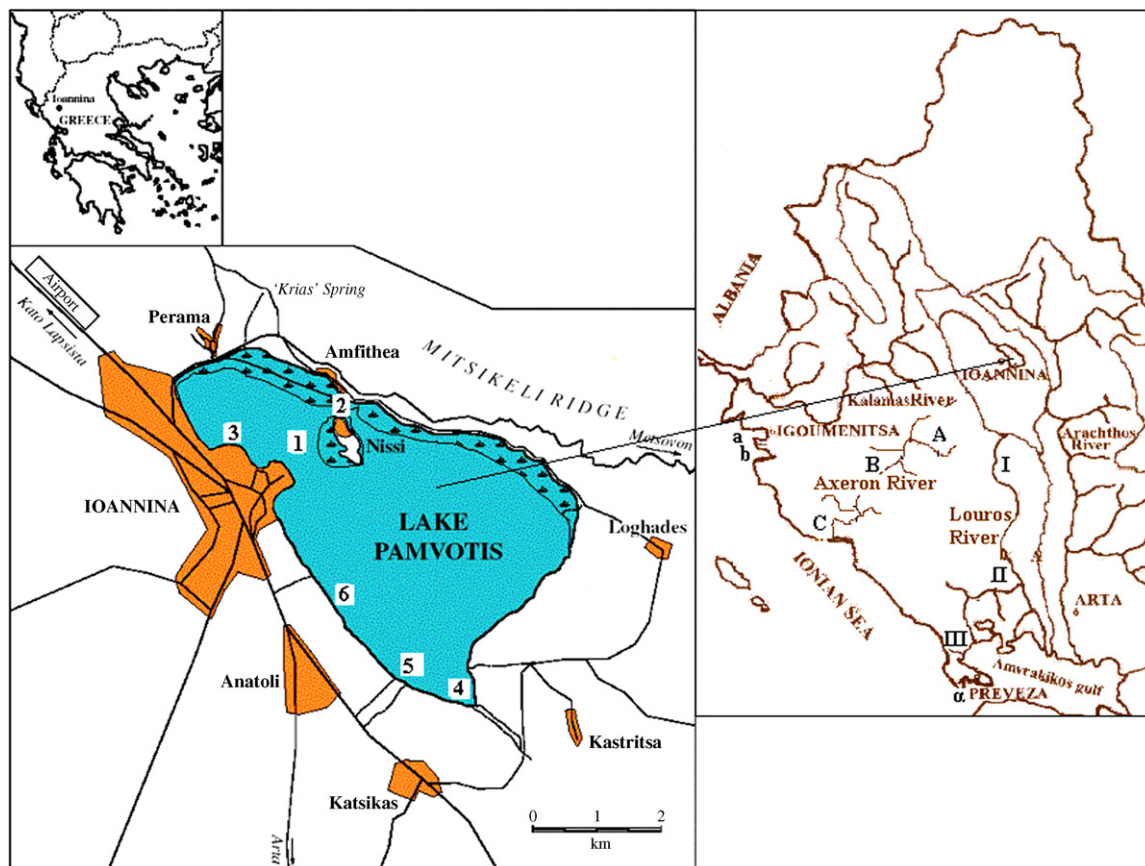
Fig. 1. Map of Greece and magnified location map showing the study areas and the selected sampling sites.

water quality in relation to the burden imposed by anthropogenic activities (Fig. 1).

Acheron (Acherontas) river is 50 km long with a cacthement area of 768 km^2 and drains in Ionian sea with a mean annual discharge of 23.5 m^3 s^{-1}. The underlying geology in the area is dominated by limestones. Its water is the main source of irrigation for approximately 85,000 m^2 of cultivated land dominated by citrus trees/fruits, maize, cotton plants and olive trees. It is estimated that Acheron river receives the run off from approximately 60,000 m^2 to 65,000 m^2 of irrigated land. Three sampling points were decided along the route (from the springs to the outfall) to monitor water quality in relation to the burden imposed by anthropogenic activities (Fig. 1).

Lake Pamvotis, NW Greece is a shallow Mediterranean lake and is situated approximately 470.25 m above the sea level. The lake occupies an area of 22.8 km^2 and its basin contains approximately 90 × l0^6 m^3 aqueous volume. The lake is located next to the city of Ioannina (150,000 inhabitants) and 40% of the catchment is used for agriculture. The basin has no naturally occurring surface outflows and is recharged by karstic springs. Drainage from the basin occurs through a system of sink holes that drain to the rivers Arachthos, Louros and Kalamas. During the last three decades, anthropogenic activity (irrigation, domestic sewage discharge and sediment deposit) has altered the trophic status of lake Pamvotis.

2.4.2. Sampling procedure

Water samples were collected in glass bottles and filtered through a Whatman 0.45 μm filter to remove the suspended solids. The filtrates were then acidified to pH < 2 with HNO$_3$ and kept at 4 °C until analysis.

3. Results and discussion

3.1. Optimization of the resin preconcentration method

3.1.1. Effect of pH

The effect of pH on the preconcentration of trace metal ions on IR-120 PLUS resin was studied by extracting 1 μg L^{-1} of each individual metal ion in the pH range of 1.0–10.0. The pH profile of the elements depicted in Fig. 2 reveals that recoveries were higher in acidic pH values which are in accordance with the cation exchange nature of the resin. Optimum recoveries were attained at the pH range of 3.0–7.0 for Cd^{2+}, 4.0–7.0 for Pb^{2+} and 4.0–6.0 for Sn^{4+}. In order to accomplish the simultaneous determination of the target metal ions, a pH value of 5.0 was chosen as an overall optimum.

3.1.2. Effect of resin quantity and contact time

The amount of resin required to achieve quantitative extraction was investigated by increasing the amount of resin from 0.5 g to 10 g. Approximately 3 g of resin we found to be adequate since no improvement was observed at higher amounts. In a like manner, the contact time of resin necessary to achieve equilibrium was assessed from 15 min to 24 h. Quantitative sorption was observed after 5 h of continues steering reaching a plateau above this value and it was therefore selected as optimum.

3.1.3. Desorption of trace elements

Three parameters were evaluated for their influence on the recovery of the target metal species from the resin. The type and concentration of the acid, the elution volume and the elution time (content time of acid with the resin). Nitric acid was selected for
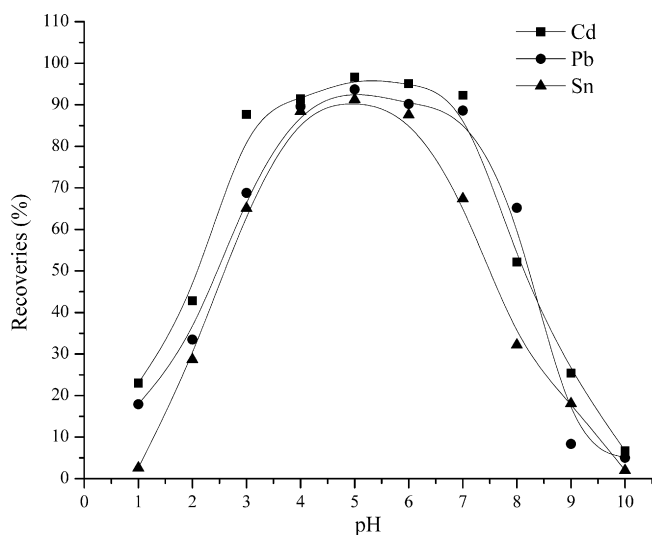
Fig. 2. Performance of the resin extraction method at various pH values.

Fig. 4. Effect of nitric acid concentration on metals elution from activated carbon.

metals recovery since it does not interfere with AAS analysis compared to other strong mineral acids like HCl and H_2SO_4. The effect of HNO_3 concentration on metal elution from the resin was studied by increasing HNO_3 concentration from 0.1 to 5.0 M and the results are depicted in Fig. 3. Under the specified experimental conditions recoveries higher than 94% were obtained with 1 M HNO_3 solution. In order to pursue maximum preconcentration 30 mL of 1 M HNO_3 was employed since larger volumes did not yield any improvement in metal recovery. To ensure reproducible recovery of the target elements from the resin 2 h of stirring was applied.

3.2. Optimization of the activated carbon preconcentration method

3.2.1. Effect of pH

It is well known that the pH value of the solution has significant influence on the overall retention of metal ions on activated carbon. For this reason, the influence of pH on to the sorption of trace elements the pH values were assessed in the range from 1 to 10. The optimal pH ranges for the individual metals did not exhibit any significant variations yielding optimum recoveries at pH 5–8
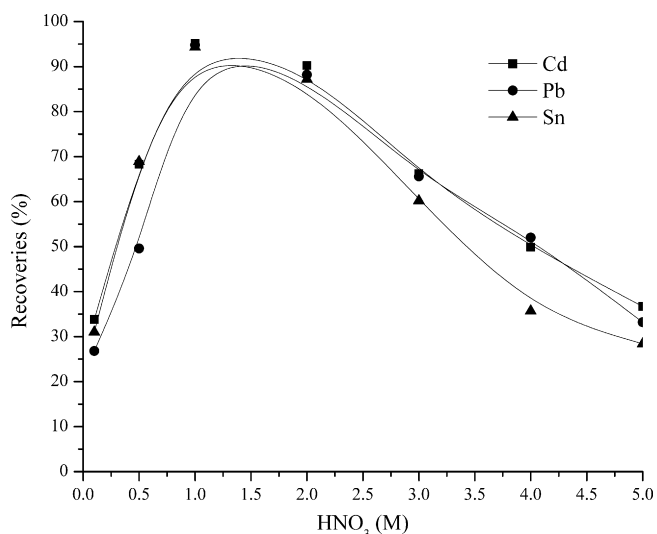

Fig. 3. Effect of nitric acid concentration on metals elution from the resin.
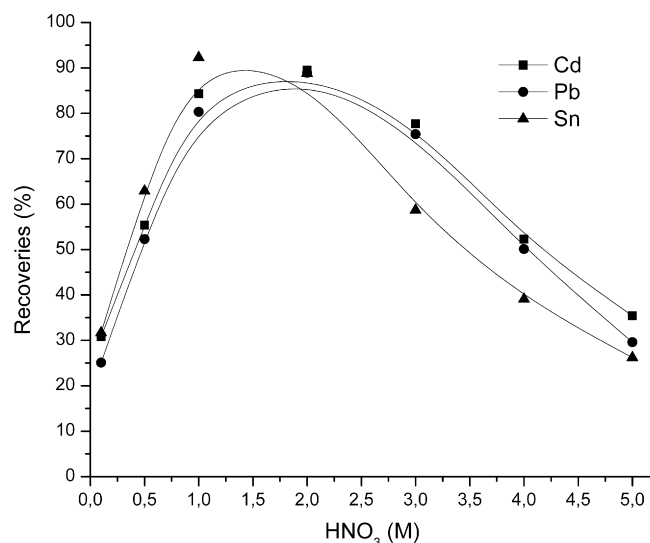
for Cd^{2+} and Pb^{2+} and at pH 4–8 for Sn^{4+}. Considering these results, a pH value of 6 was selected as optimum.

3.2.2. Effect of activated carbon quantity and contact time

The quantity of AC was varied from 50 mg to 500 mg by keeping the rest of the parameters constant. Although 100 mg was found to be quite sufficient, the working quantity of AC was fixed at 150 mg, to ensure adequate enrichment of the target elements onto AC even for large sample volumes.

The contact time of AC with sample water was varied from 15 min to 6 h. Although quantitative sorption was evident after the first hour, 2 h of contact time were finally selected in order to allow sufficient time for sorption of the metals on AC when dealing with large sample volumes.

3.2.3. Desorption of trace elements

Trace metals adsorbed onto the AC were eluted with various volumes of HNO_3 at concentrations ranging from 0.1 M to 5.0 M. The experimental data suggest (Fig. 4) that 25 mL of 2.0 M HNO_3 and 2 h of stirring ensure complete desorption of the target species from the AC surface.

3.3. Optimization of the solid phase extraction method

3.3.1. Effect of pH

Since the reaction conditions between APDC and most metal species are well established [1,28] no further effort was devoted to optimize this parameter. Based on literature data, it was decided to use a pH value of 4 as a compromise for the simultaneous extraction of all target species.

3.3.2. Effect of APDC concentration

The effect of chelating agent concentration on the analytical response was subsequently investigated by increasing the amount of APDC from 0 to 8 g L^{-1} and the results are shown in Fig. 5. Placement of excess of chelating agent, required in order to compensate for the consumption of chelating agent because of its reactivity with other metals, did not have any significant adverse effects on the performance of the reactions although a small reduction was observed. Due to the requirement for simultaneous extraction of the three metal species a value of 4 g L^{-1} was decided.
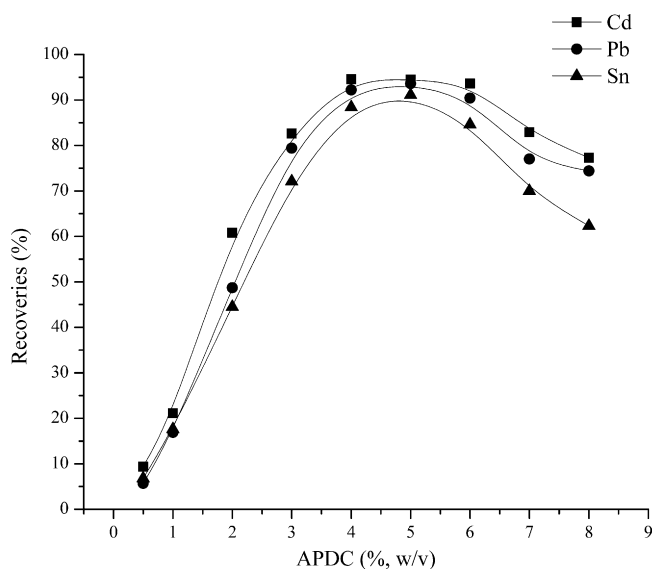
Fig. 5. Effect of chelating agent concentration (APDC) on the extractability of the target metal species with C-18 SPE.

Fig. 6. Effect of sample flow rate on the performance of solid phase extraction.

3.3.3. Effect of flow rate

Flow rate is an important parameter in solid phase extractions since it determines the sample throughput as well as the efficiency of the method. The results of Fig. 6 suggest that the optimal flow rate is 5.0 mL min^{-1} for Sn^{4+} and Cd^{2+} and 4.0 mL min^{-1} for Pb^{2+}. It was decided that a flow rate of 5 mL min^{-1} fulfils the requirement for simultaneous extraction of the three metals and was selected for further work.

3.4. Optimization of sample volume

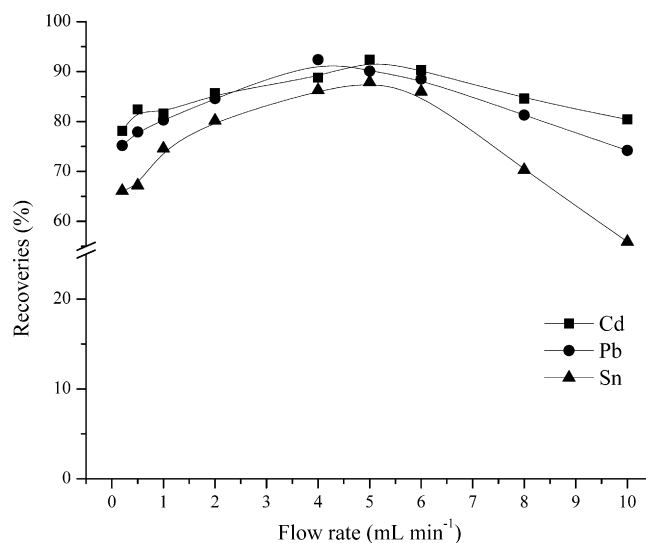The maximum sample volume that can be extracted with the examined methods is determined by a multitude of variables related to the maximum capacity of the material, the burden of the samples (including co-existing species that may compete the target elements for the available reactive sites), the required preconcentration factor and the reaction mechanism upon which metals extraction is based (cation exchange, physical adsorption or hydrophobic adsorption).

In order to accomplish maximum preconcentration and quantitative recoveries, sample volumes in the range of 50–1000 mL were extracted. Since distilled water does not contain any other species that may interfere with the extraction procedure, real samples were used to optimize this variable. It was found that 300 mL of sample volume extracted with IR-120 plus, 500 mL with AC and 100 mL with SPE provide adequately low detection limits and good reproducibility and they were therefore selected as working volumes for the monitoring survey.

Table 2
Recoveries of Cd^{2+}, Pb^{2+} and Sn^{4+} ions with Amberlite IR120+, activated carbon and solid phase extraction using GFAAS and HGAAS

	Resin % recovery (±% RSD)	Activated carbon % recovery (±% RSD)	SPE % recovery (±% RSD)
Cd^{2+} (µg L^{-1})			
0.05	95.2 ± 3.7	88.2 ± 2.5	95.5 ± 4.0
0.1	96.5 ± 2.8	90.2 ± 3.1	95.3 ± 3.5
0.2	100.2 ± 2.5	92.2 ± 3.3	98.2 ± 3.5
Pb^{2+} (µg L^{-1})			
0.1	97.4 ± 3.1	90.5 ± 3.2	101.8 ± 4.1
0.5	98.5 ± 3.2	87.2 ± 3.5	97.1 ± 3.6
1	98.7 ± 2.8	89.3 ± 2.8	100.2 ± 2.8
Sn^{4+} (µg L^{-1})			
0.1	92.8 ± 3.5	83.1 ± 3.4	93.6 ± 3.9
0.5	98.8 ± 2.7	88.1 ± 2.9	95.8 ± 3.3
1	99.1 ± 3.1	91.1 ± 2.8	96.1 ± 3.8

Table 3
Summary of analytical features of the three methods

	Cd^{2+}	Pb^{2+}	Sn^{4+}
Linearity R^2	0.9979–0.9986	0.9968–0.9985	0.9959–0.9978
LOD ($n = 7$)	0.003–0.025	0.05–0.10	0.1–0.25
LOQ ($n = 7$)	0.010–0.085	0.17–0.26	0.33–0.83
RSD (%), ($n = 7$, $C = 0.05$ µg L^{-1})	3.78–5.32	3.08–4.82	4.81–6.11
Experimental preconcentration factor	9.88–20.21	9.79–20.07	8.85–19.68
Consumptive index (mL)	10.12–30.36	10.21–24.91	11.30–25.40
Recovery (%)	88.2–100.2 (94.6 ± 3.2)	87.2–101.8 (97.5 ± 3.2)	83.1–99.1 (93.2 ± 3.3)

LOD: limit of detection and LOQ: limit of quantitation.

4. Analytical characteristics of the methods

Under the specified experimental conditions, the analytical features of the examined methods are summarized in Table 2. The recoveries offered by each preconcentration technique examined within the confines of the present study are summarized in Table 3. It is evident that SPE and resin extraction offer the highest recoveries as compared to AC extraction. This can partially be attributed to the fact that we employed physical adsorption onto activated carbon without the use of complexing agents [5,8]. t-Test analysis suggests that mean recoveries between resin and SPE are statistically equivalent at 95% probability level and they both differ significantly from AC extraction.

Tukey–Kramer multiple comparison test among the measured recoveries and the theoretical optimum value (100%) suggest that resin extraction is favorable for Cd^{2+} and Sn^{4+} and SPE for Pb^{2+}. However, AC and resin extraction offer improved RSD values (2.5–3.7% and 2.5–3.5%, respectively) compared to SPE (3.3–4.1%), although the later exhibits less fluctuation in RSD values.

In view of the above results it is evident that each preconcentration technique offers several analytical advantages and the selection of the most appropriate depends on the target elements and the required analytical performance. However, the presence of other species (organic or inorganic) in real samples may alter the analytical features observed in laboratory experiments [2,27]. In order to examine, whether such phenomena play a significant role in the analytical results, a comparison of the three methods was undertaken. The data suggest that resin extraction and SPE give equivalent results while the results produced from AC are usually lower with a few exceptions. Further examination of the data with Tukey–Kramer multiple comparison test among the measured concentrations shows that resin and SPE extraction offer in most occasions better results as compared to AC extraction. However, in several samples no differences were observed among the three methods which were found to produce equivalent results. This observation verifies the fact that sample matrix composition may affect extraction and appropriate investigation must precede any application.

5. Method application in the analysis of real samples

The results from the analysis of real samples are gathered in Table 4. As we can observe, the lowest concentration levels of Cd^{2+} were observed in lake Pamvotis and Acheron river, 0.20–0.93 $\mu g\,L^{-1}$ and 0.82–1.41 $\mu g\,L^{-1}$, respectively, while higher concentrations were observed in Louros river (1.05–2.36 $\mu g\,L^{-1}$). However, no violation of the allowable limits ((80/778/EEC, 98/83/EC), 5 $\mu g\,L^{-1}$) were observed. With regards to Pb^{2+}, contamination of the examined surface waters was far below the allowable limits given by European Union Directives (20 $\mu g\,L^{-1}$) with maximum values of 1.41 $\mu g\,L^{-1}$ in lake Pamvotis, 0.63 $\mu g\,L^{-1}$ in Acheron river and 0.49 $\mu g\,L^{-1}$ in Louros river. As far as Sn^{4+} in concerned, the pollution of lake Pamvotis and Louros river was very limited, in contrast to Acheron river where tin concentration reached up to 6.7 $\mu g\,L^{-1}$. Nevertheless, no violation of the maximum permitted concentration of 20 $\mu g\,L^{-1}$ (80/778/EEC, 98/83/EC) was observed.

The correlation matrix of lake data suggests that there are no statistically significant correlations among the three metallic pollutants in the time period of sampling which means that their concentration levels were no subject to short-term variations. In terms of spatial distribution, all metals exhibit statistically significant correlations at $p = 0.05$ in sampling points 1 and 3 while for the other sampling spots only element-specific significant correlations were observed. This means that each element undergoes different transformations or has different sources. Interestingly, the spatial

Table 4
Determination of Cd^{2+}, Pb^{2+} and Sn^{4+} in real samples

(a) Lake Pamvotis

Sampling station	12 May Cd2+	12 May Pb2+	12 May Sn4+	19 May Cd2+	19 May Pb2+	19 May Sn4+	26 May Cd2+	26 May Pb2+	26 May Sn4+	2 June Cd2+	2 June Pb2+	2 June Sn4+	9 June Cd2+	9 June Pb2+	9 June Sn4+
S1	0.47 ± 0.05	0.35 ± 0.02	BDL	0.79 ± 0.05	0.43 ± 0.03	BDL	0.52 ± 0.06	0.38 ± 0.02	BDL	0.54 ± 0.03	0.35 ± 0.02	0.19 ± 0.01	0.55 ± 0.03	0.42 ± 0.03	1.14 ± 0.1
S2	0.42 ± 0.04	0.36 ± 0.03	BDL	0.45 ± 0.04	0.47 ± 0.04	BDL	0.55 ± 0.05	0.60 ± 0.05	BDL	0.20 ± 0.02	0.80 ± 0.06	BDL	0.12 ± 0.01	0.38 ± 0.03	1.08 ± 0.1
S3	0.28 ± 0.01	0.36 ± 0.04	BDL	0.38 ± 0.02	0.49 ± 0.04	BDL	0.32 ± 0.04	0.52 ± 0.03	BDL	0.30 ± 0.02	0.34 ± 0.04	0.33 ± 0.02	0.28 ± 0.01	0.58 ± 0.05	1.06 ± 0.09
S4	0.45 ± 0.05	0.39 ± 0.02	BDL	0.68 ± 0.06	0.55 ± 0.06	BDL	0.69 ± 0.07	0.50 ± 0.03	BDL	0.85 ± 0.07	0.46 ± 0.03	BDL	0.79 ± 0.04	0.58 ± 0.04	1.20 ± 0.1
S5	0.31 ± 0.01	0.30 ± 0.01	BDL	0.31 ± 0.03	0.45 ± 0.05	BDL	0.28 ± 0.03	0.40 ± 0.04	BDL	0.33 ± 0.01	0.70 ± 0.05	0.29 ± 0.02	0.35 ± 0.04	1.41 ± 0.09	1.01 ± 0.08
S6	0.34 ± 0.03	0.36 ± 0.04	0.68 ± 0.05	0.33 ± 0.03	0.42 ± 0.03	BDL	0.62 ± 0.02	0.42 ± 0.02	BDL	0.49 ± 0.03	0.55 ± 0.04	0.35 ± 0.02	0.93 ± 0.08	0.40 ± 0.02	1.08 ± 0.09

(b) Acheron and Louros rivers

Sampling station	Acheron river (9 June) Cd2+	Acheron river Pb2+	Acheron river Sn4+	Louros river Cd2+	Louros river Pb2+	Louros river Sn4+
S1	1.13 ± 0.31	0.41 ± 0.06	1.22 ± 0.22	1.05 ± 0.09	0.22 ± 0.04	BDL
S2	0.82 ± 0.09	0.45 ± 0.05	5.75 ± 1.2	2.25 ± 1.1	0.49 ± 0.07	BDL
S3	1.41 ± 0.24	0.63 ± 0.08	2.71 ± 1.0	2.36 ± 1.1	0.46 ± 0.05	0.22 ± 0.03

BDL: below detection limit.

correlation matrix of Sn^{4+} was statistically significant in almost all sampling stations which indicates either common sources in the lake environment or high mobility which does not alter its spatial profile.

6. Conclusions

Three popular preconcentration methods based on cation exchange resin, physical absorption onto activated carbon and hydrophobic extraction of metal chelates on C_{18} cartridges were assessed and compared for the determination Cd^{2+}, Pb^{2+} and Sn^{4+} at $\mu g\,L^{-1}$ levels by atomic absorption spectrometry in natural water samples. The results from the comparison study show that resin and SPE are more effective than the activated carbon. The results suggest that resin should be preferable for the extraction and preconcentration of Cd^{2+} and Sn^{4+} while SPE offers better results for Pb^{2+}. The selection of the most suitable method depends on several factors, such as the metal of interest, sample volume available and practical operation. Resin extraction offers good analytical results but is time-consuming and requires larger sample volumes while SPE has higher analysis cost and is limited by the maximum sample flow rate.

Based on the above observations a preliminary assessment of the pollution status of three important natural water ecosystems was undertaken. The results suggest that no significant pollution issues are raised with regards to the presence of the three metal species examined while some spatial and short-term seasonal patterns were unraveled. Although these data are not adequate to infer final conclusions regarding the pollution burden of the examined ecosystems, they enable a first interpretation of water quality and aid the design of an appropriate monitoring and sampling protocol.

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