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Cd, Pb and Cu in spring waters of the Sibylline Mountains National Park (Central Italy), determined by square wave anodic stripping voltammetry

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Abstract. Square wave anodic stripping voltammetry (SWASV) was used to determine Cd, Pb and Cu in spring waters of the Sibylline Mountains National Park, Central Italy. Samples were collected from three different areas of the Park (Mount *Bove* North, Mount *Bove* South and Springs of River *Nera*) during the period 2004-2011. Physical-chemical parameters were also determined to obtain a general characterization of the waters. Very low metal concentrations were observed (i.e., Cd 1.3±0.4 ng L^{-1}, Pb 13.8±5.6 ng L^{-1}, Cu 157±95 ng L^{-1}), well below the legal limits and also below the medians of known Italian and European data. Comparing the three areas it was noted that waters from the area of the *Nera* Springs are the poorest in heavy metals and the richest in minerals, that conversely the waters of Mt. *Bove* North are the richest in heavy metals and the poorest in mineral salts, and finally that intermediate values both for heavy metals and mineral salts were observed for the waters of Mt. *Bove* South.

Key words: Heavy metals, Cd, Pb, Cu, spring waters, voltammetry.

Introduction

The ever-growing consumption of bottled mineral water worldwide - in Europe an increase of 51% has been estimated from 2006 to 2011 (Birke et al., 2010) - has recently stimulated the interest of both researchers and the general public in ways of gauging its quality through detailed knowledge of its chemical composition.

Extensive research results on Italian and European mineral waters have been published in recent years (Cicchella et al., 2010; Dinelli et al., 2010; Birke et al., 2010; Reimann and Birke, 2010; Bertoldi et al., 2011). The general interest in heavy metals refers to their potential toxicity and their compliance with national and international limits for maximum allowable concentrations.

The present work focuses essentially on the spring waters of the Sibylline Mountains National Park, an area of the Apennine Mountains in Central Italy which in the past received attention only for bottled waters, both in European (Birke et al., 2010; Bertoldi et al., 2011) and Italian (Cicchella et al., 2010; Dinelli et al., 2010) studies.

Knowledge of the Cd, Pb and Cu amongst their heavy metal contents and the ability to determine them by square wave anodic stripping voltammetry are the primary interests in this work. The selection of these three metals is due to their relevance in the toxicological evaluation of spring waters and because they are the ideal metal ions to be determined using voltammetry, which has been applied here for the first time in the present context. In fact only two attempts have been carried out in the past to use voltammetry with different electrodes and/or waveform modulations (Ben-Bassat et al., 1975; Kounaves et al., 1994).

Some major ion concentrations and other physical-chemical parameters will be also reported to give a general characterization of the waters under examination.

Comparisons will be carried out with local bottled mineral waters and with aqueduct waters distributed in the area.

Materials and Methods

Twenty-three water samples were collected in 3 areas of the Sibylline Mountains National Park (Parco Nazionale dei Monti Sibillini), Central Italy, Apennine Mountains: Mount *Bove* North (12 samples), Mount *Bove* South (5 samples) and the Springs of the River *Nera* (6 samples). Samples from spring waters (springs: *Sorgente Panico*, *Sorgente Val Ruscio*, *Sorgente L'Acqua Fiecciola*, *Fonte*

Val di Bove, *Fonte del Lupo*, *Sorgente dell'Uccelletto*, *Sorgente dell'Acero* and *Sorgenti del Nera*), bottled mineral waters (*Roana* mineral water, captation from the *Panico* spring, and *Nerea* mineral water, captation from the *Uccelletto* spring), and aqueduct waters (*Fonte Frontignano* and *Ussita* public fountains, *Sorbo* rural house, *Vallinfante* public fountain and *Rifugio Saliere* mountain hut) were collected in the period 2004-2011. Sample collection was carried out directly in polyethylene sampling bottles, which were decontaminated according to a procedure described elsewhere (Annibaldi et al., 2009).

Temperature, electrical conductivity at 20 °C (EC) (Model 30 handheld Conductivity Meter from YSI, Yellow Springs, OH, USA) and pH (Orion, 290A pH/mV meter, Thermo Electron Corporation, Beverly, MA, equipped with a pH electrode 9165BN) were measured at the sampling site. Other physical-chemical parameters considered were: total dissolved solids (TDS) (determined by water evaporation at 180°C), hardness (determined by complexometric tritation with EDTA), and Na^+, Cl^-, F^-, I^-, and NO_3^- ion contents (determined by potentiomety with ion-selective electrodes (Orion models 86-11 Ross, 9617 BNWP, 9609 BN, 9653 BN, 97-07 BNWP, respectively).

The sample treatments and voltammetric analysis for heavy metal determination were performed in a clean chemistry laboratory ISO 14644-1 Class 6, with areas at ISO Class 5 under laminar flow cabinets. Two days before analysis, the samples were acidified with ultrapure HCl, 34-37% (Romil, Cambridge, England), 2 mL acid in 1000 mL water, pH ~1.5.

The voltammetric instrumentation consisted of a Metrohm (Herisau, Switzerland) 746 VA Trace Analyzer and a 747 VA Stand equipped with a Teflon PFA cell, a thin mercury film deposited onto an Ultra Trace epoxy-impregnated graphite rotating disk as working electrode (TMFE), an Ag/AgCl, 3 mol L^{-1} KCl reference electrode and a glassy carbon rod counter electrode. Square wave anodic stripping voltammetry (SWASV) was used for metal determinations. Given the very low cadmium concentration with respect to the other metals, Cd was detemined separately from Pb and Cu, which were measured simultaneously. In the case of Cd deposition was carried out at −1050 mV for 45 min, while for Pb and Cu together a deposition potential of − 975 mV and a deposition time of 15 min were used. In both cases metal depositions were carried out with electrode rotating at 3000 rpm. The main square wave (SW) parameters applied during the anodic stripping were the same in both cases as follows: SW amplitude 25 mV, SW frequency 100 Hz, step height 8 mV, step time 100 ms. The accuracy of measurements was controlled and assured by analyzing the certified reference material NASS-5 (National Research Council of Canada) for trace metals in seawater.

Results and Discussion

Measurement results are summarized in Tables 1 and 2 for general physical-chemical parameters (in summary form) and for the three metals, respectively.

General characteristics of waters

From a general point of view (see Table 1) the waters under examination can be classified, according to Italian law, as: oligomineral waters (*acque oligominerali*), as TDS is within the range 50 to 500 mg L^{-1}; medium hardness (*durezza media*), as it is within the range 8 to 12 °F; waters suitable for low sodium diets (*indicate per diete povere di sodio*), as its Na content is below 20 mg L^{-1}; waters suitable for infant consumption (*acque destinate all'infanzia*), as fluoride is below 1.5 mg L^{-1} and nitrates are below 10 mg L^{-1}.

As regards the presence of dissolved ions it can be seen that the two areas of Mt. *Bove* (North and South) show a generally lower content than the area of the River *Nera* springs. This is also reflected in lower values of EC and TDS, which suggests that Mt. *Bove* waters are lighter than the *Nera* spring waters.

Trace metals

Cadmium shows the lowest concentrations of the three metals, with values of 1-2 ng L^{-1}, close to the detection limit for SWASV of ~0.5 ng L^{-1} (Annibaldi et al., 2009) and this fact justifies the presence of high standard deviations.

Table 1. Summary statistics from data of physical-chemical measurements carried out in the three areas studied. Mean ±SD.

Area	Temp. (°C)	EC (µS cm^{-1})	pH	TDS (mg L^{-1})	Hardness (°F)
Mt. *Bove* North	10.0±3.4	157.1±41.9	7.78±0.29	124±24	8.8±1.9
Mt. *Bove* South	6.6±2.3	152.9±20.0	7.71±0.08	105±8	8.8±1.3
Springs of the River *Nera*	8.4±0.4	256.8.1±3.7	7.70±0.10	158±6	10.0±1.8

Area	Na^+ (mg L^{-1})	Cl^- (mg L^{-1})	F^- (mg L^{-1})	NO_3^- (mg L^{-1})	I^- (µg L^{-1})
Mt. *Bove* North	0.76±0.15	1.77±0.60	0.048±0.009	1.90±0.42	1.9±0.5
Mt. *Bove* South	0.76±0.18	2.01±0.67	0.041±0.010	1.28±0.23	1.6±0.4
Springs of the River *Nera*	1.12±0.05	4.18±0.90	0.037±0.003	2.43±0.14	1.8±0.6

Table 2. Concentrations of Cd, Pb and Cu in waters collected at the Sibylline Mountains National Park, Central Italy.

Sample, date	Metal concentrations Mean ± SD (RSD%), ng L^{-1}		
	Cd	Pb	Cu
Area Mt *Bove* North			
Spring waters			
Panico spring, July 2008	1.7 ± 0.3 (18%)	16.4 ± 2.9 (18%)	102 ± 16 (16%)
Val Ruscio spring, July 2009	1.1 ± 0.2 (18%)	19.8 ± 2.5 (13%)	309 ± 17 (6%)
Val Ruscio spring, June 2011	1.2 ± 0.2 (17%)	20.5 ± 1.4 (7%)	314 ± 13 (4%)
L'Acqua Fiecciola spring, July 2009	1.6 ± 0.4 (25%)	17.7 ± 5.9 (33%)	139 ± 6 (4%)
Bottled mineral water			
Roana mineral water, November 2008	0.8 ± 0.2 (25%)	15.8 ± 1.7 (11%)	95 ± 5 (5%)
Aqueduct waters			
Frontignano public fountain, November 2004	1.1 ± 0.1 (9%)	14.6 ± 2.1 (14%)	132 ± 10 (8%)
Frontignano public fountain, July 2005	1.2 ± 0.1 (8%)	17.3 ± 3.2 (18%)	144 ± 4 (3%)
Frontignano public fountain, July 2008	1.3 ± 0.1 (8%)	16.3 ± 3.1 (19%)	141 ± 8 (6%)
Ussita public fountain, July 2008	1.5 ± 0.1 (7%)	24.6 ± 0.6 (2%)	366 ± 10 (3%)
Ussita public fountain, June 2011	1.4 ± 0.1 (7%)	21.3 ± 0.1 (1%)	362 ± 2 (1%)
Sorbo rural house, July 2009	4.4 ± 0.5*(11%)	104 ± 4* (4%)	647 ± 20* (3%)
Sorbo rural house, June 2011	2.0 ± 0.1*(5%)	101 ± 5* (5%)	610 ± 8* (1%)
Mean	1.2 ± 0.3 (25%)	18.4 ± 3.1 (17%)	210 ± 112 (53%)
Area Mt *Bove* South			
Spring waters			
Fonte del Lupo spring, July 2005	1.0 ± 0.1 (10%)	6.2 ± 0.6 (10%)	103 ± 4 (4%)
Fonte del Lupo spring, July 2008	1.2 ± 0.3 (25%)	5.8 ± 0.4 (7%)	129 ± 8 (6%)
Fonte del Lupo spring, June 2011	1.1 ± 0.1 (9%)	6.6 ± 0.2 (3%)	101 ± 3 (3%)
Val di Bove spring, June 2011	1.2 ± 0.1 (8%)	7.6 ± 0.1 (1%)	115 ± 4 (3%)
Aqueduct water			
Rifugio Saliere mountain hut, March 2011	1.2 ± 0.2 (17%)	9.8 ± 2.0 (20%)	299 ± 6* (2%)
Mean	1.1 ± 0.1 (9%)	7.2 ± 1.6 (22%)	112 ± 13 (12%)
Area Springs of the River *Nera*			
Spring waters			
Uccelletto spring, July 2008	1.1 ± 0.3 (27%)	6.7 ± 0.8 (12%)	107 ± 16 (15%)
Acero spring, 07/08	1.4 ± 0.3 (21%)	18.4 ± 0.7 (4%)	100 ± 18 (18%)
Nera spring, July 2005	1.2 ± 0.1 (8%)	10.3 ± 0.4 (3%)	83 ± 1 (1%)
Nera spring, July 2008	2.1 ± 0.5 (24%)	9.3 ± 0.9 (10%)	95 ± 10 (11%)
Bottled mineral water			
Nerea mineral water, July 2008	2.4 ± 0.4 (17%)	11.4 ± 1.3 (11%)	106 ± 3 (3%)
Aqueduct water			
Vallinfante public fountain, July 2008	0.7 ± 0.1 (14%)	13.2 ± 2.4 (18%)	99 ± 8 (8%)
Mean	1.5 ± 0.6 (43%)	11.6 ± 4.0 (35%)	98 ± 9 (9%)
Overall mean	1.3 ± 0.4 (31%)	13.8 ± 5.6 (40%)	157 ± 95 (60%)

Each value represents the mean of at least 3 measurements.
*outlier, not considered for summary statistics.

Very low values (even if ten times higher than those of Cd) are also observed for Pb, for which results of about 6-20 ng L^{-1} are obtained. Significantly higher values are obtained for Cu, which varies approximately between 100 and 300 ng L^{-1}.

Comparing the three areas, no significant differences are observed for Cd, while substantial changes occur for the other two metals. In particular, increments are observed for Pb in the order Mt. *Bove* South (average 7.2 ng L^{-1}), *Nera* Springs (11.6 ng L^{-1}), Mt. *Bove* North (18.4 ng L^{-1}), and for Cu in the order *Nera* Springs (9.8 ng L^{-1}), Mt. *Bove* South (112 ng L^{-1}), Mt. *Bove* North (210 ng L^{-1}). No significant time-variations in the metal concentrations are detected when samples of 2-3 different years are analyzed.

With very few exceptions, both mineral waters bottled in the area (*Roana* and *Nerea*) and aqueduct waters from public fountains (*Frontignano*, *Ussita*, *Vallinfante*) show approximately the same metal contents as the spring waters from which they derive. Thus, in general, neither the bottling procedures nor the municipality treatment for the aqueduct, significantly modify these waters with respect to the very low detected concentrations of Cd, Pb and Cu. Conversely some substantial metal increments are observed for sites of private houses. In particular for the old rural house in *Sorbo* increased values of factors ~2-3 Cd, ~5-10 Pb and ~6 Cu are observed, and for the *Saliere* mountain hut Cu content increases by ~3 times, while no changes occur for Cd and Pb. Such metal increments may be due to the presence of old metal pipes (possibly made of lead in several parts) that release metals into the water.

The Italian and European laws (DM 29/12/2003 and Directive 2003/40/EC, respectively) set the same concentration limits for mineral waters, i.e. 3.0 $\mu g\ L^{-1}$ for Cd, 10 $\mu g\ L^{-1}$ for Pb, 1.0 $mg\ L^{-1}$ for Cu. In Italy we also have a specific law for spring waters (DPR 236/88, whose values were confirmed with the DLgs 339/99) which sets concentration limits at 5 $\mu g\ L^{-1}$ for Cd, 50 $\mu g\ L^{-1}$ for Pb and 1.00 $mg\ L^{-1}$ for Cu (with a guideline value for Cu of 0.100 $mg\ L^{-1}$). It is easy to see that Cd, Pb and Cu concentrations in the analysed waters are well below - thousands of times lower than - the legal limits.

Comparison with literature data shows that spring waters from the National Park of the Sibylline Mountains have a content of Cd, Pb and Cu below the median content of Italian (Cicchella et al., 2010) and European (Reimann and Birke, 2010) mineral waters.

Conclusion

SWASV enabled the Cd, Pb and Cu content of spring waters, mineral waters and aqueduct waters of the Central Apennines area of Italy (Sibylline Mountains National Park) to be determined down to $ng\ L^{-1}$ level, without any enrichment procedure or pretreatment of samples.

The metal concentrations are well below Italian and European legal limits and significantly lower than the median values reported for European mineral waters; thus they are to be considered non-contaminated high-quality waters. On the basis of physical-chemical parameters, they are classified as oligomineral, medium hardness waters, suitable for low sodium diets and for infant consumption.

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