Speciation of inorganic arsenic in coastal seawater from Ionian and Tyrrhenian Seas (Sicily, Italy) using derivative anodic stripping chronopotentiometry

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Abstract The purpose of this paper was to use derivative anodic stripping chronopotentiometry (dASCP) as a sensitive and accurate technique, to determine the concentrations of dissolved As (III) and As (V) in coastal seawater samples from the Straits of Messina, the Ionian and the Tyrrhenian seas, and to investigate the relationship between the anthropogenic activities on the coastal areas and the concentration of dissolved inorganic arsenic in seawaters. The obtained data indicated that As (V) was the most abundant species, with concentration ranging from 26.7 to 307 nM, whereas As (III) levels were lower than 48 nM in all the samples. In particular, As (III) and As (V) levels significantly decreased from high to low anthropogenic activities zones ($p < 0.00001$, ANOVA), with the reference samples, from a wildlife reserve, showing the lowest values. Furthermore it was observed that human activities influenced inorganic arsenic speciation, since the zones that received high human input presented the highest As(V)/As (III) ratio.

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Introduction

Arsenic is widely present in the marine environment both as a consequence of natural sources mainly related to the process of rocks erosion, and anthropogenic sources including smelters, use of arsenical pesticides and wood preservatives agents. Arsenic occurs in the aquatic environment in different forms which vary in toxicity, with the inorganic forms, and particularly As (III), being the most toxic (Jain and Ali 2000). Particularly the toxicity of different arsenic species varies in order As (III) > As (V) > monomethilarsenate (MMA) > dimethilarsinate (DMA; Penrose 1974); for this reason speciation of arsenic in environmental samples is gaining increasing importance. Many studies provide evidence that arsenate is the most abundant species in oxygenated seawater, arsenite rarely accounts for more than 20% of total arsenic (Neff 1996), whereas the concentration of organic arsenic in surface seawater is lower than 0.07 nM (Sun et al. 1997). However arsenic speciation in seawaters depends on many factors as climatic variations, phytoplankton and bacteria population (Gonzalez-Dàvila 1995), levels of nitrogen and degree of pollution (Howard et al. 1995); particularly

it was noticed that in sewage contaminated coastal waters the 83% of total dissolved inorganic arsenic was in the reduced form (Sanders 1985). The very low levels of arsenic species in seawater, require the use of high sensitive and selective analytical techniques, capable to detect concentrations lower than 1 ppb (13.3 nmol AsL^{-1}). Hydride generation methods in conjunction with atomic absorption spectroscopy (HG-AAS) or inductive coupled-plasma atomic emission spectroscopy (ICP-AES) have been widely used for arsenic speciation in seawater due to their high sensitivity and selectivity, however a pre-concentration step and big amounts of sample are generally required (Cabon and Cabon 2000); moreover the presence of methylated arsenic compounds can produce errors in speciation of inorganic arsenic by hydride evolution directly into the spectra detector. On the contrary, electrochemical methods offer excellent possibility for differential determination of trace levels of As (III) and As (V) as they show a different electrochemical behavior. Literature reports many publications about the use of stripping voltammetry (SV), both in the cathodic or anodic mode, for sensitive and reliable inorganic arsenic speciation measurements in water systems. Arsenate is generally electro-inactive, therefore a reduction step to arsenite was necessary prior to the voltammetric determination; in the optimized electrochemical conditions detection limits ranging from 0.1 to 0.2 ppb (1.3 to 2.6 nmol l^{-1}) were obtained (Greulach and Henze 1995; Kopanica and Novotny 1998; Sun et al. 1997). Recently, the use of derivative anodic stripping chronopotentiometry (dASCP; Dugo et al. 2004; Dugo et al. 2006) was described to determine the concentrations of As (III) and As (V) in natural waters; good sensitivity and repeatability were obtained in the determination of As (V) after a prior reduction step with potassium iodide and detection limits lower than 0.1 ppb were achieved (Dugo et al. 2005). This paper aim to use dASCP to determine the concentrations of dissolved As (III) and As (V) in coastal seawater samples from the Straits of Messina, the Ionian and the Tyrrhenian seas, washing respectively the Southern and the Western province of Messina, and to investigate the relationship between the anthropogenic activities on the coastal areas and the concentration of dissolved inorganic arsenic in surface seawaters. Furthermore the correlation between the concentrations of As (V) and As (III) in zones with different anthropogenic input was assessed. There are no reliable study of dissolved inorganic arsenic in seawater of the Messina coasts. Recently there has been an increasing trend in the levels of marine pollution and sewage outfall, the WWF Italy (http://www.wwf.it) reported arsenic levels ranging from 330 to 530 nM in South of Italy seawaters. Since the resident of the studied area rely extensively upon fish and fish products as important constituent of their diet, a monitoring of arsenic seawater pollution level is of great concern both from the environmental and the nutritional point of view.

Material and methods

Study area and sampling sites

Messina (38°11′N, 15°34′E) is an important seaport located in the northern point of Sicily island, which is separated from the mainland Italy by the Straits of Messina. The Straits is 3 km wide in the North (from Capo Peloro–Messina and Scylla–Reggio Calabria) and 16 km wide in the South (from Capo Alì–Messina and Pellaro–Reggio Calabria) and links Tyrrhenian and Ionian seas. The municipality of Messina has 262,000 inhabitants for a population density of 1,241 inhabitants per square kilometer; pollution due to small scale industry is negligible, however there is considerable pollution from road and naval traffic emission and domestic waste discharge. The province of Messina spread out along the Tyrrhenian coast for about 100 km and along the Ionian coast for about 80 km. As Fig. 1 shows, five sampling zones (1–5) were chosen in the Straits of Messina, four (6–9) from the Ionian coast and four (10–13) from the Tyrrhenian coast; five seawater samples were collected in each zone. The concentrations of dissolved inorganic As was also determined in twenty samples of seawater collected in the wildlife reserve of Aeolian Islands, unaffected by human activities. Totally 85 seawater samples were analysed.

Sample collection

Seawater samples were collected in April 2004 at sixteen stations located in the studied area. Water samples were collected about 100 m far from the coast, using a submersible in line pump fitted to a

Fig. 1 Sampling zones

PVC pole from a depth of 1 m pointing upstream from a boat. Acid washed tubing was fitted to the pump and samples were collected in acid washed 1,000 ml bottles. After sampling seawater was transferred in dark polyethylene containers, spiked with HCl 1 M and hydrazinium chloride to prevent As (III) oxidation (Sun et al. 1997) and stored in ice during the transport to the laboratory, where the samples from each site were filtered trough a 0.45 μm membrane filter and stored at 4°C; the analysis were executed within a week.

Reagents

All the reagents used were of analytical grade. Hydrochloric acid (34–37%), Au (III) (1,000 mg l^{-1}) As (III) and As (V) (1,000 mg l^{-1}) standard solutions were purchased from Panreac (Barcelona, Spain). A 1,000 mg l^{-1}Au (III) standard solution (Steroglass, Perugia, Italy) was used to plate the glassy carbon working electrode. The required low concentration standards were prepared daily by dilution of stock solutions. Hydrazinium chloride was purchased from

Table 1 Electrochemical parameters for the derivative anodic stripping chronopotentiometric analysis of As (III) in seawaters

dASCP parameters	As (III)
Deposition potential	**+300 mV**
Deposition time	180 s
Anodic constant current	+2.5 µA
Final acquisition potential	500 mV
Agitation speed	1,000 rpm
Peak potential	+160 mV

Merck; KI used to reduce As (V) to As (III) was obtained from Baker J.T. (Deventer, Holland). Near-shore Seawater (CASS-4) certified by the National research Council of Canada. Was used Ultra-pure water (18.2 MΩ/cm) was prepared by a Pure Lab RO and a Pure Lab UV system (USF, Ransbach–Baumbach, Germany).

Instrumentation

Arsenic analysis were carried out on a PSA ION 3 potentiometric stripping analyzer (Steroglass, S. Martino in Campo, Perugia, Italy), which was controlled by Neotes 2.0.1 software (Steroglass). The working electrode was a glassy carbon electrode coated with a thin gold film; an Ag/AgCl electrode (3M KCl), and a platinum wire were also used as the reference and the auxiliary electrodes, respectively.

Derivative anodic stripping chronopotentiometric analysis of As (III) and As (V)

Prior to each analysis the working electrode was plated electrolyzing for 1 min at −100 mV a 1,000 mg l^{-1} Au (III) standard solution. As (III) was directly determined placing into the electrochemical cell 5 ml of seawater and 5 ml of 6M HCl; a previous study (Dugo et al. 2005) provided evidence that acidified seawater is an optimum stripping medium for the chronopotentiometric determination of As (III). The optimized electrochemical parameters for the analysis of As (III) are given in Table 1. As (V) was determined after reduction to the electro-active As (III) form with KI: 5 ml of seawater, 5 ml of 6 M HCl and 0.25 g of KI were placed into a flask closed with a Teflon stopper, and left under magnetic stirring at 80°C till the colorless solution turned to yellow, which indicated I_2 formation (about 5 min). The

sample solution was cooled in the dark to the room temperature, then the analysis was carried out; the obtained result represent the total inorganic arsenic level and As (V) concentration was determined subtracting As (III) concentration from this value. As a previous study showed (Dugo el al. 2005), good accuracy, repeatability and high sensitivity were achieved using derivative anodic stripping chronopotentiometry for inorganic As analysis in sea water (Table 2)

Statistical analysis

To study the influence of human input on As (III) and As (V) levels in coastal seawater, all the sampling sites were grouped according to their anthropogenic activities into: high anthropogenic activity H (population density >1,300 inhabitants per square kilometer, harbour and industrial activity), medium anthropogenic activity M (population density <1,300 inhabitants per square kilometer, negligible harbour and industrial activity), low anthropogenic activity L (small villages). The population density data were obtained from the National Census of 2001. The concentrations of dissolved inorganic As was also determined in twenty samples of seawater collected in the wildlife reserve of Aeolian Islands in the Tyrrhenian Sea, unaffected by human activities; these data were used as a control to asses by the analysis of variance (ANOVA) the significance of the different arsenic levels observed in seawater samples affected by anthropogenic input. The Pearson correlation test was further employed to estimate the correlation between As (V) and As (III) concentration in coastal seawater samples from zones with different anthropogenic input.

Table 2 Analytical performances of the derivative anodic stripping chronopotentiometric analysis of As (III) in seawaters

Characteristics	Performance
Repeatability ($n=5$)	4.0%
Accuracy[a]	95.0%
Detection limit[b]	1.1 nM
Linear concentration range	0–13 mM

[a] Tested with Nearshore Seawater reference material reference material provided by National Research Council (Canada)

[b] Calculated at 3 σ level

Results and discussions

Analytical method

Growing concern about heavy metals pollution has led to increasing needs to develop sensitive analytical techniques capable to detect trace and ultra-trace concentrations of metals in a variety of environmental matrices. A previous study (Dugo et al. 2005) has shown the high performances obtained using derivative anodic stripping chronopotentiometry (dASCP) for inorganic arsenic speciation in aqueous matrices without any previous sample extraction procedure nor pre-concentration step. Particularly for seawater, the accuracy, tested with certified reference material, was of 95%; the repeatability was within 4%, whereas limits of detection and quantification (expressed as 3 and 10 σ/S) were 1.1 nM (0.080 μg l^{-1}) and 3.3 nM (0.25 μg l^{-1}), respectively (Table 2). The present paper gives evidence that dASCP is a powerful tool for monitoring As pollution in seawater since it coupled high sensitivity and resolution, rapid sample preparation with low costs of the equipment; furthermore the small dimensions of the analyzer allowed its transport for in situ analysis. For all these features, dASCP is suited for routine analysis.

As levels in the Straits of Messina, Ionian and Tyrrhenian seas

The mean concentrations of dissolved inorganic arsenic at different sampling zones in the Straits of Messina, Ionian and Tyrrhenian seas are given in Table 3. As (III) and As (V) levels were highly variable at most locations, with As (V) being the most abundant species. The concentration range of As (V) observed in the Straits of Messina and in the Ionian Sea were very similar, respectively 310–26.7 and 283.4–38 nM; lower and less variable As (V) levels were found in the Tyrrhenian Sea, 119.5–48.1 nM.

Table 3 Mean levels of total dissolved inorganic As, As (III) and As (V) (nM) in seawater samples from different sampling zone; five samples from each site were analysed

	Sampling zone	Anth. act.[a]	As (III)	As (V)	As (V) /As (III)	Salinity ‰
Strait of Messina						
1	Capo Peloro	M	8.66±1.33	41.7±2.0	4.82	37.8
2	Messina Coast Road	H	12.5±1.73	98.5±2.4	7.86	36.9
3	Port of Messina	H	31.3±3.7	105.3±3.3	3.37	36.5
4	South Messina	H	44.2±3.3	301.3±8.7	6.81	37.0
M±SD (n=20)			24.1±14.9	10.25±7.56		
Ionian Sea						
5	Scaletta Zanclea	L	<1.1	53.3±1.9	>48.5	38.9
6	Capo S. Alessio	L	8.80±1.73	61.3±4.4	6.97	39.0
7	Mazzarò	M	<1.1	41.1±3.1	>37.4	38.0
8	Giardini Naxsos (Port)	H	11.3±1.5	273.3±11.1	24.2	37.5
M±SD (n=20)			5.06±5.33	107.6±99.2		
Tyrrhenian Sea						
9	Ortoliuzzo	L	4.66±1.60	71.3±7.2	15.3	38.4
10	Torregrotta	L	2.27±1.20	49.9±1.7	22.0	38.9
11	Milazzo	H	10.0±4.0	84.4±9.3	8.44	37.6
12	Gioiosa M.	M	5.87±1.60	118.0±5.6	20.10	37.0
M±SD (n=20)			5.70±3.20	82.6±24.3		
Wildlife reserve						
13	Aeolian Islands	Control	1.33±0.55	43.3±1.9	32.6	39.0
14	Aeolian Islands	Control	1.20±0.32	32.0±2.9	26.7	38.7
15	Aeolian Islands	Control	<1.1	39.6±4.4	36.0	38.8
16	Aeolian Islands	Control	<1.1	23.7±1.5	21.5	38.9
M±SD (n=20)			0.70±0.70	34.7±8.2		

[a] Anthropogenic activity: H = high, M = moderate, L = low
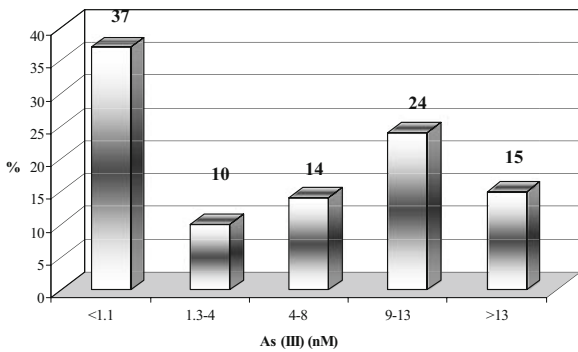
Fig. 2 Groups of concentration for dissolved As (III) in coastal seawater

Fig. 4 Relationship between dissolved As (V) and As (III) in surface seawater in the province of Messina area ($r=0.75$, Pearson correlation coefficient)

The highest concentrations of As (V) were at South Messina and Giardini Naxos Port sampling sites, which received high anthropogenic input, meanwhile the lowest at Capo Peloro, in the Northern suburbs of Messina. Particularly it is important to remark that the area of Capo Peloro is strongly interested from upwelling currents of Messina Straits carrying to surface clean deep waters from Ionian Sea. The Straits of Messina zone presented the highest mean level of As (III); at Port of Messina and South Messina sampling zones, As (III) average concentrations of 31.4 and 44.3 nM were detected, which accounted respectively for the 23 and 13% of total dissolved inorganic arsenic found in that sampling sites, probably as the result of intense human activities. Figure 2 shows, the 37% of all the studied samples presented As (III) levels lower than 1.1 nM, whereas the 39% higher than 8 nM.
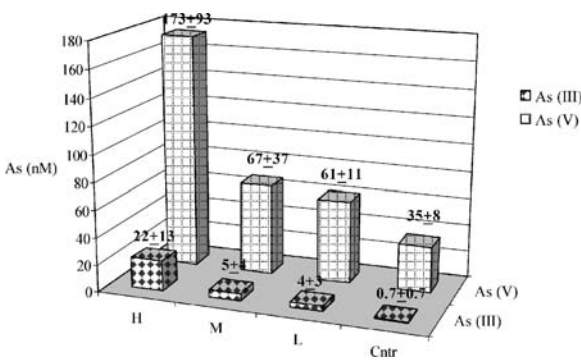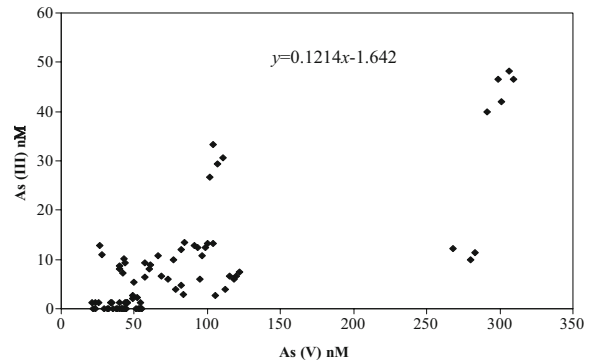
Influence of anthropogenic activity

The clear differentiation between different zones in terms of anthropogenic input, is supported by the observed maximum values of As (V) and As (III) in urban zones. In order to confirm the influence of the anthropogenic activity on dissolved inorganic As levels in seawater, As (III) and As (V) were determined in samples collected in the wildlife reserve of Aeolian Island, a zone with a very low human population where the environment remains in a relatively pristine condition. The obtained data provided evidence that As (III) and As (V) levels significantly decreased from high to low anthropogenic activities zones ($p<0.00001$, ANOVA), with the reference samples (wildlife reserve) showing the lowest values (Fig. 3). In particular the mean contents of As (III) and As (V) in the zones with high human

Fig. 3 Arsenic concentrations (mean ± SD) in zones influenced by high (H; $n=25$), moderate (M; $n=15$), low (L; $n=20$) human activities and the control (Cntr; $n=20$)
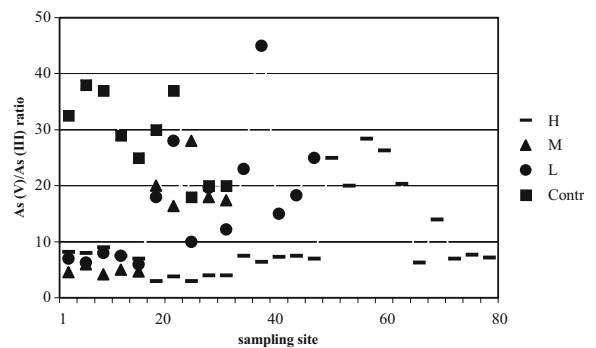

Fig. 5 As (V)/As (III) ratio found in zoned influenced by high (H), moderate (M), low (L) anthropogenic activities and the control. Samples showing not detectable concentrations of As (III) (<1.1 nM) in the low and control zones, fall out of scale

input were respectively 35 times and 4 times those found in the control.

As (V) versus As (III)

Dissolved As (III) have been compared with dissolved As (V). Figure 4 shows a positive correlation ($r=0.75$, Pearson correlation coefficient) which can be explained by the natural oxidation of organic arsenic and As (III) to As (V) in oxygenated surface seawaters. Many studies have provided evidence that dissolved As speciation in coastal seawater is mainly ruled by the biological activity in the water column (Bu-Olayan and Thomas 2001; Howard et al. 1995; Munksgaard and Livingstone 2001; Sanders and Windom 1980; Sanders 1983). Furthermore some data about the dependence of dissolved inorganic As speciation on the anthropogenic input are available. Andrade (1979) reported that in not polluted coastal seawaters As (V) is the most abundant species and As (V)/As (III) ratio ranging from 20 to 200 were found, whereas Sanders (1985) observed that in zones strongly affected by human input As (III) accounted for the 83% of total inorganic As. This study shows that in coastal seawater influenced by high or moderate anthropogenic activity, the As (V)/As (III) ratio ranged from 4 to 25; whereas in zones unaffected by human input the As (V)/As (III) ratio was >25 for the majority of the studied samples; in particular 15 out of 40 samples collected in zones influenced by low anthropogenic input and in the control area, presented not detectable As (III) levels (<1.1 nM; Fig. 5). Therefore the obtained results suggest that the anthropogenic activity on the coastal area can be considered as a factor that influence the speciation of dissolved inorganic arsenic in coastal surface seawater.

Conclusion

This study gave evidence that dASCP is a powerful tool for inorganic As speciation in seawater since it coupled high accuracy, sensitivity with short time of analysis and low instrumental cost; furthermore the small dimensions of the analyzer allowed its transport for in situ analysis. For all these features, dASCP is suited for routine analysis. Reliable As (V) and As (III) concentrations in 0.45 μm filtered coastal

seawater samples from the Straits of Messina, the Ionian and the Tyrrhenian seas, have been determined. The highest levels of inorganic As were found in the Straits of Messina area, followed by Ionian and Tyrrhenian zones which showed similar values. As (III) and As (V) levels were significantly influenced by anthropogenic input since their concentrations decreased from high to low human activities zones. Furthermore the obtained results provided evidence that As (V)/As(III) ratio were higher in regions receiving high or moderate human input respect to the control area, confirming that inorganic As speciation in coastal seawater is also influenced by water pollution from naval traffic emission and domestic waste discharge.

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