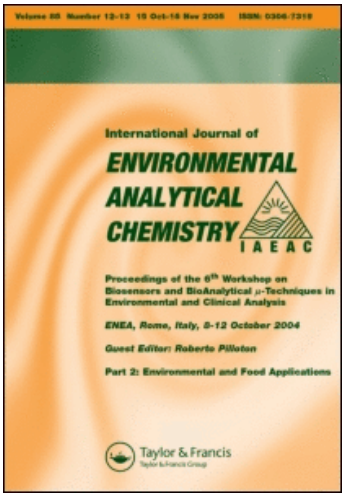

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Villa-lojo, M. C. , Beceiro-GonzÁlez, E. , Alonso-Rodríguez, E. and Prada-Rodríguez, D.(1997) 'Arsenic Speciation in Marine Sediments: Effects of Redox Potential and Reducing conditions', International Journal of Environmental Analytical Chemistry, 68: 3, 377 — 389
To link to this Article: DOI: 10.1080/03067319708030502
URL: http://dx.doi.org/10.1080/03067319708030502

Intern. J. Environ. Anal. Chem., 1997, Vol. 68(3), pp. 377–389
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ARSENIC SPECIATION IN MARINE SEDIMENTS: EFFECTS OF REDOX POTENTIAL AND REDUCING CONDITIONS

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(Received 10 February 1997; In final form 20 April 1997)

The speciation of arsenic in the environment is among others controlled by reduction, methylation and oxidation processes and therefore influenced by the prevailing redox conditions. In this study we have analyzed sediments taken from La Coruña estuary in the north west of Spain. Inorganic (trivalent and pentavalent) and the organic (MMA and DMA) arsenic speciation is related to Eh, Fe and Mn load. The variation of the arsenic species concentration and other parameters was analyzed at different depths in some of the sampling points. Low arsenic concentrations (1–10 $\mu g \cdot g^{-1}$) were found. In spite of oxidising conditions (Eh values between 31–96 mV), most of the samples showed a higher As(V) percentage than As(III). Principal component analysis was made to see sample groups and the results showed that speciation depends on reducing conditions (Eh and Mn).

Keywords: Arsenic speciation; marine sediments; principal components analysis

INTRODUCTION

Sediments existing at the bottom of the water column may reflect the current quality of the water system and can be used to detect the presence of contaminants that do not remain soluble in water. Morever, sediments may act as a potential source and sink for pollution, depending on the prevailing environmental conditions such as redox potential, pH or the presence of organic chelators.[1]

The chemistry of arsenic in the environment is complex. In general, thermodynamic considerations suggest that As(V) is the dominant specie in oxic

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environments, and that As(III) should predominate under reducing conditions. Biological activity may lead to both methylation and demethylation and contributes significantly to the formation of organic as well as inorganic forms. Methylated arsenic oxiacids have been reported in soils and sediments.[2–3] However, processes that promote methylation of As are still poorly understood. It is supposed that methylated arsenicals may enter the environment either directly as pesticides or by the biological transformation of organic or inorganic precursors.[4–7]

Redox potential (Eh) and pH should be determined to measure the posibility of As reduction in soils.[8] The redox equilibrium between As(V) and As(III) is higly pH-dependent,[9] thus, pH as well as the redox potential would have a large impact on arsenic speciation and mobility.[10–12] Masschelyn et al.[13] studied the effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. They observed that alterations in the oxidation state of arsenic, as influenced by redox potential and pH, greatly affected its solubility.

The thermodynamically unexpected conversion of arsenic species to arsenate in reducing environments was measured in laboratory studies by Holm et al.,[14] who also demostrated the importance of adsorption in controlling the concentrations of reactants and products during species interconversion reactions. According to Livesey and Huang[15] soluble arsenate is controlled by adsorption reactions in soils, rather than through the precipitation of arsenate compounds. In addition to kinetic and microbial considerations, amorphous iron and aluminium hydroxides,[16] clay content[17] and pH[16–17] are the soil properties reported to be most related to As sorption.

Under reducing conditions, arsenate minerals are too soluble to persist in soils, but arsenic sulfides were predicted to be stable.[18] Deuel and Swoboda[19] reported an increase of total soluble As under reduced conditions and attributed this increase to the reduction of ferric arsenate compounds.

Reuther[20] studied the geochemical mobility and reactivity of particulate inorganic arsenic in freshwater sediments, in relation to the degree of concentration, pH, Eh, oxygen and phosphorous load. As(III) and As(V) are known to be readily adsorbed onto amorphous hydrous iron oxides.[10] An increased solubility of e.g. iron hydroxides at low pH could lead to a release of iron-bound As from soils and sediments to waters.[21]

In this paper we have studied As(III), As(V), MMA and DMA speciation in marine sediments, as well as the relationships between them and other chemical parameters of the sediment (pH, Eh, Fe and Mn).

EXPERIMENTAL PART

Reagents

Stock standard solutions of arsenic compounds (1000 mg L^{-1}) were prepared by dissolving adequate quantities of As_2O_3 (Panreac), Na_2HAsO_4 $7H_2O$ (Panreac), $CH_3AsO(ONa)$ $6H_2O$ (Carlo Erba) and $(CH_3)_2AsO(ONa)$ $3H_2O$ (Merck) in ultrapure water. Working standards were prepared by dilution of the stock solutions. Ion exchange resins Dowex 50-X8 and Dowex 1-X8 (100–200 mesh) from Janssen Chimica were used for separation of arsenic species. All other chemicals were reagent grade.

Instrumentation

Flame Atomic Absorption Spectroscopy (FAAS) was used for iron and manganese determination with an air-acetylene flame, employing a Perkin-Elmer 2380 atomic absorption spectrophotometer equipped with hollow cathode lamps.

Hydride Generation Atomic Absorption Spectroscopy (HGAAS) was used for arsenic determination using a Perkin-Elmer MHS-10 Hydride Generator fitted to the spectrophotometer. A hollow-cathode lamp was used as the element specific ligth source.

An Orion 420 A pHmeter was employed for pH and Eh measurements.

Sampling and Sample Digestion

Marine sediments were collected in La Coruña estuary (N.W. of Spain). Fluxes of metals through the coastal environments in this zone are still low in comparison to other Spanish coast. However during the last years have witnessed a demographic and industrial growth leading to an increase of metal fluxes to the environment. It is a zone with important fishery resources, therefore contributing significantly to the economy of the region. The estuary receives inputs from agricultural zones and is influenced by the tides of the Atlantic Ocean water.

Eighteen sampling points were distributed along the estuary as shown in Figure 1. These samples were named "zones" and for their lyophilization and subsequent analysis the total sampled sediment was used. Four points (sampling sites number 7, 10, 13 and 18) were subsampled at different depths. Sediments were collected with a special gravity corer. A sediment column of 17 cm was taken.

To prevent oxidation of reduced species the samples were kept frozen at $-40°C$ prior to liophylization at less than $-40°C$ of temperature and at less

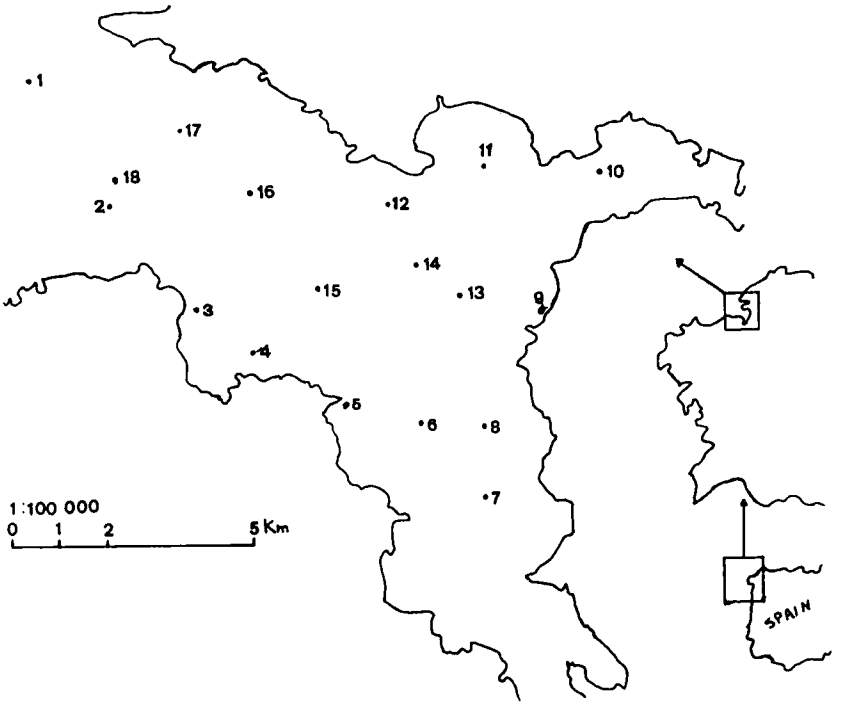

FIGURE 1 Sampling locations of the studied zone in La Coruña estuary.

than 25 Hg μm of pressure. Lyophilized samples were sieved through a 2 mm mesh and stored in topaz bottles prior to analysis. A digestion method with hydrochloric acid[22] was used which has been proved to maintain the chemical form of arsenic in the sediment.

Sediment Parameters Determination

pH and Eh

pH and Eh were determined according standard methods.[23] 2,5 mL ultrapure water were added to 1g of homogenized sediment. The mixture was shaken during 30 minutes. pH and Eh were measured with the suitable electrode.

Arsenic solid speciation

To separate the arsenic species a method described in a previous paper[24] was used. Briefly, As (III) and DMA are separated on the acetate-form of a Dowex 1-X8 (100–200 mesh) ion-exchange resin in a 20 × 1 cm column glass. As

(III) is eluated with ammonia and hydrochloric acid, while DMA remains on the resin. As (V) and MMA are separated on the H^+-form of a Dowex 50-X8 ion-exchange resin (100–200 mesh) in a 20 × 1 cm column glass. As (V) is eluated with hydrochloric acid and MMA with ultrapure water. As in the eluates is determined by HG-AAS. To determine the total arsenic concentration in the sample, 10 mL of digested solution is measured directly by HG-AAS. The arsenic species and total arsenic are quantitatively reduced to their respective hydrides by using hydrochloric acid and 3% sodium tetrahydroborate (prepared in 1% sodium hydroxide) as reductant.

Exchangeable iron

To determine exchangeable iron, 1 g of sediment is agitated in an acid medium for five minutes. The solution is adjusted up to 100 mL with the extractant solution. The acid medium is prepared by dissolving 0.1 g $CaCO_3$ and 0.088 g $(MgCO_3)_4$ $Mg(OH)_2$ $5H_2O$ in some mL of ultrapure water. 0.1 mL of concentrated H_2SO_4 and 2.5 mL of concentrated acetic acid are added. The final volume is adjusted to 1000 mL with ultrapure water. Fe was measured by FAAS.

Exchangeable manganese

To determine exchangeable manganese, 1 g of sediment is agitated in 1 M ammonium acetate (pH = 7,00) shaking for thirty minutes. The solution was adjusted up 10 mL with the extractant solution. Mn was measured by FAAS.

RESULTS AND DISCUSSION

Arsenic Speciation in Samples Named "Zones"

Results corresponding to the arsenic speciation in the total sampled sediment have been previously reported[22] and are shown in Table I. The concentration of total arsenic is below 10 $\mu g.g^{-1}$ in all samples. In general, highest contents are present in sampling points located near the coast. With respect to the inorganic arsenic content there was no clear relationship with the location of the sampling point, with As(V) as the most abundant inorganic arsenic species. The methylated forms comprised an average of 65% of the total As content in the sediment. The dominant methylated form was DMA, possible due to the biological transformation of the inorganic arsenic.[25]

TABLE I Determination of inorganic arsenic species, total arsenic, organic arsenic, Eh, Fe and Mn in sediments (zones).

SAMPLE	*Total As* ($\mu g.g^{-1}$)	*As (III)* ($\mu g.g^{-1}$)	*As (V)* ($\mu g.g^{-1}$)	*Organic As* ($\mu g.g^{-1}$)	*Eh* (*mV*)	*Fe* ($\mu g.g^{-1}$)	*Mn* ($\mu g.g^{-1}$)
1	4.34	<0.25	2.44	1.65	52.3	27.76	1.66
2	2.32	0.89	0.55	0.88	69.5	18.32	1.34
3	1.29	0.52	<0.35	0.42	68.5	14.58	1.67
4	9.93	4.04	4.56	1.33	95.1	16.46	2.33
5	6.10	0.70	1.99	3.41	96.0	21.75	3.92
6	4.41	1.68	1.80	0.94	95.9	25.96	2.13
7	5.77	<0.25	0.55	4.97	30.6	34.03	2.19
8	5.99	1.45	1.38	3.17	56.2	50.92	2.81
9	6.57	0.32	0.93	5.32	83.8	42.39	3.63
10	6.78	<0.25	0.77	5.76	59.5	112.47	0.95
11	5.53	<0.25	0.76	4.52	62.2	137.18	0.58
12	4.52	0.33	1.03	3.16	47.4	24.80	2.38
13	6.08	<0.25	0.47	5.36	77.0	32.88	2.04
14	4.51	0.57	<0.35	3.59	80.8	39.59	1.77
15	2.73	0.84	0.67	1.22	91.8	39.67	1.36
16	4.60	1.44	2.69	0.47	69.2	29.54	2.78
17	4.64	1.16	1.16	2.34	72.0	24.68	0.63
18	5.93	1.67	1.05	3.21	65.6	40.26	1.49

Arsenic Speciation at Different Sediment Depths

Total arsenic and arsenic species were studied at different depths in the sampling points number 7, 10, 13 and 18. These samples were named 1, 2, 3, and 4 respectively and letters a, b, c and d corresponding to bottom, medium, top and total sampled sediment. Results are shown in Table II.

Arsenic species concentrations were quite uniform with the depth profile. In general, organic arsenic concentrations were higher than inorganic concentra-

TABLE II Determination of arsenic species, total arsenic, Eh, Fe and Mn in marine sediments at different depths.

SAMPLE	*Total As* ($\mu g.g^{-1}$)	*As(III)* ($\mu g.g^{-1}$)	*As(V)* ($\mu g.g^{-1}$)	*MMA* ($\mu g.g^{-1}$)	*DMA* ($\mu g.g^{-1}$)	*Eh* (*mV*)	*Fe* ($\mu g.g^{-1}$)	*Mn* ($\mu g.g^{-1}$)
1b	5.13	1.26	0.80	0.80	2.27	55.8	26.95	2.42
1c	7.30	1.90	0.99	0.70	3.71	64.1	30.37	2.17
1d	5.77	<0.25	0.55	0.55	4.42	30.6	34.03	2.19
2a	5.93	1.51	1.10	0.81	2.51	68.6	64.35	1.79
2b	6.29	1.42	1.35	0.57	2.95	39.1	182.73	1.78
2c	6.96	1.99	1.57	1.00	2.40	66.3	108.89	1.61
2d	6.78	0.29	0.77	0.81	4.91	59.5	112.47	0.95
3b	3.80	<0.25	0.40	0.74	2.41	50.2	32.78	1.64
3c	5.21	0.80	0.44	0.60	3.37	60.8	36.24	3.07
3d	6.08	<0.25	0.47	0.64	4.72	77.0	32.88	2.04
4a	5.75	1.71	0.89	0.54	2.61	86.5	34.71	1.50
4b	6.88	2.09	1.44	0.16	3.19	67.7	38.12	1.67
4c	3.17	0.26	0.42	0.21	2.28	89.5	20.43	0.82
4d	5.95	2.17	1.05	0.67	2.06	65.6	40.26	1.48

tions. Regarding organic arsenic, all samples reveal higher DMA than MMA concentration. Although DMA did not present a clear variation with depth, MMA increased with depth in three of the four sampling points (number 1, 3 and 4).

Usually As (III) increases with depth, but here we find that both inorganic species As(III) and As(V) decrease. The arsenate/arsenite concentration ratios vary between 0.5–2.6 and are much lower than those reported by Ficklin[26] in lacustrine sediments from Montana with arsenate/arsenite concentration ratios of 45.2. This disequilibrium may be the result of a dynamic balance between inorganic arsenic oxidation and "in situ" microbial arsenate reduction.

pH, Eh, Fe and Mn

pH

All sampling points gave slightly alkaline pH-values of 7.9–8.6 in the sediment. No clear variation was observed with depth.

Eh

Moderately reduced sediment conditions (30.6–96.0 mV) were found, with Eh values increasing in the middle region of the estuary (Tables I and II). With respect to depth variation it was observed that the top sediment fraction had the highest redox potential.

Fe

Iron content varied between 14.6–137.2 $\mu g.g^{-1}$ (Tables I and II). These values were not very high due to alkaline soils containing low amounts of soluble Fe and Mn in the catchment area. Higher contents were found in the middle and upper part of the estuary. No clear variation was observed with depth.

Mn

Manganese content varied between 0.6–3.9 $\mu g.g^{-1}$ (Tables I and II). The highest contents occured at the begining of the estuary. With respect to depth variation it was observed that the top sediment fraction had the lowest content in three of the four points studied.

TABLE III Varimax-rotated Principal Component loadings, autoscaled data (zones).

	Factor 1	*Factor 2*	*Factor 3*	*Factor 4*
Total As	0.396	0.889	0.103	−1.076
As(III)	0.875	0.092	0.364	−0.057
As(V)	0.865	0.235	0.190	−0.239
Org. As	−0.525	0.785	−0.254	0.095
Eh	0.600	−0.073	−0.038	0.793
Fe	−0.567	0.531	0.480	0.225
Mn	0.441	0.278	−0.818	−0.025
Pct. of Var.	40.4	26.2	16.3	10.8
Cum. Var.	40.4	66.6	82.9	93.7

Principal Component Analysis (PCA)

PCA was made with the aim to reduce the original dimension of the data set (equal to the number of measured variables) to a lower number of new variables (named principal components, PCs) retaining most of the original information. In this way, it is hoped that sample groups and sample distributions can be easier viewed and analyzed.

PCA were made for each of the two data sets obtained (one for zones and another for depths). PCA was made with autoscaled data. After calculating the PCs, a Varimax Rotation was carried out in order to achieve easier interpretation of the loadings. All the tables presented here correspond to rotated PCs.

PCA-Zones

For the PCA study the variables considered were As(III), As(V), total As, organic As, Fe, Mn and Eh. Samples from zones are fairly well explained by using the first four PCs (see Table III). They cover about 92% of the initial information.

The first one explains up to 40% of the initial information and is mostly defined by the inorganic species (As(III) and As(V)). It is supposed that an important quantity of organic arsenic is obtained by biological transformation of the inorganic species. In that way, all the arsenic species present in the samples depend on As(III) and As(V) contents; this fact could explain that both species define the first factor. On the other hand, correlation between As(III) and As(V) should be expected due to their redox-dependent interaction.

The second PC (about 26% of the initial variance) is mainly defined by total as and organic As. Correlation between both variables may be expected because methylated forms comprise an average of 65% of total as in the sediments. The highest contents of organoarsenicals correspond to sampling points close to the coast, at the begining of the estuary, perhaps due to the input of agricultural

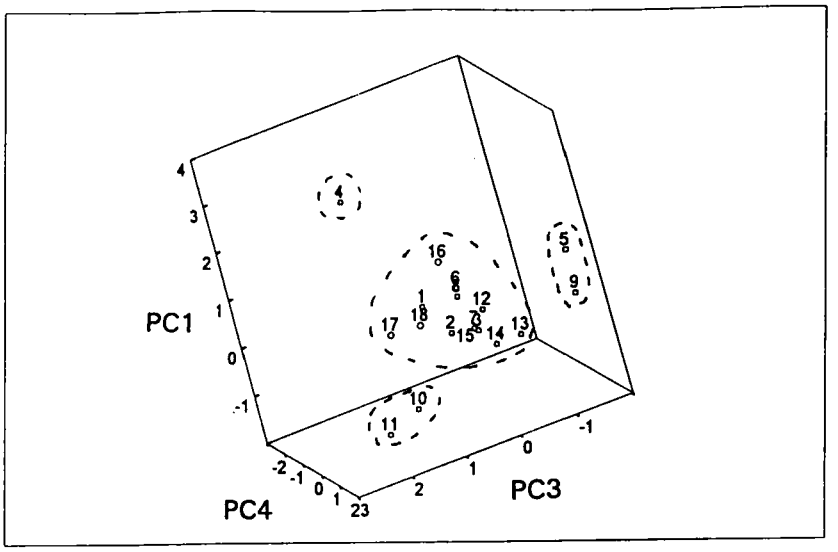

FIGURE 2 Sample scores distribution in the rotated PC1-PC3-PC4 subspace (zones).

wastes from the use of pesticides and herbicides. Similar results were reported by Reimer and Thompson,[27] who found a strong relationship between dissolved organic arsenic and total arsenic concentration in marine coastal sediments, caused by "in situ" bacterial methylation.

The third PC (about 16% of the variance) is directly linked to Mn (a variable which clearly distinguishes groups, as can be seen in Figure 2). Mn (II) forms in the sediment are capable to trap and sorb dissolved As, thus affecting the solubility and behaviour of this element.[25]

The fourth PC explains about 12% of the initial information and is defined by Eh. It is known that the redox potential is indicative for the degree of arsenic reduction in soils. In the same way, it may influence solubility and concentration in sediments.[13]

Taking all these PCs into account, the sample distribution presented in Figure 2 and 3 can be interpreted quite satisfactorily. From both figures it can be seen that sample groups are mainly due to substrate conditions and less due to species concentration. Thus, in Figure 2 Mn appears to be the discriminant factor and in Figure 3 Eh seems decisive. Mn as well as the redox potential would have an impact on substrate conditions and may influence arsenic speciation.

Probably, a clustering is not observed for the different arsenic species, because the variables defining PC1 and PC2 cause a "compensating effect". For this reason only a trend can be observed.

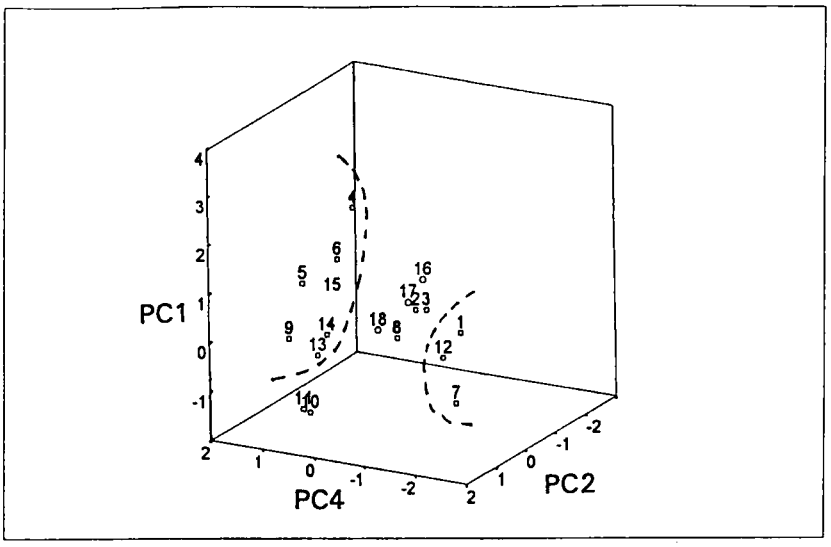

FIGURE 3 Sample scores distribution in the rotated PC1-PC2-PC4 subspace (zones).

On the right side of Figure 2, samples no.5 and 9 clearly form a defined group, with rather high values for Mn. In addition, they present high contents for total arsenic and organic arsenic, medium values for As (V) and low values for As (III).

Also the left side at the lower part shows a sample group (no.10 and 11). These samples have lower PC3 scores and values for total As, organic As, As(III) and As (V) are similar to those found for the group mentioned before. There is an interesting characteristic to be observed: samples no.10 and 11 present high Fe and low Mn contents and samples no.5 and 9 have low Fe and high Mn contents. This fact justifies that all these samples have similar values for all arsenical species. This means that for samples 5 and 9 the high Mn content may contribute to the methylation, because Mn-reduction may lead to bacterial growth.[3] For samples 10 and 11 reducing conditions (low Eh) are probably obtained due to their high Fe content,[20] thus promoting a microbial growth and consequently methylation.

Assuming a low kinetic rate for step 1 would explain medium As(V) contents (the reduction has not been completed).[28]

$$\text{As(V)} \xrightarrow[\text{reduction}]{1} \text{As(III)} \xrightarrow[\text{methylation}]{2} \text{Organic As}$$

TABLE IV Varimax-rotated Principal Component loadings, autoscaled data (depths).

	Factor 1	*Factor 2*	*Factor 3*
Total As	0.814	0.283	−0.043
As(III)	0.783	−0.477	0.339
As(V)	0.939	−0.261	−0.051
MMA	0.378	0.400	0.195
DMA	−0.115	0.738	−0.350
Eh	−0.195	−0.735	−0.124
Fe	0.645	0.282	−0.489
Mn	−0.006	0.475	0.815
Pct. of Var.	34.6	58.7	15.0
Cum. Var.	34.6	24.1	73.7

Low As(III) levels may point to the fact that trivalent As has been methylated. Furthermore when the Mn content increases, the kinetic for step 1 may decrease due to $(AsO_4)_2Mn_3$ is produced.[13]

Sample 4 appears alone in Figure 2 due to this sample has high contents for all of the variables except Fe and Mn, which present medium values.

In Figure 3 we can see different sample groups; those samples with higher PC4-scores (no. 4, 5, 6, 9, 13, 14 and 15) can be seen at the left side of Figure 3, and those samples with lower PC4-scores (no. 1, 7 and 12) can be observed at the right side of Figure 3. The central set group presents medium values for Eh, without other special characteristics.

PCA-Depths

PCA was also made on autoescaled data and a Varimax Rotation was carried out. As(III), As(V), total arsenic, MMA, DMA, Fe, Mn and Eh were considered. Table IV resumes the loadings found for each of the three first PCs. Despite total organic arsenic was considered in the previous study (zones), MMA and DMA were used when studying the vertical distribution. We supposed that the difference between both organic species could be more interesting in this case, since variation of aerobic conditions may be more significant with depth.

Arsenic species concentrations seem quite uniform within the sediment profile and clustering due to depths was not found. However it can be seen that sample groups were obtained due to reducing conditions (Eh) and DMA contents (Figure 4).

The first PC, explains up to 35% of the variance and is mainly defined by total As, As(III) and As(V). Probably, as inorganic arsenic methylation increases with depth due to higher microbial contents,[3] it may lead to a decrease of As(III) and As(V) levels with depth. This may agree with the fact that MMA

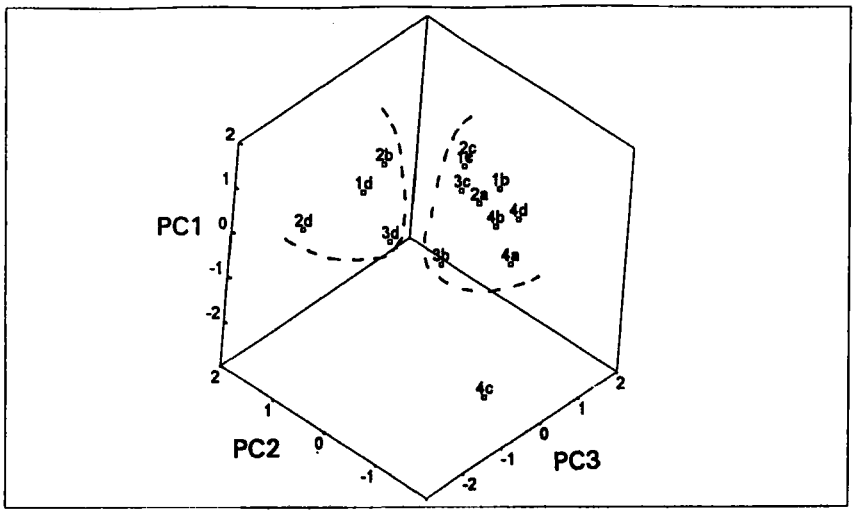

FIGURE 4 Sample scores distribution in the rotated PC1-PC2-PC3 subspace (depths).

increases with depth in three of the four sampling points (see Table II). Explanation for this PC could be similar than that for zones.

The second PC is defined by DMA and Eh (about 24% of the initial information). Correlation between both variables could be expected, because when Eh decreases (reducing conditions) a higher microbial activity is expected, with increasing DMA contents. The dominant methylated form was DMA; it could explain that this variable defined the second factor.

In Figure 4, it can be seen that those samples with higher DMA contents and lower Eh (no. 1d, 2b, 2d, and 3d) can be observed at the left side of the figure and those with lower DMA contents and Eh medium values (no. 1c, 1b, 2a, 2c, 3b, 3c, 4a, 4b and 4d) can be seen at the right side of the figure.

The third PC explains 15% of the variance. The variable which define this PC is Mn.

Acknowledgements

The authors express their thanks to the Galician Government for financial support of this project XUGA 103001A94.

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