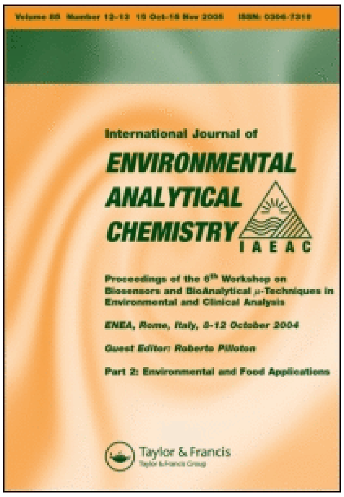

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MONITORING SULPHUR SPECIES AND METAL IONS IN SALT-MARSH PORE-WATERS BY USING AN IN-SITU SAMPLER

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An in-situ sampler is employed to monitor the composition of pore-waters at different depths in salt marshes of the Lagoon of Venice, Italy.

Pore-water concentrations of $S_2O_3^=$, S(-II), Fe(II) and Mn(II) as well as zinc, lead, cadmium and copper ions are determined by voltammetry; sulphate concentrations are measured by turbidimetry.

$S_2O_3^=$, S(-II), Fe(II) and Mn(II) concentration vs depth profiles undergo relevant seasonal changes, with higher pore-water concentrations in summer months. The concentration profiles of $S_2O_3^=$ and S(-II) show a typical depletion layer in the pore-waters of the upper sediment layers.

The trace metal ions analysed (Zn, Cd, Cu and Pb) display concentration vs. depth profiles which are almost independent of the season and which are characterised by higher concentration values in the upper sediment layer. Data from salt marshes of two sites with different pollution levels are examined.

Comparison with data relevant to unvegetated mud-flats indicates that the depletion of S(-II) in the upper pore-waters, which is mirrored by a relevant increase in trace metals concentrations, is a characteristic typical of the salt-marsh environment.

Keywords: Pore-water sampler; sulphur species; metal ions; salt-marshes; lagoon of Venice

INTRODUCTION

The study of seasonal and depth changes in the composition of pore-waters of sediments of transitional environments such as salt-marshes, is of great relevancy for understanding the interactions between reduced sulphur species[1–4] and

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metal ions[5,6] and can give important information on the possible release of toxic compounds from polluted sites[7].

Seasonal cycling of sulphur compounds and its influence on precipitation and mobilisation of metal ions have been studied in salt-marshes for instance of the northern Atlantic coast, both on the American[7–9] and European side[10]. However, some points concerning the exchange of matter between the sediment and pore-waters and the role played by bioturbation factors such as the presence of vegetation are not fully solved. The oxic conditions generated by plant metabolism can, in fact, influence the sediment layer in contact with the plants' roots (the so called rizosphere) causing two opposite effects: on one side, sulphide oxidation and related dissolution of metal ions from insoluble metal sulphides[7], on the other, the oxidation of soluble iron(II) to insoluble iron(III) oxides with concomitant trace metal adsorption and coprecipitation[10]. It was also demonstrated that pore-water biogeochemical cycles can change significantly from site to site or as a consequence of sudden physical events such as tides or rainstorms[2,11].

The development of suitable and reliable methods both for sampling[12–14] and analysing pore-waters[15–17] of intertidal or swamp sediments can help in spreading light on the overall effect which dominates in a particular environment or site. In-situ dialysis samplers were used to this aim[13,18]; they owe their popularity to the simplicity compared to other methods in which pore-waters must be extracted by centrifugation or pressure filtration. However, when dialysis samplers are used to gain anoxic pore-waters, dissolved oxygen must be removed from the compartments by a rather tedious and time consuming procedure[13].

Recently, a practical device for in-situ pore-water sampling, which allows simultaneous sampling at different depth levels, has been presented[19]. This apparatus improves and adapts to intertidal pore-water sampling, previous projects of samplers studied for deep-sea[20] or lake[21] research. At variance with previous devices[20,21], this sampler does not need to be removed for obtaining the sample, so far it allows to obtain sequential samples from the same location, with minimal adulteration of the sample and no contact with oxygen of the air[19]. Such a device is apt for periodical monitoring of the release of toxic substances from polluted sediments[22]. With respect to other samplers[23], developed mainly to study water-sediment interfacial processes, it can be used to investigate deeper layers involved in first diagenesis.

In the present paper, we examine the possibility to use this sampling device to monitor seasonal cycles of sulphur species and metal ions in the pore-waters of salt-marshes of the Venice Lagoon, in order to discriminate between the factors which rule the sulphur and metal cycles in the rizosphere (upper sediment layer) from those which are operative in deep layers (not influenced by plants).

EXPERIMENTAL

Location and sampling

The study was performed in the Venice Lagoon, a shallow water basin (average depth ca. 60 cm), with an average tidal excursion of 60 cm and a sedimentation rate of about 3 mm/yr[24].

The analysed pore-waters were sampled mainly in the salt-marsh 1, a low-middle marsh (according to the classification of ref. (6)) placed in the locality named "Pili", in proximity of the industrial area of Porto Marghera. For trace metals, pore-water samples were gained also from salt-marsh 2, which is located in proximity of one of the three mouths which connect the lagoon with the Adriatic Sea, north of Sant'Erasmo island and east of Lazzaretto Vecchio island. It has been previously shown that trace metal levels both of surface water[25] and sediments[26] in site 2 are lower than in site 1. Details on the composition of the lagoon sediments of the area where salt-marsh 1 is located, were reported elsewhere[27]. In particular, Zn, Cu, Pb and Cd occurred in superficial sediments in concentrations many times higher than those of their natural background with values around 1,000 mg/kg, 100 mg/kg, 80 mg/kg and 5 µg/kg, respectively.

Both salt-marshes 1 and 2 are covered by halophytic plants with dominance of *Arthrocnemum fructicosum* (L.) Moq. The sediments are reddish brown and rich in living and decomposing roots till ca. 30 cm depth; at greater depths, a diffuse blackening pervades the sediment, which rapidly becomes definitely black. This colour change is synonymous with the presence of ferric oxide precipitate in surface layers[6] and the precipitation of insoluble FeS and FeS_2 (pyrite) at depth[5,6].

Pore-waters in the salt-marsh 1 were collected in 1994, on February (winter), on April (spring), on July (summer) and on November (autumn) always in low tide conditions. Sampling in site 2 was carried out on July, 1995.

Pore-waters were gained with the *in situ* sampler shown in Figure 1, which consists in a rectangular base nylon block, provided by milled-in chambers, whose sampling ports are covered with a Millipore membrane (pore size 0.45 µm). This sampler differs from the device presented recently[19] because of the presence of lateral juts (interposed between the sampling ports) and because of the different shape (linear vs. V-shaped) and smaller volume (20 ml vs. 30 ml) of the sampling chambers. The juts are introduced in order to further decrease the possible effects of vertical percolation flows along the device walls, while the linear shape of the chambers should minimise the perturbation caused by the device to natural pore-water flows in the sediment; the smaller chambers volume is aimed to improve the spatial resolution of the device from ± 4 cm to ± 3 cm[19].

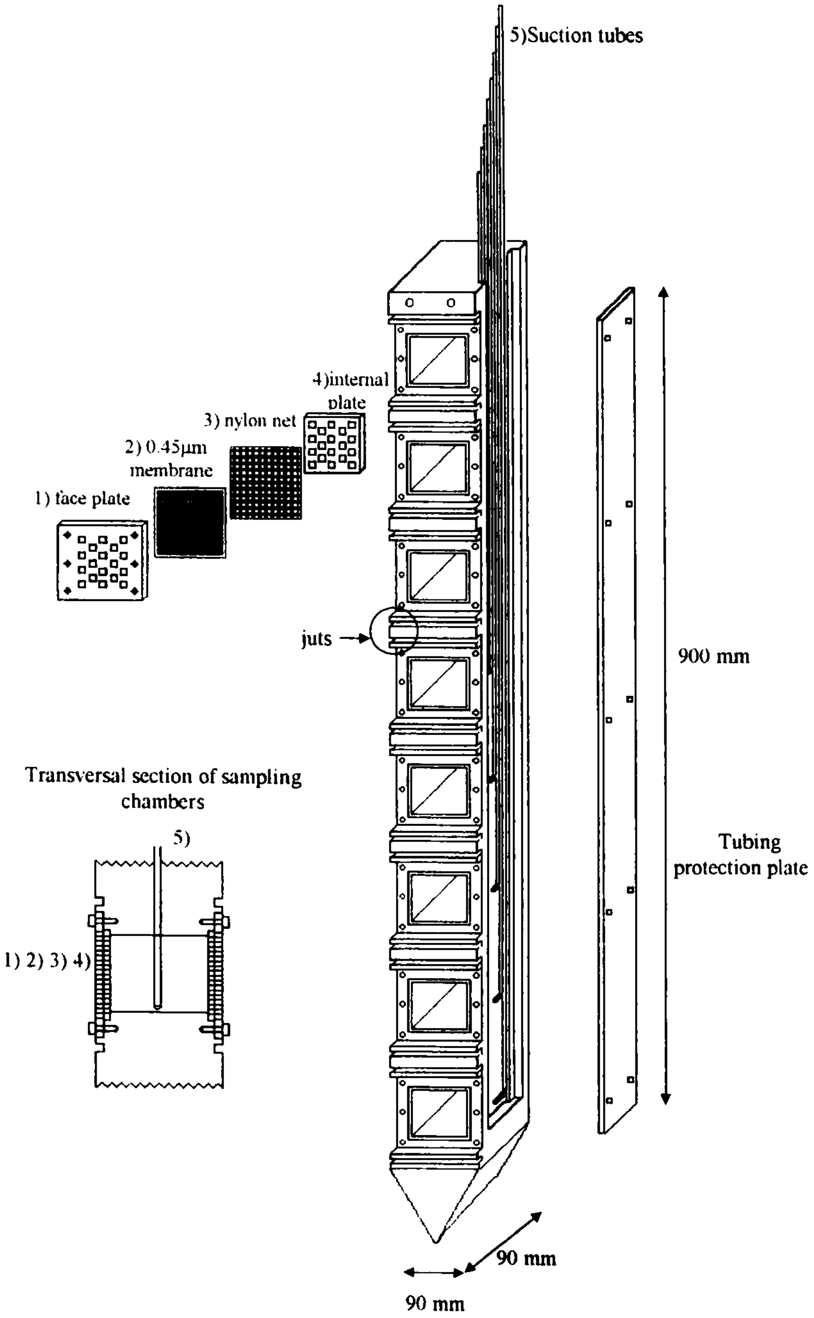


FIGURE 1 Scheme of the pore-water sampler

The sampler was cleaned and conditioned according to usual recommended procedures[28]. It was placed in the study site using the procedures described in ref. [19]. Briefly, after setting the device into sediments, residual air present in the chambers was removed by suction with a hand pump. The silicone tubes, which allow sampling of the pore-waters without removal of the apparatus, were sealed by closing a series of stopcocks. Sampling was carried out, after a proper equilibration time (typically two weeks[19]), by opening one stopcock and gently sucking with a syringe; the syringe contained the sample up to the analysis time (a couple of hours later). At the end of the suction no free volume was left inside the syringe which was sealed by closing a stopcock at the syringe inlet. No further manipulation or filtration of the pore-water was operated: syringes were kept in the dark in a nitrogen atmosphere. The sampler was left unattended on the study site all along the year of sampling, with a signal marking its position. Previous report[19] showed good agreement between data gained using *in situ* sampling and "classical" core-squeezing; this indicates a quick equilibration between the pore waters sampled in the chambers and the pore-water in the sediment, which is favoured by the scarce resistance that the double port design of the sampling chambers assures with respect to horizontal pore-water fluxes.

All laboratory analysis were carried out at room temperature (22 ± 2°C) and completed within few hours (typically 6–7 hours) after sampling.

Analytical methods and instrumentation

Sulphate was determined by turbidimetry[29]. A Metrohm mod.605 pH-meter equipped with a glass electrode with internal Ag/AgCl reference electrode was used for pH measurements. Conductivity was measured with CRISON mod. micro CM 2202 conductivity meter.

Multi-component voltammetric analysis were carried out by differential pulse voltammetry, using a Princeton Applied Research polarograph model 384B associated with a model 303A static mercury drop electrode (operating in SMDE mode). Instrumental conditions were: pulse height 70 mV, step time 0.2 s, scan rate 20 mV/s; the obtained voltammetric patterns displayed features in agreement with literature findings[30].

An Ag/AgCl was used as reference electrode. In order to avoid drifts in its potential as a consequence of precipitation of AgS (black), frequent substitution of the internal filling solution was carried out, usually every 4–5 samples, when using a reference electrode compartment with one frit, and every 20–22 samples with a double frit separator. The auxiliary electrode was a Pt-wire.

Reduced S(-II) was determined in the crude sample at the ambient pH by cathodic stripping voltammetry (scan from –0.400 to –1.700 V, deposition time: 0s), without degassing the solution[22]. The cathodic peak observed around –0.66 V is really the sum of H_2S, HS^- and any polysulphide species (S_x^{2-}) and is defined as total S(-II)[31].

The same cathodic scan in the same subsample allows one to detect also Fe(II) and Mn(II) which are reduced to metal giving two reduction peaks at –1.46 and –1.57 V, respectively[30].

The determination of Pb, Cd and Cu ions was carried out in the same subsample, after being acidified to pH 2 by addition of Suprapur® HCl 30% Merck (typically 20 µl of HCl per 10 ml of sample) and degassing in order to remove H_2S. The anodic stripping scan performed after a deposition at –1.05 V for 30 min, gave three peaks at –0.72, –0.55 and –0.34 V for Cd(II), Pb(II) and Cu, respectively. In the case of copper, which in the reducing conditions of sulphide containing pore-waters, can be present as Cu(I) or Cu(II)[32], it must be noted that the anodic stripping method did not allow separation of Cu(I) and Cu(II) peaks. We refer to the observed stripping peak as total soluble copper.

Thiosulphate, sulphite and zinc were analysed at pH 4, after addition of 2 ml of 0.5 M acetate buffer to 5 ml of sample. Degassing with nitrogen allowed the complete elimination of H_2S[22]. $S_2O_3^{2-}$ and SO_3^{2-} were determined from the currents of the cathodic stripping peaks at –0.08 and –0.52 V, respectively; no detectable SO_3^{2-} was determined in all the examined samples. Zinc was determined by anodic stripping voltammetry in the same subsample, after a deposition at –1.30 V for 3 min (stripping peak at –1.14 V).

The metal species detected by the above described methods include complexes and small colloidal aggregates (size ≤ 5 nm) which are labile at the pH of the measurement[22] and diffuse and dissociate quickly enough to give a voltammetric current identical to that of the same concentration of free metal ion[33].

Spiking of the pore-water samples with increasing concentrations of each one of the detectable analytes show linearity between peak currents and concentrations. This allowed us to obtain quantitative data by using the standard addition method.

Detection limits, determined as previously described[22], result: 0.2 µM for S(-II); 1 µM for $S_2O_3^{2-}$, 2 µM for SO_3^{2-}, Fe(II) and Mn(II); 2 nM for Cu_{tot}, Cd(II) and Pb(II) and 25 nM for Zn(II).

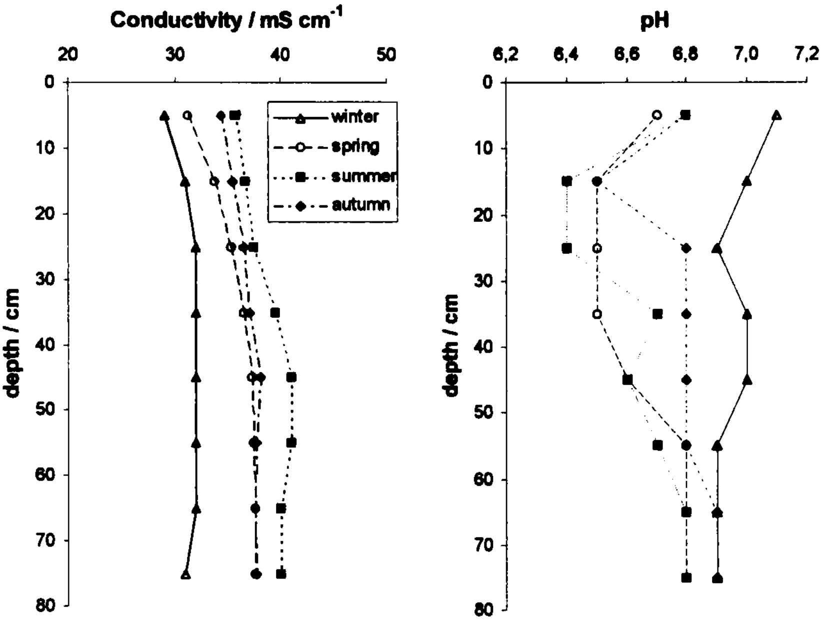
All reagents used were of analytical grade, apart HCl and sodium acetate which were of Suprapur®(Merck) quality. Extra pure Nitrogen (>99.9999 %) from Siad was used to purge the solutions.

Calculations

The equilibrium distribution of Zn, Pb and Cu species with inorganic ligands were calculated by using the program MINEQL+ ver. 3.01b[34,35], following a procedure similar to the one used by Giblin et al.[7,9] and taking into account the same inorganic ligands considered by those authors. In particular, HS^- was calculated from total S(-II), pH and salinity; pE values, calculated from HS^-/S^0 ratios, were used to evaluate $(Cu^+)/(Cu^{2+})$ ratios[8]. Chlorinity, Cl‰, was estimated from conductivity which correlates with salinity (S‰), as reported in the literature[36], according to the relationship[37]: Cl‰ = S‰ / 1.80655.

RESULTS AND DISCUSSION

The seasonal profiles for the different analytes shown in Figures 2- 4 refer to data gained in salt-marsh 1, while Figure 5 compares the trace metal profiles obtained from the pore-waters sampled both in site 1 and 2.



a) b)

FIGURE 2 Seasonal dependence of the conductivity/depth and pH/depth profiles in the pore-waters of salt-marsh 1

Figures 2 shows the dependence on season and depth for conductivity and pH data. Conductivity data display a slight increase with increasing depth. Seasonal trends indicate lower conductivity in winter and higher conductivity in summer pore-waters; this probably reflects an increase in the concentration of dissolved salts caused by higher water evaporation rates in warmer periods.

pH values show marked seasonal changes with the more acidic value ($pH = 6.4$) being recorded in summertime, at 15 and 25 cm depths. These trends parallel with those obtained for Fe(II) (see below), in agreement with previous literature findings which showed a direct correlation between H^+ activity and Fe(II) concentration values[9].

The concentration profiles of SO_4^{2-}, shown in Figure 3a, are characterised by increasing values with increasing depths, with no particular seasonal change. Such a trend is observed also for the SO_4^{2-} concentration normalised for changes in conductivity (i.e. in salinity[37]) of the pore-water at different depths (see Fig.3b). The normalised SO_4^{2-} concentration was calculated as follows:

$$[SO_4^{2-}]_n = [SO_4^{2-}]_x \cdot C_o/C_x$$

where $[SO_4^{2-}]_n$ is the normalised sulphate concentration, $[SO_4^{2-}]_x$ is the measured sulphate concentration at depth x, C_o is the conductivity of surface water and C_x is the conductivity of the pore-water at depth x. The evidence that this ratio is higher than the sulphate concentration in surface water (20 mM) indicate that sulphide oxidation is occurring. The decrease in sulphate excess in upper pore-waters can be related to the vegetated nature of this layer, where the presence of organic sulphur is expected to be prevailing[38]. Similar trends were observed also for pore-waters of other salt-marshes of the Lagoon of Venice[39].

Thiosulphate (see Figure 3c) is detected only in three spring samples and in one summer sample. The scarcity of thiosulphate in salt-marsh pore-waters when compared to its presence in the 10–40 µM range in mud-flat pore-waters[22], appears linked to the presence of the vegetated layer: plants activity, with their exhudates, increases the metabolic activity of both anaerobic and aerobic bacteria[2], with the final result that redox processes are complete and fast. For this reason thiosulphate, which is a good substrate for oxidation, reduction and disproportionation reactions[40], is continuously removed from pore-waters by such a rapid turnover.

Thiosulphate can be produced by sulphide reoxidation under both oxic and anoxic conditions, via chemical or biological pathways[41,42]. The evidence that, in the studied salt-marsh, $S_2O_3^{2-}$ concentrations higher than the detection limit are determined only in few spring and summer samples (when biological activity is higher), is opposite to the one observed in mud-flat, where a chemical origin behind thiosulphate accumulation in pore-waters was supported by the increase in its concentration in winter time[22].

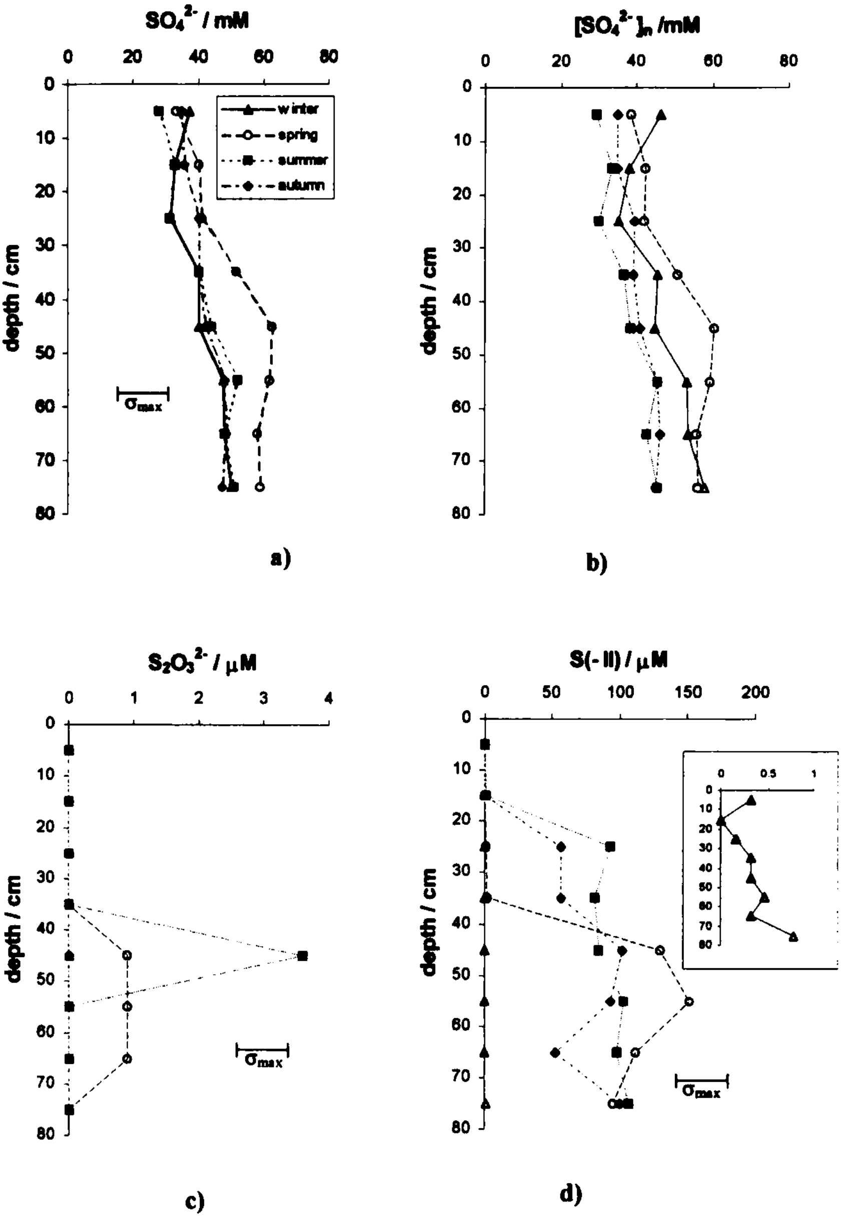


FIGURE 3 Seasonal concentration/depth profiles of sulphur species in the pore-waters of salt-marsh 1: a) sulphate; b) normalised sulphate; c) thiosulphate; d) S(-II). Error bars correspond to the maximum standard deviations, σ_{max}, calculated on five replicate determinations on each sample

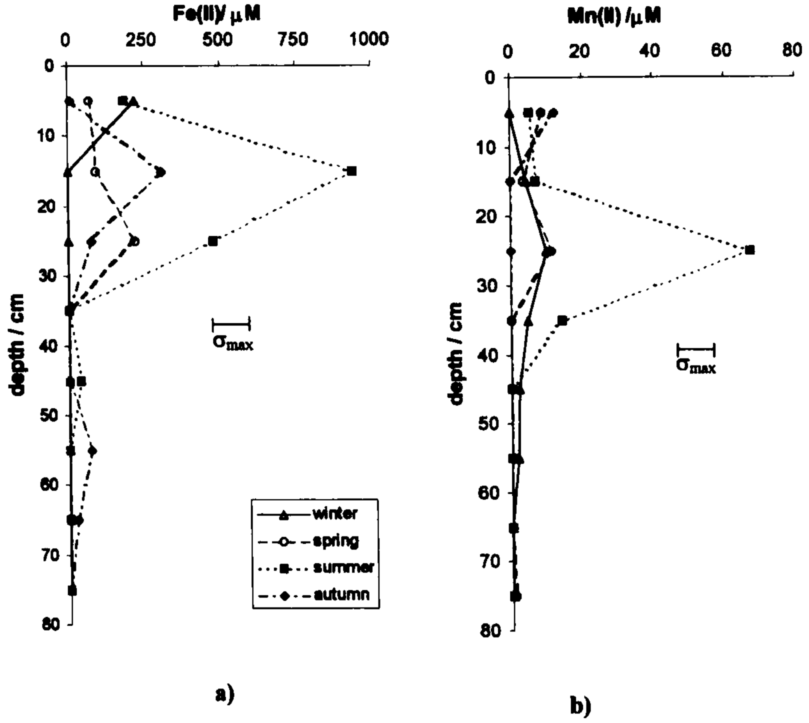


FIGURE 4 Seasonal concentration/depth profiles of Fe(II) (a) and Mn(II) (b) in the pore-waters of salt-marsh 1. Error bars correspond to the maximum standard deviations, σ_{max}, calculated on five replicate determinations on each sample

The profile of S(-II), shown in Figure 3d, undergoes relevant seasonal variations. Concentrations in the first 15 cm are very low in any season, even in spring and summer samples. This depletion in the upper pore-waters can be related to less reducing conditions caused by plants activity. This evaluation is confirmed by the evidence that the sulphide depletion layer deepened in spring probably as a consequence of increased plant metabolism. Also the comparison with pore-waters data relevant to an unvegetated mud-flat in the same site[22], confirms this hypothesis: upper mud-flat pore-waters are in fact characterised by higher S(-II) concentrations which reach, for instance, 160 μM at 15 cm depth in summer. In the salt-marsh, below the depletion layer, a steep increase in concentration is observed with maxima of 152 μM at 55 cm depth in spring and of ca. 100 μM at 25 cm depth in summer and 45 cm depth in autumn. Much lower concentrations characterise the winter profile (S(-II) < 1 μM).

In the layers where high S(-II) concentrations are found, sulphide production is expected to be greater than removal. This reflects in the precipitation of insoluble iron sulphides which are responsible for the blackening of deeper sediments. At these depths the metabolic activity of plants is no more able to cause the consumption of reduced sulphur, besides sulphur reducing bacteria still find a great amount of available organic substrates which support their production of S(-II). These bacteria can operate also in the upper layers, but the reduction products cannot diffuse in pore-waters being reoxidised by reactions with Fe(III) oxides (which are more abundant in the upper sediment layers, as indicated by their reddish-brown colour[6]), with sulphur oxidising bacteria or with oxygen driven into the sediment by plant activity[42,43].

The presence of quite high concentration of S(-II) even in the deepest samples can be related to the presence of available organic substrates, produced from dead roots and rhizomes, and perhaps from the excretion of dissolved organic compounds from living roots.

The Fe(II) profiles, reported in Figure 4a, are characterised by relevant seasonal variability with a maximum concentration of 936 μM, detected at 15 cm during summer sampling. On the other side, winter samples are characterised by low Fe(II) concentrations, always below the detection limit, apart the top sample.

Maximum Fe(II) concentration values are typically settled in the upper layers, between 5 and 15 cm, in the brown vegetated layer; below this depth, values decrease progressively up to undetectable concentrations in almost all the deepest samples. The high Fe(II) concentrations in the upper layers are related to sulphur cycle and plants biochemistry. In *spartina* populated salt-marshes high concentrations of iron(II) were observed in the vegetated layer[4], this ion being stabilised in solution by complexation with thiols and other sulphur containing organic compounds. Such a complexation could also mitigate the Fe(II) toxicity to plants. The evidence that detectable amounts of Fe(II) are measured also at depth where S(-II) is present (e.g. 25 cm depth in the spring profile) can be explained by a cycle in which bacteria produce organic ligands able to reduce Fe(III) from colloidal particles as well as to complex the so produced Fe(II)[44]. Also the contribution of Fe(II) exchanged with colloidal particles of small size (in the 5 nm range) cannot be neglected, since these species can be electroactive[33].

Mn(II) (see Figure 4b) is detected all through the year in the upper 35 cm layers with a maximum of 67 μM in the summer profile at 25 cm depth; in samples deeper than 55 cm, Mn(II) is almost undetectable. The "average" high concentrations of Mn(II) are related to indirect reduction by sulphide[42] together with direct microbial reduction since bacteria which generate free sulphide, act also as Fe/Mn reducing organisms[45]. A biological pathway for Mn(II) production

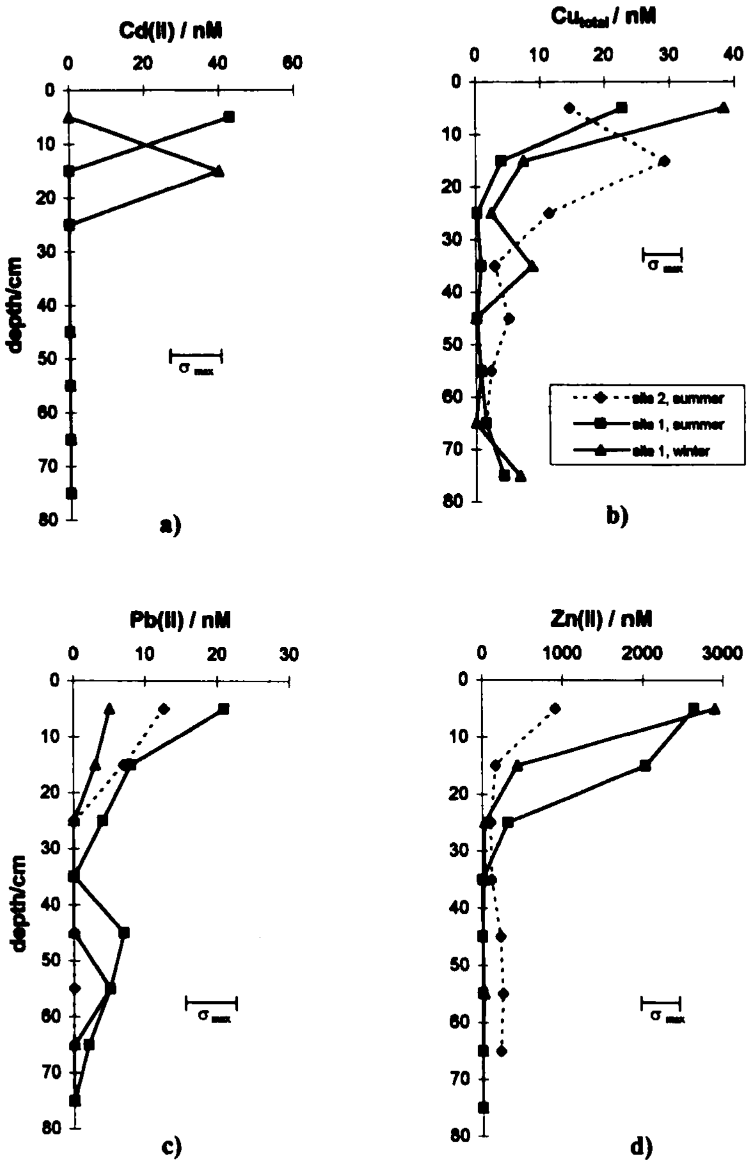


FIGURE 5 Seasonal concentration/depth profiles of trace metals in the pore-waters of salt-marsh 1 (full line) and 2 (dashed line): a) Cd(II); b) total soluble copper; c) Pb(II); and d) Zn(II). Error bars correspond to the maximum standard deviations, σ_{max}, calculated on five replicate determinations on each sample

agrees with the evidence that higher Mn(II) concentration are measured in summer, when biological activity is higher.

As shown in Figure 5a, Cd(II) determinations in the pore-waters sampled in salt-marsh 1 indicate concentrations which are almost always below the detection limit. In the few top samples where this metal ion has been detected, its concentration never exceeded 45 nM. Only two seasonal profiles (winter and summer) are shown in Figure 5a, since no further relevant changes characterise the other profiles. No cadmium was detected in the pore-waters of salt-marsh 2.

As far as the other three trace metals are concerned, they show average concentrations in the order Zn(II) > Cu_{tot} > Pb(II). Relevant profiles show depth distributions of similar shape and which do not change significantly with seasons (Figures 5b, c and d); they are characterised by maximum concentrations always settled in the upper 25 cm. When entering the sulphidic layer (35 cm depth), the trace metals concentrations rapidly decrease to lower values. Concerning site 1, again for the sake of simplicity, only the summer and winter profiles are shown.

In salt-marsh 1, Pb(II) displays a maximum concentration of 21 nM in the summer top sample. Concentration levels in deeper pore-waters decrease significantly, however with a second maximum in the 10 nM range at 45 – 55 cm depths. In the superficial layer of site 1, copper concentrations range between ca. 20 and 40 nM (maximum of 38 nM in winter). Zn (II) concentrations in the upper layer of salt-marsh 1, reach values between 2800 and 3000 nM.

The comparison with data of salt-marsh 2, sampled in summer (see dashed lines in Figures 5b, c, d) indicates that the Cu and Pb profiles are characterised by comparable concentration values for both salt-marshes, while higher concentration levels characterise the Zn(II) profile in salt-marsh 1. This evidence is probably related to pollution of site 1 by wastes from a blende working plant for zinc production, which operated in Marghera up to few years ago[26,27].

The increase in trace metals concentrations in the pore-waters of the vegetated layer can be explained both with the formation of metal complexes with organic ligands, which prevents the precipitation of metal sulphides[46], as well as with sulphide depletion caused by plant activity[7]. It is worth to note that a relevant role of trace metals complexation by organic ligands is evidenced at any depth level when one tries to model trace metal data by taking into account their precipitation and complexation reactions with inorganic ligands (see Experimental). The free metal ions concentrations, calculated by the computer program MINEQL, indicate that supersaturation conditions hold for Zn and Pb with respect to the formation of sphalerite (ZnS) and galene (PbS), and for Cu with respect to covellite (CuS) for upper and chalcocite (Cu_2S) for deeper pore-waters. Supersaturation conditions indicate severe complexation of the examined trace metals by ligands different from the main inorganic ligands generally used in this kind of modelling[7,9] (see Experimental). These unknown ligands are expected to be organic ligands which can be present at high concentration levels in salt-marsh pore-waters. Further specialised studies would be necessary in order to ascertain the quality and quantity of such ligands as well as their role in overall biogeochemical cycles.

As a final remark, it is worth to note that for all the trace metal analysed, concentrations in the upper pore-waters are, in any case, significantly higher (more than two order of magnitude) than relevant concentrations in surface waters of the Venice Lagoon[25]. This means that when the salt-marsh is submerged by lagoon waters during high high tides, a concentration gradient which favours the diffusion of metal ions from the pore-water to surface waters is expected to be operative.

CONCLUSIONS

The results presented here show that the use of *in-situ* pore-water samplers in combination with voltammetric methods of analysis allows one to study periodical changes in the concentrations of sulphur species and metal ions in salt-marsh pore-water. The obtained patterns and seasonal cycles show some characteristics which are typical of the salt-marsh environment. In particular, the active role of halophyte plants in promoting sulphide oxidation and in increasing metal ions concentrations in upper pore-waters, is evidenced.

These observations can have practical consequences when thinking to use polluted sediments for reclaiming new lands or for the restoration of eroded salt-marshes.

The information here obtained can constitute the basis for further studies aimed to extend this kind of investigation to a larger number of sampling stations, so taking into account also the role of environmental heterogeneity and temporary events such as rainstorms or exceptional tide conditions.

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