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The behaviour of arsenic in muddy sediments of The Bay of Biscay (France)

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Abstract—We have studied particulate and dissolved arsenic species in sediment and porewaters at sites in the Bay of Biscay, France, ranging in depths from 150 to 2,800 m. At all stations, major redox species (oxygen, nitrate, ammonia, total and reactive iron and manganese, sulphate and sulphur) reflect early diagenetic depth sequences of redox reactions comparable to other marine environments. Vertical distributions of dissolved and particulate As species and major redox species are related to changes in redox conditions and their major carrier phases, such as Fe and Mn-oxides. Arsenic diagenesis appears strongly dependent on Fe cycling. A subsurface maximum of dissolved As and surface enrichment of particulate As correspond to dissolution and precipitation of Fe (III) phases. Except for the shallowest and most bioturbated site, flux calculations show three different vertical diffusive As fluxes: two upwards and one downwards. Phase changes of recycled As result in local accumulations of reactive As at different redox fronts. Mass-balance calculations indicate that the upward As flux toward the oxidized layer can explain the enrichment of HCl extractable particulate As in this layer. A portion of the upward diffusing As can escape the sediment and may be fixed onto settling Fe-oxides by adsorption or co-precipitation and contribute to reactive particulate As input (i.e., As is recycled across the water sediment interface). *Copyright © 2003 Elsevier Ltd*

1. INTRODUCTION

Like many trace elements, arsenic (As) is essential to many marine organisms, yet can be toxic in high concentrations (Cutter and Cutter, 1995). The marine cycle of As is coupled to biologic processes, i.e., As is taken up and incorporated by living organisms where As can inhibit biologic functions (Plana and Healy, 1978). The geochemical cycle of As in the marine environment is complex due to the existence of its two redox states [e.g., As (III, V)] and multiple organic compounds, such as arsenobetaine and other arsenosugars, arsenocholine, or methylated arsenicals, each of them having its own biochemical and geochemical reactivity (Geislinger et al., 2002). An important process is the adsorption of As onto sedimentary particles (Pierce and Moore, 1982; Michel et al., 1997). Arsenic speciation is strongly influenced by redox conditions (Pierce and Moore, 1982; Belzile, 1988; Belzile and Tessier, 1989; Mucci, 1996; Sullivan and Aller, 1996; Smedley and Kinniburgh, 2002). The principal As species in oxidized water is arsenate, As (V). The arsenite, As (III), species occurs in oxygen-depleted or anoxic low Eh environments (Langmuir et al., 1999). The speciation of As plays an important role controlling mobility and toxicity. For example, arsenate species are usually more strongly adsorbed than arsenite (Pierce and Moore, 1982; de Vitre et al., 1991). Under more reducing conditions, dissolved As can precipitate as insoluble sulphides.

This study is a part of the Oxybent program, which focuses on the mechanisms of benthic biogeochemistry and their role in the preservation of sedimentary signals. We collected sediment cores at four sites at the Aquitaine margin in the Bay of Biscay with contrasting depth, organic matter content, sedimentation rate, and bioturbation intensity (Chaillou et al., 2002). The Bay of Biscay is a large sedimentary basin, fed by several rivers

(Loire, Charente, Gironde, Adour, Bidassoa, and Ebre) transporting suspended matter to the ocean. The southern French Atlantic coast is enriched in As due to the presence and exploitation of As-bearing ores (GÉODE, 1997). Since, in addition, the redox conditions in the muddy sediments of the Bay of Biscay have been extensively studied (Anschutz et al., 1998; Hyacinthe et al., 2001; Chaillou et al., 2002), modern sediments of the Bay of Biscay are excellent for examining As diagenesis. The oxidation/reduction state (redox conditions) of sediment and the presence of major diagenetic phases (Mn/Fe-oxides, S-species) are important parameters governing transformation and distribution of trace metals and particularly As. In the oxic part of the sediment column, for example, As is usually adsorbed on Fe-oxides and to a lesser extent on Mn-oxides and -hydroxides (Edenborn et al., 1986; Belzile, 1988; Langmuir et al., 1999; Smedley and Kinniburgh, 2002). The oxidation of the organic matter using oxidants present in the sediment yields reduced products and creates chemical gradients and fluxes in the first centimetres of sediments. Sedimentary Mn, Fe, and S-species are involved in these processes (Froelich et al., 1979; Kostka and Luther, 1994; Hulth et al., 1999; Anschutz et al., 2000), and then they can influence the distribution of As: control its release to the bottom water or its fixation in the sediments.

The objective of this study is to characterize the vertical distribution of dissolved and particulate As species in the muddy sediments of the Bay of Biscay and explain the behaviour of As in terms of fluxes and diagenetic recycling. The impact of As diagenesis on the geochemical record in modern sedimentary environments is evaluated to differentiate the origins (authigenesis/pollution) of As.

2. MATERIAL AND METHODS

2.1. Study Area

The Bay of Biscay is a semienclosed basin on the eastern side of the Northern Atlantic Ocean. Several French and Spanish rivers feed the

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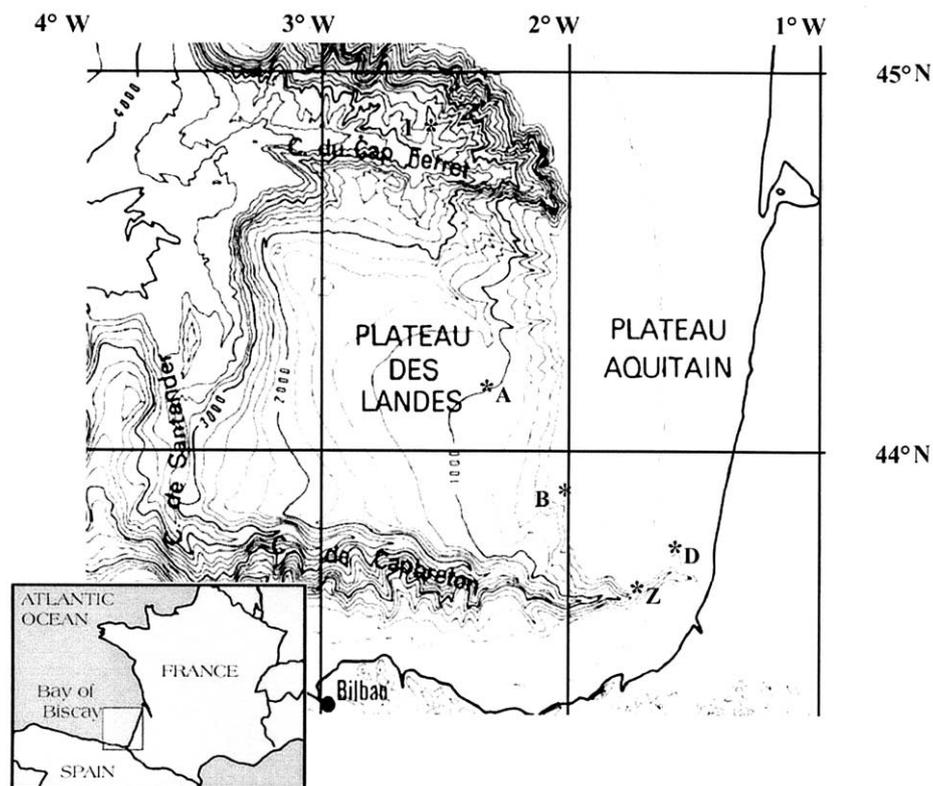


Fig. 1. Map of the southeastern part of the Bay of Biscay showing the locations of Oxybent 9 (June 1999) stations and station Z of Sedican II (September 2001).

sedimentary basin transporting approximately 3.7×10^6 t yr⁻¹ of suspended particulate matter, of which the Gironde accounts for ~60% (OSPAR commission, 2000). The suspended matter transported by the Lot-Garonne-Gironde and Adour river systems is enriched in nonferrous metals such as Cd, Zn, Ba, and As. This is due to mining and ore treatment activities going back to the late 19th century (Roux and Simonet, 1987; Blanc et al., 1999; Schäfer and Blanc, 2002). Most of the sediment is retained in the coastal zone, but 2–3% of the particles cross the continental shelf and settle on the abyssal plain (Rush et al., 1993).

Sediment samples were collected in June 1999 during the OXYBENT 9 cruise. Undisturbed sediment cores were collected at depths ranging from 150 to 2800 m depth in the southeastern part of the Bay of Biscay on the slope of the Aquitaine margin (stations A, B, and D) and close to the canyon of Cap Ferret (station I; Fig. 1). A core station Z, 400 m depth, collected in a flat region near the canyon of Capbreton was sampled for porewater speciation analysis only in September 2001 (SEDICANII cruise). The sediment at the stations located above 700 m

(D, B, and Z) is in contact with North Atlantic Central Waters. Station A is under the influence of a branch of Mediterranean outflow waters (Table 1). The temperature of both water masses ranges from 10.5 to 13°C. The sediment at station I is overlain by North Atlantic Deep Waters, with a temperature of 4°C.

2.2. Sample Collection and Treatment

Cores were collected with a multicorer, which allows sampling the sediment/water interface with minimum disturbance. Overlying water was collected immediately after core recovery for dissolved O₂ measurements, using the Winkler method (Strickland and Parsons, 1972). Profiles of porewater O₂ were measured on board using a cathode-type mini-electrode (Revsbech, 1983; Helder and Bakker, 1985; Revsbech and Jørgensen, 1986). The cores were kept at bottom water temperature using an insulating device. Subsamples were taken with 0.5 cm resolution from the surface to 4 cm and with 1 cm resolution in the rest of the core. Porewater was extracted by centrifugation at 5000 rpm for 20

Table 1. Features of the surficial samples of Oxybent (June 1999) and Sedican (September 2001) stations.

	Station I	Station A	Station B	Station D	Station Z
Geographic position	44°49'00N 2°33'00W	44°10'00N 2°22'00W	43°50'00N 2°03'00W	43°42'00N 1°34'00W	43°40'38N 1°37'70W
Depth (m)	2800	1000	550	150	400
Temperature (°C)	4	12	12	12.5	12
O ₂ bottom water (μmol L ⁻¹)	253	200	215	235	208
%C _{org} interface	1.39	1.51	1.83	2.32	
%C _{inorg} interface	2.75	3.37	2.12	1.59	
Maximum sedimentation rate (mg cm ⁻² yr ⁻¹)	17	36	80		

min under inert N₂-atmosphere. The supernatant was immediately filtered (0.2 µm, syringe filter SFCA NALGENE purged by N₂), acidified (HNO₃; suprapur) for dissolved metals analysis, or frozen for nutrient analysis. Samples for As speciation analysis (station Z) were stored in acid-cleaned (3 d in HCl 10%, thoroughly rinsed with MilliQ-water) 15-mL borosilicate glass bottles at 4°C under N₂ atmosphere and analysed within 48 h. On the samples from station Z, only dissolved As-species, dissolved O₂, Fe, and Mn were analysed. Despite the precautions taken to avoid oxygen contamination, we cannot exclude the possibility that traces of O₂ may have affected the measured porewater concentration of redox-sensitive species during core slicing and filtration.

Dissolved nitrate ($\Sigma\text{NO}_3^- = \text{NO}_3^- + \text{NO}_2^-$) and NH₄⁺ were analysed by flow injection analysis according to Anderson, (1979) and Hall and Aller (1992). The precision was ±0.5 µmol/L for ΣNO_3^- and ±5% for NH₄⁺. Dissolved Mn was measured by flame atomic absorption spectrometry (Perkin Elmer AA 300). Dissolved Fe was analysed by the ferrozine procedure described by Stookey (1970). The precision of both methods is ±10%. Sulphate was measured with a nephelometric method (AFNOR, 1997) with precision better than 2%.

Total solid-phase element contents were determined on 30 mg freeze-dried samples digested in a mixture of 2 mL HF, 250 µL HNO₃ 70%, and 750 µL HCl 30% according to the procedure described by Loring and Rantala (1992). All acids used were of suprapure quality. Sediment was also extracted with an ascorbate solution (50 g of NaHCO₃, 50 g of Na-citrate, 20 g of ascorbic acid for 1 L solution; buffer at pH 8). This procedure removes the most reactive Fe (III) phases, all Mn (III, IV) oxides and oxihydroxides, and their associated trace metals (Kostka and Luther, 1994; Anschutz et al., 1998; Hyacinthe et al., 2001). A separate extraction was carried out with 1N HCl to determine acid-soluble Mn and Fe. This reagent is used to dissolve acid volatile sulfides (AVS), carbonate, amorphous Fe-oxihydroxides, Fe-monosulphides, and also extract elements from clay minerals (Kostka and Luther, 1994; Hyacinthe et al., 2001; Keon et al., 2001). For both procedures, ~1 g of wet sediment was leached for 24 h at ambient temperature with 25 mL of the reagent. The centrifuged solution was then diluted with 0.2 mol/L HCl for Fe and Mn analysis and with 1% HNO₃ for trace metal analysis. Iron and manganese were analysed using flame atomic absorption spectrometry (Perkin Elmer AA 300).

Total As (As_{tot}) in solid-phase digests and porewater (dissolved As_{tot} = As (III) + As (V)), was analysed after prereduction of As (V) by KI/ascorbic acid (0.1 mol/L/0.06 mol/L) in 2.4 mol/L HCl, using hydride generation flow injection atomic absorption spectrometry (HG FIAS, Perkin Elmer AA300) as described by Yamamoto et al. (1985). Arsenite in the porewater was measured without the prereduction step, and As (V) was calculated as the difference between dissolved As_{tot} and As (III). The analysis of nonreducible As species (e.g., Arsenobetaine) requires an additional digestion of the dissolved phase and thus, these species were not detected by this technique (Michel et al., 1997). However, organo-As species are considered minor as i) their role in vertical transfer processes in the water column is small, and ii) their contribution to total As concentrations in river and wetland sediments is negligible (Michel et al., 1997; Keon et al., 2001; Smedley and Kinniburgh, 2002). The analytical methods were continuously checked against international certified reference materials (MESS-2, SL-1, and NIST 1646). Accuracy was within 9% and precision generally better than 10% for concentrations 10 times higher than detection limits (±3% for Mn and ±7% for Fe).

2.3. Flux Estimates

In the absence of resuspension and bioturbation, molecular diffusion is the main transport mechanism in sediment (Berner, 1980). The vertical diffusive flux of dissolved species was estimated using Fick's first law:

$$J = -\varnothing D_s (\Delta C/\Delta Z)$$

where J is the diffusional flux (µmol cm⁻² yr⁻¹), ΔC/ΔZ is the concentration gradient, ϕ is porosity, D_s is the bulk sediment diffusion coefficient corrected by tortuosity, i.e., D_s = D₀/θ² where θ is tortuosity and D₀ the molecular diffusion coefficient in water (Berner, 1980). The D₀ values obtained from Li and Gregory (1974) were corrected for the

in situ temperature at the time of sampling; tortuosity (θ) is assumed to be equal to 1 - ln(ϕ²) (Boudreau, 1996). This method was adopted to calculate instantaneous fluxes, including the flux of dissolved As at the water/sediment interface.

3. RESULTS AND DISCUSSION

3.1. Sediment Accumulation Rate

The sedimentation rates were determined at the four sites from the distribution of excess ²¹⁰Pb (²¹⁰Pb_{xs}; Chaillou et al., 2002). Maximum sediment accumulation rates at stations B, A, and I (0.15, 0.068, and 0.033 cm yr⁻¹, respectively) are inversely related to distance from the continent and to depth (Table 1). At station D, the ²¹⁰Pb_{xs} distribution is almost vertical, indicating very high sedimentation rates or intense mixing. The presence of polychaetes and burrows down to 40 cm suggests more intensive bioturbation than at the other stations, which are deeper and more distant from continental sediment sources. There are no ²¹⁰Pb_{xs} data for station Z, but polychaetes and burrows observed down to 10 cm depth, indicate biologic mixing at this station. Although station Z is located near the edge of the Capbreton Canyon, the bottom at the site itself is flat. X-ray radiography (SCOPIX, X-ray imaging system associated with image analysis software) of a sediment core from station Z shows unlaminate sediments with no evidence of slumping (data not shown). At all stations, the median grain size determined by laser diffraction (MALVERN-Mastersizer) is similar (roughly 10 µm). Although the dataset from station Z does not allow direct comparison with the other sites for all diagenetic parameters, it provides additional information on the vertical distribution of As redox species.

3.2. Characterization of the Redox Conditions

3.2.1. Major dissolved species

The oxic-suboxic boundary is an important horizon in early diagenesis as it controls the distribution of sensitive redox species such as U, Mo, Re, Cd, and As (Thomson et al., 1990; Gobeil et al., 1997; Moore et al., 1988; Martinez et al., 2000; Mucci et al., 2000; Chaillou et al., 2002). The five sites studied are well oxygenated, with dissolved oxygen in the bottom waters of 200 to 300 µmol L⁻¹. In the sediment, O₂ penetration depths range from 5 mm at station D to 50 mm at station I, with comparable values for stations Z and D (Fig. 2). Nitrate concentrations in the bottom waters at stations A and I were 15 and 20 µmol L⁻¹, respectively (Fig. 3). Below the oxic layer of the sediment, NO₃⁻ concentrations were close to zero, whereas dissolved NH₄⁺ increased towards the bottom of the cores (Fig. 3). Dissolved Mn appeared where O₂ concentrations approached zero. At stations A, B, Z, and D, the Mn²⁺ profiles showed distinct maxima (13, 25, 117, and 43 µmol L⁻¹, respectively; Figs. 4a and 7) below the oxic layer. Dissolved Mn in the lower part of the cores was lower, but constant. Dissolved Fe first appeared below dissolved Mn, at the depth where nitrate was minimum (Figs. 4b and 7).

The sulphate concentration was relatively constant with depth and equal to the SO₄²⁻ concentration in seawater, except at station D and to a lesser extent at station B. At station D, SO₄²⁻ decreased with depth from 28.9 mmol L⁻¹ at the water/sediment interface to 20.4 mmol L⁻¹ at 38 cm depth. At station

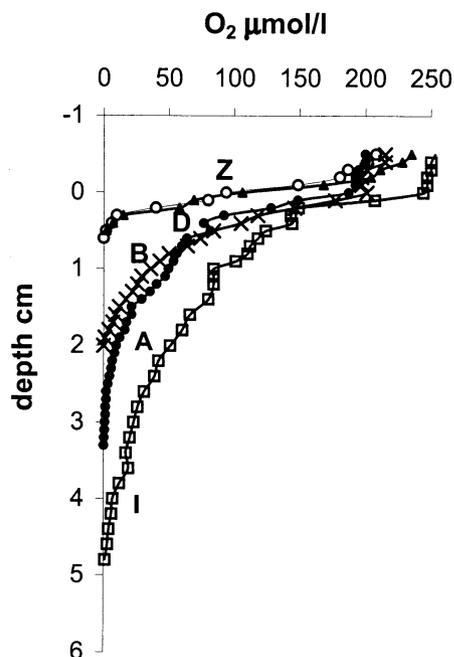


Fig. 2. Porewater profiles of oxygen in $\mu\text{mol L}^{-1}$ vs. depth for Oxybent stations D, B, A, and I and station Z.

B, SO_4^{2-} concentration decreased to 24.6 mmol L^{-1} at 38 cm depth (Fig. 5). Dissolved sulphides were not analysed. We noted no smell of sulphide during core processing, but we observed a few black patches near the base of the cores from the deepest stations and black colour of the sediments at station D, indicating H_2S production at a low level (see below).

The distribution of dissolved redox species in the four cores follows the classical pattern: disappearance of oxidizing species (O_2 , NO_3^-) close to the surface and emergence of reduced

species (NH_4^+ , Mn^{2+} , and Fe^{2+}) below (Froelich et al., 1979; Postma and Jakobsen, 1996).

3.2.2. Solid phases: Fe, Mn, and S

The distributions of particulate Fe and Mn are similar in the four cores (Fig. 4a,b). At the three deepest stations, maximum total particulate Mn (Mn_{tot}) occurs near the oxic/anoxic boundary where oxidation of Mn^{2+} (derived from the anoxic sediment) forms authigenic Mn-oxides and oxy-hydroxides (Fig. 4a). In core D there is no distinct peak of Mn-oxihydroxide at the oxic/anoxic horizon, possibly because of rapid mixing (Fig. 4a). However, the high content of Mn_{asc} in the first decimetre of the sediment core suggests that Mn is diagenetically recycled close to the sediment/water interface.

Maximum particulate Fe concentrations occur below the water/sediment interface, indicating relative enrichment compared to the surface sediment. Solid-phase Fe includes residual Fe, authigenic or excess-Fe, and sulphide-Fe. Selective digestions may separate different Fe fractions. The profiles of Fe_{asc} and Fe_{HCl} are parallel, with higher concentrations in the Fe_{HCl} fraction ($100\text{--}200 \mu\text{mol g}^{-1}$ higher; Fig. 5b). Ascorbate-extractable Fe_{asc} consists of amorphous Fe (III)-oxides only. Fe_{HCl} contains amorphous Fe (III)-oxides plus AVS-Fe and Fe in carbonates and clay minerals (Kostka and Luther, 1994). In the surface layer of stations B, A, and I, Fe (III)-oxide concentration is above $50 \mu\text{mol g}^{-1}$. Below this layer, particulate reactive Fe (both, Fe_{asc} and Fe_{HCl}) is lower and constant. This is attributed to the reduction of Fe-oxides, increasing dissolved Fe^{2+} concentrations. At station D, there is no subsurface peak in reactive-Fe, but reactive Fe-oxides persist far below the oxic layer i.e., in the anoxic sediment, probably due to the vertical mixing.

At each of the four stations, the lowest total sulphur (S_{tot}) concentrations occurred in the sediment surface layer. The cores from the stations I, A, and B showed relatively constant

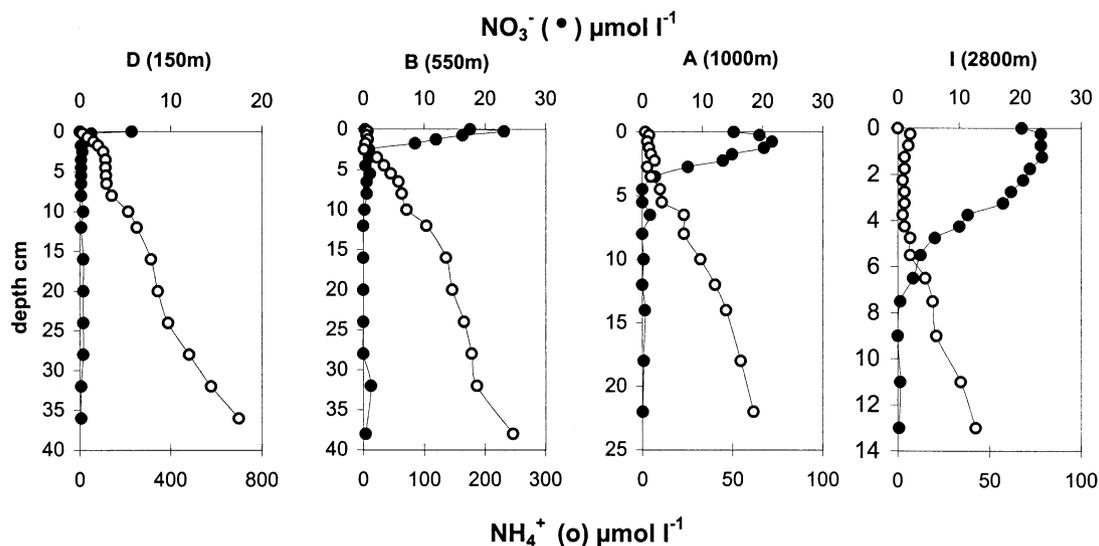


Fig. 3. Porewater profiles of NO_3^- (black dots) and NH_4^+ (open dots) in $\mu\text{mol L}^{-1}$ vs. depth for Oxybent stations D, B, A, and I.

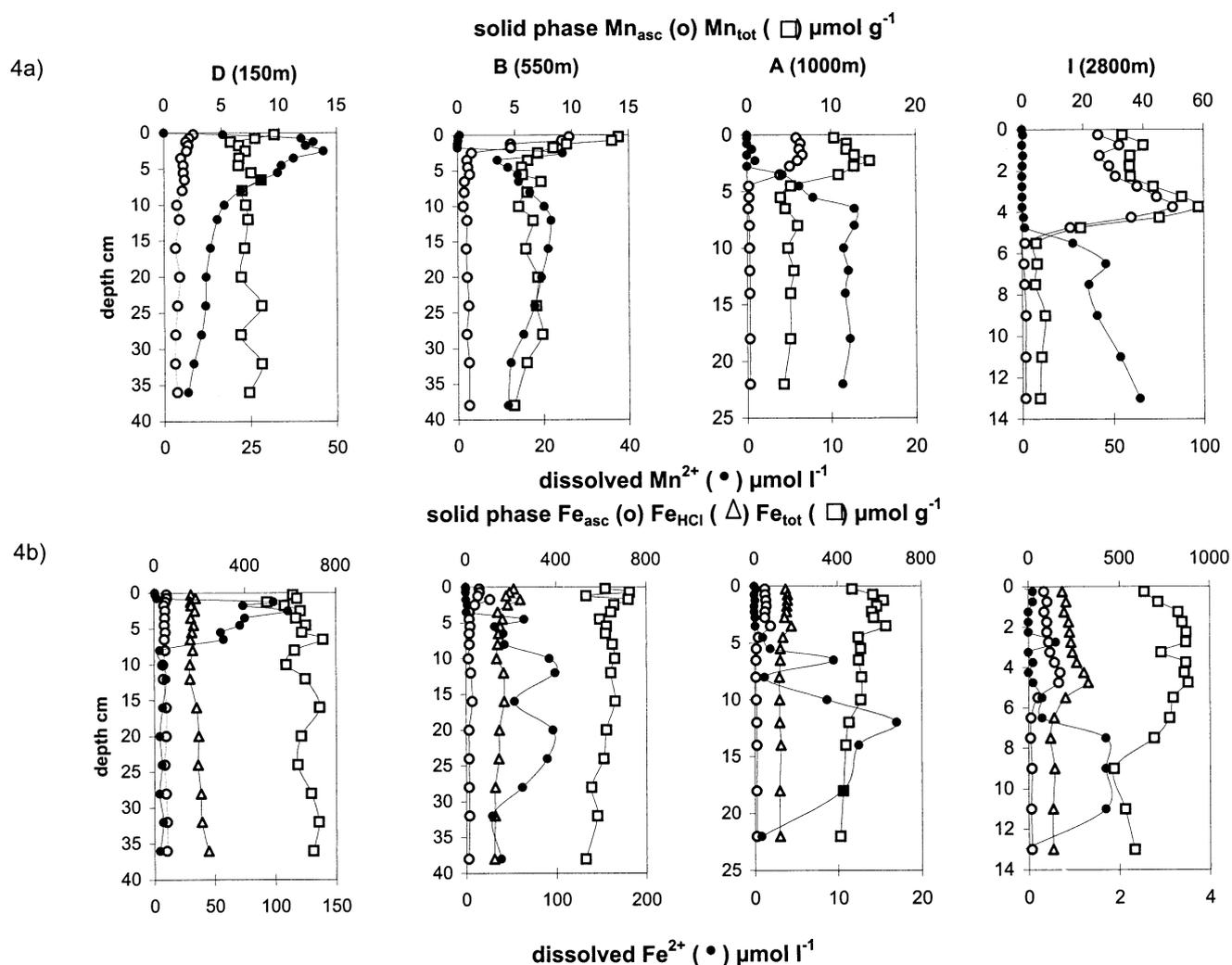


Fig. 4. (a) Porewater and reactive solid-phase profiles of Mn vs. depth for Oxybent stations D, B, A, and I. Mn extracted by ascorbate is symbolised by open dots and total Mn-fraction by open squares. (b) Porewater and reactive solid-phase profiles of Fe vs. depth for Oxybent stations D, B, A, and I. Fe extracted by ascorbate is symbolised by open dots, Fe extracted by HCl by open triangles, and total Fe-fraction by open squares.

S_{tot} concentrations with values below $30 \mu\text{mol g}^{-1}$ (Fig. 5). The presence of particulate S in continental margin sediments is often attributed to authigenic iron-sulphide minerals, formed during organic carbon mineralization by sulphate reduction (Bernier, 1970; Jørgensen, 1982). The first authigenic compound formed during this reduction step is generally amorphous FeS, which is slowly converted to more crystalline FeS₂ in the presence of sulphides (Jørgensen, 1982). At stations I, A, and B, small black dots at the surface of the sediment slices suggest trace quantities of FeS. At station D, the presence of Fe-monosulphides was confirmed by i) the sediment's black colour below 5 cm, ii) the characteristic odour of H₂S emanating during HCl leaching, and iii) the Fe_{HCl} profile (Fig. 4b). Indeed, the Fe_{HCl} concentration increased immediately below the Fe-oxide rich horizon. These observations suggest that sulphide production is more important at station D than at the deepest stations. The decrease of porewater SO₄²⁻ at the bottom of the core confirms the importance of sulphate reduction.

3.3. The Vertical Distribution of As

3.3.1. Porewater profiles

The profiles of total dissolved arsenic are consistent with other studies of marine sediments (Peterson and Carpenter, 1986; Belzile and Tessier, 1989; Mucci et al., 2000). In the upper part of the cores, dissolved As concentrations increase with depth and reach maximum values within 3–10 cm. The only exception is station I (Fig. 6a). This maximum, which coincides with maxima in Fe²⁺ and Mn²⁺ profiles, is attributed to the reduction and dissolution of oxidized solid-phase As. The depth of As reduction/dissolution coincides with the depth where dissolved Fe first appears and both, dissolved As and Fe diffuse toward the oxic/anoxic boundary (Figs. 6a and 7a). At the bottom of the nitrate-rich layer, Fe seems to be rapidly oxidized and removed from the porewater. However, precipitation of As appears to occur closer to the sediment/water

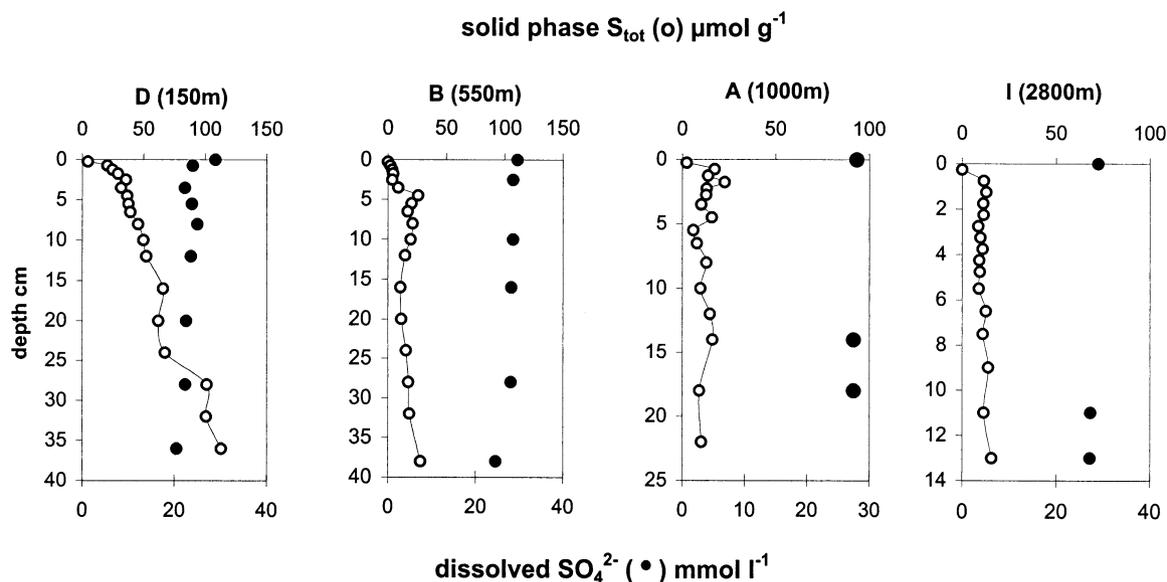


Fig. 5. Profiles of particulate S (open dots) and porewater SO_4^{2-} (black dots) vs. depth for Oxybent stations D, B, A, and I.

interface. Maximum dissolved As concentrations are $\sim 0.8 \mu\text{mol L}^{-1}$ (D), $0.4 \mu\text{mol L}^{-1}$ (B), and $0.2 \mu\text{mol L}^{-1}$ (A and I), and are much higher than bottom water concentrations of $0.015 \mu\text{mol L}^{-1}$ (typical seawater values are $0.02 \mu\text{mol L}^{-1}$; Andrae and Froelich, 1984; Sullivan and Aller, 1996). The dissolved As profile is consistent with upward diffusion from 3 to 10 cm depth followed by adsorption or precipitation in the oxic layer.

Speciation analysis of porewater in core Z, collected at 400 m depth, indicates that As (V) is the dominant species in the bottom water and at the sediment/water interface (Fig. 7b). Total dissolved As increases strongly with the appearance of Fe^{2+} , which was also observed at the other stations (Fig. 7a). The relative proportion of As (III) increased with depth and reached $\sim 100\%$ of dissolved total As at 2 to 3.5 cm (Table 2, Fig. 7b). At 4.5 and 13 cm depth, the relative As (III) proportion decreased to roughly 75%, indicating the significant presence of an unidentified As species (representing 25% of As_{tot}). According to the operational definition of the analytical technique, this should be As (V). The hydride generation protocol we used does not measure methylated As-species, and methylated As-species typically represent $<5\%$ of As_{tot} in marine sediments (Michel et al., 1997). Therefore, we assume the unidentified species to be inorganic.

We do not consider contamination by O_2 during sampling as a possible explanation for the apparent As (V)-excess, because all samples (some of which show 100% As (III)) were treated identically and because O_2 diffusion over the 10 cm distance from the bottom of the core to the deepest subsample is not likely. In the case of O_2 contamination, chemical oxidation kinetics (As (III) \rightarrow As (V)) by dissolved O_2 is too slow to cause an increase in As (V) (Rüde, 1996; Cherry et al., 1979). Intense bioturbation as observed at station D might establish local environments, containing more oxidized phases such as Mn-oxides within strongly reduced zones, causing partial oxidation of As (III) (Scott and Morgan, 1995; Mucci et al., 2000).

However, the apparent As(V) excess occurs only in the lower part of the core, where i) bioturbation is probably limited, and the sediment is strongly reducing. These strong anoxic conditions could result in reduction of more refractory organic matter or more crystalline Fe-oxides (e.g., goethite) associated to a release of dissolved Fe as suggested by the Fe^{2+} profile (Fig. 7a). This suggests two additional possibilities: first, As (V) could be released from inner surfaces of more crystalline Fe-oxides or from organic matter into porewater. The presence of As(V) requires that reduction is kinetically inhibited. The second possibility is that the As is released from colloidal particles ($<0.2 \mu\text{m}$) during the prerelution step of the analysis (KI/ascorbic acid in 2.4 mol/L HCl; 1 h). We assume that As associated with colloidal particles (e.g., amorphous carbonates or sulphides) is inaccessible to hydride generation and thus the prerelution step might represent an additional "attack" of the porewater. However, if this is true, it remains unclear whether the additional reagents, the high HCl concentration during the prerelution step, or reaction time control the destruction of colloidal particles.

3.3.2. Solid-phase profiles

The concentration of total particulate arsenic (As_{tot}) in the uppermost sediment layer of the Bay of Biscay is $\sim 20 \mu\text{g g}^{-1}$ (Fig. 6b). At the three deepest sites, there are subsurface peaks of As_{tot} parallel to peaks in particulate-extractable Fe and Mn (Fe_{asc} , Fe_{HCl} , Mn_{asc}). This suggests that in the oxic layer, As is linked to Fe and/or Mn-oxides. Manganese oxides and organic matter play an important role as As-carriers to river, lake, and coastal sediments (Peterson and Carpenter, 1983, 1986; Moore et al., 1988; Tingzong et al., 1997). However, in our sediment profiles, As_{tot} shows a strong decrease at exactly the depth where Fe_{asc} and Fe_{HCl} decrease (1.75 cm, 3.5 cm, and 4.75 cm at stations B, A, and I, respectively; Fig. 4b and 6b). The similarities in the distributions of solid As_{tot} and Fe-oxides

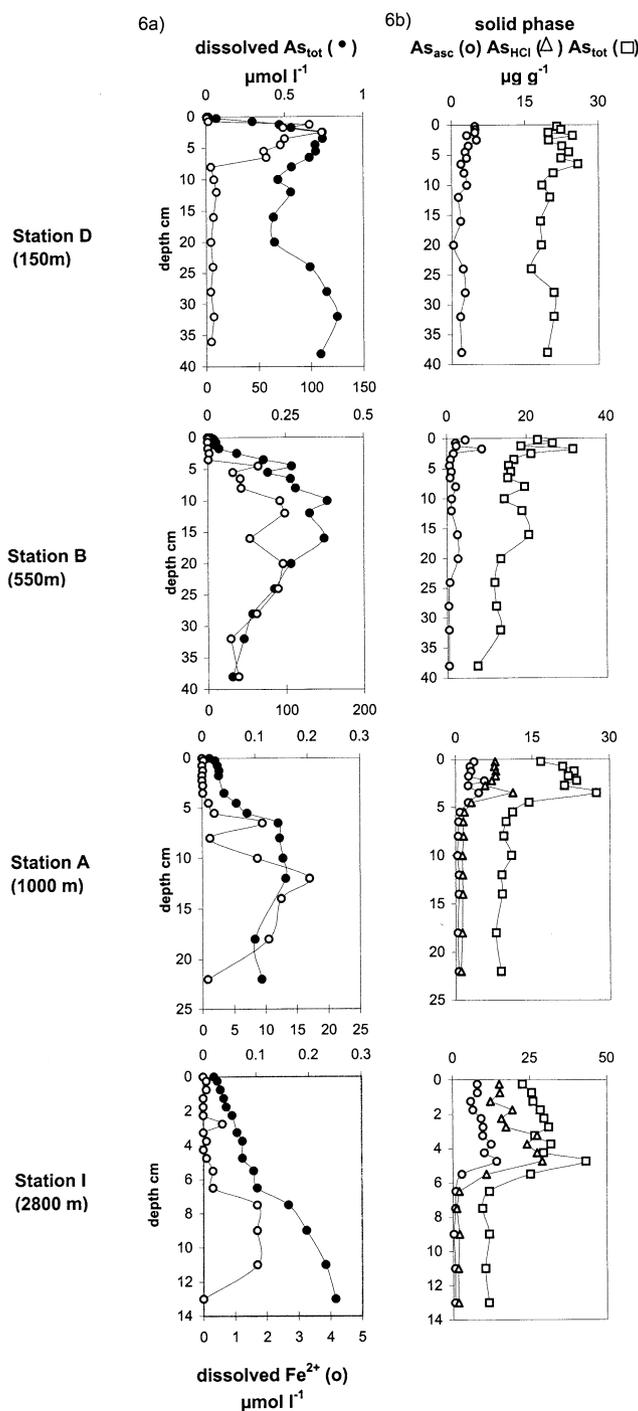


Fig. 6. (a) Porewater profiles of total As (black dots) and Fe²⁺ (open dots) vs. depth for Oxybent stations D, B, A, and I. Total dissolved As corresponds to As (III) + As (V). (b) Solid phase of As vs. depth: As extracted by ascorbate (open dots), As extracted by HCl (open triangles), and total As-fraction (open squares).

suggest that the diagenetic Fe cycle controls the particulate As-distribution and that Fe-oxides are the principal As-carrier phase in the Bay of Biscay sediment. Several other investigations of coastal sediments have shown that Fe (III)-oxides control early diagenetic behaviour of As where sediment chemistry is not dominated by Mn-oxides (Peterson and Carpenter, 1983; Widerlund and Johan, 1995; Sullivan and Aller, 1996;

Mucci, 1996; Mucci et al., 2000). Maximum particulate As ranges from 27 μg g⁻¹ at station D to 47 μg g⁻¹ at station I (Fig. 6) and is clearly higher than reported for other coastal environments (1–20 μg g⁻¹; Onishi and Sandell, 1955; Woolson, 1977). At the deepest station, As_{tot} concentrations decrease below the peak to constant values between 10 and 12.5 μg g⁻¹ at the bottom of the cores, which can be considered as the

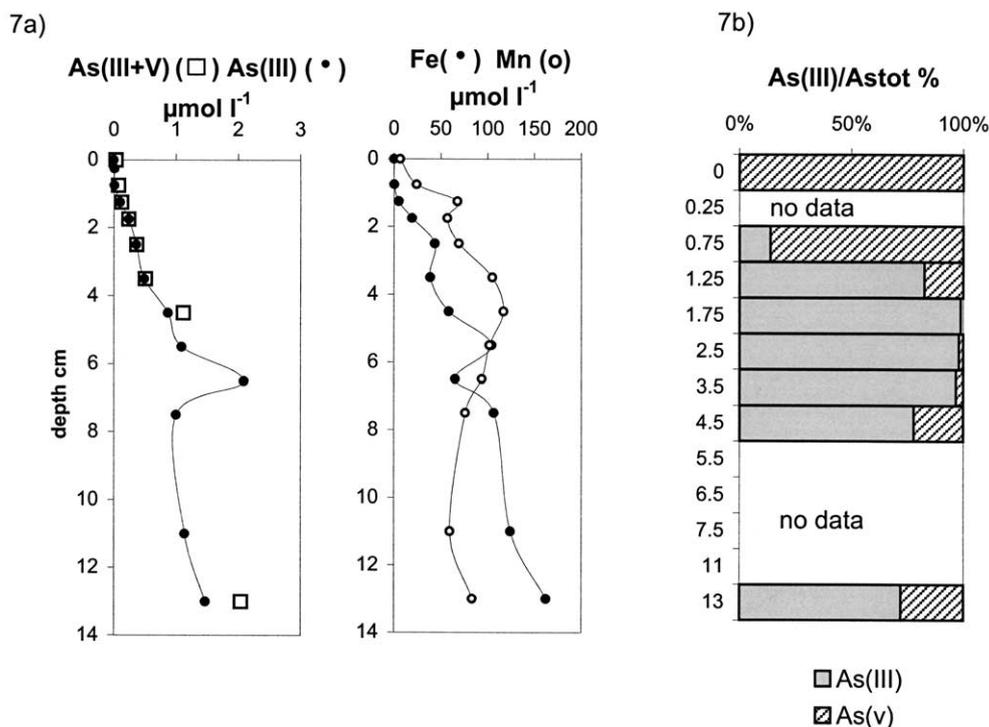


Fig. 7. (a) Porewater profiles of As (III) (black dots) and As (III + V) (open squares) in $\mu\text{mol l}^{-1}$ vs. depth compared to the distribution of dissolved Fe (black dots) and dissolved Mn (open dots) for the Sedican station Z (400 m). (b) Relative contribution of As (III) to As (III + V) in % for the Sedican station Z.

average residual or non-redox-sensitive As in this area. The decrease in particulate As_{tot} is coupled to As release into porewater. The profiles of extractable As (As_{asc} and As_{HCl}) parallel the profile of As_{tot} and show subsurface enrichment and constant and low As content deeper in the sediment. Although, particulate As_{tot} at station D showed no clear subsurface enrichment, the highest particulate As values nevertheless occurred in the uppermost 10 cm of the sediment. In contrast to the other stations, the As_{tot} concentration is higher than in the bottom of core D than residual As elsewhere. Biologic mixing probably explains this distribution.

Table 2. Results of the speciation analysis of pore water As in the sediment of the station Z (400 m) collected in September 2001.

Depth (cm)	As_{tot} (nmol/L)	As(III) (nmol/L)	As(III)/ As_{tot} (%)
0	31	0	0
0.25		10	
0.75	72	10	14
1.25	121	100	83
1.75	237	240	101
2.5	367	360	98
3.5	506	490	97
4.5	1116	870	78
5.5		1090	
6.5		2090	
7.5		1000	
11		1140	
13	2040	1470	72

3.4. The Diagenetic Behaviour of As

The total As content in the surficial sediments of the Bay of Biscay is similar to the As content of the particulate matter carried by the major rivers of the Adour/Garonne basin (20 to $25 \mu\text{g g}^{-1}$; Schäfer et al., 2002). This is consistent with the known conservative behaviour of As, suggesting no significant change of As distribution during the estuarine mixing (Michel et al., 1997). Beginning in the 19th century, chronic As pollution in the Gironde-Adour fluvial system has been caused by industrial and mining activities. However, the subsurface As_{tot} -maxima of the different cores cannot be interpreted as a direct sedimentary record of this pollution, because the thickness of the As_{tot} -enriched layer is inversely correlated with the sedimentation rate. For example, the 6-cm-thick layer enriched in As_{tot} at station I represents several decades of deposition whereas the 2 cm layer of station B only represents a few years. Although the As_{tot} input may have varied over time, the strong correspondence of As_{tot} and Fe (III)-oxides content suggests that early diagenesis is the dominant process controlling the As distribution, masking eventual sedimentary signals caused by variable As inputs.

Arsenic is transported to the sea floor in both organic and inorganic form. The latter is mainly associated with Fe, Mn, and Al-oxides. During burial As is exposed to well-defined redox sequence (Smedley and Kinniburgh, 2002). In addition to its own redox sensitivity, the diagenetic behaviour of As depends on the diagenesis of the major carrier phases: Arsenic, mainly present as As (V) in the oxic layer, is reduced to As (III)

and simultaneously released into the porewater when Fe (III)-oxides are reduced in the upper part (1–5 cm) of the cores (Figs. 6 and 7a,b). Dissolved As can then diffuse upwards and be fixed onto particles by adsorption or co-precipitation in the oxic zone or diffuse downwards to the zone of sulphate reduction and interact with dissolved or particulate sulphides (Edenborn et al., 1986; Legeleux et al., 1994; Widerlund and Johan, 1995; Mucci, 1996; Mucci et al., 2000).

Precipitation and/or adsorption of upward diffusing As create an As maximum value located just above the maximum porewater concentration (Fig. 6). A comparison of the porewater profiles of Fe, Mn, and As shows that dissolved total As is released at the same depth as dissolved Fe (Fig. 6 and 7a). Oxygen, Fe-, and Mn-oxides can oxidize As (III), which diffuses towards the oxic part of the sediment. Chemical oxidation of As (III) by dissolved O₂ is slow (Cherry et al., 1979; Råde, 1996) compared to oxidation by Mn-oxides, which serve as a catalytic electron transfer medium in the presence or absence of oxygen (Andrea, 1979; Peterson and Carpenter, 1983, 1986; Moore et al., 1988; Kuhn and Sigg, 1993; Scott and Morgan, 1995). The oxidation rate is independent of the As concentration (Scott and Morgan, 1995) but may be controlled by surface reactions. Little is known about the effect of Fe-oxides on the oxidation kinetics of As. Although Mn-oxides play an important role as an oxidizing agent for As authigenesis, the adsorption of As (V) on Fe-oxides is favoured due to the negative surface charge of Mn-oxides at circum neutral pH (Kuhn and Sigg, 1993; Stumm and Morgan, 1996). Adsorption or co-precipitation is confirmed by the selective extractions. In the zone of maximum As_{tot} enrichment, As_{asc} increases only slightly, accounting for ~30% of the excess particulate As obtained after subtraction of the estimated background value. In contrast, As_{HCl} accounts for more than 90% of excess As. Variations in total As are clearly caused by forms of As that are not dissolved by ascorbate reagent. This suggests that As in the oxic sediment is mostly linked to amorphous Fe (III)-oxides and other As-carriers such as clay minerals. Below the Fe redox boundary, the difference between As_{tot} and As_{HCl} is constant, around 10 µg g⁻¹. This As-fraction may be considered as residual and non-redox-sensitive and may be associated with phases inaccessible to reduction by ascorbate, such as crystalline Fe-oxides.

Downward diffusing As can be fixed by carrier phases such as authigenic iron monosulphides or pyrite or form distinct As sulphides (Edenborn et al., 1986; Legeleux et al., 1994; Widerlund and Johan, 1995; Mucci et al., 2000). At the deeper stations (I, A, and B), where sulphate reduction is weak, no significant increase with depth of particulate Fe_{tot}, Fe_{HCl}, or Fe_{asc} was observed, indicating concentration of authigenic Fe-monosulphides that can fix As is low. However, the porewater is sensitive to diagenetic processes, and total dissolved As exhibits a clear downward gradient. This suggests that As diffuses toward sediment layers deeper than were sampled by our cores, where it may precipitate as As₂S₃ or AsS (Fergussen and Gavis, 1972; Huerta-Diaz et al., 1998; Smedley and Kiniburgh, 2002).

At station D, the decrease of dissolved Fe and As with depth below the subsurface maximum indicates efficient trapping of dissolved As, probably by authigenic iron sulphides (Legeleux et al., 1994; Mucci et al., 2000). The profiles of As_{tot} show

significant enrichment below 25 cm, which confirms anaerobic authigenesis at the bottom of core D. The amount of As fixed in the As_{asc} fraction is not sufficient to explain the increase in As_{tot} (Fig. 6). The balance could be a particulate Fe-As-S phase, such as pyrite (FeS₂), or As-minerals without Fe (AsS or As₂S₃), that are more resistant to ascorbate leaching than Fe-monosulphides. Core D shows a clear increase of S_{tot} with depth and complete removal of Fe²⁺ at 8 cm, yet dissolved As remains high and even increases below 25 cm depth. In our samples, oxidation of less than 1% of excess As could explain the porewater values at this depth. Oxygen contamination during sampling cannot be completely ruled out, and is unlikely to have caused the increase considering the relatively slow oxidation kinetics of As (III) (the oxidation time of As (III) in seawater ranges from several months to one year, Johnson and Pilson, 1975). Because all the subsamples were treated the same way, eventual O₂ contamination should have occurred in all the samples, which was not the case. The dissolved As increase below 25 cm may be due to local environments (presence of more oxidized, As-bearing phases) or retarded As release from inner surfaces of more crystalline Fe-oxides, or to mineralization of refractory organic matter by sulphate-reducing microorganisms.

3.5. Remobilisation and Diffusional Fluxes of Arsenic

Careful examination of dissolved As profiles exhibits two distinctive upward fluxes. The first is from the suboxic maximum to the base of the oxic layer, exactly at the level of the Fe-redox boundary. The second is located in the oxic layer, from the base of the oxic layer towards the water/sediment interface. These fluxes can be created by the gradients of two distinct dissolved oxyanions, As (V) and As (III), as suggested in Figure 7. Arsenate may dominate in the oxic porewater and As (III) in suboxic and anoxic porewater.

The dissolved As data can be used to estimate upward fluxes and mobility of As. The gradients calculated at stations B, A, and I are similar. The amount of recycled As that is due to molecular diffusion can be estimated from the ratio of diffusive flux to particle accumulation rate. The upward flux at the level of the Fe-redox boundary corresponds to a theoretical enrichment in reactive As of 5.5, 12, and 17 µg g⁻¹ for stations B, A, and I, respectively. We compare these calculated values to the observed authigenic contents (Fig. 6b) produced in the uppermost part of the sediments, i.e., to recycled As. The oxidation of upward diffusing, dissolved As (probably As (III); see above) from the suboxic area to the base of the oxic layer increases the amount of reactive As by the mass of recycled As. For the three stations, the mass calculated from the fluxes of recycled As is 60% to 80% of the measured reactive As (As_{HCl}). Therefore, a major part of As that diffuses upward is probably trapped in the oxidized surface layer.

The second diffusive flux of As (probably as As (V); see above), across the oxic layer may transport dissolved As to the overlying bottom water. At sites B, A, and I, the flux across the oxic layer is 2.0, 1.3, and 1.0 nmol cm⁻² yr⁻¹, respectively. However, As released to bottom water may be trapped immediately by carrier-phases such as amorphous Fe-oxides, that are continuously supplied to the sediment surface in the Bay of Biscay (Anschutz et al., 2002). Assuming that all As released to

the bottom water is fixed onto settling particles, the minimum inputs of recycled As estimated from maximum sedimentation rates are 1.9, 2.6, and 4.3 $\mu\text{g g}^{-1}$ at site B, A, and I, respectively, or 18%, 38%, and 36% of the sedimentary reactive As input. Our data further suggest that reactive As represents 40–50% of the sedimentary particulate As flux at the water/sediment interface, which is twice what Widerlund and Ingri (1995) reported for the Kalix River estuary.

The downward diffusive fluxes of dissolved As at stations B and A were 0.89 and 0.35 $\text{nmol cm}^{-2} \text{y}^{-1}$, resulting in an addition of 0.8 and 0.7 $\mu\text{g g}^{-1}$ of particulate As. These estimated enrichments (probably as As_{HCl}) are relatively small compared to the As_{tot} content and explain why the profiles of particulate As do not show enrichment at the bottom of these cores.

4. CONCLUSIONS

Diagenesis of As in Bay of Biscay sediments is strongly coupled to Fe cycling and thus to redox conditions, and is determined by the flux of organic matter to the sea floor. Particulate matter deposited on the sediment surface contains $\sim 20 \mu\text{g g}^{-1}$ of As, of which more than 50% is refractory and not affected by redox changes. The reactive, HCl extractable fraction of total As (As_{HCl}) comprises freshly settled and recycled As, representing 25–35% and 10–20% of particulate As_{tot} , for stations I and A, and B and D, respectively. Early diagenetic redox processes follow the classical sequence with disappearance of oxidizing species (O_2 , NO_3^-) close to the surface and emergence of reduced species (NH_4^+ , Mn^{2+} , and Fe^{2+}) below (Froelich et al., 1979). These redox changes strongly modify As concentrations in porewater, resulting in different concentration gradients, fluxes, and particulate As concentrations. Within the uppermost 10 cm of the sediment, upward and downward fluxes intensively recycle As, particularly at the level near the Fe-redox boundary and close to the water/sediment interface.

Upwards diffusing As is fixed on the particulate phase near the Fe-redox boundary. The amount of this recycled As is similar to the amount forming the subsurface peak of authigenic particulate As_{HCl} . The second flux, near the sediment/water interface, releases dissolved As to the overlying bottom water, where it later is fixed probably onto amorphous Fe-oxides and thus will contribute to the reactive particulate-As input by sedimentation as recycled As. Downward As fluxes indicate removal of As from the porewater, possibly due to scavenging by sulphide phases.

Speciation analysis of porewater As reveals the presence of operationally defined As (V) in the anoxic part of the sediment. Possible explanations for this observation include local environments containing more oxidized phases; release of As (V) from inner surfaces of more crystalline Fe-oxides or from refractory organic matter; and different/additional sample treatment during speciation analysis that may release As from dissolved/colloidal As binding phases and keep As inaccessible to hydride generation.

The distribution of As in the sediment of the Bay of Biscay is mainly controlled by early diagenetic redox processes, and variations in As_{tot} should not be interpreted as a sedimentary record of As transport to the sediment. The non-redox-sensitive fraction (residual As) does not show important variations in

sediment cores covering the last 250 yr, suggesting that As transport to coastal sediments has not been influenced by mining activities in the Adour/Garonne basin.

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