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a b s t r a c t

Understanding trace metal behaviour in estuarine environments requires sampling strategies and analytical methods adapted to strong physical and geochemical gradients. In this study, we present a specific sampling strategy covering a wide range of hydrological conditions during nine cruises in 2003–2007 to characterise the behaviour of three dissolved metals (uranium, vanadium and molyb- denum) in surface and bottom water along the salinity gradient of the highly turbid macrotidal Gironde Estuary using a solid–liquid extraction. Uranium behaved conservatively whatever the water discharges observed. The slight dissolved U depletion compared to the theoretical dilution line between the fluvial and marine end-members occasionally observed in the low salinity range (0–3) was attributed to the mixing of different water bodies of the Gironde tributaries. In contrast, dissolved V behaviour was largely influenced by the hydrological conditions, showing increasingly pronounced addition with decreasing freshwater discharges, (i.e. increasing residence times of water and particles in the estuary). This addition of dissolved V in the low- to mid-salinity range was attributed to desorption processes observed in the Maximum Turbidity Zone (MTZ). The distribution of dissolved Mo concentrations along the salinity gradient was highly variable. Apparent conservative, and non-conservative behaviours were observed and were related to the concomitance of desorption from SPM, inputs from sediments for additive distribution and biological uptake and removal into sediments for subtractive distribution. Based on the whole database (2003–2007), annual net fluxes to the coastal ocean were estimated for dissolved U $(15.5–16.6 \text{ t yr}^{-1})$ and V $(31.3–36.7 \text{ t yr}^{-1})$.

1. Introduction

Estuaries play a major role in geochemical cycles of trace metals. Processes occurring in these mixing environments with various physical and chemical gradients affect the partitioning between particulate and dissolved phases reactivity and bio-availability of metals. Understanding trace metal behaviour is crucial for the assessment of potential impacts on the coastal ocean. In oxic aquatic freshwater environments, uranium (U), vanadium (V) and molybdenum (Mo) are present in their soluble oxidized state: U(VI) as bicarbonates complex in majority (Osmond and Ivanovich, 1992), V(V) as $VO_2(OH)^{2-}$ (Sadiq, 1988) and Mo(VI) as MoO_4^{2-} (Collier, 1985).

In most studied estuaries, U behaved conservatively along the salinity gradient (Windom et al., 2000). However, in few cases, some local depletion was observed in the low salinity range, and

was attributed to changes in alkalinity (Toole et al., 1987; Van Den Berg et al., 1991; Sarin and Church, 1994). Few papers have reported on V geochemistry in estuarine environments suggesting generally conservative behaviour (e.g. Scheldt and Rhine estuaries, Van der Sloot et al., 1985; Tamar Estuary, Van Den Berg et al., 1991). However, local subtraction was also observed and was attributed to local O_2 depletion in the water column (Shiller and Mao, 1999), as its solubility is more important in oxic environments (Wehrli and Stumm, 1989; Emerson and Huested, 1991). In sediments, V may be released from pore water during Organic Matter (OM) degradation (Audry et al., 2006). Although, V is not considered as a priority pollutant (Directive 2000/60/EC, European Council, 2000)), it may have inhibitory effect on enzymatic activity (Jandhyala and Hom, 1983) and its concentration levels in bivalves is surveyed along the French coast (French National Mussel Watch programme RNO, 2006). In contrast, Mo is well known for its toxic effects (e.g. Goldberg et al., 2002), although it is also essential for N_2-fixing cyanobacteria (Bortels, 1930; Fogg and Wolfe, 1954). Dissolved Mo abundance and biological activity are lower in the marine parts of estuaries (Howarth and Cole, 1985), reflecting its conservative

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behaviour observed in most estuaries. However, Mo removal from estuarine waters has also been observed (Dalai et al., 2005) and release into sediment pore water during early diagenesis followed by resuspension may locally and temporarily add dissolved Mo to the water column of the Gironde Estuary (Audry et al., 2007).

In this study we present dissolved U, V and Mo concentrations and distributions along the salinity gradient of the Gironde Estuary, which are much less documented than those of other more commonly studied elements (e.g. Cd, Cu, etc.). Although the estuarine behaviour of dissolved U, V and Mo has been studied in several estuaries, further investigations are required during contrasting hydrological conditions to (1) document and compare their respective behaviours along the salinity gradient of the same estuary, (2) report on their responses to variations in hydrological conditions and/or (3) present the net fluxes estimates of U, V, Mo exported out of the Gironde Estuary.

2. Study area and methods

2.1. Gironde Estuary

The Gironde Estuary is one of the largest (625 km^2) fluvio-estuarine systems of the European Atlantic Coast (Fig. 1). Its main tributaries, the Garonne and Dordogne Rivers, account for a mean annual freshwater input of 820 m^3 s^{-1} (1990–2007 period; Port Autonome Bordeaux). The Gironde Estuary is a partially mixed to well-mixed meso- to macrotidal estuary with tidal amplitude of 1.5–5.5 m (Hayes, 1975). During tidal cycle ocean water inputs have been estimated 30–40 times higher than fluvial inputs (Allen et al., 1977). The estimated residence time of fluvial water varies from a few days during flood events to w86 days during low freshwater discharge (Castaing and Jouanneau, 1979; Saari et al., 2008). The asymmetrical progression of the tidal wave towards the upstream of the estuary and the residual density circulation induce a pronounced permanent Maximum Turbidity Zone (MTZ) with Suspended Particulate Matter (SPM) concentrations in surface waters superior to 1 g l^{-1} (Castaing, 1981). The total suspended sediment mass in the MTZ has been estimated at w5 × 10^6 tons (Jouanneau and Latouche, 1981).

2.2. Sampling

During 2003–2007, nine cruises were performed along the salinity gradient of the Gironde Estuary (0–34) onboard the RV "Coˆtes de la Manche'', covering different seasons and a wide range of hydrological situations. The cruises included stable low water discharge situations (September 2006; Q¼169 m^3 s^{-1}; GIMER-CAD2) and a flood period (March 2007; Q¼2600 m^3 s^{-1}; GIMER-CAD3; Fig. 1), with an average annual freshwater discharge of w750 m^3 s^{-1} during the 2003–2007 period (Fig. 1).

At each sampling point, salinity, temperature, pH and oxygen level were measured with a multi-parameter probe (YSI 6920) calibrated the same day. Surface water (1 m below air-water interface) and bottom water (1 m above water-sediment interface) were sampled with decontaminated 5-l Niskin bottles and immediately transferred into acid pre-cleaned PP bottles (500 ml), previously rinsed with estuarine water of the site. Then, 130 ml were immediately filtered through 0.2 mm Nucleopore® polycarbonate filters and split into two aliquots. One aliquot (125 ml) was acidified (ultrapure HNO$_3$, 1/1000) to a pH < 2 and stored in an acid pre-cleaned PP bottle at 4 °C in the dark until trace metal analysis. The second aliquot (5 ml) was stored in a PP bottle at —20 °C until dissolved inorganic phosphate (DIP) analysis. Clean techniques were used to minimize contamination during sampling, handling and onboard analysis (Patterson and Settle, 1976).

Suspended Particulate Matter (SPM) concentrations were determined by filtration (Whatman GF/F, 0.7 mm, pre-weighed) of precise water volumes. Filters were then dried onboard at 50 °C until constant weight and re-weighed in the laboratory. SPM for Particulate Organic Carbon (POC) analysis was retrieved by pumping and centrifugation of important volumes of estuarine waters (up to 400 l), as described in Scha¨fer et al. (2002) and dried at 45 °C.

2.3. Laboratory analysis

2.3.1. Dissolved U, V and Mo analyses by solid–liquid extraction and ICP-MS

Analysing dissolved trace metals in estuarine waters has to deal with (1) low and variable concentrations along the salinity
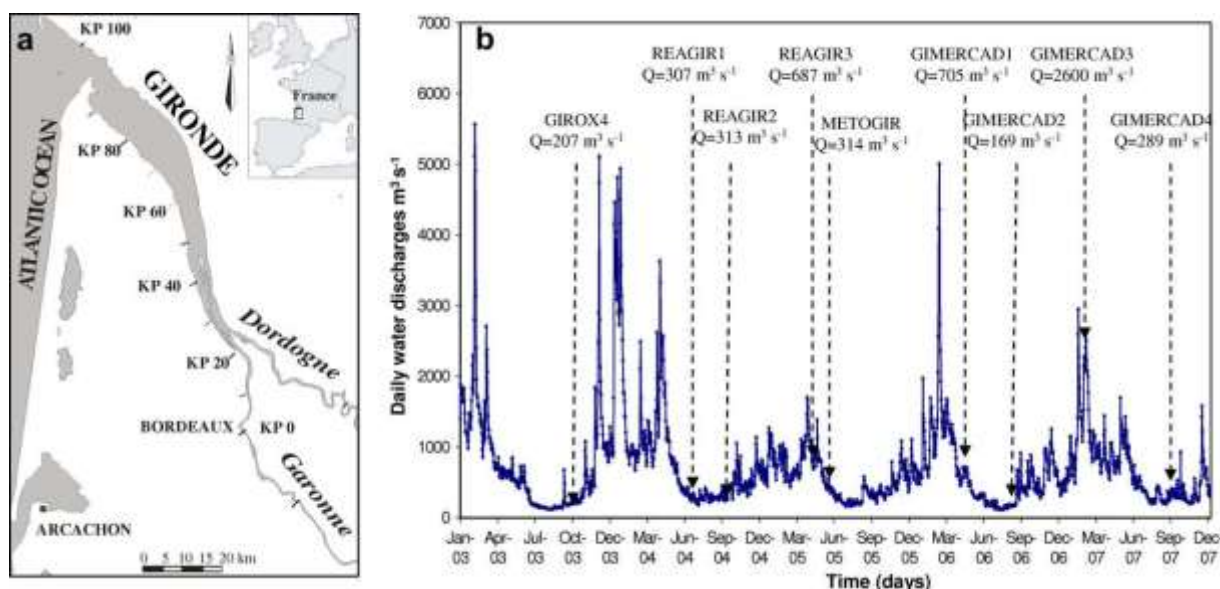

Fig. 1. a) Map of the Gironde Estuary and its two major tributaries, the Garonne and Dordogne Rivers; b) daily water discharge in the Gironde Estuary from January 2003 to December 2007. The nine sampling cruises are indicated by arrows.

gradient, (2) changing sample matrixes due to estuarine processes (e.g. flocculation, OM degradation etc.) and (3) the presence of the salt matrix, known to induce significant physical and chemical interferences during ICP-MS analyses. Several adapted methods have been used to separately study U, V and Mo in estuarine environments, based on metal specific procedures and material. For example, Windom et al. (2000) and Sarin and Church (1994) measured U by ion-exchange combined to alpha counting and by isotope-dilution followed by ICP-MS quantification, respectively. Dissolved V concentrations were analysed using different techniques such as catalytic colorimetric methods (Shiller and Mao, 1999) and separation/preconcentration by Chelex 100® resin prior to ICP-AES measurements (Auger et al., 1999). Dilution of the saline matrix prior to direct ICP-MS measurement was used to determine dissolved Mo concentrations (Dalai et al., 2005). However, dilution only limits the physical interferences and cannot be applied to elements with too low concentrations and/or affected by isobaric interferences.

In this study, we analysed simultaneously dissolved U (U_D), V (V_D) and Mo (Mo_D) after matrix separation and preconcentration by solid–liquid extraction, using $Digi$SEP Blue® cartridges (SCP SCIENCE), with amino-di-acetate as the functional group. The setup consisted on a 6 ml $Digi$SEP Blue® cartridge coupled to an acid pre-cleaned PP reservoir (70 ml) at the top and to a peristaltic pump (Gilson; 2 ml mn^{-1}) and tub at the bottom. The matrix separation/preconcentration procedure is based on the method reported by Kingston et al. (1978) and is divided into four steps (Fig. 2). Each step and parameter (flow rate, pH, reagent volumes, preconcentration factors, etc.) of the procedure was controlled and optimised to obtain low blank values, best recoveries and reproducibility of metal analyses (Table 1). The evolution of the (''single-use'') cartridge performances during multiple-use and -regeneration cycles of the same cartridge (more than 50 separation–regeneration cycles) has also been assessed (Table 1). This rapid and economic matrix separation and preconcentration technique has proven to be

		U	V	Mo
Blank values	mean	0.001	0.002	0.010
n ¼160	standard deviation	0.002	0.004	0.011
Detection limit $3s$		0.001	0.016	0.010
Reproducibility between cartridges	RSD	2%	1%	5%
Multiple use (n ¼50)	RSD	<10%	<10%	<10%
CASS-4	certified values	3	1.18 Ť 0.16	8.78 Ť 0.86
n ¼18	measured values	2.7 Ť 0.17	1.17 Ť 0.10	6.2 Ť 0.7
	recovery	90%	100%	66%
	reproducibility RSD	6%	9%	11%
NASS-5	certified values	2.6	1.2	9.6 Ť 1.0
n ¼9	measured values	2.55 Ť 0.31	1.15 Ť 0.12	6.93 Ť 0.97
	recovery	98%	96%	72%
	reproducibility RSD	12%	10%	14%

reliable and adapted for the simultaneous determination of U_D, V_D and Mo_D in estuarine and coastal seawater samples.

Concentrations of U_D, V_D and Mo_D were then measured by ICP-MS (Thermo X7) with external calibration under standard conditions. Accuracy and analytical precision were continuously quality checked for all the cartridges used by analysis of international certified reference materials (CASS-4; NASS-5; Table 1). This method provided quantitative recoveries (>97%) and excellent precision (Table 1) for U_D and V_D, when using the same cartridge several times (25–50 times) and for different cartridges (Table 1). Molybdenum showed lower recoveries of 66% (CASS-4, n ¼ 19) and 70% (NASS-5, n ¼ 9). However, suitable precision and reproducibility between cartridges allowed correcting Mo_D concentrations to 100% recovery. This correction did not modify the observed distribution of Mo_D along the Gironde Estuary salinity gradient, where dissolved Mo concentrations varied by a factor of w30 (Fig.5).

2.3.2. Particulate Organic Carbon (POC) and Dissolved Inorganic Phosphate (DIP) analyses

Representative aliquots (w50 mg) of dry, homogeneized SPM samples were acidified with HCl (2 M) to remove carbonates and dried at 60 °C for 24 h. Samples were then analysed with a LECO CS-125 analyser with precision better than 5%, according to the method described in Etcheber et al. (1999). POC contents are expressed as percentage of dry weight of SPM, abbreviated as POC%. DIP was analysed within a month after sampling according to the ascorbic acid-molybdate blue method (Murphy and Riley, 1962) and measured spectrophotometrically.

3. Results

1. Hydrological conditions

Based on the freshwater discharges of both major tributaries (Garonne and Dordogne Rivers), the hydrological situations during the 9 cruises between September 2003 and October 2007 can be classified into 4 contrasting water level types: exceptional drought (<200 m^3 s^{-1}: 09/27/03, GIROX4; 09/07/06, GIMERCAD2), typical low freshwater discharge (w300 m^3 s^{-1}; 07/18/04, REAGIR1; 10/09/04, REAGIR2; 07/08/05, METOGIR; 10/01/07, GIMERCAD4), low/mean water discharge (w700 m^3 s^{-1}: 05/10/05, REAGIR3; 05/12/06, GIMERCAD1) and flood (w2600 $m^3 s^{-1}$; 03/04/07, GIMERCAD3) were observed.
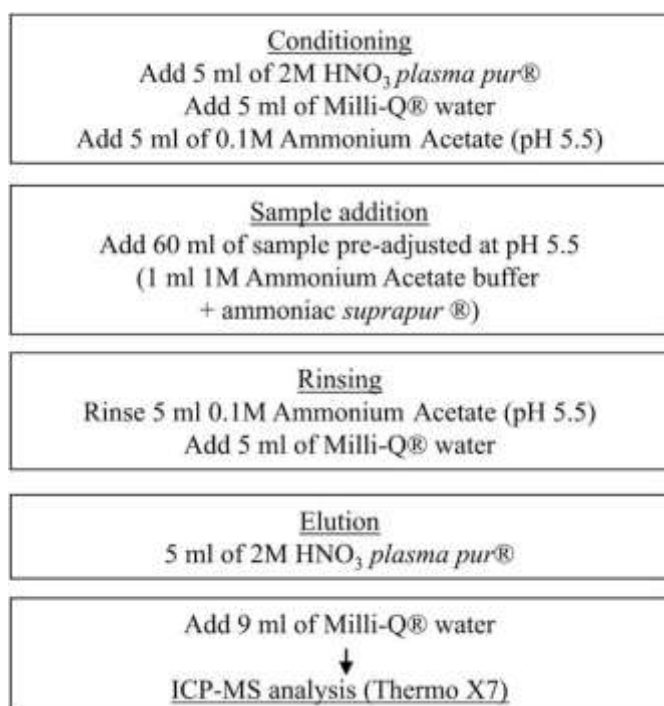

Fig. 2. Protocol steps of the solid–liquid extraction using $Digi$SEP Blue® cartridge.

Fig. 3. U_D and SPM distribution along the salinity gradient (0–35) of the Gironde Estuary during the nine sampling cruises (freshwater discharges, Q in m^3 s^{-1}). The lines in the graphics represent the theoretical dilution lines between the freshwater and seawater end-members. Deviation of measured concentrations from these lines suggests either addition or subtraction.

3.2. SPM and DIP distribution along the salinity gradient

Relation between spatial distribution and concentrations of SPM, hydrological conditions and intrusion of saline waters in the Gironde Estuary are well-documented (Iouanneau et al., 1983; Elbaz-Poulichet et al., 1984; Sottolichio and Castaing, 1999). In the present study, maximum SPM concentrations in surface water (6000 mg l^{-1}; September 2003) were generally

observed during severe drought level and the presence of the MTZ is mainly localized from freshwater to a mid-salinity range to $S\frac{1}{4}$15–20 due to low fluvial water discharges (Figs. 3–5). In May 2005 and 2006 (REAGIR3, GIMERCAD1), maximum concentrations were observed at mid-salinity range, probably caused by low/mean water levels. Afterwards, concentrations decreased roughly until values less than 10 mg l^{-1} (seawater end-member; Figs. 3–5).
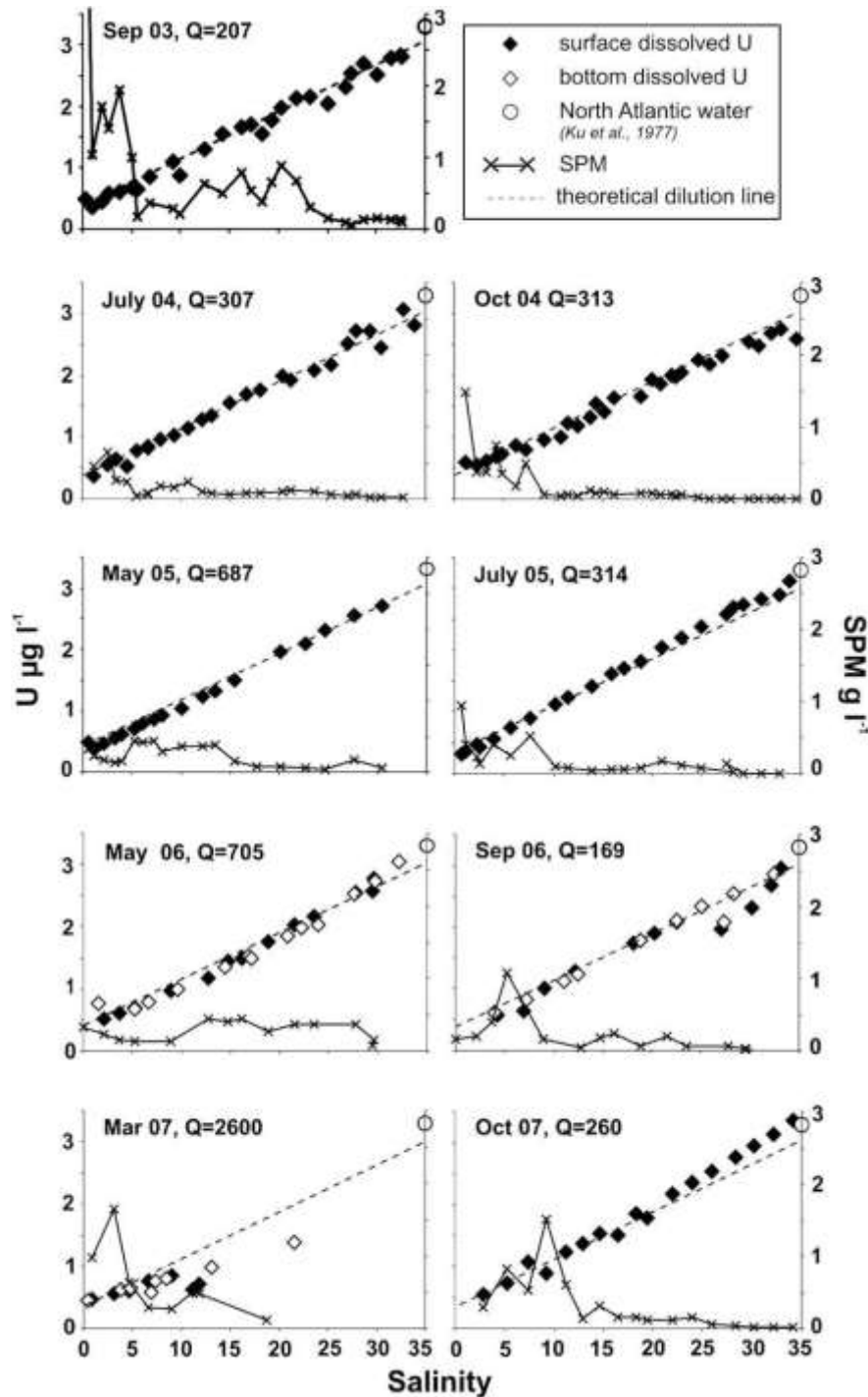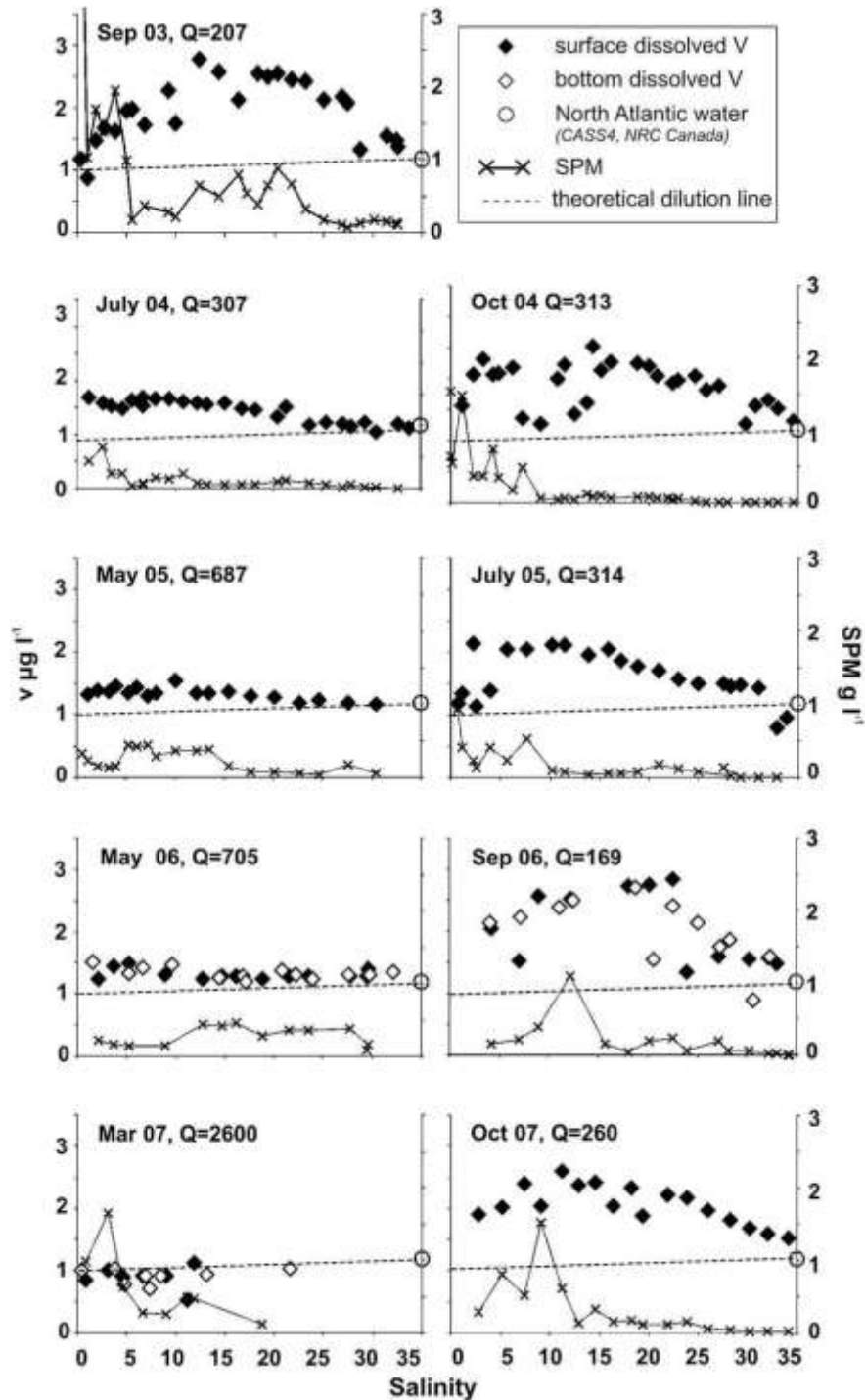
Fig. 4. V_D and SPM distribution along the salinity gradient (0–35) of the Gironde Estuary during the nine sampling cruises (freshwater discharges, Q in $m^3 \ s^{-1}$). The lines in the graphics represent the theoretical dilution lines between the freshwater and seawater end-members. Deviation of measured concentrations from these lines suggests either addition or subtraction.

In October 2007, DIP concentrations along the salinity gradient showed a typical bell-shaped distribution, with decreasing concentrations towards the higher salinity corresponding to seawater dilution (Fig. 6; Deborde et al., 2007).

3.3. Uranium distribution along the salinity gradient

Dissolved U concentrations measured for the 9 longitudinal profiles ranged from 0.32 to 3.37 $\mu g \ l^{-1}$ and were similar for both surface and bottom water of the same salinity (Fig. 3). (s.d.<5%; cf. May 2006, October 2006, September 2007). Note that these concentrations are in the same range as those observed by Windom et al. (2000) in other estuaries. In the Gironde Estuary, U_D concentrations at the main freshwater end-member (Garonne River, contributing w70% of freshwater and w80% of dissolved U) were clearly lower (0.50 T 0.10 $\mu g \ l^{-1}$) than the seawater end-member (3.3 T 0.3 $\mu g \ l^{-1}$; S¼ 34.1), which reached slightly lower concentrations than typical values of North Atlantic oceanic
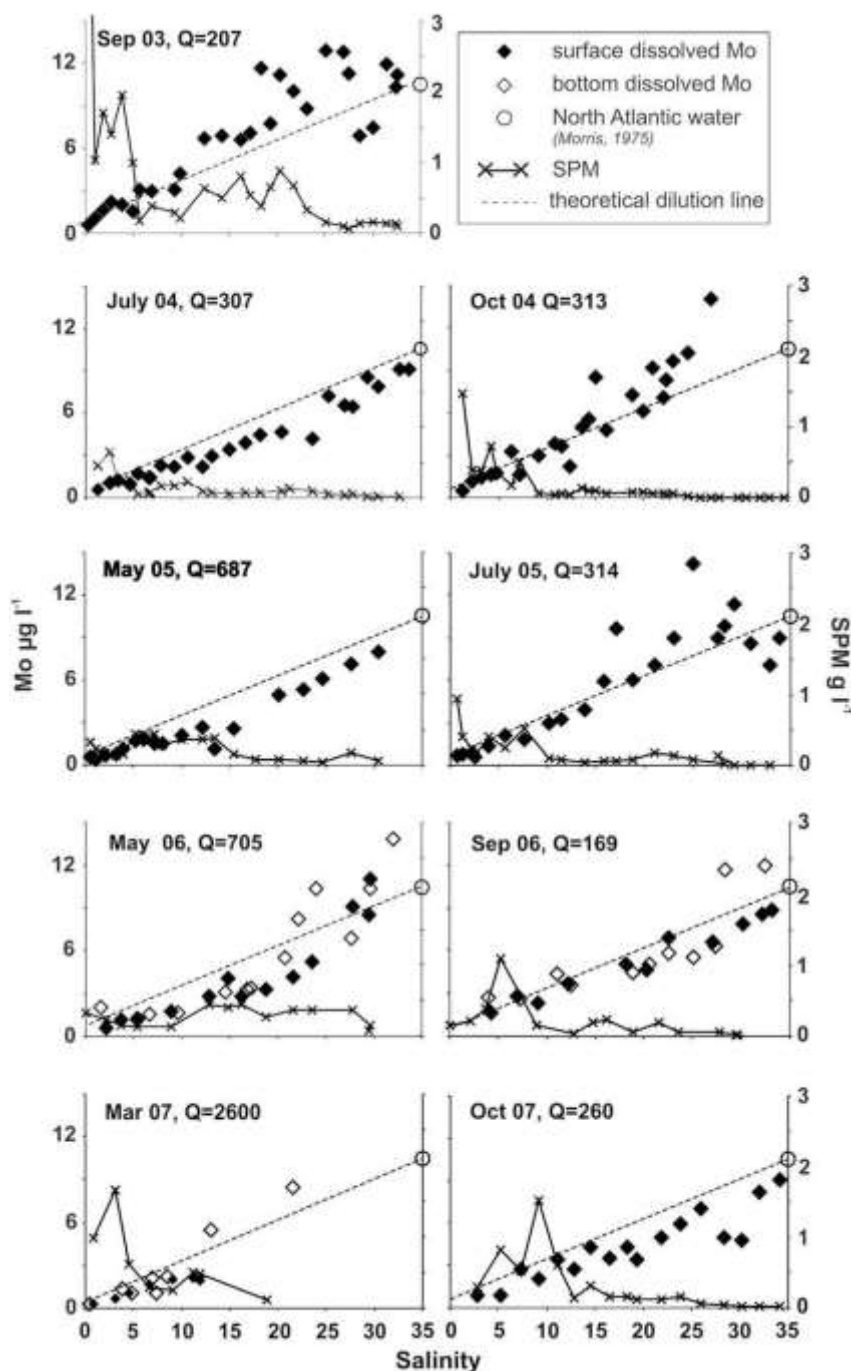
Fig. 5. Mo$_D$ and SPM distribution along the salinity gradient (0–35) of the Gironde Estuary during the nine sampling cruises (freshwater discharges, Q in m^3 s^{-1}). The lines in the graphics represent the theoretical dilution lines between the freshwater and seawater end-members. Deviation of measured concentrations from these lines suggests either addition or subtraction.

water (3.36 mg l^{-1}, Ku et al., 1977), whatever the hydrological situation. Between these two end-members, U$_D$ concentrations followed the theoretical dilution line indicating conservative behaviour whatever the hydrological situation and the MTZ position/intensity. Only at few points in the low salinity range, U$_D$ concentrations plotted below the dilution line (Fig. 3). The differences between measured and expected values (w0.25 mg l^{-1}) cannot be explained by analytical uncertainties (Table 1) suggesting that this represents a local and/or temporal anomaly (cf. 4. Discussion).

3.4. Vanadium distribution along the salinity gradient

Dissolved V concentrations were similar in surface and bottom water of the same salinity (s.d.<6%; cf. May 2006, October 2006, September 2007; Fig. 4). They ranged from 0.89 mg l^{-1} to 2.76 mg l^{-1} (Fig. 4), which is higher than those measured in the English Channel (0.76–1.43 mg l^{-1}; Auger et al., 1999) and on the Louisiana Shelf (0.32–1.70 mg l^{-1}; Shiller and Mao, 1999). The V$_D$ concentration levels were rather similar (1.0–1.5 mg l^{-1}) in the freshwater and seawater end-members (North Atlantic Coastal Ocean values
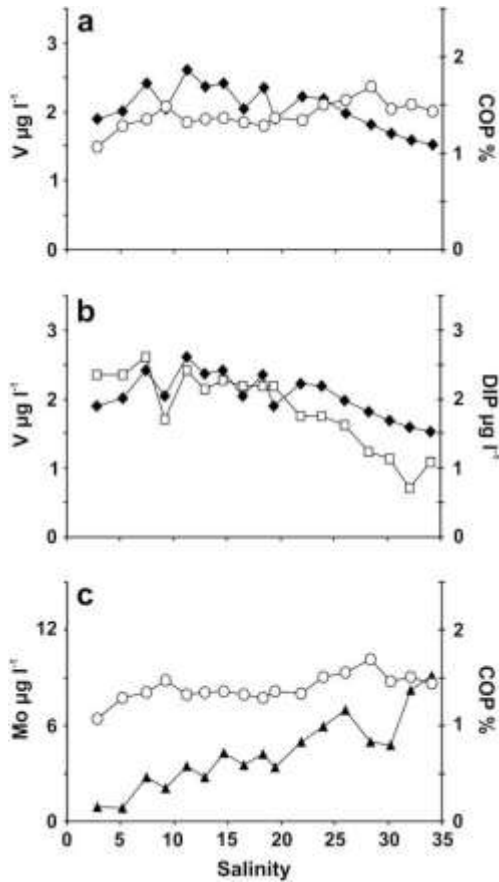
Fig. 6. Relation between a) V_D (black diamond; $mg\,l^{-1}$) and POC% (white circle), b) V_D (black diamond; $mg\,l^{-1}$) and DIP (white square) and c) Mo_D (black triangle; $mg\,l^{-1}$) and POC% (white circle) along the Gironde Estuary salinity gradient (0–35) during October 2007.

$_W 1.18\ mg\,l^{-1}$, e.g. CASS-4; Morris, 1975) and followed (conservative; e.g. March 2007) or not (non-conservative) the theoretical dilution lines.

3.5. Molybdenum distribution along the salinity gradient

Along the salinity gradient, high spatial differences (factor 30) were observed for both surface and bottom dissolved Mo concentrations (Fig. 5). Surface values ranged from 0.32 ∓ 0.2 $mg\,l^{-1}$ at the freshwater end-member to 9.16 ∓ 2.0 $mg\,l^{-1}$ at the seawater end-member (North Atlantic Oceanic water 10.5 $mg\,l^{-1}$; Morris, 1975), which are in the same range than those observed in the Chao Phraya River Estuary (0.02–11.2 $mg\,l^{-1}$, Dalai et al., 2005). However, in September 2003, October 2004 and July 2005, higher local values (until 14.1 $mg\,l^{-1}$) were observed at high-salinity range (Fig. 5). Between both end-members, Mo_D showed very different distribution patterns with 1) Mo_D concentrations following the theoretical dilution line (conservative behaviour; e.g. July 2004, September 2006), 2) Mo_D subtraction in the mid-salinity range (May 2005, May 2006, October 2007) or 3) Mo_D addition in the mid- to high-salinity range (September 2003, October 2004; Fig. 5). Like U_D and V_D, Mo_D concentrations showed similar distribution patterns in surface and bottom water. However, bottom water values were lower during May 2006 and September 2006, representing 70–100% of surface water concentrations, whereas during March 2007 bottom water values were higher.

4. Discussion

1. Uranium

The sampling strategy applied during contrasting freshwater discharges showed profiles where surface and bottom U_D followed the theoretical dilution line between the marine and freshwater end-members, suggesting globally conservative behaviour in the Gironde Estuary, except for locally and temporarily apparent subtraction in the low salinity range (Fig. 3). Conservative U behaviour is coherent with what has been observed for most estuaries (e.g. Windom et al., 2000). However, local subtraction has also been reported in the Amazon shelf (Swarzenski et al., 1995), in the Savannah Estuary (Windom et al., 2000), and in Delaware and Chesapeake estuaries (Sarin and Church, 1994), where it was attributed to important U sequestration in salt marshes (Church et al., 1996). In the Gironde Estuary, previous studies have reported both conservative behaviour inferred from dissolved ^{238}U activities measured in the Gironde fluvial-estuarine system (Saari et al., 2008) and non-conservative U behaviour suggesting U_D removal in the low salinity range (Smith et al., 2001; Audry et al., 2007). This apparent U_D variation may probably reflect variable contributions of the Dordogne River (0.2 ∓ 0.1 $mg\,l^{-1}$; Masson, 2007) or the Garonne River (0.6 ∓ 0.1 $mg\,l^{-1}$; pers. comm.) draining U-rich areas with Permian outcrops (Coynel et al., 2007). However, these anomalies are rather small and do not affect the overall distribution of U_D along the salinity gradient (Fig. 3). The eight U_D profiles obtained during severe drought level to mean freshwater discharge closely followed the dilution line, with increasing amplitude of concentrations (up to 13%) towards the higher salinity (seawater end-member October 2004: 2.7 $mg\,l^{-1}$; October 2007: 3.3 $mg\,l^{-1}$; Fig. 7). Those variations could be attributed to (1) destabilization of uranyl carbonate complex and/or (2) biological uptake and/or (3) U adsorption to metal oxides at the water-sediment interface during tidal flooding over intertidal mud flats (Barnes and Cochran, 1993; Shaw et al., 1994; Church et al., 1996). The equation of the relation U/salinity (Fig. 7) is slightly different from that reported by Audry et al. (2007), as the authors based the relation on water sampled from salinity 0–19 and on higher riverine end-member concentrations (see discussion above). Thus, the hypothesis of U sequestration by the sediment of the Gironde Estuary up to 50% (Audry et al., 2007) could be considered as over-estimated, as no clear subtractive behaviour was observed along the salinity gradient during the nine cruises discussed here. However, similar surface and bottom U_D concentrations (Fig. 3) support the work of Audry
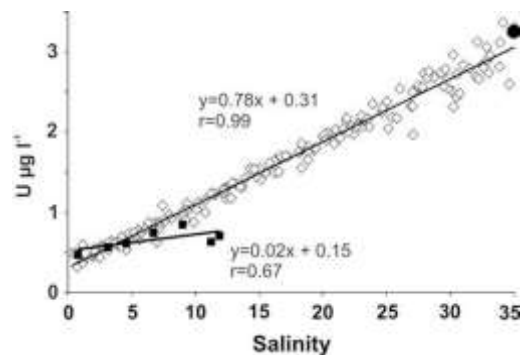

Fig. 7. Distributions of U_D concentrations ($mg\,l^{-1}$) measured along the salinity gradient. White diamonds represent concentrations measured during drought level to medium freshwater discharge conditions. Black squares represent concentrations measured during the flood event (March 2007). Black circle corresponds to the U_D of North Atlantic Oceanic water.

et al. (2007) reporting (1) negligible inputs of U from sediments, soft mud and dredging-related resuspension (estimated at 0.5%, 0.3% and 0.2%, respectively, of annual fluvial inputs) and (2) inefficient U sequestration.

During the flood event (March 2007), the distribution showed lower concentrations with larger amplitude (from salinity 1–12; Fig. 7) suggesting a non-conservative and un-equilibrated distribution. In fact, during floods, the water residence time in the estuary is greatly reduced, and may be not sufficient to allow complete mixing of freshwater masses of different origins (Dordogne and Garonne Rivers) and saltwater bodies, inducing a more 'noisy' distribution between the two end-members.

4.2. Vanadium

V_D behaviour along estuarine salinity gradients is few documented and has never been studied in the Gironde Estuary. The present data set aims at documenting V_D behaviour in this estuary for contrasting freshwater discharges. Distributions of V_D in the Gironde Estuary followed non-conservative behaviour. During drought and very low water discharge, the summits of the bell-shaped concentration curves (similar to those observed for Cd; Kraepiel et al., 1997; Michel et al., 2000) along the salinity gradient reached values of up to w3-fold higher than values expected for conservative mixing (Fig. 4). Moreover, during mean river discharge and especially during flood, the V_D distribution along the salinity gradient followed the theoretical dilution line, probably due to a higher dilution of added V_D. This V_D behaviour is original and clearly different from those reported for the Rhine, Scheldt (Van der Sloot et al., 1985) and Tamar estuaries (Van Den Berg et al., 1991), where V_D behaviour was non-conservative at low salinity and conservative in the mid- to high-salinity range. The sampling strategy revealed sensitivity of apparent V_D behaviour to freshwater discharge, i.e. addition becoming more visible during low freshwater discharge.

Vanadium addition in both, surface and bottom waters of the Gironde Estuary suggests that V dissolution prevails over sequestration (September 2006, Fig. 4), even in bottom water of the MTZ which may be strongly O_2-depleted during low discharges (Robert et al., 2004; Audry et al., 2006). In the water column, increasing V_D during drought to low/mean freshwater discharge may reflect (1) release from OM degradation and/or (2) desorption from SPM. In general, OM degradation in the MTZ results in decreasing POC in surface SPM. Thus, increasing V_D with decreasing POC was reported to result from OM degradation processes in the Tyro and Bannock Basins (Van der Weijden et al., 1990). However, no such relationship between V_D and POC occurred during different situations (e.g. October 2007, typical low water level, Fig. 6a), suggesting that OM degradation in the water column did not release V_D, in contrast to the soft mud of the Gironde Estuary freshwater reaches (Audry et al., 2006). In this estuary, additive phosphate behaviour along the salinity gradient has been attributed to predominance of desorption over OM degradation (Deborde et al., 2007). As $VO_2(OH)^{2-}$ and HPO_4^{2-} are two oxi-anions stereochemically close, we compared their distribution during October 2007 (Fig. 6b). Increasing V_D and phosphate concentrations suggest that V_D addition may be due to desorption processes occurring in the water column. The V desorption efficiency in the MTZ was experimentally assessed by mixing freshwater SPM with river water and low salinity estuarine water ($S < 2$; pers. comm.), suggesting that 10–50% of particulate V may be desorbed from Garonne River particles by saline estuarine waters, depending on salinity and solid/liquid mixing proportions (reflecting SPM concentrations). Applying this range of potential desorption to the V_D data of the different profiles in the estuary and to particulate V fluxes in the Garonne River, suggested that desorption of 10–20% of particulate V entering the estuary may

explain the observed addition in the salinity gradient and the resulting net V_D fluxes at the estuary mouth (see below). Accordingly, long water and particle residence time during low discharge may result in maximum V_D desorption from SPM and explain the observed maximum V_D concentrations in the mid-salinity range.

4.3. Molybdenum

Few studies have reported distribution of Mo_D along estuarine salinity gradients (Head and Burton, 1970; Dalai et al., 2005; Audry et al., 2007). Based on monthly monitoring profiles on the Chao Phraya Estuary, Dalai et al. (2005) have reported a strong linear relationship between salinity and Mo_D, suggesting conservative behaviour. In the present study, the sampling strategy revealed a wide range of different Mo_D behaviours: rather conservative (July 2005, September 2006; Audry et al., 2007), additive (September 2003, October 2004) and subtractive (July 2004, May 2005, May 2006 and October 2007; Fig. 5). During severe drought, both subtractive (September 2006) and additive (September 2003) profiles were observed, suggesting that hydrological conditions alone cannot explain Mo_D distributions along the salinity gradient of the Gironde Estuary (which was observed for V_D distribution). Therefore, intra-estuarine processes were investigated in order to better understand the variable Mo_D behaviours.

4.3.1. Additive Mo distribution

The possible processes contributing to additional Mo_D in the estuary are 1) OM degradation in the MTZ, 2) Mo_D release from reductive processes in the MTZ, 3) Mo_D desorption from SPM and 4) inputs from sediment. During early diagenesis, Mo is partly released from OM degradation into the soft mud pore water and from reduction of Mn-oxides (Robert, 2003; Audry et al., 2006). The first hypothesis of Mo release associated to OM degradation in the MTZ (such as early diagenesis), was investigated by comparing POC and Mo_D (as for V, part 4.2.). Distributions did not exhibit close correlation (Fig. 6c), suggesting low Mo_D release from OM mineralisation in the downstream part of MTZ, where addition occurred. Reductive dissolution of Mn-oxides and increasing Mn^{2+} concentrations (Mn_D) in bottom water (reduction of Mn_xO_y to Mn^{2+}; e.g. Froelich et al., 1979) were reported for the Gironde Estuary (e.g. Audry et al., 2006). As Mo release from Mn-oxides reduction occurs in the Gironde Estuary sediments (Robert, 2003), we tested this hypothesis for the present data set from the MTZ. For this, we plotted Mo_D and Mn_D concentrations (measured by solid–liquid extraction and GF-AAS measurement) in the Gironde sediments together with the respective values in surface and bottom water of the nine profiles (Fig. 8). In the sediments, two relationships linking Mo_D to OM degradation on the one hand and to Mn-oxides reduction on the other were clearly established (Fig. 8a; Robert, 2003). Although Mn_D concentrations in the water column were clearly lower than in the sediment, Mo_D tended to increase with increasing Mn_D, as observed in the sediment. The relationship however was not significant (Fig. 8b). Accordingly, OM degradation and reductive processes in the MTZ may probably play a minor role in the observed Mo_D addition.

Maximum Mo adsorption on oxide minerals occurs in oxic environment at pH 3–5 and at low ionic strength (Wedepohl, 1978; Shimmield and Price, 1986; Goldberg et al., 1996; Goldberg and Forster, 1998). Thus, in estuarine waters with pH_W 7–8 and increasing ionic strength, Mo is likely to be desorbed from SPM to the water (Jones, 1975; Smedley et al., 2002). We estimated the excess Mo concentrations to those expected from the theoretical mixing line to 30–40% of the theoretical value (up to 110% in October 2004). The experimentally assessed potential desorption of Mo from Garonne River SPM suggested that 10–50% of particulate
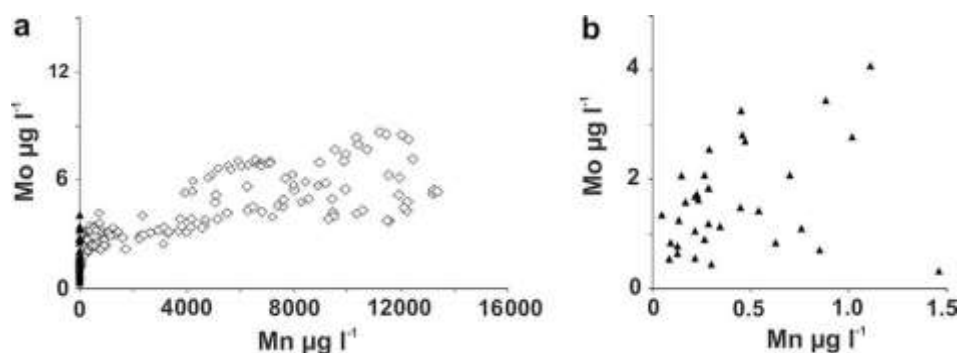
Fig. 8. a) Mo_D and Mn_D concentrations ($mg\,l^{-1}$) measured in the MTZ for the nine profiles (black triangle) and in the sediments (white diamond) of the Gironde Estuary. The dotted line shows Mo_D release from OM degradation and the dashed line the Mo_D release from reduction of Mn-oxides in sediments (Robert, 2003). b) Zoom on Mo_D and Mn_D concentrations ($mg\,l^{-1}$) in surface water of the MTZ during the nine profiles (black triangle).

Mo concentrations may be desorbed in the turbidity gradient, depending on SPM concentrations (pers. comm.). In contrast to the case of V, the potential Mo desorption from fluvial SPM cannot account for the 'excess Mo_D' along the salinity gradient, even when assuming the maximum potential desorption of 50%. Thus, in the Gironde Estuary, SPM desorption probably contributes to Mo_D addition, but is far from being the only/dominant process involved.

In contrast to U_D and V_D, higher Mo_D concentrations were observed in bottom water than in surface water for $S \leq 10$, during the flood (March 2007; Fig. 6), and also during subtractive distribution in May and September 2006 along the whole salinity gradient, suggesting Mo_D release from sediment to the water column (estimated to 0.17 t year by Audry et al., 2006). This may probably be attributed to (1) release of interstitial water and/or (2) resuspension of Mo-rich particles, which may be degraded in the water column. Suboxic sediments were reported to show Mo enrichments in polyframboids (iron sulfide microniches) together with low levels of redox sensitive metals (e.g. U, V), suggesting Mo sequestration from porewater even before pyrite concretion form by sulphate reduction (Elbaz-Poulichet et al., 2005; Tribovillard et al., 2008). In the Gironde sediments, intense sulphate reduction provides enough sulphide ($>0.1\ mM$) to support precipitation of authigenic Mo sulfides (with or without Fe; Zheng et al., 2000; Audry et al., 2006, 2007). Thus, assuming that Mo-rich particles may theoretically form in the suboxic zone of Gironde sediments, remobilisation of surface sediment (e.g. dredging activity) could transfer these particles into the oxic bottom water, where their dissolution may induce addition of Mo_D, whereas U_D and V_D remain unchanged.

4.3.2. Subtractive Mo distribution

Subtractive Mo behaviour was observed in July 2004, May 2005, May 2006 and October 2007 (Fig. 5). Possible explanations for the apparent Mo_D subtraction are (1) biological uptake and/or (2) Mo sequestration by sediments. Molybdenum is known as a central component of several enzymes essential to N_2-fixing cyanobacteria plankton (e.g. Bortels, 1930; Fogg and Wolfe, 1954; Marino et al., 2003). Thus, local Mo_D depletion in high Mo_D-concentrated seawater can be connected to temporary phytoplankton uptake (e.g. Manheim and Landergren, 1978), as observed in the Southampton Waters (Head and Burton, 1970). In the Gironde Estuary, Chlorophyll-a distribution along the salinity gradient suggests primary production from spring to beginning of autumn, except in the MTZ (Irigoien and Castel, 1997). Accordingly, primary production in spring and autumn may also contribute to the Mo_D subtraction observed downstream from the MTZ in July 2004, May 2005, May 2006, September 2006 and October 2007 (Fig. 5).

In the Gironde Estuary, Mo removal from sediment porewater was observed but considered negligible for the water column as Mo_D distribution was close to the theoretical dilution line (Audry et al., 2007). However, we revised this hypothesis and considered that Mo sequestration could influence Mo distribution because (1) variable Mo behaviours including subtraction were observed for the present data set and (2) precipitation of authigenic Mo is possible (see discussion part 4.3.1.). Still, quantifying Mo removal remains difficult as the approach described by Li and Chan (1979) cannot be applied (Mo-salinity relationship intercept corresponds to negative concentrations). We proposed then a different method to estimate the daily 'deficit Mo' over a whole profile by subtracting the observed Mo_D concentrations to the theoretical concentrations given by the conservative distribution between end-members. The removal rate R ($kg\ d^{-1}$), defined as: $R \frac{1}{4} Q*dMo$, where Q is the daily river water input into the estuary ($690\ m^3\ s^{-1}$, May 2005), and dMo the mean 'Mo deficit' over the salinity gradient ($1.23\ mg\ l^{-1}$, May 2005), was of 73 kg d^{-1}. This removal represents more than seven times the dissolved fluvial inputs (10 kg d^{-1}, unpublished data) and points out the major role of the ocean end-member on the Gironde Mo_D distribution. However, this removal rate was not estimated over a year because of the highly dynamic Mo_D distributions.

4.3.3. Molybdenum balance

For the nine profiles, Mo_D distributions changed from addition to subtraction, showing concentrations with similar distances from the theoretical dilution line (e.g. September 2003 and 2006, Fig. 6). Daily Mo_D addition may be estimated from the difference between net Mo_D fluxes at the estuary mouth (Boyle et al., 1974, 1982; see next Section 4.4.) and daily gross Mo_D fluxes entering the estuary. In July 2005, addition observed was of 190 kg d^{-1} (e.g. net fluxes 200 kg d^{-1}, gross fluxes 10 kg d^{-1}) which suggested that, at the daily timescale, Mo_D addition (July 2005) and subtraction (May 2005, 73 kg d^{-1}) over three months may be relatively of the same order. Assuming that none of these processes prevails, one may suppose that addition and subtraction widely counterbalance each others and that the resulting mass balance is not very different from what would be expected from conservative behaviour. Accordingly, the observed highly dynamic Mo_D behaviour probably results from the concomitance of reversible release/sequestration cycles involving SPM, biological uptake and water-sediment exchanges, and their kinetic balances with respect to water residence time (up to 3 months; Castaing and Jouanneau, 1979; Saari et al., 2008). Physical estuarine phenomena such as tidal currents, tidal bore, flood events or dredging play an important role on

estuarine sediment resuspension and may therefore act as key factors influencing the Mo_D distribution between the riverine and ocean end-members of this estuary.

4.4. Estimation of net fluxes to the coastal ocean

Estuaries play a major role in trace metal transport at the continent–ocean interface. Dissolved and particulate metal fluxes entering the Gironde Estuary (gross fluxes) have been well-documented due to long-term high-resolution observation at the different fluvial entries (e.g. Schäfer et al., 2002; Masson et al., 2006). However, estimating metal fluxes exported to the coastal area (net fluxes) is more difficult, as it depends on the metal behaviour. Furthermore, the existing net flux estimates only take into account dissolved net fluxes of elements with conservative (e.g. U) or additive behaviour (e.g. Cd; Michel et al., 2000). In the case of a strictly conservative behaviour (U) the dissolved net fluxes are equivalent to the dissolved gross fluxes. From the gross fluxes calculated on the Garonne River at the upstream limit of tidal influence, we estimated annual U net fluxes of 13.2 t yr^{-1}, 15.5 t yr^{-1}, 6.5 t yr^{-1}, 8.0 t yr^{-1} and 8.2 t yr^{-1}, respectively, in 2003, 2004, 2005, 2006 and 2007.

In the case of additive metal behaviour, flux estimates are based on an assumed conservative distribution in the 20–35 salinity range leading to a theoretical concentration at $S = 0$ (C_0). The net flux is then estimated from the following equation: $F_{net} = Q_{dwd} x\ C_0$, with Q_{dwd}: daily water discharge at the instant t and C_0: theoretical concentration at salinity 0 (Boyle et al., 1974, 1982; Meybeck, 1992; Michel et al., 2000). Accordingly, V_D daily net fluxes estimated from the different profiles ranged from 46 kg d^{-1} (July 2004) to 207 kg d^{-1} (March 2007). Although extrapolation to the annual timescale probably bears important uncertainty, the orders of magnitude of annual V_D net fluxes were estimated from the relation between daily water discharges and daily net fluxes measured during the sampling campaigns (equation type potency, $y = 65,447\ x^{-0.565}$, $R = 0.88$). The results obtained suggest that during the studied period, annual V_D net fluxes were rather similar from one year to the other: 33.6 t yr^{-1} (2003), 36.7 t yr^{-1} (2004), 31.3 t yr^{-1} (2005), 32.3 t yr^{-1} (2006) and 33.5 t yr^{-1} (2007). In contrast, Mo_D annual net fluxes were not estimated because of the variable behaviour of this element. However, we estimated daily net Mo_D fluxes from additive metal profiles (Fig. 6) to 150 kg d^{-1} and 200 kg d^{-1} for severe drought water discharges (September 2003) and low water discharge (July 2005) respectively. Those increasing daily net fluxes with low, increasing freshwater discharges (≈ 100 m^3 s^{-1}) reflect the relevance of sediment resuspension processes on the Gironde Estuary Mo_D balance.

5. Conclusion

The sampling strategy described in this paper pointed out the relevance of monitoring during contrasting water discharge situations in order to understand the variability of trace metal distribution. The acquisition of the present rare database on U_D, V_D and Mo_D behaviour in estuarine environments allows distinguishing three different distribution patterns for these oxi-anions in the Gironde Estuary. Uranium showed a permanently conservative behaviour, whereas the apparent V_D was more or less additive as a function of river water discharges, involving residence time and V_D desorption from SPM in the MTZ. Molybdenum distribution was highly variable suggesting both additive and subtractive behaviours implying concurrent and/or reversible processes occurring simultaneously with different kinetics.

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