



Speciation of dissolved copper and cadmium in the Loire estuary and over the North Biscay continental shelf in spring

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ABSTRACT

Dissolved cadmium and copper species were measured in the Loire estuary and the North Biscay Bay continental shelf (France) in spring 2002. Metal behaviours along the salinity gradient, metal fluxes from the Loire system and surface distributions on the continental shelf were described and compared with the ones obtained at a period of higher discharge (i.e., winter 2001). Vertical distributions at different stations were also examined with the aim to assess whether the Loire inputs affect the Cu and Cd speciation over the continental shelf. In the Loire estuary, different metal behaviours were observed from winter. Cu and its various species mostly followed a theoretical dilution line whereas a Cd addition composed of chloro- and organic complexes was observed. According to our estimations, the Cu flux was composed, as in winter, of 40% hydrophobic organic complexes. On the other hand, Cd organic complexes accounted for less in the total dissolved metal flux than they did in winter (55 and 78% for spring and winter, respectively). On the continental shelf, a C₁₈Cu-to-TDCu ratio of 40% was observed in the stratified area under Loire influence. For Cd, the organic fraction was relatively important in the surface waters near the mouth of the estuary and decreased deeper and seaward. Thus, the Cu and Cd speciation on the North Biscay Bay continental shelf are firstly determined by the extent of the estuarine plume. Beyond the estuarine influence, biological processes appeared to be the origin of the observed variations.

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1. Introduction

A large number of studies have been conducted on cadmium and copper in estuaries. In the case of Cd, they have shown unambiguously that this metal, bound to suspended matter, is mobilised when river water mixes with seawater. However, the mechanism at the origin of the desorption is not fully understood, though speciation calculations have suggested formation of stable chlorocomplexes (Comans and van Dijk, 1988). The behaviour of Cu varies from one estuary to the other and can show seasonal variations within a particular system (Ackroyd et al., 1986; Bourg, 1988; Cobelo-García and Prego 2003; Waeles et al., 2005a). Several investigations have been devoted to the speciation of Cu in estuarine environments (Baeyens et al., 1998; Buck et al., 2007; Jones and Bolam, 2007; Santos-Echeandía et al., 2008). However, some of

them were restricted to a certain section of the system of concern and the ones that have examined the speciation of Cu over a large salinity gradient were focused on relatively small systems (e.g., Shank et al., 2004a, b). Thus, studies on large estuarine plumes have not been carried out and the variations of metal speciation in such systems are largely unknown.

Different types of methods can be used to determine the speciation of Cd and Cu in seawater: electrochemical stripping measurements or metal determinations after chromatographic separations (extractable C₁₈ metal). Electrochemical stripping methods at natural pH determine inorganic trace metals (free metal ions and inorganic complexes) and may include a fraction of relatively labile organic complexes (Achterberg and Braungardt, 1999). Because labile Cd species can represent a significant fraction of the total dissolved Cd pool in seawater, such a method can be easily implemented to directly determine the inorganic/organic speciation of this metal. In this study, labile Cd species were measured with a stripping chronopotentiometric method (i.e., PSA) with a mercury film electrode. In the case of Cu, various investigations

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within the estuarine and coastal media have determined that usually more than 99% of metal is organically complexed (Donat et al., 1994; Shank et al., 2004a). Using ligand competition (e.g., Lucia et al., 1994), it is possible to estimate the concentrations of free ions and the conditional stability constants of the natural metal complexing ligands. In the present study, the approach by Mills and Quinn (1981) based on solid-liquid chromatography was carried out. After separation on C₁₈ columns, direct electrochemical measurements of Cu in the two separated fractions allowed us to distinguish the hydrophobic organic fraction from the hydrophilic organic fraction.

The Loire River provides the main source of freshwater to the North Biscay Bay continental shelf. The small tide currents in this area together with high freshwater discharges from the Loire lead to a large plume, which spreads along the South Brittany shore and to a vertical salinity stratification (Lazure and Jegou, 1998). Few studies about trace metals have been carried out in this system. Except one by (Boutier et al., 1993), they were generally focused on particulate matter or considered only the low salinity section of the estuary (Jouanneau et al., 1998; Piron et al., 1990; Thouvenin et al., 1997).

The study reported here was conducted in the whole salinity gradient of the Loire estuary – North continental shelf system. In a first paper, we described the results obtained in winter 2001 (Nutrigas campaign) for copper and cadmium speciation in the Loire estuary and the surface waters of the continental shelf (Waeles et al., 2004). Under winter conditions, a large area of the North Biscay continental shelf was affected by Cu and Cd inputs. Partitioning between hydrophobic and hydrophilic organic Cu was relatively constant along the salinity gradient of the shelf whereas association of Cd with organics decreased from the mouth of the estuary to the offshore waters. In this work, we report the spring 2002 data (Gasprod campaign), which have been obtained for a period of lower discharge. Our main objective was to examine the distribution of dissolved Cu and Cd species under a lower extent of the low salinity waters and thus to assess the relative influence of the fluvial inputs and of the autochthonous biological processes on metallic speciation over the continental shelf. Our objectives were also to describe and compare with winter data, the Cu and Cd behaviours in the Loire estuary and the fluxes of the various dissolved metallic species to the continental shelf.

2. Materials and methods

2.1. Sampling and filtration

The sampling was performed between April 8 and April 21 (GASPROD cruise, Programme PNEC-Golfe de Gascogne, RV Thalassa). Seventy samples were collected at different stations; nine of them were located in the Loire estuary (stations L1–L9); the others (stations 1–39) on the North Biscay continental shelf between the river mouth and the shelf break (Fig. 1). Sampling was generally done at 5 m depth but some stations, situated between the mouth of the Loire estuary and the shelf break (stations 6, 14, 23 and 30) were sampled at different depths. Polypropylene bottles, specifically designed for trace metal analysis (Noex[®]-modified by INSU, France), were used with a Kevlar cable and a Teflon messenger. Washing, sample processing and storage were conducted as described in Waeles et al. (2004).

2.2. Analyses of the various copper and cadmium species

The C₁₈ method has been used for the quantification of hydrophobic organic copper complexes (C₁₈Cu) and inorganic and

hydrophilic organic Cu complexes (non-C₁₈Cu). The extractable C₁₈ fraction, which is a subset of the organically complexed pool, is liable to greatly affect copper bioavailability (Elbaz-Poulichet et al., 1994). This method has been implemented in estuarine, coastal and oceanic systems (Mills et al., 1982, 1989; Mills and Quinn, 1984; Donat et al., 1986; Osterroht et al., 1988; Elbaz-Poulichet et al., 1994; Martin et al., 1994; El Sayed and Aminot, 2000; Waeles et al., 2005a). After extraction on C₁₈ columns (Isolute[®]200 mg, IST), the two obtained fractions and total dissolved copper (TDCu) were analysed using a stripping chronopotentiometric method (SCP) on a gold disk electrode as described in Riso et al. (1997a).

Total dissolved cadmium (TDCd) and labile cadmium species were measured by another chronopotentiometric method, i.e., potentiometric stripping analysis, with a mercury film electrode (Riso et al., 1997b). Organic Cd concentrations (OrgCd) were estimated by the difference between TDCd and LabCd concentrations.

These electrochemical stripping methods are appropriate for total dissolved Cu and Cd quantification in organic-rich estuarine and coastal waters since they are poorly affected by organic matter and thus require no pretreatment by UV irradiation. Table 1 lists the electrochemical conditions along with precision, reproducibility and detection limit. In order to check the accuracy of the methods, various certified reference seawater samples were analysed before the start of the campaign (Table 2).

2.3. Salinity, chlorophyll *a* and nitrate measurements

Salinity was measured with an SBE 25 CTD Seabird[®]-type probe. A quantitative estimation of in situ chlorophyll *a* (chl *a*) was performed by using a profiler and computing the relationship between in situ fluorescence of the profiler and chl *a* values. Chl *a* in the water samples was measured using a fluorimetric method (Lorenzen, 1966), accurate to $\pm 0.1 \mu\text{g L}^{-1}$. Nitrate was measured with a Technicon Analyser II following the procedure described by Tréguer and Le Corre (1975) with a precision of $\pm 0.05 \mu\text{M}$.

3. Results and discussion

3.1. Hydrology

The North Biscay Bay continental shelf is regularly subject to low salinity events, which are related to the northwards water-flow from the Loire along the South Brittany shoreline (Lazure and Jegou, 1998). In spring 2002, the extent of low salinity waters was relatively important as indicated by the horizontal gradient, from 32.0 in the mouth of the estuary up to 35.5 in the offshore waters. This situation followed a 3-month period with a fluvial discharge of $1000 \text{ m}^3 \text{ s}^{-1}$ on average. However, the flow of the Loire River in spring 2002 was not as large as the one encountered in winter 2001, the latter being preceded by a 3 month mean flow rate of $1800 \text{ m}^3 \text{ s}^{-1}$. From Fig. 2a, two domains can be distinguished according to the extent of the Loire plume. On one hand, the eastern area, from the mouth of the estuary to the South Brittany point, is stratified as displayed by the vertical distribution of salinity at stations 14, 23 and 30 (Fig. 3). On the other hand, the western part of the study area is well-mixed as confirmed by the salinity distribution at station 6 (Fig. 3).

Nitrate concentrations in surface waters (Fig. 2b) were in the range 1.0–30 μM . In the offshore waters, nutrient concentrations were smaller than those typically found in this area in winter (Morin et al., 1991). According to Maguer et al. (2009), this suggests the onset of the offshore spring bloom in this area.

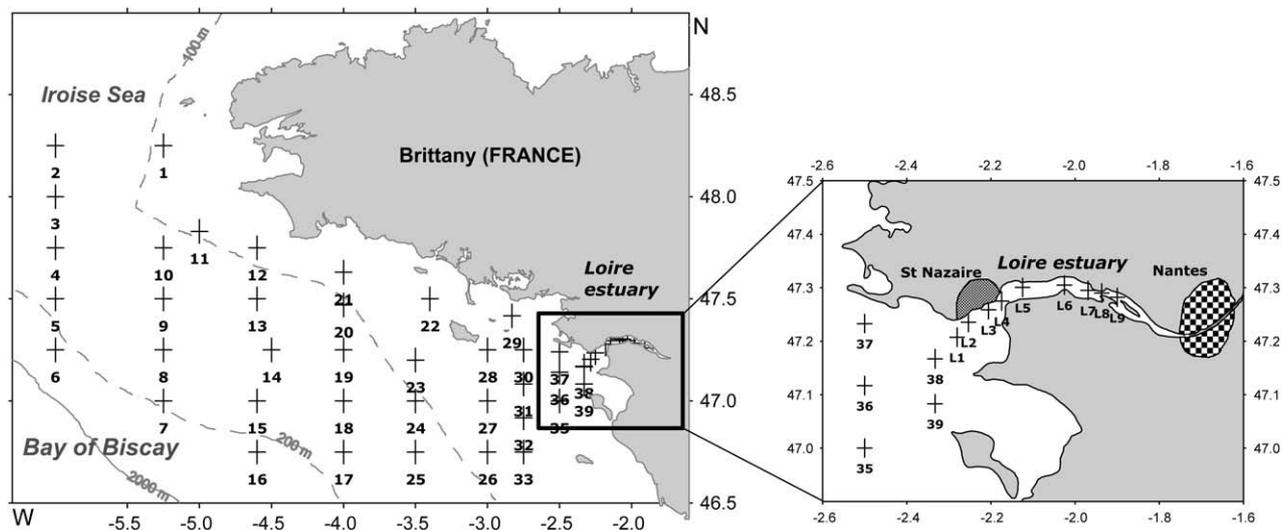


Fig. 1. Study area and location of the sampling points.

3.2. Dissolved metal behaviours in the Loire estuary

In spring 2002, TDCu in the Loire estuary was in the range 9.4–23.6 nM. Examination of the various dissolved forms indicated $C_{18}Cu$ concentrations that varied between 2.8 and 7.8 nM and non- $C_{18}Cu$ levels in the range 6.6–15.8 nM. Thus, total dissolved Cu concentrations and the ones observed for its various species were close to the ones encountered in winter 2001.

In the case of Cd, total dissolved levels were found in the range 0.17–0.49 nM. LabCd concentrations varied between n.d. and 0.27 nM, whereas OrgCd concentrations fluctuated from 0.12 to 0.25 nM. TDCd and LabCd levels in spring 2002 were approximately twice higher whereas OrgCd was in the same range as the ones previously observed.

Fig. 2a illustrates the dissolved Cu salinity distributions in the Loire estuary. TDCu and its various organic species mostly followed a theoretical dilution line. This nearly conservative behaviour is different from the positive deviation observed for TDCu and $C_{18}Cu$ in winter 2001.

It is well established that copper behaviour varies from one estuarine system to the other, but variations within the same system have been much less documented (Ackroyd et al., 1986; Bourg, 1988; Waeles et al., 2005a). Within the Loire estuary, the difference observed between winter and spring may originate from the fluctuation of the water discharge. Since floods took place before the winter sampling cruise, they likely favoured important inputs of organic ligands by the river, particularly of non-polar hydrophobic organic ones (Elbaz-Poulichet et al., 1994). Thus, these organic ligands may have been at the origin of the Cu addition in

winter by inducing a copper desorption from suspended particles during the estuarine mixing. Such a Cu addition linked to that of non-polar hydrophobic organic complexes was also reported in winter for the Penzé estuary (Waeles et al., 2005a). Using the competition ligand approach (CLE-CSV) in an organic-rich system (Cape Fear estuary-South Atlantic Bight), Shank et al. (2004a, b) showed that allochthonous organic ligands have strong complexing capacities and that a significant fraction of these ligands are C_{18} extractable. According to these authors, strong Cu ligands occurred at concentrations of 0.23 DOC. In the Loire estuary, DOC concentrations were measured in the range 100–300 μM (Middelburg and Herman, 2007) and behave almost conservatively suggesting that the findings of Shank et al. that terrestrially-derived ligands control the behaviour of Cu in estuaries can be generalized to many temperate systems. Using reverse titration, Santos-Echeandía et al. (2008) indicated that concentration of strong binding Cu ligands is ~ 5 nM in the Vigo Ria. In this relatively uncontaminated system, 90% of the dissolved metal was associated with these strong organic ligands.

Fig. 2b displays the Cd-salinity distribution. TDCd has a non-conservative behaviour with a strong positive deviation from linearity indicative of a dissolved metal addition in the system. The rise in TDCd concentrations occurred in the salinity range 0–12 and was particularly strong from 0.17 to 0.49 nM. LabCd behaves almost like TDCd suggesting that the addition of dissolved Cd corresponded mainly to the formation of Cd-chlorocomplexes from particle-desorbed cadmium (Comans and van Dijk, 1988; Dai et al., 1995). This input of labile complexes was also observed in winter in the same salinity range. At higher salinity ($S = 12$), one should note that the TDCd decrease did not follow a theoretical dilution line in contrast to that of LabCd. Thus, an addition of organic complexes, as the ones previously observed in the Loire (Waeles et al., 2004) and the Penzé estuary (Waeles et al., 2005b, 2008b) should be considered. As a matter of fact, distribution of the estimated OrgCd fraction showed an addition of organic Cd complexes in the salinity range 5–22 with an increase of concentrations from 0.12 to 0.25 nM. It should be noted that this addition was not as high as the one measured in winter 2001; the latter occurred in the salinity range 12–27 with an increase of concentrations from 0.06 to 0.25 nM.

According to several authors (Gerringa et al., 1996; Gobeil et al., 1987), the input of organic cadmium in estuaries can be a consequence of the degradation of particulate organic matter within the

Table 1
Electrochemical conditions of PSA and SCP methods.

Method	PSA (Cd)	SCP (Cu)
Working electrode	Mercury film	Gold disk
Deposition potential vs Ag/AgCl (mV)	–1200	–350
Angular velocity (rpm)	4130	4130
Deposition time (min)	15	5
Stripping	Chemical oxidation	Applied current of 2 μA
Reproducibility ($n = 9$)	4% (at 0.1 nM level)	2% (at 3.1 nM level)
Precision ($n = 6$)	7%	4%
Detection limit (nM)	0.01	0.17

Table 2
Analysis of certified reference materials by PSA and SCP methods.

	Cd certified value	Cd by PSA (n = 3)	Cu certified value	Cu by SCP (n = 3)
NASS-5	0.20 ± 0.03	0.18 ± 0.03	4.7 ± 0.7	4.3 ± 0.3
CASS-3	0.27 ± 0.04	0.25 ± 0.04	8.1 ± 1.0	7.8 ± 0.5
SLEW-2	0.17 ± 0.02	0.16 ± 0.02	25.5 ± 1.7	27.0 ± 1.1

benthic compartment. In the Loire system, Billen et al. (1986) have shown that large amounts of particles are discharged in the outer estuary under elevated water-flow conditions. These sediment-deposited particles could be an important source of organic cadmium. However, in this stratified estuary, the amount of organically complexed metal transferred from the sediment to the upper layers is probably reduced. Thus, it is more likely that the organic Cd addition originates from a metal desorption in the water column. According to our results about Cd particulate speciation in the Penze estuary (Waeles et al., 2005b), this desorption occurs from iron/manganese oxides, probably as the result of competition between $\text{Ca}^{2+}/\text{Mg}^{2+}$ and Cd^{2+} ions. The importance of organic Cd complexation in winter can result, as for Cu, from the elevated water-flow conditions before the sampling. Indeed, it has been shown by Miller (1999) that periods of prolonged rainfall significantly increase inputs and concentrations of organic matter in estuarine waters. As for Cu, the behaviour of Cd in estuaries should be controlled in a great extent by the input of strong terrestrially-derived organic ligands.

3.3. Fluxes of the various dissolved species

Metal concentrations in the riverine source waters were quantified as previously reported in Waeles et al. (2004). A mean flow rate of $1000 \text{ m}^3 \text{ s}^{-1}$ was used here which corresponds to the average of the values recorded during the 2 months preceding our sampling cruise. For Cu, the total dissolved flux was 216 kg day^{-1} . About 39% of the metal flux was composed of non-polar hydrophobic complexes (C_{18}Cu). In the case of Cd, the output of total dissolved metal has been estimated to 8.5 kg day^{-1} and the labile and organic forms of Cd were calculated as being 45 and 55%, respectively, of the metal flux.

As expected, total dissolved Cu and Cd fluxes from the Loire estuary were lower than the ones calculated for winter (i.e., 343 and 14 kg day^{-1} for TDCu and TDCd respectively) mainly because of the differences in water discharge between the two seasons.

The relative contribution of the various dissolved Cu species was close to the one found in winter 2001. Copper that exists essentially as organic complexes in estuaries is exported at $\sim 40\%$ as hydrophobic complexes.

The composition of Cd fluxes showed however a higher contribution of LabCd complexes in spring compared to winter (i.e., 45 vs 22%). Oppositely, organic Cd complexes accounted for more in the winter flux (78%) compared to the spring Cd flux (55%).

A comparison with the Gironde estuary, that represents the other major source of freshwater for the Bay of Biscay, indicates that TDCu and TDCd fluxes are of the same order for both systems. Fluxes from the Gironde estuary reported by Michel et al. (2000) were in the range 92–293 and $12\text{--}20 \text{ kg day}^{-1}$, for copper and cadmium respectively.

3.4. TDCd and TDCu distribution over the continental shelf

Fig. 4a,b illustrate the TDCu and TDCd distributions in the surface waters of the North Biscay continental shelf in spring 2002. For Cu, the influence of the Loire is relatively important considering that North Atlantic Ocean typical values are in the range 0.9–1.5 nM (Kremling, 1985) and that North West European shelf break concentrations vary from 0.8 to 2.0 nM (Le Gall et al., 1999). Concentrations above 2.0 nM were observed in a large eastern part of the studied domain, with the highest values ($>3.5 \text{ nM}$) being found close to the mouth of the Loire estuary and along the south Brittany shoreline. For Cd, the influence of the Loire was weaker. TDCd concentrations above those of the North Atlantic Ocean (0.02–0.08 nM, Kremling, 1985) and those of the North West European shelf break (0.07–0.11 nM, Le Gall et al., 1999) were found only at a few stations.

As expected, TDCu and TDCd levels in the North Biscay Bay continental shelf in spring 2002 were lower than the ones found in winter 2001 (i.e., 1.7–8.0 and 0.11–0.26 nM for Cu and Cd, respectively), considering the difference in metal fluxes between these two seasons. The maximum in Cd concentration was confined within the estuary in spring, whereas it was situated close to the mouth but outside of the estuary in winter. That the Cd maximum was not situated in the same area is linked to the differences in metal behaviour: in winter, the input of OrgCd to the dissolved phase was more important than in spring and occurred at higher salinities.

A comparison of our data with that of the Galician shelf waters (Santos-Echeandía et al., 2009) indicates very similar TDCu concentrations in both areas. The temporal trend of the Cu concentrations was similar to the one we observed in the North Biscay with higher levels during high continental runoff period (winter). For Cd, lower concentrations were reported for the Galician shelf (TDCd generally $<0.06 \text{ nM}$) and the temporal trend differed from the ones observed in the North Biscay. Because of the limited influence of the low-Cd-content freshwater of the Vigo Ria, the highest Cd levels on the Galician shelf were reported during dry season when upwelling events occurred.

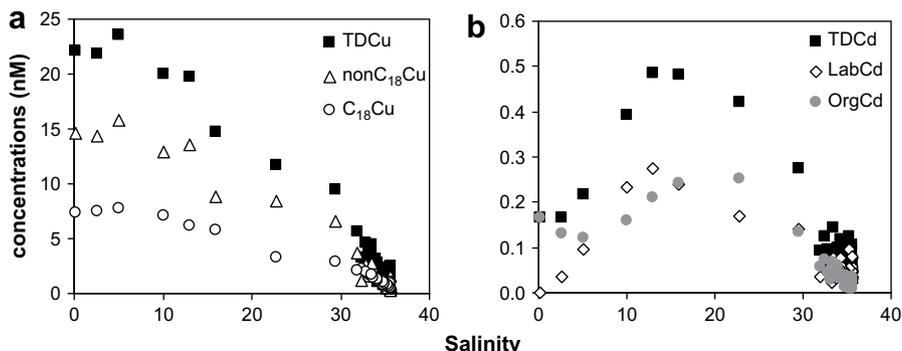


Fig. 2. (a) Copper, and (b) cadmium salinity distributions in spring 2002.

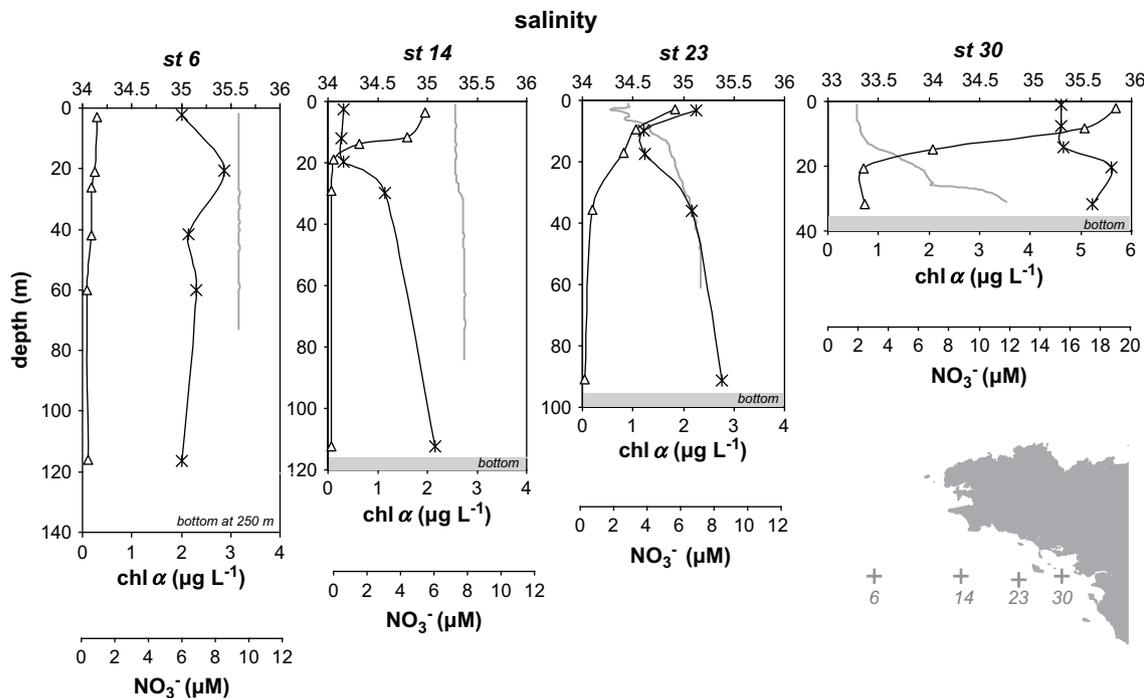


Fig. 3. Vertical distributions of salinity (grey line), NO_3^- (X) and chl α (Δ) in spring 2002.

3.5. Dissolved metal species distribution over the continental shelf

Fig. 4c,d depict the distributions of Cu and Cd dissolved species in the surface waters of the North Biscay Bay continental shelf in spring 2002. C_{18}Cu -to-TDCu ratios were close to 40% in the eastern part of the studied domain, whereas higher ratios were observed westwards with values in the range 36–64%. In winter 2001, few fluctuations of the C_{18}Cu -to-TDCu ratio were reported over the whole continental shelf ($42 \pm 8\%$). Thus, our results suggest that Cu speciation on the continental shelf is first determined by the Loire River inputs. As a matter of fact, our estimations for winter and spring indicated that Cu fluxes from the Loire estuary were composed at approximately 40% by C_{18}Cu species. Depending on the intensity of the river water discharge, the area under influence of the Loire River with a C_{18}Cu -to-TDCu ratio of 40% is more or less extended.

LabCd-to-TDCd contribution (Fig. 4d) varied from $\sim 40\%$ to values above 70%. The lowest ratios were measured in the coastal area, close to the estuary, whereas the highest ratios were found in western area. Such a rise from east to west in the LabCd contribution was also reported in winter 2001. However, lower ratios were measured at this season with values close to 20% near the mouth of the estuary and values around 50% seaward of the studied domain. Besides this variation along the salinity gradient, our data also highlight a seasonal variation in the Cd speciation over the continental shelf. The lower LabCd contribution in winter in the continental shelf, which is equivalent to a higher organic complexation, should be related to the intense supply of organically complexed metal within the Loire estuary at this season.

Cu and Cd speciation over the Loire plume appears to be mainly controlled by estuarine processes and particularly by their binding with terrestrially-derived organic ligands. According to Shank et al. (2004a), these ligands have strong complexing capacities and thus will maintain both metals in the dissolved phase.

3.6. Vertical distribution of Cu and Cd over the continental shelf

Fig. 5 depicts the vertical distribution of TDCu and C_{18}Cu -to-TDCu ratio at four stations situated between the mouth of the estuary and the shelf break. In the stratified area (stations 30, 23 and 14), TDCu levels were in the range 1.24–3.65 nM and highlight decreasing values with depths. The C_{18}Cu -to-TDCu contribution was close to 40% at stations 30 and 23 and shows few variations (46 ± 2 and $39 \pm 4\%$, respectively). At station 14, a rise of the C_{18}Cu -to-TDCu ratio was observed with depths: i.e., from 36% at the surface to 53% at 20 m depth. In the well-mixed area (station 6), TDCu concentrations were quite constant over the whole water column (1.0 ± 0.2 nM). However, a significant variation of the C_{18}Cu contribution was observed. The C_{18}Cu -to-TDCu ratio varied from 49% in surface to 79% at 12 m depth. Deeper, relatively high values ($\sim 60\%$) were also observed.

Our results indicate that the surface waters of the continental shelf are generally enriched in dissolved copper. This is linked to the dispersal of the Loire water in surface. Under strong influence of the Loire River (stations 30 and 23), the C_{18}Cu -to-TDCu ratio is close to 40% over the whole water column and the speciation of Cu seems thus controlled by the Loire inputs. Under weak influence of the Loire (stations 14 and 6), the Cu speciation showed much more fluctuations. The highest contribution of the C_{18}Cu fraction was observed at station 6 but did not correspond to the highest chl α values (Fig. 3). The strong complexation of copper with hydrophobic organic complexes could be linked to the stressful conditions of phytoplankton in well-mixed waters. It has been shown that phytoplanktonic species that are regularly driven under the euphotic area, release high amounts of dissolved organic matter (Wafar et al., 1983). This organic matter could have a strong influence on Cu speciation. It is worth noting that the dominant species at this station were *Chaetoceros* sp. and *Pseudo-nitzschia* sp. (Cras-sous, personal communication). On the other hand; at station 14 (stratified area), the C_{18}Cu -to-TDCu maximum was situated close to the nutricline (between 20 and 30 m, for NO_3^- distribution, see Fig. 3), under the production zone. The strong complexation of

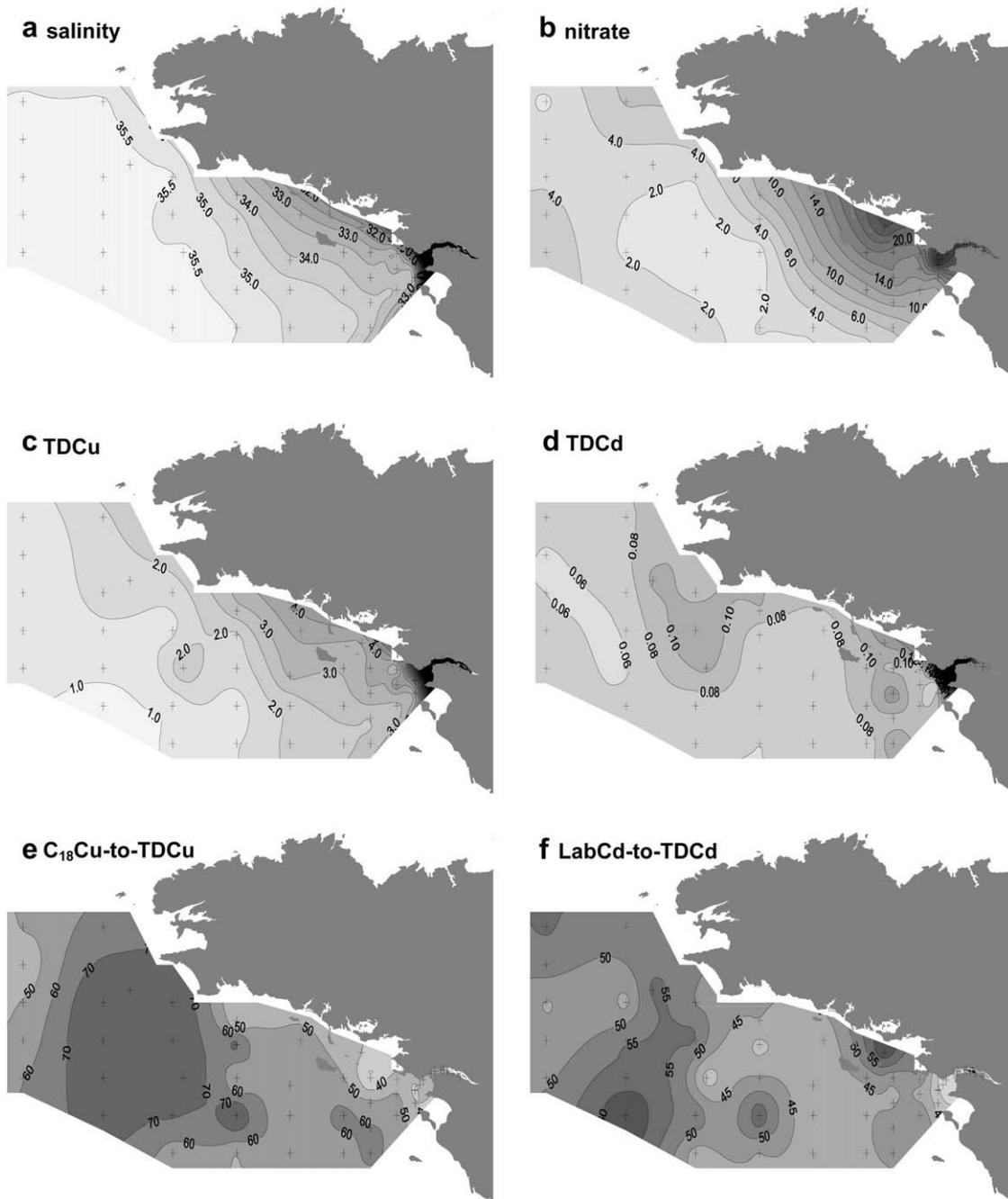


Fig. 4. Distributions of surface (a) salinity, (b) nitrate (μM), (c) TDCu (nM), (d) TDCd (nM), (e) C_{18}Cu -to-TDCu ratio (%), and (f) surface LabCd-to-TDCd ratio (%) in spring 2002.

copper with hydrophobic organic ligands can correspond here to the hydrolysis of organic matter (Cauwet et al., 1990). This hydrolysis is followed by a rapid polymerization of organic matter and lead to the formation of polysaccharides that are part of the C_{18} extractable compounds (Elbaz-Poulichet et al., 1994).

The vertical distributions of TDCd are presented in Fig. 6. Almost constant TDCd concentrations (0.08 ± 0.01 nM) were found from top to bottom in the well-mixed area (station 6). In the stratified area (stations 14, 23 and 30), few variations along the water column were found with TDCd values that varied from 0.06 to 0.11 nM.

More interesting are the variations of dissolved Cd species. For convenience, we report here the vertical distributions of the OrgCd-to-TDCd ratio instead of the LabCd-to-TDCd one. In the stratified area (stations 14, 23 and 30), profiles were characterised by two

maxima. The first maximum was found in surface. The contribution of the organic fraction was particularly important close to the estuary (station 30) and, as noted earlier (Section 3.5), decreased westward. At station 30, the maximum was particularly important in surface together with a strong decrease toward depth confirming that the Loire estuary is probably the main source of organic Cd for the surface waters. The study by Scarponi et al. (1995) on the Po River plume also highlighted such a distribution of organic Cd in term of both distance from the mouth and depth confirming the hypothesis of an estuarine origin. The second maximum was observed at stations 14 and 23 under the euphotic zone, at 20- and 30-m depth, respectively. According to a previous study on dissolved Pb (Waeles et al., 2008a), one can expect a notable degradation of particulate organic matter at these depths where particles

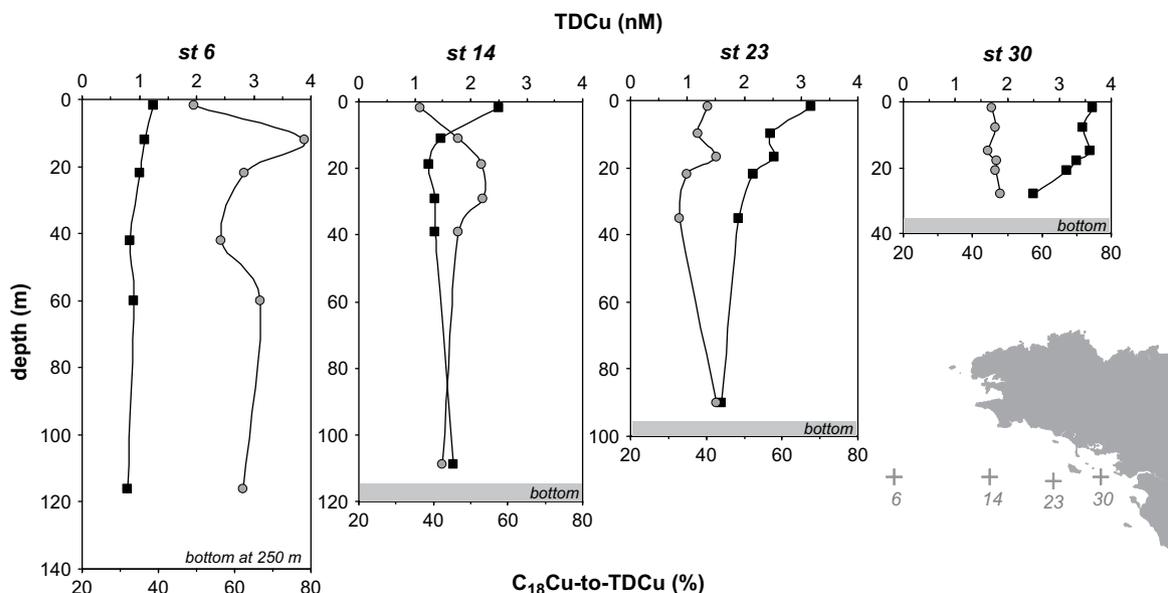


Fig. 5. Vertical distributions of TDCu (■) and $C_{18}Cu$ -to-TDCu ratio (●) in spring 2002.

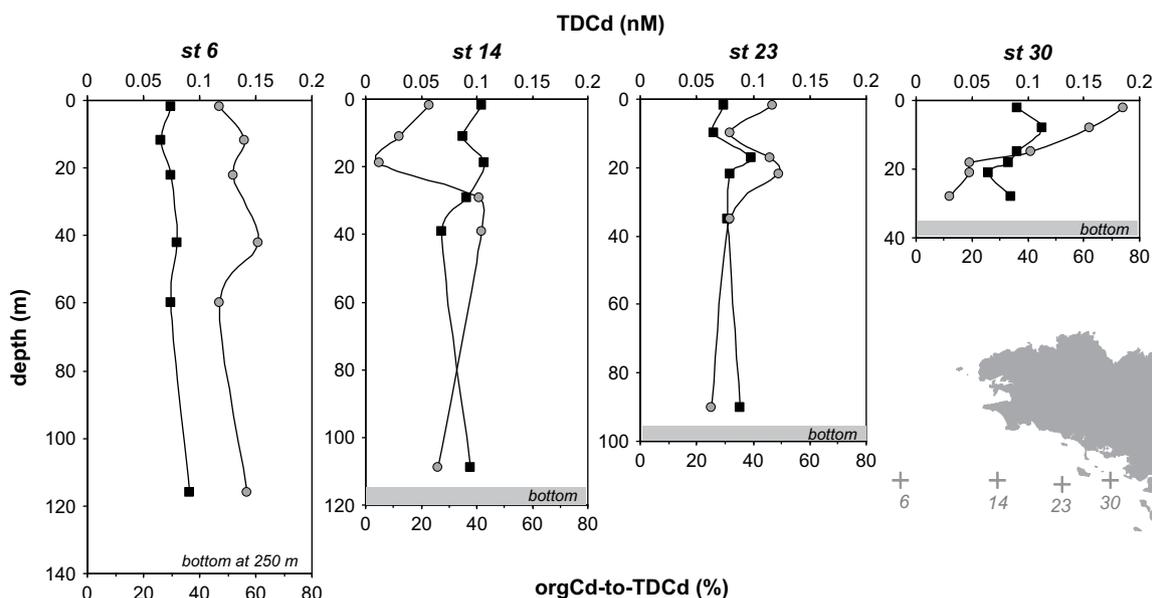


Fig. 6. Vertical distributions of TDCd (■) and OrgCd-to-TDCd ratio (●) in spring 2002.

are trapped. Our results indicate, as did those by Scoullou et al. (2006) that this degradation of organic matter in the pycnocline/thermocline acts as a potential secondary source of metal ligands and thus could have a significant impact on Cd speciation. In the well-mixed area, OrgCd accounted for a relatively high and constant fraction ($53 \pm 5\%$). The relatively high organic ratio at this station could be linked to an input of organic ligands following the degradation of organic matter. It can be also linked, as for copper, to a release of hydrophobic organic complexes by phytoplanktonic species under stressful conditions.

4. Conclusion

Our results on Cu and Cd speciation in this study have shown that the behaviour of both metals may vary within the Loire system.

More or less marked positive deviations were observed which occurred at variable salinities. The importance of the organic metallic fraction in the addition processes suggests that the Cu and Cd behaviours are controlled at least partially by the nature and the amount of organic matter supplied by the river.

According to our estimations, differences in metal behaviours from winter to spring has little influence on the dissolved Cu flux which is composed of 40% $C_{18}Cu$ for both season. On the other hand, Cd flux composition varied seasonally with organic complexes that accounted for 78 and 55% in winter and spring, respectively.

The effect of the Loire inputs on the North Biscay Bay continental shelf was detected for the two metals. Cu and Cd speciation on the shelf is largely determined by the extent of the estuarine plume. For Cu, it appears as a $C_{18}Cu$ -to-TDCu ratio of 40% over the stratified area under Loire influence. For Cd, the organic fraction is particularly

important in the surface waters near the mouth of the estuary and decreases deeper and seaward. Within the estuarine plume, terrestrially-derived strong organic ligands are probably the main factor for controlling Cu and Cd speciation. Beyond the estuarine influence, autochthonous biological processes such as hydrolysis of organic matter or phytoplankton exudation appear on the contrary to be most influential.

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