The significant role of colloids in the transport and transformation of organic carbon and associated trace metals (Cd, Cu and Ni) in the Rhône delta (France)

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Received 7 April 1994; accepted 1 May 1995

Abstract

The distribution of organic C and trace elements (Cd, Cu, and Ni) between truly dissolved and colloidal phases was determined in May 1992, in order to better understand their behavior during estuarine mixing in the Rhône delta (France). Colloidal material (10^4 Daltons–0.4 μm) was separated with an ultra-clean cross-flow filtration system. A considerable part of the organic C and trace metals studied, used to be considered to occur in the so-called “dissolved” pool, is associated with colloidal material. The significant correlation between colloidal organic C and colloidal Cu suggests an important involvement of colloidal organic material in the transport of this element. The correlation between Ni, Cd and organic matter mainly occurs in the truly dissolved fraction, suggesting that the truly dissolved organic C is important for these two elements. Truly dissolved and colloidal organic C and trace-metal fluxes transported from the River Rhône to the northwestern Mediterranean Sea were estimated.

1. Introduction

The distinction between “dissolved” and “particulate” phases in aquatic chemistry used to be operationally defined by a filtration with ca. 0.45 μm pore size filters (Goldberg et al., 1952). This definition has been challenged by recent works on colloids and/or submicrometer particles (Honeyman and Santschi, 1989,1992; Koike et al., 1990; Whitehouse et al., 1990; Honeyman, 1991; Wells and Goldberg, 1991; Benner et al., 1992; Longhurst et al., 1992). The abundance of colloidal particles (1 nm–1 μm; Vold and Vold, 1983) has been shown to represent one of the major factors in the backscatter of light in the ocean (Morel and Ahn, 1991; Stramski and Keifer, 1991). Several papers have critically emphasized the role of colloidal material in the biogeochemistry of trace elements, radionuclides and organic pollutants in aquatic environments (Santschi et al., 1987; Honeyman and Santschi, 1989,1991,1992; Baskaran et al., 1992; Baskaran and...
Santschi, 1993; Thieria et al., 1991; Buffle and Van Leeuwen, 1992; Benner et al., 1992; Farrington, 1992; Guo et al., 1994; Martin et al., 1995). For example, Martin et al. (1995) reported that a significant part of organic C and trace elements (up to 89% for Fe) in the so-called "dissolved" phase was actually associated with colloidal material in the Venice Lagoon. Baskaran et al. (1992) showed that a large fraction of natural 234Th (up to 80%) in the Gulf of Mexico water was colloidal. According to Buddemeier and Hunt (1988), radionuclide transport in groundwater is essentially associated with particles smaller than 0.2 μm. It is becoming ascertained that the simple classification of trace elements into particulate and dissolved fractions, without any consideration of the colloidal fraction, may be inadequate to understand their detailed biogeochemical cycling.

Colloidal material is particularly important due to its high specific surface area and, hence, potential adsorptive capacity which might control the partitioning of an element or compound between dissolved and particulate phases. Honeyman and Santschi (1988) have pointed out that our ability to model trace-element transport is largely limited by a lack of detailed understanding of the quantitative factors that influence the distribution of trace elements between dissolved and sorbed phases in natural systems. In fact, colloids can be considered as an additional ligand enriched in different types of functional groups able to complex with trace elements and hence should be taken into account by Surface Complexation Models (SCMs; Davis and Kent, 1990).

Honeyman and Santschi (1989, 1991) recently proposed that one of the processes responsible for the large variation in scavenging rates could be "colloidal pumping" or "Brownian pumping", i.e. the transfer of dissolved species to large aggregates via colloidal intermediates. This process involves mainly two steps: (1) the rapid formation of metal–colloid surface site complexes (i.e. adsorption), and (2) the slow agglomeration and coagulation of these colloids to macroparticles. However, Nelson et al. (1985) reported that colloidal organic C found in natural aquatic systems was able to largely inhibit the adsorption of reduced plutonium to suspended sediment particles. This might imply a reversibility of the "colloidal pumping" process (transformation from the particulate to the dissolved phase through colloidal intermediates). Our recent studies in the Venice Lagoon showed that this "colloidal pumping" process did not always act in ideal manner. For instance, Mn in the Venice Lagoon does not show any important coagulation during mixing between freshwater and seawater although the adsorption of dissolved Mn onto colloidal particles is likely (Martin et al., 1995). An experimental study by Yan et al. (1992) showed that during the mixing of unfiltered river water with seawater, Fe concentration (< 0.4 μm) increased considerably at low salinity, suggesting that some deflocculation of the coarse Fe-bearing colloidal aggregates occurs during mixing. In this case, the interaction between dissolved and colloidal phases greatly affects the distribution of trace elements. Indeed, this is related to the stability and hence the residence times of colloids in aquatic systems. Enriched organic material able to stabilize colloids in the water column has been considered to be responsible for this phenomenon. Conversely, Moran and Buesseler (1993) reported that the residence time of colloidal 234Th in continental shelf waters off New England is ~ 0.5 days. This suggests that colloid aggregation might not be rate-limiting in controlling the scavenging of 234Th and, by analogy, other particle-reactive trace metals. These controversial results should imply that the "colloidal pumping" process is largely related to the physicochemical characteristics of waters where the colloids are dispersed.

It can be assumed that the so-called "colloidal pumping" will be more pronounced during estuarine mixing. So far, however, comprehensive studies on the role of colloids in trace-metal distributions in natural estuarine systems are still limited.

The aim of this study is to illustrate the role of colloidal material in the transport of trace metals and organic C in a large river estuary system: the Rhône River delta (France).

2. Materials and methods

The Rhône River is the main source of sediments and freshwater (50%) to the western Mediterranean Sea, with an average water discharge of 1700 m³/s
and a solid discharge of $4.5 \times 10^6$ tonne/yr. The mixing zone is highly stratified with a thin surface plume extending several kilometers southward off the river mouth. This river plume has been considered to have an important effect upon the rates and processes occurring in the water column and in the sediments. We selected a period with relatively high river discharge (May 1992) when the Rhône plume is well defined so as to examine its impact on the partitioning of organic C and trace metals between particulate, colloidal and dissolved phases. The study area is illustrated in Fig. 1.

Surface samples were taken from a small rubber boat, by immersing capped 10 l acid-cleaned polypropylene bottles about 20 cm below the surface. Within 2 h of sampling, 15 l of water were filtered in the laboratory using acid-cleaned Nuclepore filters (0.4 μm, Ø 142 mm) and a Teflon filter holder in a closed pressurized system (pure N₂ gas). Both the filter holders and connectors were made of PTFE and are precleaned by soaking in acid. To avoid any adsorption or release onto/from the Nuclepore filter, we discarded the first 1–2 l of the filtrate. Then, 50 ml prefiltrate were collected for

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![Diagram](image_url)

**Fig. 1.** The study area in the Rhône delta in May 1992.
DOC analysis with HgCl₂ added as a preservative. 500 ml prefiltrate were acidified to pH 2 with concentrated HNO₃ (Suprapur) for total dissolved trace-metal analysis. Another portion of the samples (~ 1 l) was filtered through precombusted Whatman fiber-glass filters (GF/F, 0.7 μm) on a glass filter holder (Millipore), and these filters were stored for later POC measurement. The remaining prefiltrate (~ 10–12 l through the Nuclepore filter) was processed by cross-flow ultrafiltration so as to isolate colloids from the truly dissolved phase.

The CFF system consists of a Millipore Pellicon cassette (Millipore Corp.), an air-driven pump (Teflon), a polypropylene reservoir, teflon tubing and connectors, and valves. We used a PTGC membrane (polysulfone) cassette with a nominal molecular weight cutoff of 10⁴ and a filter area of 0.462 m² in an acrylic housing. The polysulfone membrane corresponds to a pore size of ~ 3 nm, which approximates to the lower size limit of colloidal particles. Before processing samples, the CFF system was carefully cleaned with 0.1 HNaOH followed by several acid washes (Fig. 2). Between the samples, the system was cleaned by flushing with Milli-Q water, cycling with 0.1 HNO₃, and then with Milli-Q water. Finally ~1000 ml samples were

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**Fig. 2.** Clean procedure for the cross-flow ultrafiltration system.
flushed through so as to condition the system. Ultrafiltration was then carried out continuously under the concentration mode (with a permeate pressure < 10 psi) until the sample volume was reduced ~1 l. During this operation, 500 ml permeate for trace-metal analysis and 50 ml for organic C measurement were collected. The prefiltered \( V_p \) and the colloidal concentrate volume \( V_c \) were recorded to determine the concentration factor \( F = V_p/V_c \). Some more detailed information on the CFF experiment has been described elsewhere (Martin et al., 1995). The above prefiltration or ultrafiltration operations were all conducted under a clean bench in order to minimize contamination.

In order to confirm that the prefiltration system, commonly used for trace-metal analysis (Nuclepore, polypropylene bottles, etc.) is suitable for organic C studies, samples were also taken in glass bottles and filtered under reduced vacuum with a glass filter holder (Millipore) on precombusted glass fiber filters (Whatman GF/F, 0.7 μm). Intercomparison was then carried out for dissolved organic C from the two sampling and prefiltration systems.

Organic C was determined in the so-called total dissolved (in the prefiltrate, DOC < 0.4 μm), truly dissolved (in the ultrafiltrate, UOC < 3 nm), colloidal (retained fraction from ultrafiltration, COC) and particulate fractions. DOC, UOC and COC were measured by high-temperature catalytic oxidation method (HTCO) using a TOC-5000 from the Shimadzu corporation (Cauwet, 1994). The oxidation of organic compounds is performed by direct injection of the sample into a furnace, at 680°C onto a catalyst made of 1.2% Pt coated SiO₂. The CO₂ formed is analyzed by a non dispersive infra-red (NDIR) detector. Particulate organic C (POC) was measured according to the method of Cauwet (1983).

Cu, Ni, and Cd concentrations were measured in both the acidified prefiltrate and ultrafiltrate by graphite-furnace atomic-absorption spectrophotometry (GFAAS) after extraction in a Class 100 clean room using a method modified from Danielsson et al. (1982). Recoveries were 90–105% when compared to the NASS-4 standard seawater reference material (Canada). The colloidal concentration was calculated by the difference between the total dissolved and the truly dissolved concentration.

Contamination risk arising from the CFF system has been tested in two ways. The first was designed to test the maximum blank of the whole system with Milli-Q water. In this case, 10 l Milli-Q water was recycled throughout the whole CFF system for ~2 h. The second was designed to check the system recovery \( R(\%) \) of samples.

\[
R(\%) = 100 \times \frac{(F - 1) \times C_u + C_c}{F \times C_p}
\]

where \( F \) is the concentrate factor of the CFF process; \( C_u \) is the concentration passing through the membrane (<10⁴ Daltons or truly dissolved); \( C_c \) is the concentration of retained material (concentrated solution or colloids with a size between 10⁴ Daltons and 0.4 μm); \( C_p \) is the concentration in the solution after prefiltration (<0.4 μm). After adding HgCl₂ as a preservative, the retentate COC sample can be stored for several months without precipitation. However, some precipitation is found in the concentrated samples for trace-metal analysis even after acidification. So, the recovery check was only available for organic C. Then, a loss of material occurs during the ultrafiltration operation when \( R(\%) < 100 \). Conversely, the system has been contaminated when \( R(\%) > 100 \).

It should be noted that the colloidal metal concentration calculated by difference might be questionable because of the lack of the mass balance of the different fractions of metals from ultrafiltration. In this respect, we used freshwater from the River Seine (France) to test for possible adsorption of metals onto the CFF membrane. Concentration variations during CFF recycling were determined in the ultrafiltrate as a function of time (up to 136 min). Results (see Martin et al., 1995) showed that concentration variations were not significant; therefore, the adsorption of metals onto the membrane is likely not important on a time scale of minutes to 2 h, whilst our ultrafiltration process is usually <15 min. In fact, another study has already calculated the mass-balance from CFF processing (with a membrane similar to ours), and the recoveries have been shown to be acceptable (72–124%) (Whitehouse et al., 1990). Assuming that contamination during the ultrafiltration process would be negligible, the amounts added appear to be small. What cannot possibly be ignored, however, is the breakthrough of colloidal C.
or trace metals from the retentate into the ultrafiltrate. So, further experiments on the mass balance for ultrafiltration are still necessary to confirm the colloidal trace-metal concentration calculated by difference as mentioned in this study.

3. Results and discussion

3.1. Validity of the prefiltration and crossflow ultrafiltration systems for DOC and trace metal analysis

In order to ascertain the validity of the prefiltration system commonly used for trace-metal study, an intercomparison of DOC concentrations obtained with the two prefiltration systems (see methods above) is shown in Fig. 3, which suggests that the data are within ±5% of the ideal relationship, with the exception of the sample at P129, which might be caused by some occasional errors during the sample processing or analysis. Nevertheless, this comparison shows an overall acceptable variation, indicating that the prefiltration system constructed with Nuclepore filters is suitable for organic C studies.

As noted earlier, the validity of the CFF system has been checked in two ways. The blanks of organic C and trace metals after recycling for about 2 h through the CFF system are compared to those in

<table>
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<tr>
<th>Station</th>
<th>(V_p) (l)</th>
<th>(V_r) (ml)</th>
<th>(F)</th>
<th>(C_u) ((\mu)M)</th>
<th>(C_p) ((\mu)M)</th>
<th>(C_c) ((\mu)M)</th>
<th>Recovery (%)</th>
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<td>616.07</td>
<td>12.99</td>
<td>100.00</td>
<td>143.75</td>
<td>252.00</td>
<td>77.71</td>
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<td>1645.11</td>
<td>2.92</td>
<td>115.92</td>
<td>147.92</td>
<td>225.08</td>
<td>103.66</td>
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<td>138.00</td>
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<td>94.46</td>
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<td>605.52</td>
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<td>119.17</td>
<td>200.33</td>
<td>95.44</td>
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<td>7.17</td>
<td>113.92</td>
<td>127.83</td>
<td>187.67</td>
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<td>72.17</td>
<td>81.67</td>
<td>129.58</td>
<td>97.36</td>
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\(V_p\) = initial sample volume for ultrafiltration; \(V_r\) = retentate volume; \(F\) = concentration factor; \(C_u\) = truly dissolved organic carbon concentration; \(C_p\) = total dissolved organic carbon concentration; \(C_c\) = organic carbon concentration in the retentate fraction.

Fig. 3. Intercomparison of DOC values between two filtration systems.
Table 2
Compartmentsof organic carbon in the Rhône delta in May 1992

<table>
<thead>
<tr>
<th>Station</th>
<th>Salinity</th>
<th>SPM (mg g⁻¹)</th>
<th>TOC (µM)</th>
<th>UOC (µM)</th>
<th>UOC/TOC (%)</th>
<th>DOC (µM)</th>
<th>DOC/TOC (%)</th>
<th>COC (µM)</th>
<th>COC/DOC (%)</th>
<th>COC/TOC (%)</th>
<th>POC (µM)</th>
<th>POC/SPM (%)</th>
<th>POC/TOC (%)</th>
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<td>R124(2)</td>
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<td>38.33</td>
<td>246.0</td>
<td>100.00</td>
<td>40.66</td>
<td>143.75</td>
<td>58.44</td>
<td>43.75</td>
<td>30.43</td>
<td>17.79</td>
<td>102.2</td>
<td>3.2</td>
<td>41.6</td>
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<td>187.9</td>
<td>115.92</td>
<td>61.69</td>
<td>147.92</td>
<td>78.71</td>
<td>32.00</td>
<td>21.63</td>
<td>17.03</td>
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<td>10.5</td>
<td>9.33</td>
<td>170.7</td>
<td>120.33</td>
<td>70.51</td>
<td>138.00</td>
<td>80.86</td>
<td>17.67</td>
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<td>32.7</td>
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<td>138.75</td>
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<td>113.92</td>
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<td>127.83</td>
<td>86.16</td>
<td>13.92</td>
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<td>61.85</td>
<td>119.17</td>
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<tr>
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<td>4.90</td>
<td>125.4</td>
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<td>105.42</td>
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<td>5.59</td>
<td>88.1</td>
<td>16.7</td>
<td>51.9</td>
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</table>

TOC = total organic carbon; UOC = truly dissolved organic carbon; COC = colloidal organic carbon; DOC = total dissolved organic carbon; POC = macroparticulate organic carbon.
fresh Milli-Q water analyzed by the same methods. The differences show, respectively, ~ 5 μM (± 10%) for organic C, ~ 0.30 pM (± 20%) for Cd, 18 pM (± 20%) for Cu, and ~ 13 pM (± 20%) for Ni. These blanks are overall low as compared to trace-metal and organic C concentrations normally encountered in coastal environments.

As far as the organic C is concerned, tests were also undertaken by calculating the mass balance of the CFF system (Table 1). 85–100% recovery is obtained for most of the samples. Relatively low recovery (~ 78%) is found for the river water sample, which would suggest that the adsorption of organic C onto the polysulfone membrane could be significant during the low-salinity sample processing. We have not made any correction for this kind of deficiency because such a correction could be misleading, since we are not sure which fraction of C is lost, although the missing fraction is most likely colloidal. If so, we may have underestimated the COC concentration. Anyway, the performance of an ultrafiltration system can vary with the solute concentration and the nature of the sample (Whitehouse et al., 1989); this mass balance is important in evaluating the validity of the ultrafiltration system. Overall, the the modified Millipore CFF system appears to be suitable for both organic and inorganic trace studies.

3.2. Significance of the colloidal fraction

Organic C

Table 2 shows the concentrations and variations of the various forms of organic C in the Rhône delta in May 1992.

DOC concentrations, ranging from 81.7 to 147.9 μM, are consistent with those previously measured in the same area (Cauwet et al., 1990). DOC depicts an overall conservative behavior during estuarine mixing (Fig. 4A).

The concentration of particulate organic C (POC) represents 2.9–16.7% of the concentration of suspended particulate matter (SPM). These values are in agreement with those reported by Cauwet et al. (1990). POC (%) decreases almost exponentially when the turbidity increases.

COC contributes 8–30% of the DOC with a maximum value in the river water. This is in good agreement with the results reported by Sempéré (1991) in the same area. The removal of organic colloids appears evident as shown by its distribution as a function of salinity (Fig. 4B). However, what is the fate of the removed COC? The flocculation of colloidal material and hence its transformation into macroparticles during estuarine mixing is a classically recognized process. However, whenever the truly dissolved organic C is considered, an excess is found as compared to its theoretical dilution line (Fig. 4C). Thus, the removed COC must be transferred not only into macroparticles but also into the
<table>
<thead>
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<th>Station</th>
<th>Salinity</th>
<th>Cd</th>
<th>Cu</th>
<th>Ni</th>
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<td>(C_p) (nM)</td>
<td>(C_c) (nM)</td>
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<td>0.014</td>
</tr>
<tr>
<td>P125F</td>
<td>26.2</td>
<td>0.16</td>
<td>0.17</td>
<td>0.005</td>
</tr>
<tr>
<td>P129</td>
<td>38.1</td>
<td>0.08</td>
<td>0.09</td>
<td>0.006</td>
</tr>
</tbody>
</table>

\(C_a\) = truly dissolved fraction; \(C_p\) = total dissolved fraction; \(C_c\) = colloidal fraction.
truly dissolved phase. This phenomenon is extremely interesting, albeit to some extent surprising because it is well accepted that flocculation of colloids is one of the most important process occurring during estuarine mixing. In fact, as noted earlier, there is some experimental evidence indicating that the deflocculation of colloidal aggregates during the estuarine mixing is also possible (Yan et al., 1992). Fletcher et al. (1983) also observed an increase in “dissolved” Fe concentration in the low-salinity range of estuary.

A positive correlation between SPM and COC would suggest a direct relationship between colloidal organic particles and macroparticles. Based on Th and Be isotope partition data, Honeyman and Santschi (1989) proposed an empirical relationship between colloidal mass concentration \((C_c)\) and SPM concentration \((\text{kg l}^{-1})\):

\[
\log C_c = 0.7 \times \log (\text{SPM}) - 0.26
\]

However, using the field data from this study, the relationship between colloidal organic C concentration and SPM can be described by:

\[
\text{COC} = 4.34 + 1.56 \times \text{SPM} \quad (R = 0.63, n = 13)
\]

Assuming that colloidal material contains 50% C (Moran and Moore, 1989; Wells and Goldberg, 1991), then:

\[
C_c (\text{mg l}^{-1}) = 1.0 \times 10^5 + 3.7 \times 10^4 \text{SPM (mg l}^{-1})
\]

The relationship between the colloidal and macroparticulate mass concentrations is potentially important with respect to the interaction between colloids and macroparticles because it is related to many physico-chemical processes, such as those observed in adsorption/desorption experiments (Morel and Gschwend, 1987).

On the basis of the above discussion, the organic C transfer between the truly dissolved, colloidal and macroparticulate phases appears to be fairly complicated. Next to the traditionally recognized estuarine flocculation process, a reverse process might transfer the colloidal organic C into truly dissolved phase. As a first estimate, 35% of POC (22 \(\mu\)M) and 25% of COC (8 \(\mu\)M) are removed between the river end-member and a salinity \(\sim 20\). At the same time, 20% of the truly dissolved organic C (17 \(\mu\)M) is found in excess. Accordingly, 13 \(\mu\)M of the total organic C (TOC) is removed during this process. As far as the excess of UOC is concerned, colloidal organic C and particulate organic C (via colloids) represent the most likely source. In the latter case, suspended particles such as microplankton would be transferred into colloids in order to maintain the equilibrium between macroparticles, colloids, and dissolved solutes. They represent an opposite process to the “colloidal pumping” described by Honeyman and Santschi (1989). In this context, we suggest that the “colloidal pumping” process would probably operate in two ways. On the one hand, it can scavenge trace elements from the truly dissolved fraction into the macroparticulate phase via colloids, and on the other hand it can transfer both colloidal aggregates and macroparticles to truly dissolved phase via colloids.

It is widely recognized that the estuarine zone is an active region where organic material is trapped, but the mechanism involved during estuarine mixing is more complicated than expected when a colloidal phase is considered.

**Trace metals**

Total dissolved Cu and Ni concentrations in the river end-member are 23.4 nM and 20.5 nM, respectively (Table 3). These values are slightly lower than those previously reported (Huynh-Ngoc et al., 1988; Zhang and Wollast, 1990; Guan, 1990; Elbaz-Poulichet et al., 1995). Colloidal Cu has a concentration between 0.67 nM and 9.15 nM, representing between 20 and 40% of the total Ni concentration. There are many controversial results on Cu behavior in estuaries in the literature (conservative, mobilization from particles and removal from solution). Cu seems to behave conservatively in the Rhône estuary according to this study (Fig. 5) even when the colloidal Cu is involved, which is in good agreement with the observations of Guan (1990).
Conversely, colloidal Ni is removed in the Rhône estuary (Fig. 6C). Since the truly dissolved Ni predominates in the total "dissolved" fraction, the removal in the colloidal fraction does not change significantly the total dissolved Ni distribution along the salinity gradient. As a result, both total "dissolved" and truly dissolved Ni show conservative behaviors (Fig. 6A and B).

The Cd concentration variation in the studied area has been well documented. Our results on the total dissolved Cd concentration are in good agreement with those published earlier (Elbaz-Poulichet et al., 1987, 1995; Guan, 1990). Colloidal Cd makes up from 0 to 38% of the total dissolved Cd. For most samples, the colloidal Cd proportion to total dissolved Cd is less than 10%.

As far as Cd behavior in estuaries is concerned, it is generally accepted that mobilization processes from particulate matter occur when river water mixes with seawater, resulting from the reduction of free Cd²⁺ activity by chloride and sulfate complexation (Com-
Typical examples have been provided in the Western Scheldt (Duinker et al., 1982), the Amazon (Boyle et al., 1982), the French and Chinese estuaries (Edmond et al., 1985; Elbaz-Poulchiet et al., 1987). In the Rhône estuary, a slight and variable maximum of total dissolved Cd is observed in the low-salinity region which is very similar to the distribution pattern obtained by previous studies in the same zone (Elbaz-Poulchiet et al., 1987). As mentioned above, this feature is assumed to be attributed to desorption processes from particles and sediments. However, based on our observation, this process is also related to colloidal material. If we couple the distribution of colloidal Cd and truly dissolved Cd, a remarkably asymmetrical relation can be shown. This might imply that the maximum of dissolved Cd is resulting mainly from the desorption both from colloidal particles and macroparticles. We suggest that the total dissolved Cd distribution is actually the apparent result of the variation of the truly dissolved Cd (Fig. 7). This process is related to the organic C transformation between colloidal and truly dissolved phases. Both truly dissolved Cd and C have a maximum value at the station with a salinity of ~10 and their variation as a function of salinity is rather similar. Next to the relation between trace metals and organic C, the competition between particulate and dissolved organic C seems possible as suggested by Fig. 8, which shows a negative correlation between total dissolved Cd and macroparticulate organic C (%). A similar relationship has been observed in the Venice Lagoon (Martin et al., 1995).

These observations show that interaction between dissolved and colloidal phases may occur, in addition to the “well known” flocculation phenomenon occurring during estuarine mixing. Colloidal particles might also deflocculate and hence increase the dis-
solved concentration. In this case, low concentrations of colloidal trace metals could indicate short residence times and colloids need to be introduced into the water from suspended particles such as plankton in order to maintain the colloidal pumping model in a steady state.

3.3. Transport of organic C and trace metals by colloidal materials

A significant correlation between colloidal organic C and colloidal copper occurs in the Rhône delta (Fig. 9A). This relationship suggests that Cu is associated mainly with organic matter in this size fraction. One possible reason is the complexation of Cu by functional groups (e.g. hydroxyl and carboxylic) associated with colloidal matters.

The tight association between “dissolved” Cu and organic materials has long been recognized (e.g. Hasle and Abdullah, 1981; Florence, 1983; Kramer and Duinker, 1984; Schreiber et al., 1990). Such Cu–organic complexes are totally ill-defined but are believed to be highly stable in seawater. Hasle and Abdullah (1981) reported that Cu complexes extensively with organic and colloidal materials in the coastal seawaters off Norway. Kramer and Duinker (1984) also found that organic colloids (therein > 5000 Daltons) play an important role in the binding of copper in the upper part of the Scheldt Estuary through complexation or adsorption. Schreiber et al. (1990) showed in a batch culture experiment, that Cu complexes mainly with organic compound(s) with a molecular weight of $3 \times 10^4$ Daltons. Results from this study confirm that Cu complexation in estuaries is most likely dominated by organic matter with high molecular weight.

However, this interpretation appears to conflict with the conservative behavior of colloidal Cu observed during the estuarine mixing. Indeed, it is difficult to understand how colloidal Cu could remain conservative whenever colloidal organic C is removed if we considered that colloidal Cu was mainly controlled by colloidal organic material. What is critical is that such a relationship between Cu and organic C is not occasional. A very similar pattern is observed in two Arctic estuaries, Ob and Yenisey (Dai and Martin, 1995). Assuming that the DLVO theory (Derjaguin, Landau, Verwey and Overbeek) is still suitable for explaining colloid behaviour during estuarine mixing, we must suspect that different classes of colloidal organic materials exist, probably composed of at least two subfractions: one refractory (conservative) and the other one removed across the river–ocean interface. This suggests that the colloidal organic C pool is heterogeneous, and able to further fractionate Cu into different species. Given
the high stability of organic Cu complexes, dissolved, and colloidal Cu remain conservative during estuarine mixing, whereas colloidal organic C could be heterogeneous and be partly removed.

Ni and Cd also show a significant linear relationship but with the truly dissolved organic C. This suggests that the complexation for Ni and Cd with organic material may occur mostly in the truly dissolved phase, most likely with low-molecular-weight organic material (Fig. 9B and C). Such a functional difference of various fractions of organic materials for different trace elements has also been suggested in the Venice Lagoon (Martin et al., 1995).

3.4. Reassessment of the river input fluxes

In order to better estimate the fluxes to the open Mediterranean derived from simple river discharge and related concentration data, changes in the concentration of elements which occur in the mixing zone must be taken into consideration. Whenever an element behaves conservatively, the net river input is equal to its river flux. Otherwise, a correction factor must be included to account for gains or losses resulting from biogeochemical processes within the estuarine zone. Based on this study, we are able to specify the fate of organic C and trace metals during the estuarine mixing in the Rhône delta and hence to compute the net river input.

River discharge is quite constant during the survey and is very close to the annual average of 1696 m$^3$/s. The corrected net fluxes from the Rhône River are shown in Table 4.

The estimate of the DOC discharged by the Rhône River is $9 \times 10^4$ tonne/yr. This value is somewhat lower than previously estimated by Kempe et al. (1991), i.e. $9.5-13.2 \times 10^4$ tonne/yr. The DOC flux includes $7 \times 10^4$ tonne/yr transported as truly dissolved materials and $2 \times 10^4$ tonne/yr transported as colloidal materials. The particulate organic C flux is estimated to be $4 \times 10^4$ tonne/yr. Thus, the river input of organic C by colloids is almost half the macroparticulate discharge. This strongly demonstrates the importance of colloids for transporting the organic C in the Rhône River.

The estimate of the net input of "dissolved" Cu is 79 tonne/yr, which is slightly smaller than that of Dorten et al. (1991). This flux includes that transported by colloids (25 tonne/yr). The total dissolved Ni flux is estimated to be 58 tonne/yr of which about one tenth is colloidal. This total dissolved flux corresponds to the minimum limit estimated by Guieu

<table>
<thead>
<tr>
<th>Elements</th>
<th>Species</th>
<th>Concentration (nM)</th>
<th>Correction factors</th>
<th>Flux corrected (tonne/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>Total dissolved</td>
<td>23.4</td>
<td>1.0</td>
<td>79</td>
</tr>
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<td>Truly dissolved</td>
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<td>1.1</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>Colloidal</td>
<td>9.2</td>
<td>0.8</td>
<td>25</td>
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<tr>
<td>Nickel</td>
<td>Total dissolved</td>
<td>20.5</td>
<td>0.9</td>
<td>58</td>
</tr>
<tr>
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<td>Truly dissolved</td>
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<td>1.0</td>
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<td>2.0</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Colloidal</td>
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<td>0.6</td>
<td>0.3</td>
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<td>Organic carbon</td>
<td>Total dissolved</td>
<td>143.8</td>
<td>1.0</td>
<td>$9.2 \times 10^4$</td>
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<td></td>
<td>Truly dissolved</td>
<td>100.0</td>
<td>1.2</td>
<td>$7.7 \times 10^4$</td>
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<tr>
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<td>0.7</td>
<td>$1.9 \times 10^4$</td>
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<tr>
<td></td>
<td>Particulate</td>
<td>102.2</td>
<td>0.65</td>
<td>$4.3 \times 10^4$</td>
</tr>
</tbody>
</table>

The mean river water discharge is 1696 m$^3$/s.

The correction factor is defined by the "effective" river end-member concentration divided by the measured river end-member concentration.

Table 4
Reassessment of the Rhône river inputs to the northwestern Mediterranean Sea
et al. (1993). As for Cd, our estimate is 3 tonne/yr for the total dissolved flux, corresponding to the maximum limit calculated by Guieu et al. (1993). As with Ni, colloidal material carries about one tenth of the total dissolved Cd discharged from the river.

The above estimates of the river input are only based on one campaign of the investigation, and do not allow us to establish a reliable budget from the Rhône River to the northwestern Mediterranean. However, they emphasize that the differentiation between the colloidal and the dissolved phases is potentially important for the calculation of river input of trace metals and organic C at a global scale. Indeed, there is some evidence that most ocean colloidal material is of local biological origin (Sigleo et al., 1982, 1983; Wells and Goldberg, 1991). This indicates that the colloidal phase of metals or C measured in river and estuarine systems must be removed from the water column just like small particles. Most likely, this removal happens on the continental shelf and hence alters the "dissolved" input from land into the open ocean. This process has been ignored until now and needs to be taken into consideration to reassess the mean ocean residence time of most trace metals.

4. Conclusions

The regulation of the chemical composition of natural waters by the interactions between solution and particles (including colloids) and between particles has been well recognized. However, this regulating process is far from being well understood. It may probably involve some poorly known processes, such as the dynamical interactions between truly dissolved and colloidal fractions. If the "colloidal pumping" process emphasizes the importance of colloids in scavenging trace elements via coagulation, the reverse process might also be critical. There is some evidence that the behavior of trace elements during estuarine mixing is largely related to their capacity for complexation with organic materials in truly dissolved, colloidal and macroparticulate phases.

Colloidal material transports a significant part of "dissolved" organic C and trace metals. The colloidal fraction of organic C and trace metals of riverine origin may be removed on the continental shelf. The global significance of such processes must be investigated.

Further studies should be undertaken to understand the whole system including solutes, colloids and macroparticles so as to reassess the dynamical two-way "colloidal pumping" process.

Acknowledgements

We greatly acknowledge the support of the Commission of the European Communities in the framework of the international project "EROS 2000" (European River Ocean System) under the contract of STEP-CT 90.0080'dscn' and STEP-CT90.0065 (Transport, Transfer and Transformation of Trace Metals in Estuaries). The sampling campaign was partly financed by the program "PNOC" (Programme Nationale d'Océanographie Côtière). The authors wish to express their acknowledgements to Mrs. V. Berthou for her technical assistance during the analysis of organic C. Peter A. Statham is greatly acknowledged for his helpful comments and suggestions. Finally, we also acknowledge Mark L. Wells and an anonymous reviewer for critical and constructive reviews of the manuscript.

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