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Evolution of particle size and concentration in the Rhône river mixing zone: influence of salt flocculation

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The salt induced flocculation phenomenon is often proposed as a major mechanism influencing the deposition of the suspended matter near the mouth of major rivers. However, depending on the particular mixing conditions between fresh water and marine water and on suspended solids (SS) reactivity, salt induced aggregation may be a minor factor controlling fast deposition of SS. This work combines field studies and laboratory experiments in order to assess the importance of salt induced flocculation in the case of the saltwedge estuary of the Rhône river. Sampling of the mixing zone has been performed in contrasted hydrodynamic conditions from a low water discharge period ($500 \text{ m}^3 \text{ s}^{-1}$) to a small flood event ($2400 \text{ m}^3 \text{ s}^{-1}$) for particle counting and salinity measurements. Through laboratory experiments, it is shown that the Rhône river particulate matter has a poor average reactivity regarding salt induced flocculation. Considering the hydrodynamics of the estuary, we show that the evolution of the concentration of large particles ($> 5 \mu\text{m}$) can be explained by settling and dilution. In contrast, the smallest measured fraction ($2\text{--}5 \mu\text{m}$) shows a more complex behavior and settling processes alone cannot explain the observed particle concentrations during the field studies. Four hypotheses are discussed for explaining the $2\text{--}5 \mu\text{m}$ particle concentration evolutions.

Keywords: Rhône river; Estuarine mixing zone; Aggregation; Sedimentation; Particle counting

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1. Introduction

With a mean water discharge of $1700 \text{ m}^3 \text{ s}^{-1}$ at Beaucaire (France) and a mean solids discharge of 4.6 tons per year, the Rhône river represents the major fresh water and particle input in the western Mediterranean sea. The solids discharge of the Rhône river has both a high inter-annual variability (1–8 tons per year) and an annual variability with about 70% of the solids discharge carried during flood events of more than $3000 \text{ m}^3 \text{ s}^{-1}$ (Pont, 1996). Several studies have shown that the particles carried by the Rhône settle in a relatively small area close to the mouth of the river. Guieu et al. (1993) have estimated that 75% of the flux of particulate matter to the Mediterranean sea accumulates in a region representing only 17% of the total area of the Gulf of Lions continental shelf. Furthermore, studies conducted using plutonium as a suspended matter tracer concluded that more than 50% of the total sediment flux to the bottom was concentrated in a region that represents less than 0.1% of the total deposition area (Noel, 1996; Thomas, 1997). The hydrodynamics and mixing of river water with marine water in the Rhône estuary is typical of a microtidal saltwedge estuary. The salt water forms a wedge in the river bed underneath the freshwater layer. The extension of this wedge is mainly controlled by the river discharge. During low water discharge period (about $500 \text{ m}^3 \text{ s}^{-1}$), the salt intrusion can extend up to 20 km inland, and during high water discharge ($2500 \text{ m}^3 \text{ s}^{-1}$ and more), the salt wedge is pushed seaward to the river mouth (Eisma, 1993). Beyond the river mouth, the freshwater forms a plume that flows over salt water. The shape and extension of the Rhône river plume is influenced by wind and the surrounding coastal circulation (Estournel et al., 1997; Marsaleix et al., 1998). At the mouth of the river, the suspended matter is exported to the coastal zone along two major pathways. A part of the suspended matter is exported seaward in the freshwater layer and forms the so-called surface nepheloid layer (SNL). Another part sinks rapidly and contributes to the formation of the bottom nepheloid layer (BNL) (Aloisi et al., 1982; Naudin et al., 1997). To explain the formation of the BNL and the accumulation of the suspended matter in a small region near the river mouth, salt induced flocculation phenomena are often referred to. Indeed, during the mixing, the suspended matter experiences an important change in the physicochemical properties of the water. The ionic strength increases and hydrodynamic conditions are completely modified. Depending on their nature, the suspended matter will behave differently during these physicochemical changes. This is well demonstrated by following the concentrations of size fraction of several species. For example, despite the fact that dissolved organic matter shows a globally conservative behavior during the mixing, this is not the case of the high molecular weight (HMW) organic species. These HMW organic matter are removed from the dissolved pool of organic matter in the low salinity region of estuaries (Santschi et al., 1997; Fox, 1983; Sholkovitz, 1976). The rapid elimination of dissolved and colloidal chemical species during the first stage of the mixing has often been attributed to flocculation processes (Fox, 1983; Sholkovitz, 1976). However, these observations are mainly based on the monitoring of the transfer of one species from the “dissolved” pool ($<0.45 \mu\text{m}$) to a “particulate” pool ($>0.45 \mu\text{m}$). This has almost never been coupled with particle size measurements, and changes between two fractions for some species do not imply a significant global change in size for the whole of the suspended matter. In-situ observations of the size distributions in estuaries never show clear evidence of a significant growth of particle size in the first stage of the mixing. On the contrary, a decrease of mean particle size and settling velocities has been observed in some estuaries (Eisma, 1986). The chemical changes occurring in estuaries

are favorable to a destabilization of the suspended matter, because the increased ionic strength reduces the electrostatic repulsion between particles, but it has not been demonstrated yet whether salt induced flocculation can play a significant role in the transfer and sedimentation of SS in the Rhône river estuary. Evaluation of the role of salt induced flocculation in enhancing the global sedimentation flux requires the proper measurements of size distribution large than $1\ \mu\text{m}$ all along the mixing zone. In this paper, we study the evolution of the particle size distribution from 2 to $200\ \mu\text{m}$ along the mixing zone of the Rhône river estuary during contrasted hydrodynamic conditions.

2. Experimental methods

2.1. Field studies

Field experiments were conducted during three different hydrodynamic flow regimes: one low water discharge in April 7–12, 1997 ($500\ \text{m}^3\ \text{s}^{-1}$, SPM in river: $8\ \text{mg l}^{-1}$), one medium water discharge in May 12–16, 1997 ($1400\ \text{m}^3\ \text{s}^{-1}$, SPM in river: $10\ \text{mg l}^{-1}$) and one high water discharge

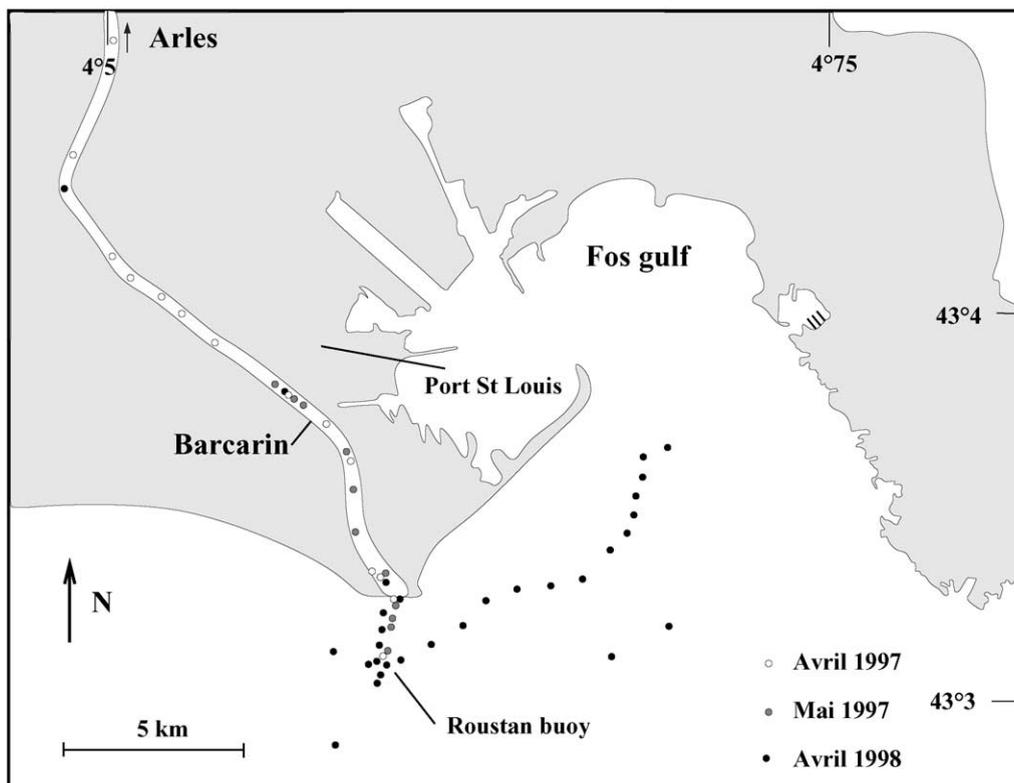


Fig. 1. General situation maps of the sampling region.

in May 14–22 1998 ($2400 \text{ m}^3 \text{ s}^{-1}$, SPM in river: 70 mg l^{-1}). Sampling was conducted from an inflatable boat for the river samples and on board the R/V *Thetis II* (CNRS/INSU), for sampling in the river plume during the May 1998 field study. For each field study, the sampling was performed over a period of one week. The sampling zones were determined by the position of the saltwedge intrusion in the river. Both horizontal and vertical profiles were sampled. Vertical profile samples were taken at various depths with a Niskin bottle. A river water reference was taken upstream of the first salt occurrence. This was done at Arles at low water discharge and at Barcarin at medium and high water discharges (Fig. 1). Sampling of the highest salinity investigated was done at the Roustan buoy, 2 km from the river mouth, for the first two campaigns and outside the plume for the last field campaign. On each sample (surface and depth), the suspended matter content was measured by filtration on a $0.7 \mu\text{m}$ filter. The water was also analyzed for particle counting using a portable particle counter (Pacific Scientific) for the river points and a laboratory particle counter (Hiac Royco) for the plume samples. The particle counting was done immediately after sampling except for the May 1998 river samples due to unfavorable hydrodynamic regimes. Therefore, these river samples from each profile in the river were brought back to the riverbank for analysis less than 1 h after sampling. In order to assess the bias due to delay in measurement, some samples were analyzed after 1 h and 4 h to evaluate the size evolution. For the small size classes (ie. less than $50 \mu\text{m}$) the evolution was inferior than 10% 4 h after sampling. More important variations (up to 40%) was noticed for large size classes. In April and May 1997, the salinity was measured by a CTD (Seabird), in May 1998, the salinity was directly measured on the sampled water by a conductimeter (WTW). During the three field studies, one transect has also been done for surface water along the mixing zone from zero salinity up to the Roustan buoy. For the last field study, the transect covered the entire mixing zone from zero salinity to outside the plume, and it was sampled over a period of two days.

2.2. Laboratory experiments

Aggregation experiments were conducted in the laboratory with both natural suspended matter from the Rhône river and clay minerals (Smectite and Illite). Smectite and Illite are present in the SS of the Rhône river (Garnier et al., 1991). For the aggregation experiments, Rhône river water was sampled at Arles just after a $3500 \text{ m}^3 \text{ s}^{-1}$ flood in November 1997. The suspended matter content of this sample was $1151 \pm 16 \text{ mg l}^{-1}$. Before proceeding to the experiment, the raw water sample was left under steady condition for 30 min in order to remove sand. The SS content after settling was 480 mg l^{-1} . The aggregation protocol consisted of slowly adding 250 ml of a 40 g l^{-1} NaCl solution to an equal volume of settled Rhône river water. The same protocol was used for clay mineral aggregation experiments. A volume of 250 ml of a 40 g l^{-1} NaCl solution was slowly added to an equal volume of a 480 mg l^{-1} solution of clay. For both natural particle and clay mineral aggregation experiments, the evolution of the size distribution of the particles was followed during the mixing using a laser particle size analyzer (Malvern mastersizer S). The rate of salt addition was constant with a value of 0.1 ml s^{-1} for all experiments and was verified by continuously measuring conductivity during the experiments.

3. Results

3.1. Freshwater/sea water mixing conditions

The periods for the field studies were chosen to observe contrasted hydrodynamic conditions in the Rhône river mixing zone. As an example, Fig. 2 shows the position of the saltwedge for the medium river discharge ($1400 \text{ m}^3 \text{ s}^{-1}$). The dotted line represents the river bottom as estimated from the depth at each sampling station. The crosses correspond to a measured salinity of 20 g l^{-1} and water thickness between 10 and 30 g l^{-1} is marked by a bar at each station. Surface salinities are also indicated at three locations. As salinity profiles were sampled over a period of about a week, hydrodynamic variations between the different sampling days introduce some variation in the position of the saltwedge. These variations are, however, moderate compared to the changes between the different field studies. Indeed, the saltwedge has been found 17 km upstream Roustan buoy during the low water discharge field experiment ($500 \text{ m}^3 \text{ s}^{-1}$) and just prior to the river mouth at large water discharge ($2400 \text{ m}^3 \text{ s}^{-1}$). Variations in surface salinities were also important, the salt concentration of surface water at the Roustan buoy was comprised between 10 g l^{-1} during low water discharge in April 1997 and 2 g l^{-1} during the small flood in May 1998. During the low and medium water discharge periods, the thickness of the water layer between 10 and 30 g l^{-1} increased notably about 4 km upstream the Roustan buoy. We believe from our field observations that this may be due to an acceleration of the stream velocity in the sampling location. Such stream velocity acceleration at the mouth of the Rhône river has been measured and discussed by other authors (Broche, 1998; Kashiwamura and Yoshida, 1978).

3.2. Particle size distribution measurements

The evolution along the salinity gradient of the particle concentrations at the Rhône river surface for the three field experiments is presented on Fig. 3. In order to compare the concentrations, they are normalized by the mean river concentration given in Table 1. The most striking feature is the difference between particles larger than $5 \mu\text{m}$ and particles between 2 and

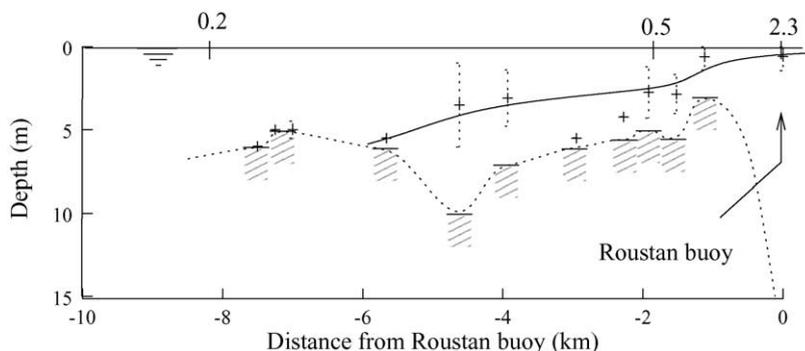


Fig. 2. Saltwedge position during the medium river discharge field study. Crosses represents 20 g l^{-1} salinity and the water layer between 10 and 30 g l^{-1} is symbolized by a vertical bar. The dotted line correspond to the estimated bottom depth.

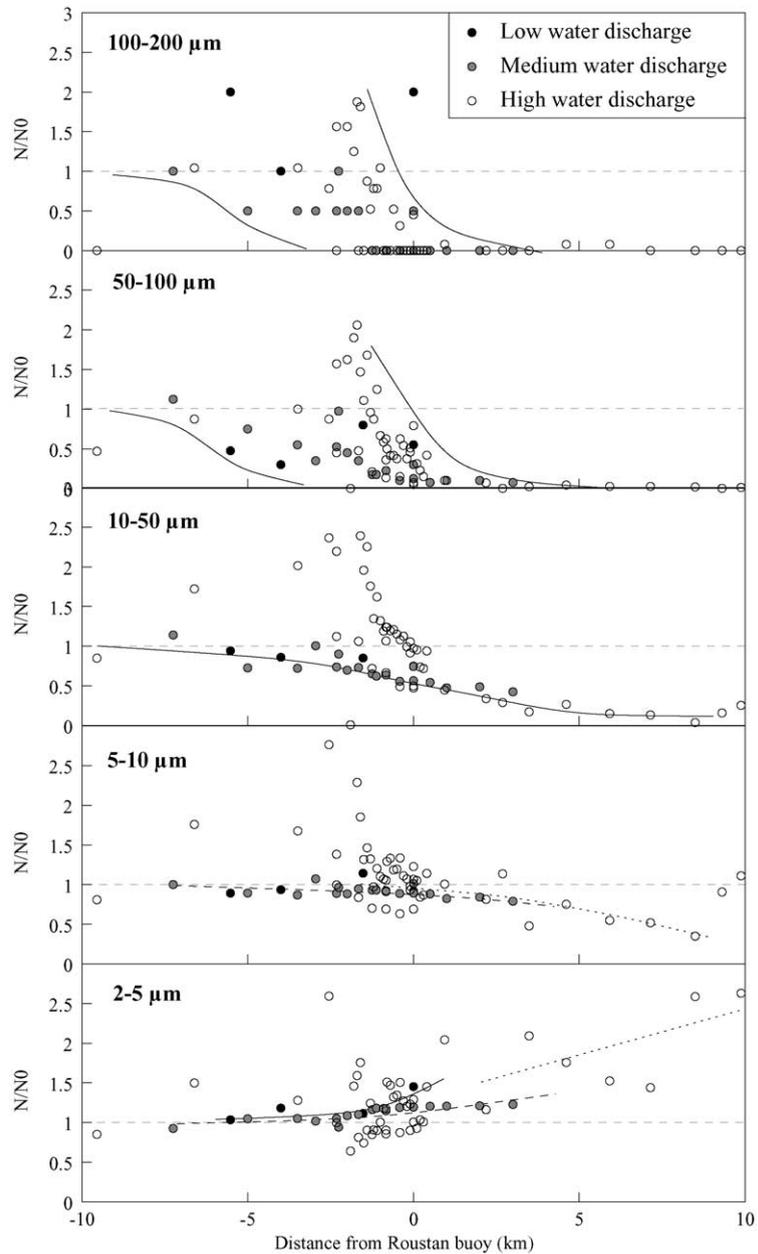


Fig. 3. Evolution of the normalized particle concentrations (N/N_0) for the different field studies with the position in the mixing zone.

5 μm . Indeed, the surface concentration of particles larger than 5 μm starts to decrease about 5 km upstream of the Roustan buoy, whereas, the 2–5 μm particle concentration tends to increase. The downstream concentration decrease in the largest measured particles is faster as their diameter increases. Almost all 100–200 μm particles are removed from the surface water 2.5 km after the

Table 1
Mean size distribution in river water

Low water discharge ($500 \text{ m}^3 \text{ s}^{-1}$)	μm	2–5	5–10	10–50	50–100	100–200
	part ml^{-1}	3800	3500	8200	20	0.5
Medium water discharge ($1400 \text{ m}^3 \text{ s}^{-1}$)	μm	2–5	5–10	10–50	50–100	100–200
	part ml^{-1}	6000	5000	3500	40	2
High water discharge ($2400 \text{ m}^3 \text{ s}^{-1}$)	μm	2–5	5–10	10–50	50–100	100–200
	part ml^{-1}	30 000	20 000	10 000	100	8

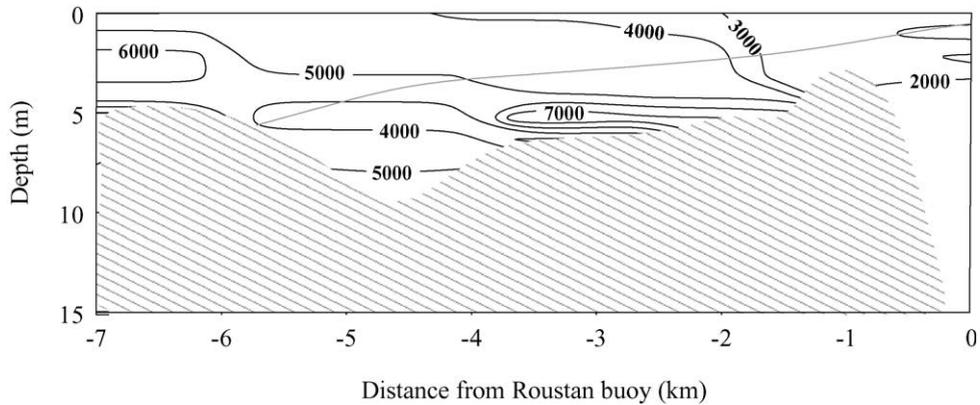


Fig. 4. Concentration of $10\text{--}50 \mu\text{m}$ particles in the beginning of the mixing zone during medium river discharge ($1400 \text{ m}^3 \text{ s}^{-1}$). This solid line indicates the average position of 20 g l^{-1} salinity.

Roustan buoy whereas surface concentration of $5\text{--}10 \mu\text{m}$ particles are only divided by 2 about 8 km off the Roustan buoy. Another interesting point is the increase of the particle surface concentrations 2 km upstream the Roustan buoy during the high water discharge field study. In this part of the estuary, all particle concentrations are twice that of the river. Although not sampled the same day, this is also observed on vertical profiles in the river for medium and low water discharge. For example, at the beginning of the salt wedge, the $10\text{--}50 \mu\text{m}$ particle concentrations increase notably in depth, but surface water is not affected as much as in the case of the flood (Fig. 4).

3.3. Laboratory aggregation experiments

The mean size evolutions obtained with clay minerals and Rhône river particles samples are shown on Fig. 5. For both clays, the mean size of the particles started to increase quickly as soon as the NaCl concentration reached 2×10^{-2} and $5 \times 10^{-2} \text{ mol l}^{-1}$ for Smectite and Illite, respectively. An equilibrium size was obtained after about 5 min aggregation time. Concerning the natural river water sample, no abrupt evolution of the size of the particle was observed. The

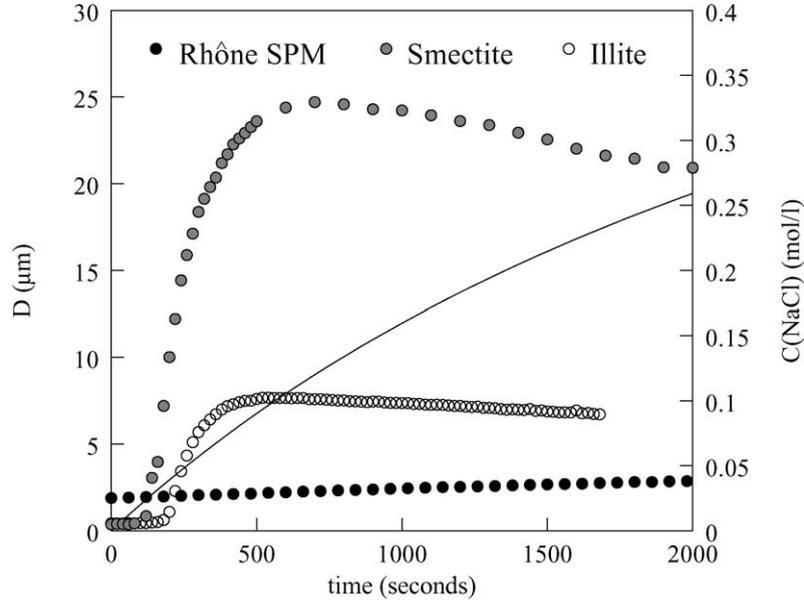


Fig. 5. Comparison of aggregation kinetic of Rhône SS, Smectite and Illite under the same conditions.

evolution of the size was very slow with a mean size less than two times greater than initial value after 30 min stirring.

4. Discussion

4.1. Mixing conditions and aggregation kinetics

Particle aggregation and adsorption are not instantaneous processes. The kinetic aspect of reactions become even more important in estuaries where the residence time is short. This kinetic limitation has been noted for the behavior of trace metals in the case of the Rhône river (Elbaz-Poulichet et al., 1996). Concerning salt induced aggregation, the reaction kinetics depend on, the electrostatic repulsion between particles which is dependent on the salinity. It has been shown that aggregation is optimal for salinities between 1 and 7 g l^{-1} (Eisma, 1993). Secondly, higher particle concentrations favor faster aggregation. It is generally considered that when shear collision dominates, the kinetics are proportional to the particle volume fraction. In the case of our laboratory experiments, despite the very high SS concentration, the aggregation kinetics remain slow (Fig. 5). This implies that the average reactivity regarding salt induced aggregation is poor for the natural river SS.

The work of Naudin et al. (1997) has shown that the mixing time of surface water depends strongly on wind and is on the order of several hours. During this transport, the largest particle settle and the SS concentration decreases quickly. Taking into account the slow growth in size of the SS at high concentration, it is not obvious that salt induced aggregation could play a role in enhancing the settling at the mouth of the river.

4.2. The case of 5–200 μm particles

The surface stream velocity can be estimated from both the experimental field work of Naudin et al. (1997) and numerical simulation (Estournel et al., 1997). To test which settling velocities are needed to explain the evolution of the 5–200 μm particle concentrations, we assume an average plume surface velocity and mixing rate. The mixing rate δ ($\text{ml l}^{-1} \text{s}^{-1}$) is defined so that an initial concentration $C_{fw}(0)$ when mixed with water at a concentration C_{sw} evolves as follows:

$$C_d(t) = \frac{C_{sw}\delta t + C_{fw}(0)}{1 + \delta t}. \quad (1)$$

From Eq. (1), it is possible to calculate the concentration corrected from dilution effects using:

$$\tilde{C}(t) = C(0) + (C(t) - C_d(t)) \quad (2)$$

If the evolution of this corrected concentration is assumed to be due to a simple settling law, we can write

$$\underbrace{AD \frac{d\tilde{C}}{dt}}_{\text{mass variation}} = \underbrace{-\tilde{C}(t)AV_s}_{\text{outward flux}} \quad (3)$$

where A and D are, respectively, the basal area and the height of the fluid volume where settling is considered, $\tilde{C}(t)$ and V_s are the corrected concentration and settling velocity. Considering a constant plume velocity noted V_p , we can replace time by traveled distance in the plume $t = d/V_p$. Integrating Eq. (3) and replacing t we have:

$$\tilde{C} = \tilde{C}_0 \exp \frac{-V_s d}{V_p D} \quad (4)$$

Using Eq. (4) it is possible to adjust the parameter $V_s/V_p D$ to fit the observed evolution. Fig. 6 shows the best adjustment. We have $V_s/V_p D = 3.3 \times 10^{-5}$, 10^{-4} and 1.7×10^{-4} , respectively for 5–10, 10–50 and 50–100 μm particles with $D=0.1$ m and $V_p=0.6$ m s^{-1} . The adjustments are of course not very accurate in simulating experimental variations. The assumptions made (constant mixing rate, constant plume surface velocities, etc.) could explain much of the variation compared to the predictions. However, the trends are in good agreement with previously published settling velocity data (see Table 2 and Syvitski et al., 1995).

4.3. The case of 2–5 μm particles

The increase of the 2–5 μm particles is observed for the three field studies and therefore constitutes a reproducible feature of the SS transfer processes. Another behavior, which has been observed only during the high water discharge field study, is the very high variability of the 2–5 μm particle concentration in the plume. We assume that this variability is related to a resuspension mechanism, which is favored at the river mouth and increases all particle concentrations observed on Fig. 3. Particle resuspension is not continuous in time and space, so it involves a fluctuating source of particles for the surface layer. The smallest particles do not settle and are exported seaward. These exported particles may follow very different pathways and contribute to a highly heterogeneous river plume.

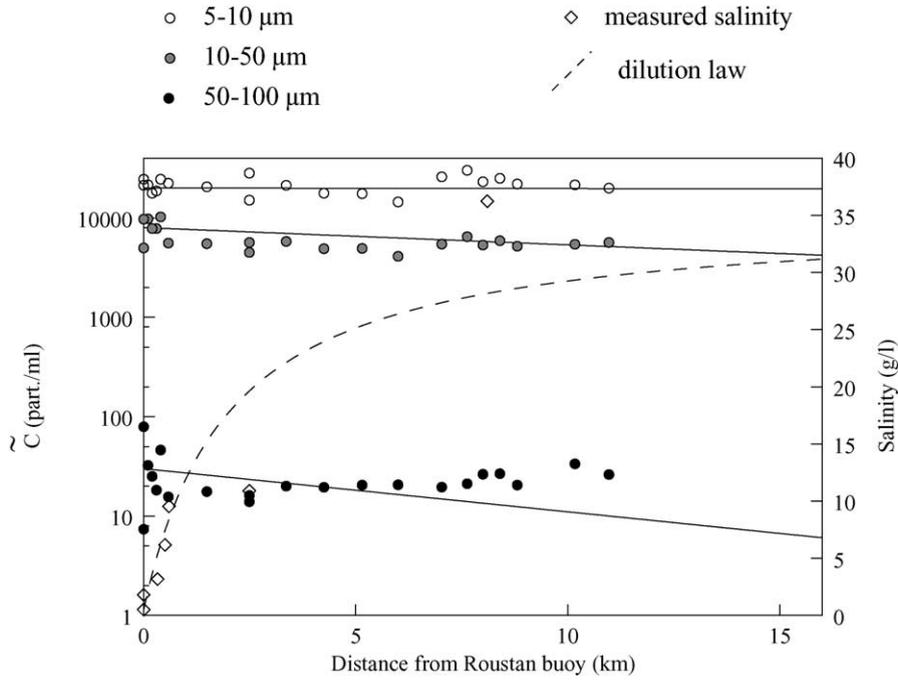


Fig. 6. Comparison between measured and predicted concentrations of dilution corrected concentrations of 5–10, 10–50 and 50–100 μm particles and of salinity as a function of the distance from the Roustan buoy.

Table 2
Predicted settling speed compared to data from Syvitski et al. [20].

	Mean size (μm)		
	3.5	30	75
<i>Our estimations</i>			
$V_p = 60 \text{ cm s}^{-1}$	2×10^{-6}	6×10^{-6}	2×10^{-4}
$V_p = 20 \text{ cm s}^{-1}$	8×10^{-7}	3×10^{-6}	5×10^{-6}
<i>Syvitski's data</i> (Syvitski et al., 1995)			
Maximum	1.15×10^{-5}	2.19×10^{-5}	2.88×10^{-5}
Mean value	2×10^{-6}	4.08×10^{-6}	5.59×10^{-6}
Minimum	5.91×10^{-11}	7.79×10^{-10}	3.39×10^{-9}

Beyond this resuspension area, there is a clear tendency toward a concentration increase in the Rhône plume. At least four hypotheses could explain such an increase: larger particle break-up, primary production, colloid aggregation or even simple mixing with a particle-rich saline water source.

4.3.1. Break-up mechanism

Particle break-up has already been proposed by several authors to explain size decrease in regions where settling is negligible (Eisma, 1993; Yan et al., 1992). Size distribution measurements alone cannot prove break-up. However, two observations favor such a mechanism. Quantitatively, only a small amount of the larger aggregates would constitute a largely sufficient stock of small 2–5 μm particles to explain the concentration increase. Qualitatively, the conditions encountered in the beginning of the mixing zone favor aggregate break-up. Indeed, it has been noted that several organic species involved in floc cohesion are desorbed in the low salinity region (Eisma, 1993). The remobilization of these organic species may yield the aggregates more fragile. We also suspect the surface stream velocity to increase in the low salinity region as shown by the interface layer thickening (see Fig. 2). An increase in the velocity gradient coupled with more fragile aggregates may promote break-up.

4.3.2. Primary production

The Rhône river mixing zone is known to be a region of high primary production. The fresh water, rich in nutrients, promotes the growth of microorganisms. Among these microorganisms, some are in the size range between 2 and 5 μm . Very few data exist in terms of cell numbers in the Rhône river plume. Eisma et al. (1991) published cell counting measurements in the Rhône river in February 1985. Between the mouth of the river and the Roustan Buoy the cell number per milliliter increase by 6000 cell ml^{-1} . Considering an increase of 6000 cell ml^{-1} every 2.5 km, Fig. 7 shows the increasing trend compared to the measurements in May 1998. The dotted lines correspond to the hypothesis of 25%, 50% or 100% of the cells being in the range 2–5 μm . Apart from the very high variability, the trend predicted from Eisma's cell data are consistent with

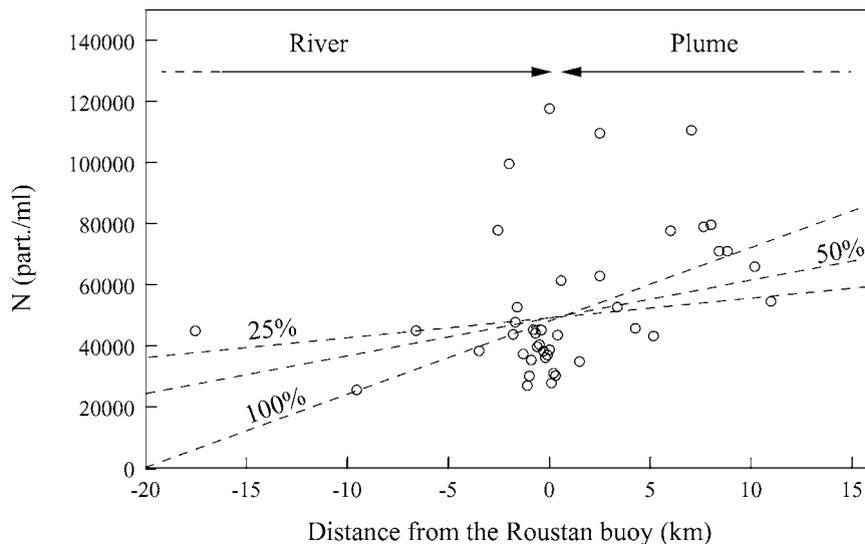


Fig. 7. Concentration of 2–5 μm particles as a function of the distance from the Roustan buoy measured during the high water discharge field study. The dotted lines correspond to increase tendencies predicted by the Eisma's cell measurements (Eisma et al., 1991) (see text).

observations. Therefore, primary production could explain, at least partly, the increase of 2–5 μm especially in the river plume.

4.3.3. Colloidal aggregation

Several authors have shown that colloids represent about 10% or less of the SS mass (Eisma et al., 1991; Santschi et al., 1995; Pham and Garnier, 1998). In terms of particle number, this represents a very important concentration. Strictly quantitatively, colloids could be the source of 2–5 μm aggregates. Two main unknowns remain however. First, the precise quantity and reactivity of these colloids are largely unknown and very difficult to measure in situ. Secondly, the kinetic aspect of the aggregation reaction is also very important and not at all trivial to evaluate. Further insight in the possible participation of colloids in the increase of 2–5 μm particle increase would certainly benefit the use of aggregation numerical models.

As the colloid concentration represents only about 10% of the SS concentration, it would slightly modify the global sedimentation flux. However, these colloids are the preferential support of pollutants due to their high specific surface. This problem is, therefore, crucial not on a quantitative point of view but for the qualitative properties of deposited materials.

4.3.4. Salt water origin

The mixing origin of the small particles seems unlikely. Indeed, salt water almost never contains more 2–5 μm particles than does freshwater. The only case where salt water was more concentrated than the freshwater was in the river during low water discharge period. Fig. 8 shows the increase of the 2–5 μm particle concentration in the salted layer from the river mouth to the beginning of the salt wedge. But in this case, even if one considers the most extreme concentrations, the mixing between freshwater and saline water could only explain a maximum of 25% of the 2–5 μm particle concentration increase.

Therefore, despite the case where it could slightly increase the concentration of small particle, the mixing process cannot generally explain the 2–5 μm particle concentration increase.

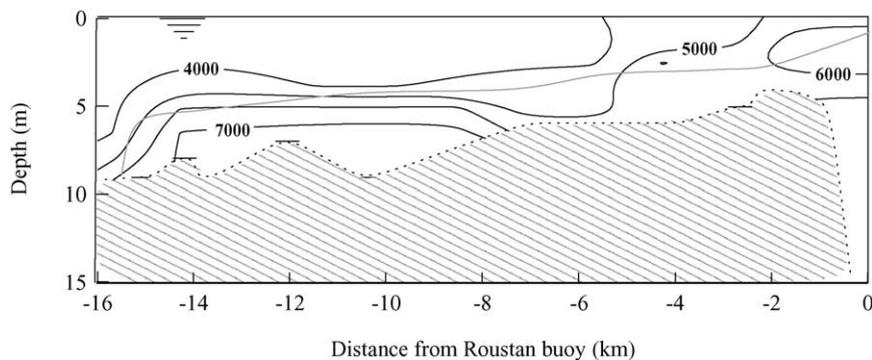


Fig. 8. Concentration of 2–5 μm particles in the beginning of the mixing zone during low river discharge ($500 \text{ m}^3 \text{ s}^{-1}$). The grayed solid line indicates the average position of 20 g l^{-1} salinity.

5. Conclusion

Elucidation of the SS transport and deposition in estuary requires accurate knowledge of hydrodynamic conditions. We show that in the case of surface particle concentrations, where mixing conditions are best known, it is possible to identify the main mechanism explaining the sediment deposition in the prodelta. Concerning the largest measured particles ($> 5 \mu\text{m}$), we show that a combination of dilution and settling explain the observed concentrations. The determined settling speed are in agreement with previously published data. Smaller particles between 2 and $5 \mu\text{m}$ display a more complex behavior. Break-up, resuspension and primary production certainly affect their concentration in the river and the plume. According to laboratory experiments, the Rhône river suspended matter appear to have a poor average reactivity toward aggregation. However, it cannot be excluded that colloid aggregation could also participate to the formation of particle in the 2– $5 \mu\text{m}$ range. A more quantitative insight into aggregation processes affecting colloids would need to be explored further using a numerical model.

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References

- Aloisi, J.C., Cambon, J.P., Carbonne, J., Cauwet, G., Millot, C., Monaco, A., Pauc, H., 1982. Origine et rôle du néphéloïde profond dans le transfert des particules au milieu marin. application au golf du Lions. *Oceanologica Acta* 5 (4), 481–491.
- Broche, P., 1998. Experimental study of the rhone river plume. Part I: physics and dynamics. *Oceanologica Acta* 21, 725–738.
- Eisma, D., 1986. Flocculation and de-flocculation of suspended matter in estuaries. *Netherlands Journal of Sea Research* 20, 183–199.
- Eisma, D., 1993. *Suspended Matter in the Aquatic Environment*. Springer, Berlin.
- Eisma, D., Bernard, P., Cadee, G.C., Ittekkot, V., Kalf, J., Laane, R., Martin, J.M., Mook, W.G., Van put, A., Schuhmacher, T., 1991. Suspended-matter particle size distribution in some west-European estuaries. Part I: particle size distribution. *Netherlands Journal of Sea Research* 28 (3), 193–214.
- Elbaz-Poulichet, F., Garnier, J.M., Guan, D.M., Martin, J.M., Thomas, A.J., 1996. The conservative behaviour of trace metals (Cd, Cu, Ni, and Pb) and As in the surface plume of stratified estuaries: example of the Rhône river (France). *Marine Chemistry* 42, 289–310.
- Estournel, C., Kondrachoff, V., Marsaleix, P., Vehil, R., 1997. The plume of the Rhône: numerical simulation and remote sensing. *Estuarine Coastal and Shelf Science* 17 (8), 899–924.
- Fox, L.E., 1983. The removal of dissolved humic acid during estuarine mixing. *Estuarine Coastal and Shelf Science* 16, 431–440.

- Garnier, J.M., Martin, J.M., Mouchel, J.M., Thomas, A.J., 1991. Surface reactivity of the Rhône suspended matter and relation with trace element sorption. *Marine Chemistry* 36, 267–289.
- Guiou, C., Zhang, J., Thomas, A.J., Martin, J.M., Bruncottan, J.C., 1993. Significance of atmospheric fallout on the upper layer water chemistry of the north western Mediterranean. *Journal of the Atmospheric Chemistry* 17, 45–60.
- Kashiwamura, M., Yoshida, S., 1978. Outflow dynamics at a river mouth. 16th Coastal Engineering Conferences ASCE, Hamburg, Germany, pp. 2925–2944.
- Marsaleix, P., Estournel, C., Kondrachoff, V., Vehil, R., 1998. A numerical study of the formation of the Rhône river plume. *Journal of Marine Systems* 14, 99–115.
- Pont, D., 1996. Evaluation of water fluxes and sediment supply. Meddelt, Venezia, October 2–5.
- Naudin, J.J., Cauwet, G., Chretiennot-dinet, M.-J., Deniaux, B., Devenon, J.-L., Pauc, H., 1997. River discharge and wind influence upon particulate transfer at the land–ocean interaction: case study of the Rhône river plume. *Estuarine Coastal and Shelf Science* 45, 303–316.
- Noel, M. H., 1996. Le plutonium comme traceur du transfert et de l'accumulation des apports particulaires du Rhône en Méditerranée Nord Occidentale. Ph.D. Thesis, Université Paris XII-Val de Marne.
- Pham, M.K., Garnier, J.M., 1998. Distribution of trace elements associated with dissolved compounds ($<0.45\ \mu\text{m}$ – $1\ \text{nm}$) in freshwater using coupled (frontal cascade) ultrafiltration and chromatographic separations. *Environmental Science and Technology* 32, 440–449.
- Santschi, P.H., Guo, L., Baskaran, M., Trumbore, S., Southon, J., Bianchi, T.S., Honeyman, B.D., Cifuentes, L., 1995. Isotopic evidence for the contemporary origin of high-molecular weight organic matter in oceanic environments. *Geochimica et Cosmochimica Acta* 59, 625–631.
- Santschi, P.H., Lenhart, J.J., Honeyman, B.D., 1997. Heterogeneous processes affecting trace contaminant distribution in estuaries: the role of natural organic matter. *Marine Chemistry* 58, 99–125.
- Sholkovitz, E.R., 1976. Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. *Geochimica et Cosmochimica Acta* 40, 831–845.
- Syvitski, J.P.M., Asprey, K.W., Leblanc, K.W.G., 1995. In-situ characteristics of particles settling within a deep-water estuary. *Deep-Sea Research Part II* 42, 223–256.
- Thomas, A.J., 1997. Input of artificial radionuclides to the gulf of Lions and tracing the Rhône influence in marine surface sediments. *Deep Sea Research Part II* 44, 577–596.
- Yan, L., Stallard, R.F., Crerar, D.A., Key, R.M., 1992. Experimental evidence on the behavior of metal bearing colloids in low-salinity estuarine water. *Chemical Geology* 100, 163–174.