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Nearshore dynamics of nutrients and chlorophyll during Mediterranean-type flash-floods

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Abstract – A year-long study in the Bay of Banyuls-sur-Mer (France) assessed the inputs from the local intermittent Baillaury River and the stimulation of nearshore phytoplankton blooms. During flash-floods, dissolved inorganic nitrogen, phosphate and dissolved organic carbon concentrations in the river were neither correlated to the river discharge nor to the season. Silicate was correlated to the river discharge. The particulate organic matter load was diluted in a mineral matrix (3–4%) but had a high nutritional quality at the beginning of the flash-flood. The offshore response to the single major flow event (October 2005) was monitored daily during two weeks at 350 m (8 m water depth) and 1.4 km from the river mouth (long-term monitoring station, 27 m water depth). The flash-flood signal was partly hidden at the shallowest site by swell resuspension of bottom sediments. At the deepest station, three phases were identified: (1) at the beginning of flow, river dissolved inputs dilute conservatively leading to increased dissolved inorganic nitrogen and silicate concentrations and decreased seawater salinity, (2) during the main turbid pulse, phosphate is released and (3) after the water column cleared, diatom photosynthesis occurred at 3 m below the water surface, leading seven days after the flow peak discharge to a high of 2 μg L^{-1} of chlorophyll *a*, which vanished three days later. The nutrients and salinity recovered their pre-flow values at that time. This dynamics of nutrients and chlorophyll during a flash-flood event is consistent with long-term monitoring data.

Key words: Flash-flood / Intermittent river / Nutrients dynamics / Nearshore ecosystem / NW Mediterranean

Résumé – Dynamique littorale des sels nutritifs et des pigments chlorophylliens durant des crues éclair méditerranéennes. Les apports du fleuve intermittent Baillaury et la stimulation d'efflorescences phytoplanctoniques littorales ont été mis en évidence lors d'un suivi annuel dans la baie de Banyuls-sur-Mer (France). Durant les crues éclair de l'année, les concentrations en azote inorganique dissous, en phosphate et en carbone organique dissous dans le fleuve n'étaient corrélées ni au débit, ni à la saison, alors que celles en silicate étaient corrélés au débit. La matière organique particulaire apportée par le fleuve était diluée dans une fraction minérale (3–4%) mais avait une bonne qualité nutritionnelle au début de la crue. La réponse marine à la crue la plus importante de l'année (octobre 2005) a été observée quotidiennement durant deux semaines à 350 m (8 m de profondeur) et 1.4 km de l'embouchure (station de suivi à long terme, 27 m de profondeur). La signature de la crue était en partie masquée au site le moins profond par la resuspension du sédiment causée par la houle. Par contre, à la station la plus profonde, trois phases ont pu être identifiées : (1) au début de la crue, les apports dissous du fleuve se diluent de façon conservative, conduisant à une augmentation des concentrations en azote inorganique dissous et en silicate, en parallèle d'une diminution de la salinité, (2) au cours du pic de turbidité, des phosphates sont relargués et (3) quand la colonne d'eau s'est éclaircie, la photosynthèse des diatomées commence à 3 m sous la surface, conduisant sept jours après le pic de la crue à un pic de 2 μg L^{-1} de chlorophylle *a*, qui a disparu trois jours plus tard. À cette date, les sels nutritifs et la salinité ont retrouvé leur niveau précédent la crue. Cette dynamique des sels nutritifs et de la chlorophylle au cours d'une crue éclair est en accord avec les données du suivi à long terme.

1 Introduction

Rivers channeled large amounts of materials of land-origin to coastal zones. In the north western Mediterranean Sea, which generally is considered oligotrophic (Lefèvre et al. 1997), the Rhône River has an outflow significant enough to influence the productivity of a large part of the Gulf of Lions (Blanc et al. 1969; Morel et al. 1990). In addition to the Rhône River, the Gulf of Lions also receives fresh water inputs from six other permanent rivers: the Orb, Hérault and Aude Rivers at its center and the Agly, Têt and Tech Rivers in its southwestern part (Fig. 1a). While the Rhône River discharge is partly regulated by Alpine dams, the other six permanent rivers along the

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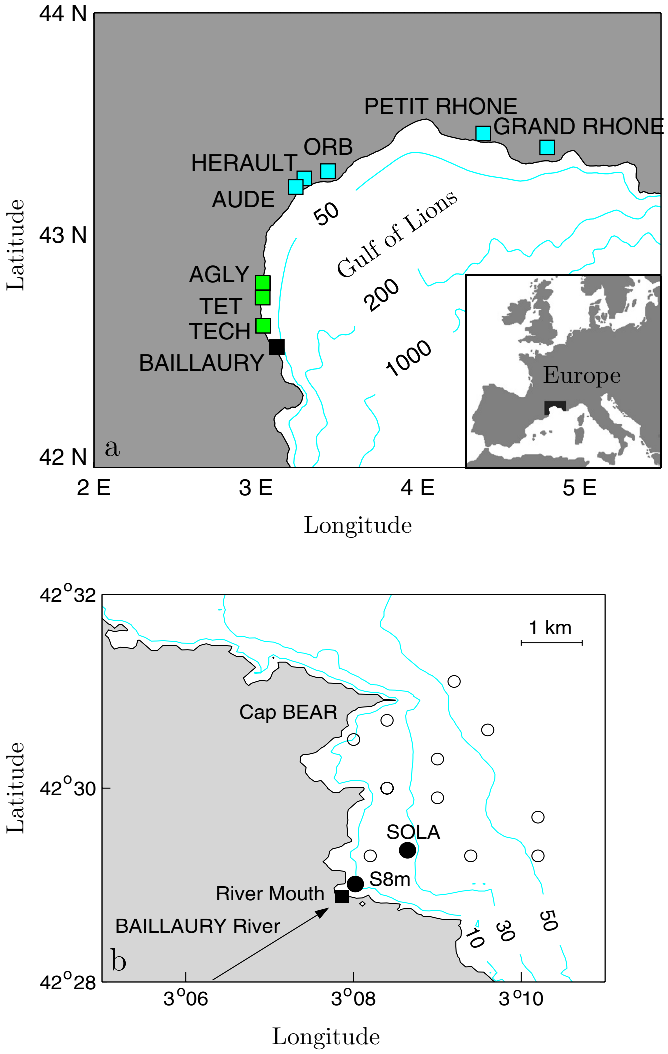

Fig. 1. (a) Bathymetric map of the Gulf of Lions. Gray squares: the locations of the permanent rivers. Black square: location of the intermittent Baillaury River at Banyuls-sur-Mer. (b) Detail of the coastal region around the Baillaury River. Filled square indicates the river mouth where discharge was measured and river samples were taken. Filled circles mark the offshore sampling stations, at 350 m (S8m, 8 m water depth) and 1.4 km (SOLA station, 27 m water depth) from the river mouth. Salinity, temperature and turbidity profiles were carried out on October 17, 19 and 20, 2005 at the thirteen stations marked by circles.

Gulf of Lions have a characteristic Mediterranean-type flow regime, that is, a very low median discharge punctuated by intense and brief flow events caused by mesoscale convective systems (Rigo and Llasat 2005). Freshwater discharge can be multiplied by a factor of 10 during such events which frequently affect the Mediterranean coast (Estrela et al. 2001).

An important characteristic of the hydrologic pathways along the Gulf of Lions coast are the many intermittent rivers with nearly null discharges except during flash-floods. Although their contribution to the ecosystem productivity is often not accounted for, these intermittent rivers can be considered as a paradigm for Mediterranean-type rivers with the ratio of flash-flood discharges to the mean annual water discharge reaching maximal values. Moreover, while the general hydrologic regime of Mediterranean-type rivers is well known (UNEP/MAP 2003), the detailed kinetics of flooding and any associated nutrient loads remain poorly documented (Tournoud et al. 2006).

In this paper, we document the impact of flash-flood events in a small embayment located in the south western end of the Gulf of Lions, at Banyuls-sur-Mer (France) (Fig. 1a). While earlier studies in this area focused on the primary production further offshore (deeper than 90 m, 15 km offshore), as stimulated by Atlantic waters, deep water upwelling or Rhône River inputs (Neveux et al. 1975; Coste et al. 1977), Jacques (1970) suggested the primary production could be stimulated by the conjunction of swells and/or local river inputs after monitoring a 50 m deep station (3 km offshore). In this latter study, neither dissolved inorganic nitrogen nor silicate concentrations were measured and local river inputs were only determined by salinity values. Since 1997, five nutrients and Chlorophyll *a* have been monitored weekly at a 27 m deep station in the Bay of Banyuls-sur-Mer (1.4 km offshore), together with salinity and temperature. A recent one year survey of the littoral phytoplankton community in the bay (Charles et al. 2005a) suggested that nutrient availability primarily depended on low salinity water intrusions and drove seasonal changes in the phytoplankton community structure. However, the dynamics of the nutrients during the low salinity intrusions could not be assessed with the sampling strategy used during this study. Indeed, the randomness of Mediterranean intermittent river floods and their brevity imply maintaining a long-term strategy for tracking the phenomenon along with having the flexibility to adopt a high frequency sampling strategy during peak discharges, irregardless of their timing.

We have focused on flash-flood events caused by intense localized rainfall in the small watershed of the Baillaury River, the main river draining into the Bay of Banyuls-sur-Mer. Baillaury River inputs were monitored with high frequency samplings during each flow event between October 2004 and October 2005. The impact of the quality and quantity of the river inputs on the dynamics of the nutrients and phytoplankton at sea are assessed. In particular, the impacts of the flow event and the swell resuspension were discriminated and the role of flash-floods in stimulating phytoplankton blooms is addressed based on the present study and long-term weekly monitoring data.

2 Materials and methods

2.1 Study site description: Hydrological, biochemical and meteorological monitoring

The Baillaury River, an intermittent river on the southwest of the Mediterranean coast of France (Fig. 1a), drains a steep watershed of 18 km^2 mainly covered by vineyards. No industrial activity or waste-water treatment plants are present in the Baillaury drainage basin. The river empties into the southern cove of the Bay of Banyuls-sur-Mer (Fig. 1b).

The Baillaury River is permanently monitored with automatic stream gauges (data available at the Hydrological data bank web site, French Ministry for Ecology and Sustainable Development; www.hydro.eaufrance.fr/accueil.html).

Long-term environmental monitoring is conducted in the bay at the Service d'Observation du Laboratoire Arago (SOLA) station (42°29.357′N / 3°8.645′E, 27 m water depth, 1.4 km offshore) since 1997 as part of the French national program for long-term monitoring of coastal areas (SOMLIT, www.domino.u-bordeaux.fr/somlit_national). The water column is sampled once a week at depths of 3 and 24 m, and 13 parameters (temperature, salinity, dissolved oxygen, pH, ammonia, nitrate, nitrite, phosphate, silicate, particulate organic carbon, particulate organic nitrogen, total suspended matter, and Chlorophyll a) are measured. Correlations between salinity and nutrients concentrations were computed.

Hourly averaged wind speed and direction and pressure were measured by Météo-France at Cap Béar, 3 km north of the SOLA station. Significant wave height and period were measured by using an RD Instruments® Acoustic Doppler Current Profiler located 35 km north of the SOLA station, in front of the Têt River mouth, at 27 m depth (Plate-forme d'Observation de l'Environnement Méditerranéen du Littoral Languedoc-Roussillon maintained by the Centre d'Étude, de Formation et de Recherche sur l'Environnement Marin).

2.2 Sampling strategies: the Baillaury River and the Bay of Banyuls-sur-Mer

The permanent stream gauging station is located 5 km upstream. Because the reliability of dissolved flux estimates depends on the reliability of the estimates for the corresponding water discharge, the instantaneous water discharge was also monitored at the river mouth during flow events. The sampling frequency depended on the discharge dynamics (hourly during discharge increase, every 4 hours during discharge decrease) and all discharge events between October 2004 and October 2005 were monitored. River discharge estimates (10% precision) were based on water depth and free surface velocity measurements at a measured topographic cross-section. Dissolved and particulate, organic and inorganic concentrations were measured in water samples taken with a sampling bucket every 6 to 8 hours at the water surface (when the river discharge was above 5 m^3 s^{-1}) in the center of the river mouth cross-section. Dissolved and particulate fluxes are computed by multiplying corresponding concentration by the river discharge. Since sampling was carried out at the water surface, particulate concentrations correspond to the finest fraction expected to remain in suspension at sea. Bed load transport was not measured. In February and October 2005, eight and thirteen water samples in duplicate were taken at the river mouth, respectively.

The marine response in the Bay of Banyuls-sur-Mer to the major flow event during the study period was sampled eight times, for ten days after the flow began. Water samples were taken offshore (Fig. 1b), at distances of 350 m (S8m, 8 m water depth) and 1.4 km (SOLA station, 27 m water depth) from the river mouth. At station S8m, samples were taken at the free surface with a sampling bucket while at the SOLA station, sea water was collected using a 12 L Niskin bottle at 3 m and 24 m below the water surface. Salinity, temperature and turbidity profiles were carried out using a Seabird® 9/11 plus CTD at eleven stations (Fig. 1b) before, during and after the main peak of the flow (October 17, 19 and 20).

2.3 Analytical methods

Both river and sea water samples were pre-filtered at 200 μm to eliminate large plant fragments and particles.

Dissolved nutrient contents were assessed from two 50 ml sea water samples. Samples were filtered on pre-combusted (450 °C) Whatman GF/F filters and used for inorganic nutrients and dissolved organic carbon (DOC). For the river samples, the expected high DOC concentrations permitted us to simplify the sampling protocol for DOC filtered on pre-rinsed Whatman GF/F filters only. We measured the maximum bias introduced by this technique as being 21 μmol L^{-1}, based on a measurement of the ratio of the total organic carbon (TOC) available from a filter to the filtered volume. Ammonia (NH_4^+) was immediately assayed according to Koroleff (1969). Samples for nitrate (NO_3^-), nitrite (NO_2^-), silicate ($Si(OH)_4^0$) and phosphate (PO_4^{3-}) determinations were frozen in plastic bottles (−20 °C). They were assayed using an automated colorimetric technique (Skalar® Auto-Analyser) according to standard methods (Wood et al. 1967; Benschneider and Robinson 1952; Mullin and Riley 1955; Murphy and Riley 1962). Two 5 ml samples for DOC were collected in pre-combusted glass tubes, acidified (5 drops of HCl, 1 N) and sealed with Teflon®-lined screw caps. DOC was analyzed with the high temperature catalytic oxidation technique (Cauwet 1994) on a Shimadzu® TOC 5000 analyser. Relative standard deviations estimated on duplicate for solutes was on average 5%, with a maximum value of 30% for phosphate when concentrations were low (data not shown).

Total suspended matter (TSM) mass was measured on duplicate samples filtered with pre-rinsed and pre-weighed Whatman GF/F filters (rinsed with distilled water, dried for 24 h at 60 °C and weighed to the nearest 10^{-4} g). After filtration and rinsing briefly with distilled water to remove dissolved salts, each sample was dried for 6 h at 60 °C and then re-weighed. Relative standard deviation estimated on duplicate for TSM was on average 10%, with a maximum value of 25% (data not shown). Grain size distribution of the TSM was assessed on 1 L water samples using a Malvern® Mastersizer 2000 laser particle size analyser. The pre-filtration step on the 200 μm mesh did not affect significantly the grain size distribution of TSM. The discarded fraction was mainly composed of leaves in our samples.

A second set of duplicate water samples were filtered on pre-combusted (450 °C) Whatman GF/F filters, dried for 6 h at 60 °C and then frozen (−20 °C) for particulate organic carbon and nitrogen (POC, PON). POC and PON were measured after acidification (HCl, 1 N) using a Perkin Elmer® 2400 CHN analyser. Relative standard deviation estimated on duplicate for POC and PON was on average 10%, with a maximum value of 30% for lowest POC and PON content (data not shown).

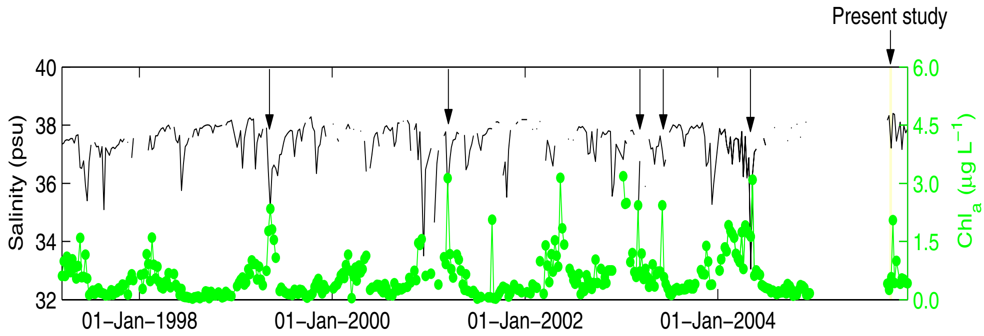

Fig. 2. Eight-years of weekly monitoring of Chl_a and salinity at the SOLA station at 3 m below water surface. Breaks indicate interruptions in data collection. Shaded area and arrow labeled present study is the intensive monitoring of the October 2005 flow event. Other five arrows indicate the Chlorophyll *a* peaks preceded by low salinity events.

The nutritional quality for marine benthic invertebrates of this organic matter was described by the ratio of total amino acids (THAA) to enzymatically hydrolysable amino acids (EHAA) contents. THAA and EHAA were measured when there was sufficient amount of TSM (more than 100 mg L^{-1}). A 1 L river water sample was centrifuged at 2952 g for fifteen minutes and the pelleted material was assayed for THAA and EHAA following the procedures detailed in Grémare et al. (2003a) which are based on those in Mayer et al. (1995).

Chlorophyll *a*, *b* and *c* and phaeophytin pigments were assayed spectrofluorometrically. Duplicate 100 ml water samples were filtered on pre-rinsed Whatman GF/F filters, and were immediately frozen in liquid nitrogen. Filters were ground with a freshly broken end of a glass rod and extracted in 90% acetone (final concentration) for 12 h at 4 °C. After shaking, samples were centrifuged at 4 °C at 800 RCF (Relative Centrifugal Field) and the fluorescence of the extracts was measured on a Perkin Elmer® LS 55 spectrofluorometer (Neveux and Lantoine 1993). Relative standard deviation estimated on duplicate for Chlorophyll *a* was on average 10%, with a maximum value of 50% (data not shown).

Bacteria cell counts were performed using a Becton Dickinson Fac Scan flow cytometer from duplicate 1 ml samples filtered at 50 μm, preserved with 2% neutralized formalin, stored in liquid nitrogen (Troussellier et al. 1995) and their nucleic acid stained with 0.5 ml of SYBR-II (Molecular Probes Inc.®, procedure described in Lebaron et al. 1998). Final concentration of the dye was 0.025% [v/v]. Stained cells were enumerated according to their side-angle-scattered light (SSC) and green cell fluorescence (FL1) collected through a 530 ± 30 nm bandpass filter. About a thousand events per second were counted with a threshold value set between 52 and 60 (depending on the sample quality) and SSC and FL1 voltage set to 375 *V* and 535 *V*, respectively. Relative standard deviation estimated on duplicate for bacteria was on average 10%, with a maximum value of 20% (data not shown).

At the SOLA station, DOC and bacteria concentrations are not measured in the context of the SOMLIT long-term monitoring program. Only Chlorophyll *a* and phaeophytin *a* are measured by fluorimetry, according to the techniques in Yentsch and Menzel (1963) and using the equations of Lorenzen (1966).

3 Results

3.1 Correlation of low salinity, nutrients and Chlorophyll *a* values at sea

Figure 2 shows eight years of salinity and Chlorophyll *a* concentrations measured weekly at the SOLA location, 3 m below the water surface. Low salinity episodes were often observed during the on-going long-term survey. At the SOLA station, the salinity correlates negatively with concentrations of dissolved inorganic nitrogen (DIN being the sum of nitrate, nitrite and ammonia, $R^2 = 0.64$) and silicate ($R^2 = 0.43$) measured weekly (p-value < 0.0001). The largest DIN (10.3 μmol L^{-1}) and silicate (19.1 μmol L^{-1}) concentrations were recorded when the salinity (33.05 psu) was lowest. In contrast, correlation between salinity and phosphate concentration was not significant (p-value = 0.1624).

The Chlorophyll *a* time series (Fig. 2) shows some short-term increases (up to 3.5 μg L^{-1}) super imposed on a strong seasonal variation marked by low values (below 0.5 μg L^{-1}) in summer. Five out of the fourteen Chlorophyll *a* peaks can be directly related to low salinity episodes recorded in the long-term survey (shown by arrows in Fig. 2).

One year monitoring of the Baillaury River discharge and dissolved loads during flash-flood events

Based on the Hydrologic Data Bank available for the Baillaury River (1967-2004), the Baillaury River had a few flash-flood events every year between October and May, while only one flood event was recorded during the last ten years between May and October. From October 2004 to October 2005, the Baillaury River flowed into the Bay of Banyuls-sur-Mer on only three occasions (all in 2005): February 8–9; September 8; October 13–20. These floods were all flash-floods, lasting less than seven days. The duration (less than one day) and the intensity (discharge was lower than 5 m^3 s^{-1}) of the September flood were less important compared to the other two flood events. In February, the river flowed to the bay for two days and water discharge peaked at 33 m^3 s^{-1}. During the seven days long October flow event, most of the water runoff occurred within the last three days. Water discharge peaked first on October 13 at 10 m^3 s^{-1}, and again, at 7 p.m. and 11 p.m.

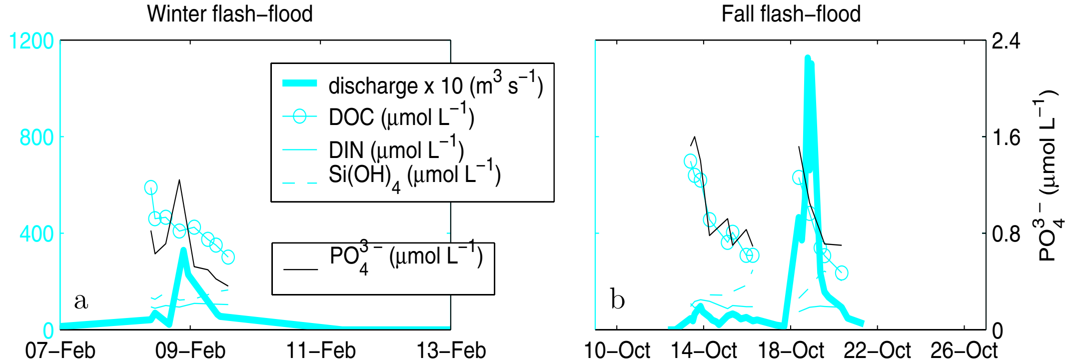

Fig. 3. Baillaury River discharge and concentrations of DOC, DIN, $Si(OH)_4^{\emptyset}$ and PO_4^{3-} during two of the three flow events (a) winter 2005 and (b) fall 2005. Gap in Fig. 3b represents discharge below 5 m^3 s^{-1} at the river mouth.

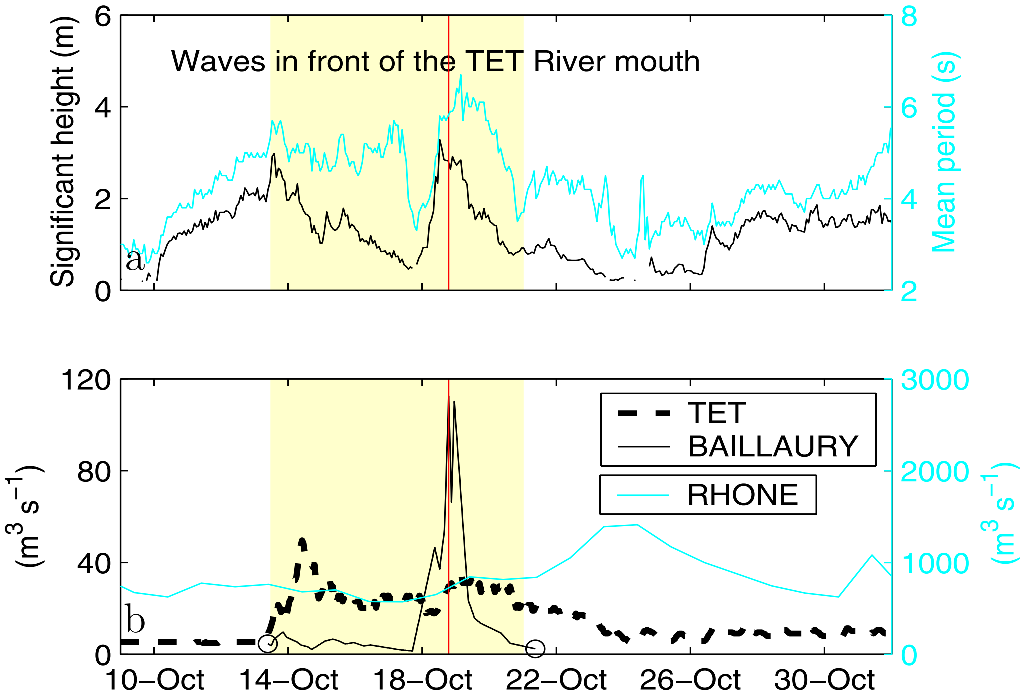

Fig. 4. Wave parameters (a) and local and regional rivers discharge (b) from October 9 to November 1, 2005. Shaded area indicates the October 2005 flow event duration and the vertical black line indicates the discharge peak at 7 p.m. on October 18.

on October 18 at 110 m^3 s^{-1}. The October 2005 flow event was the major flow event in terms of water discharge over the study period.

Figures 3a and b show concentrations of dissolved inorganic nutrients (silicate, phosphate and DIN) and DOC in the Baillaury River during these winter (February 8–9) and fall (October 13–20) flow events. During flow events, (1) the dilution pattern of most solutes was not correlated to the water discharge, except for silicate and (2) for each solute this pattern was similar from one event to the other (Figs. 3a and b). DIN concentrations remained nearly constant during the flow events. Phosphate and DOC concentrations had similar patterns and concentration ranges in Winter and Fall events. The Baillaury River solutes elementary ratios ranged from 60 to 120 for N / P and was around 0.5 for N / Si during both flow events.

3.2 Meteorological and hydrological conditions during October 2005 flow event

Three days before the October 2005 flow event began, a strong wind (20 m s^{-1}) was blowing from the SE while during the flash-flood and until October 27, the wind decreased with changing directions. A second strong SE wind episode lasted from October 27 until November 1. Both SE wind episodes were accompanied by moderate waves with a 2 m significant height (H_s) and mean period (T_m) of less than 6 s (Fig. 4a). The largest waves were recorded just before each Baillaury River pulse peak, on October 13 and 18. Significant height and mean period were quite similar on both days (3 and 3.3 m, and 5.6 and 5.8 s, respectively). The water discharge of nearby perennial rivers is represented by the Têt River (Fig. 4b). The Têt discharged increased abruptly on October 14 from 5 m^3 s^{-1} to 50 m^3 s^{-1} and then steadily decreased until October 25 to

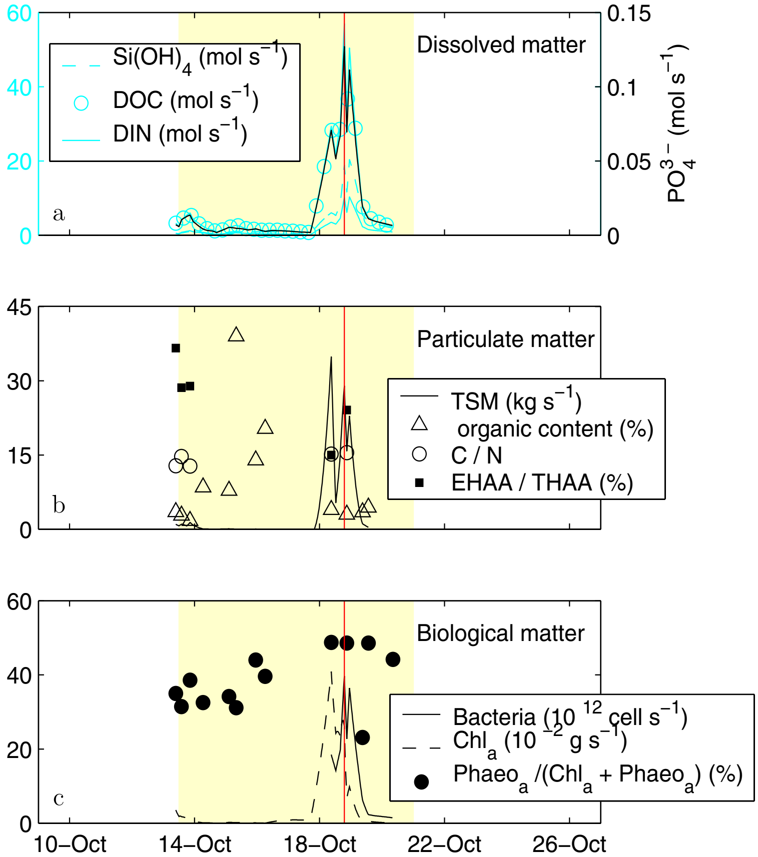

Fig. 5. Dissolved (a), particulate (b) and biological (c) Baillaury River flux. Shaded area indicates the October 2005 flow event duration and the vertical black line indicates the discharge peak at 7 p.m. on October 18.

return to a flow rate of 5 m^3 s^{-1}. On the regional scale, the Rhône River discharge was constant and below 1500 m^3 s^{-1} (average discharge between 1970–2005) over the same time period (Fig. 4b).

3.3 The river inputs during the October 2005 flood event

Figure 5 displays dissolved and suspended fluxes measured at the river mouth during the October 2005 flow event. More than 90% of the total runoff of 10^7 m^3 was discharged between October 18 and October 19. Instantaneous solute fluxes followed the river discharge dynamics (Fig. 5a). Table 1 summarizes the total inputs of dissolved and suspended components during October 2005 flow event. In particular, phosphate inputs were very low, around 1% the DIN.

Total suspended matter (TSM) fluxes reached maximum values at the beginning of the major flow pulse (October 18), the solid flux peak preceding the highest peaks of water discharge (Fig. 5b). During that time, median diameter of particles ranged from 20 to 33 μm, with 80% of the particles smaller than 70 μm. The organic content of the TSM varied inversely with TSM fluxes. The organic content increased from below 5% during the water discharge pulses up to values of at least 15% between the two discharge pulses (October 13 and 18). Similarly, the C/N ratio remained nearly constant at around 15 during the two discharge pulses and increased to 100 in between (data not shown), when the detection limit for PON (10 μg L^{-1}) was reached. In contrast, the ratios between enzymatically hydrolyzable and total hydrolyzable amino acids decreased from 0.37 to 0.15 between October 13 and 18. The relationship between fluxes of the TSM, biological fractions and the water discharge was not clear (Fig. 5c). The Chlorophyll *a* flux, like the TSM flux, preceded the discharge peak while bacteria load peak was synchronous with the discharge peak. The ratio of phaeophytin *a* to the sum of phaeophytin

Table 1. Total water, sediment and nutrients Baillaury River inputs for the October 2005 flow event. Particulate organic carbon (POC) and nitrogen (PON), silicate, phosphate, and dissolved inorganic nitrogen (DIN), and dissolved organic carbon (DOC).

	Total riverine input
Water	10^7 m^3
Sediment	1.93×10^6 kg
POC	80.0×10^5 mol
PON	5.1 10^5 mol
$Si(OH)_4^0$	17.3×10^5 mol
PO_4^{3-}	0.1×10^5 mol
DIN	8.9×10^5 mol
DOC	46.0×10^5 mol

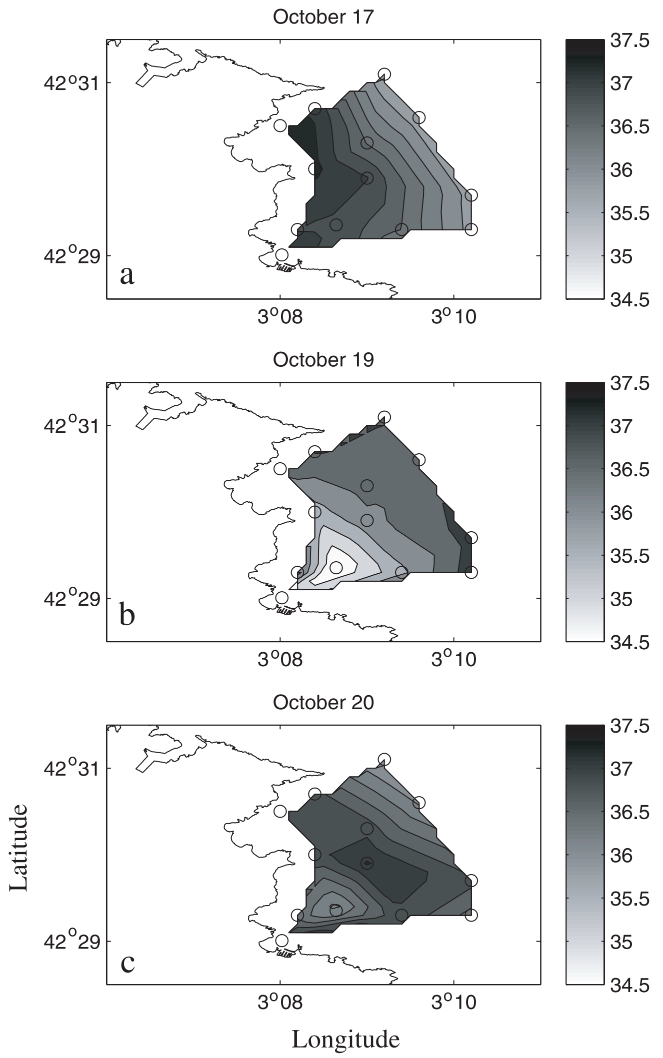

Fig. 6. Salinity maps at 1 m below free surface on the October 17, 19 and 20, 2005.

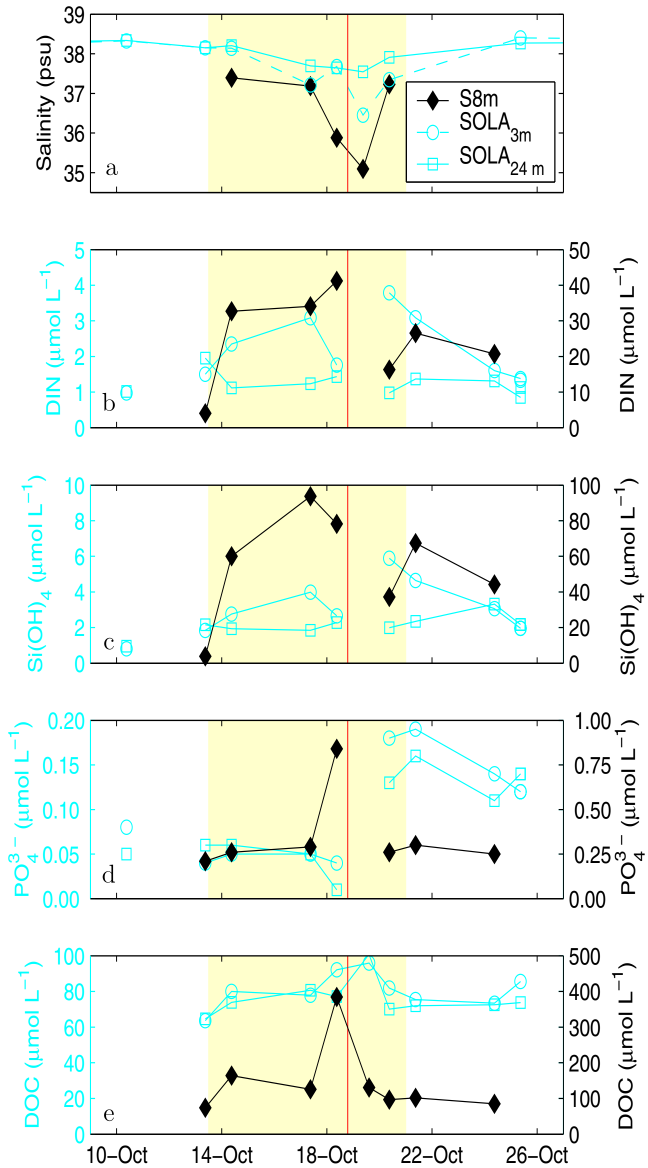

Fig. 7. Time evolution of salinity (a), dissolved inorganic nitrogen (b), silicate (c), phosphate (d), dissolved organic carbon (e) concentrations at the three sampling sites. Shaded area indicates the October 2005 flow event duration and the vertical black line indicates the discharge peak at 7 p.m. on October 18.

and Chlorophyll *a* remained high (close to 0.5) during the entire flow event. Within the TSM, the ratio between accessory pigments (Chlorophyll *b*/ Chlorophyll *c*) ranged between 3 and 10.

3.4 The marine response to the October 2005 flood event

Before the main river flush, surface salinity showed slight spatial variations, decreasing from 37 psu nearshore to 36 psu offshore (Fig. 6a). Salinity maps on October 19 further indicated that the river influence area covered only the southern part of the bay, with salinity falling to 35 and 34.4 psu, 1 m below the water surface at the S8m and SOLA stations, respectively, while marine values (37 psu) were recorded offshore (Fig. 6b). The salinity time evolution at the S8m and SOLA stations (Fig. 7a) indicated that water freshening reached its maximum on October 19 and was synchronous at both stations. After the river discharge stopped, low surface salinity values were recorded offshore (36 psu), separated from the nearshore low salinity area by a band of higher salinity (37 psu) values in the middle of the bay (Fig. 6c). At the SOLA station, salinities recovered their pre-flow level within 7 days following the major flow pulse (October 25).

DIN (Fig. 7b) at the S8m station increased dramatically (October 14) from the very beginning of the river flood. It remained high (30 μmol L^{-1}) during 4 days, with an increase to 45 μmol L^{-1} at the beginning of the major river flow pulse (October 18). Unfortunately, the accidental loss of October 19 samples meant the changes in DIN concentration immediately after the major river flow pulse are unknown. On October 20, DIN concentrations had dropped to around 15 μmol L^{-1}. DIN surface concentrations at the SOLA station, although ten times smaller, showed a similar time evolution to the S8m station data during the first phase of the river flow (until October 17). At the beginning of the major river flow pulse (October 18), DIN concentrations at the SOLA station decreased abruptly and then doubled by the day after the major river flow pulse. Thereafter, surface DIN concentrations decreased steadily to their pre-flow values within the ten days following the discharge peak. Changes in bottom water concentrations remained limited and values were low (1.5 μmol L^{-1}). Silicate concentrations (Fig. 7c) had the same time evolution as DIN concentrations.

Phosphate (Fig. 7d) at both the S8m and SOLA stations, whatever the depth, had no concentration increase during the first phase of the river flood. Values were very low, although five times larger at S8m (0.25 μmol L^{-1}) than at SOLA. Phosphate concentrations at S8m showed a strong increase to 0.95 μmol L^{-1} at the beginning of the major river flow pulse while it continue to decrease at SOLA. Two days after the major river flow pulse, phosphate concentrations had recovered their pre-flow value at S8m while they had been multiplied by four at SOLA for both sampling depths. At the SOLA station, phosphate concentrations, although decreasing slightly, remained high during five days and recovered their pre-flow level, ten days after the major river flow pulse (data not shown). Changes in DOC (Fig. 7e) concentration followed the same pattern as phosphate at the S8m station, with a maximum of 400 μmol L^{-1} at the beginning of the major river flow pulse (October 18). Concentrations decreased immediately after the flush to pre-flow concentration levels (100 μmol L^{-1}). At the SOLA station, the DOC concentration peaked one day later than at S8m and decreased again, faster at 24 m depth that at 3 m depth.

TSM peak (Fig. 8a) at the S8m station reached 200 mg L^{-1} and preceded the major river flow pulse. At SOLA, the TSM peak occurred one day later and the TSM concentrations were far lower than at S8m (less than 10 mg L^{-1}) with similar values both close to the bottom and at the surface. The median particle diameter of the TSM at S8m was 17 μm. A transitory deposit of sediment with diameter ranging from 10 to 30 μm was observed after the flow event (October 25) on the bottom at the SOLA station. TSM peaks correlated with minimal organic content (Fig. 8b), similar to observations in river. The C/N ratio values (>10) suggested that most of organic fraction in the TSM during the major river flow pulse did not have a characteristic marine phytoplankton signature (Fig 8c).

Chlorophyll *a* at the S8m station showed a marked concentration peak before the major river flow pulse and in phase with the TSM peak (Fig. 9a). The accessory pigments signature was the same as in the river with Chlorophyll *b* / Chlorophyll *c* ratio around 5 (data not shown) and the phaeopigments ratio suggests that this matter was highly degraded (Fig. 9b). At the SOLA station, Chlorophyll *a* concentration peaked at 2 μg L^{-1} in the surface water on October 25, seven days after the main river flush, and vanished within the three following days, coming down to 0.7–0.8 μg L^{-1} (Fig. 9a). At this time, the C/N ratio was 10, close to the Redfield ratio for marine phytoplankton, and the phaeopigments ratio had returned to values consistent with fresh organic matter five days after. Over this period, the accessory pigments signature at the SOLA station indicated dominance of chromophyte of marine origin with Chlorophyll *b* / Chlorophyll *c* lower than 1. Bacteria load peaked at 3.8 × 10^{8} cell L^{-1} at S8m on October 18, in phase with the Chlorophyll *a* peak of river origin. On October 20, bacteria load decreased to 1.5 × 10^{8} cell L^{-1} at S8m, the same value that was recorded at SOLA during the study (data not shown).

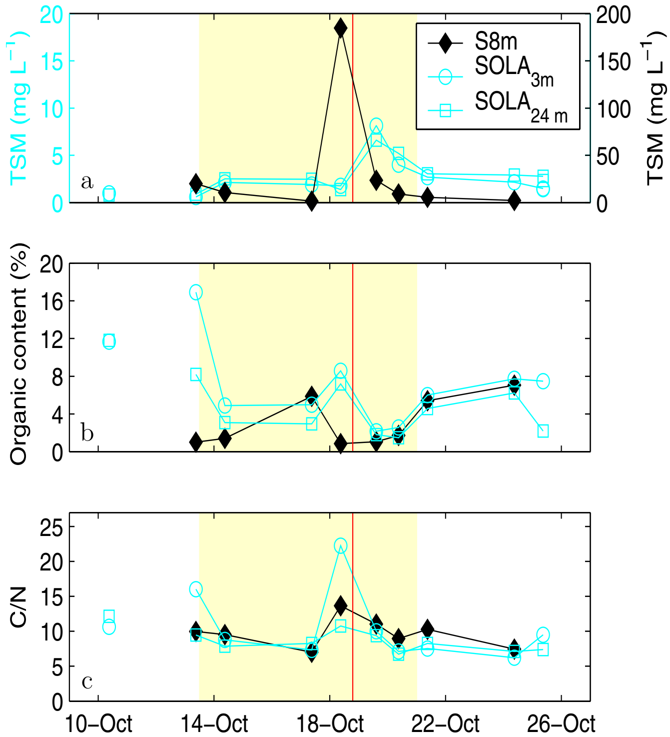

Fig. 8. Time evolution of total suspended matter (a), organic content (b) and C/N ratios (c) at the three sampling sites. Shaded area indicates the October 2005 flow event duration and the vertical black line indicates the discharge peak at 7 p.m. on October 18.

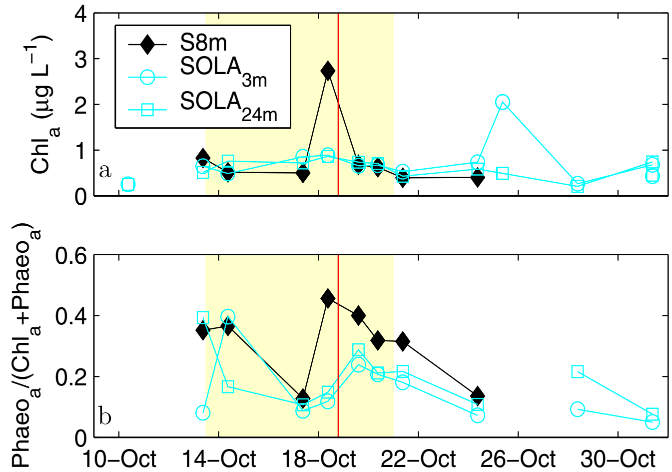

Fig. 9. Time evolution of chlorophyll *a* concentrations (a) and phaeophytin$_a$ / (phaeophytin$_a$+chlorophyll *a*) ratio (c) at the three sampling sites. Shaded area indicates the October 2005 flow event duration and the vertical black line indicates the discharge peak at 7 p.m. on October 18.

4 Discussion

4.1 The Baillaury River flow regime and the breakthrough of riverine inputs

The similarities between the solute concentrations during two river flash-floods in two different seasons suggested that even if intensities of the water runoffs differed, the processes involved in the solute transport were similar. Hence, the October event is considered representative of the general processes during a flash-flood of the Baillaury River. Moreover, sampling the river loads together with the river discharge allows the breakthrough of dissolved and particulate components transported in the Baillaury River to be estimated.

During flow, DIN concentrations showed only small changes with river discharge suggesting the source of DIN in the watershed was present in excess relative to the amount of soil washing. The drainage basin of the Baillaury River is the well-know Banyuls grape-growing region. Once a year, during February and March, the vineyard soils are treated with nitrogen and phosphorus additives. The measured patterns of DIN suggests that these elements may accumulate in the soil and be the source of the DIN in the river discharge. During flow events, phosphate and DOC concentrations behaved similarly (concentrations rose up and decreased with water discharge) which suggested that phosphate and DOC stocks were limited relative to the inorganic nitrogen in the watershed soils. In contrast to the other inorganic nutrients, silicate concentrations showed a dilution-like pattern, that is a lowered concentration as the discharge increased and vice-versa. Silicate is produced during soil diagenesis, which is a slow process relative to the time scale of a flash-flood.

As emphasized by the UNEP experts (UNEP/MAP 2003), the sampling frequency of typical water quality monitoring programs does not allow a reliable determination of sediment flux. The sampling frequency of this study described well the quantity and quality of changes in the TSM during the October 2005 flash-flood episode. However, our TSM load values underestimated the depth-averaged TSM load, because the heaviest fractions transported near the river bed were not monitored.

The organic content of the TSM (3–4%) decreased even further as the particle flux increased, suggesting dilution of the organic fraction by a suspended mineral fraction. These organic content values are comparable to those recorded at the SOLA station after sediment resuspension (Grémare et al. 1998; Charles et al. 2005b). The organic C/N ratio and the relative importance of the phaeophytin *a* contribution suggested that this matter is mostly plant detritus. EHAA/THAA ratio (values between 0.37 and 0.15) were within the range of what was previously described for the total marine suspended organic particles in the bay (Charles et al. 2005b). Based on this index, the organic matter at the start of the flow had a nutritional quality that was comparable to values measured on sedimenting marine matter after a phytoplankton bloom (Medernach et al. 2001). However, the POM nutritional quality decreased during the flow event.

In summary, the lack of significant correlation between discharge and most particulate or solute concentrations is consistent with other surveys of flash-floods in small Mediterranean catchments (Tournoud et al. 2003). The POM in the flash-flood waters in the Baillaury River was always highly diluted, but had a good nutritional quality at the start of the flow. The solute loads during flow events mainly consisted of DOC, silicate and DIN, while the phosphate load was very small.

4.2 Dilution or resuspension?

The salinity spatial distributions (Figs. 6a, b and c) within the bay before, during and after the Baillaury River major discharge peak indicated that the only Baillaury River flow event impacted the Bay of Banyuls-sur-Mer in October 2005. The main regional river, the Rhône River, flowed under or at its average level. The Têt River flushed before the Baillaury River, lowering the water salinity of coastal waters in the outer part of the Bay of Banyuls-sur-Mer but this less saline water did not enter the bay during our monitoring period. This situation is not a general rule for the Bay of Banyuls-sur-Mer, where the coastal circulation can lead to onshore-offshore exchanges or leave the bay isolated, depending on meteorological forcing (Guizien et al. 2006).

The seawater quality monitoring at the stations S8m and SOLA suggested that the Baillaury flow inputs were not the sole process causing changes in the concentrations of the measured dissolved and particulate components. At the S8m station, the increase of DIN and silicate concentrations preceded the salinity lowering (Figs. 7a, b and c). During the Baillaury flow event, moderate swells were also observed in the bay which may have interfered in the monitoring of the riverine inputs discharged in the bay. These swells could have caused sediment resuspension. A mobility parameter (Nielsen 1992), which indicates the ability of waves to move the bottom sediment, peaked at 30 at the SOLA station and 615 at the S8m station on October 13 and October 18, respectively. We conclude that no resuspension occurred at SOLA during the flow event while at S8m, the bottom sediment was intensively destabilized. Grémare et al. (2003b) had suggested that resuspension of bottom sediment caused by a strong winter storm in 1999 induced a temporary increase of both DIN and phosphate concentrations. Yet, lowered salinities (37 psu) were also recorded during this 1999 storm indicating simultaneous freshwater inputs. In this region, river flash-floods and swells often occur simultaneously, making the independent assessment of their effects difficult when based exclusively on observations.

In order to identify if the dilution process was dominant, we computed the ratio of the difference between the concentration at sea $C_M(t)$ and in the river $C_R(t)$ at a given time t to the difference between the initial concentration at sea $C_M(t_0)$ (before the flow event) and in the river $C_R(t)$ at time t for all solutes. Assuming homogeneous mixing over a given volume, for dilution only and conservative transport (no addition, no loss), this ratio should be the same for all solutes. In addition, for the river inputs, this ratio would also be equal to the ratio of $S(t)$, the sea salinity at time t, to $S(t_0)$, the initial sea salinity before the flood (time t_0):

$$\frac{S(t)}{S(t_0)} = \frac{C_M(t) - C_R(t)}{C_M(t_0) - C_R(t)}. \quad (1)$$

The assumption underlying this equation is expected to be valid outside areas of strong spatial gradients. Based on the

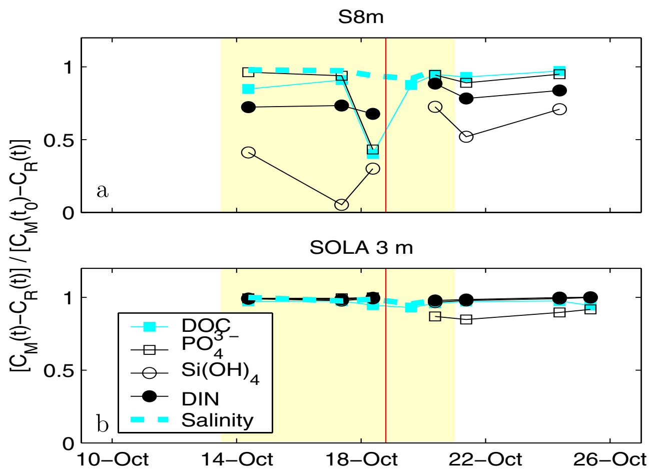

Fig. 10. *Time evolution of the dilution factor of dissolved nutrients (DIN, $Si(OH_4)^0$, PO_4^{3-}), dissolved organic carbon and salinity. Shaded area indicates the October 2005 flow event duration and the vertical black line indicates the discharge peak at 7 p.m. on October 18.*

surface salinity spatial distributions (Figs. 6a, b and c), this requirement was met at both the SOLA and S8m stations on October 17, 19 and 20. But on October 18, the S8m station was in the leading edge of the river plume (turbid surface limit position was 42°29.035′ N and 3°08.240′ E at 10 a.m. on October 18). Fig. 10 compares the time evolution of the sea salinity ratio to the time evolution of solute ratios for DOC, phosphate, silicate and DIN concentrations at the S8m and SOLA stations.

At S8m, it appears that while ratios for both phosphate and DOC followed the salinity ratio (except on October 18), DIN and silicate had larger concentrations at sea than only dilution of river solutes would estimate. The additional DIN and silicate are attributed to the effect of swells. The sedimentary nitrate reduction layer can be easily destabilized during a resuspension event releasing DIN to the overlying water column (Berner 1980). Similarly, resuspension causes the release of sediment pore water enriched in silicates by biogenic silica dissolution.

The explanation for the discrepancy at S8m on October 18 between phosphates or DOC ratios and salinity ratio is less clear. Although the hypothesis underlying equation (1) was not verified at that time at S8m, such large phosphate and DOC increases before the river water discharge peak are unlikely to result from dissolved river inputs only. Looking at the time evolution of TSM at S8m showed that the TSM was ten times larger on October 18 compared to October 13 while swells strength was similar. Hence, the origin of the TSM increase on October 18 is more likely to be the transfer of the large river particulate flux of October 18. This estimates the retardation between the river mouth and the S8m station as less than one day, and at two days for the SOLA station. Bacteria and degraded pigments increases were associated with this TSM increase at S8m. Hence, the simultaneous increases in phosphate and DOC concentrations at S8m on October 18 may be due to biogeochemical reactions (lytic process due an osmotic stress, bacterial degradation, desorption) within the river particulate matter transported to sea. Meanwhile, the second swell event on October 18 may also have further destabilized the bed sediment, releasing phosphate from deeper diagenetic layers.

At SOLA near the surface, the ratios for all solutes followed the salinity ratio during the flow event, except for DOC which exhibited a slight excess during the flow discharge peak, suggesting that transport of the river dissolved inputs within the low salinity surface water layer dominates over resuspension further offshore. The elementary ratios N/P and N/Si, 3 m below the free surface at SOLA, had values close to those in the river (around 50 and 0.7, respectively) consistent with the dominance of non-reactive transport during the flow event and with the good correlation obtained in the SOMLIT weekly monitoring between salinity decrease and DIN and silicate concentrations increases. However, the non significant correlation between salinity and phosphate concentration is not explained.

4.3 Phosphate release during reactive transport after the flow event

After the flow event, silicate, DIN and DOC recovered their pre-flash-flood values, while phosphate reached concentrations that cannot be explained by the dilution of dissolved river inputs. Indeed, while the N/Si ratio remained close to the river value until October 25, the N/P ratio dropped back to its pre-flash-flood marine value of 15 for 5 days (October 20 until October 25), due to the increase of phosphate. The transport of the October 18 phosphate peak from S8m to SOLA (Fig. 7d) was ruled out by the DOC concentrations time evolution at S8m and SOLA. Indeed, the DOC concentration peak was attenuated during its transport from S8m to SOLA the following day and DOC concentrations recovered their pre-flash-flood values on October 21 (Fig. 7e). Hence, the enhanced phosphate concentrations at the SOLA station until October 25 cannot be explained by only advection-diffusion of the S8m station peak on October 18, supporting the inferred reactive transport processes. We suggest that similar to the phosphate peak release at S8m on October 18, reactive processes at SOLA are linked to the enhanced turbidity at 3 m below the free surface between October 18 and 21 (Fig. 8). We suggest that either detritic material brought by the flood (plant fragments) may have stimulated a regenerating microbial activity at sea or desorption of adsorbed phosphorus may have occurred. In any case, this delayed phosphate appearance when water freshening is no longer detectable is consistent with the non significant correlation between salinity and phosphate in the SOMLIT weekly monitoring. The long-term data also suggest that a delayed phosphate appearance is characteristic of flash-flood events.

4.4 Flash-flood effects on the nearshore chlorophyll dynamics of the Bay of Banyuls-sur-Mer

The most striking feature recorded at sea following the river flash-flood was the abrupt increase of the Chlorophyll *a* concentration from 0.7 to 2 μg L^{-1} in surface water at the SOLA station. This increase occurred seven days after the river discharge peak. The time delay between the nutrients inputs and their utilization by primary producers results from the growth rate of the phytoplankton and may also be interfered with because of the turbidity generated by the river flow from October 18 until October 21. After October 21, the water column cleared, allowing photosynthetic activity. The Chlorophyll *a* peak on October 25 was accompanied by an increase in the N/Si ratio while both solute concentrations decreased, indicating silicate consumption and suggesting that the primary production resulted from diatom growth. Phytoplankton species however, were not sampled and identified during this study. On October 28, the Chlorophyll *a* peak had vanished and nutrients concentrations returned to their pre-flash-flood values on October 31. During October 2005, the weekly monitoring of salinity, nutrients and Chlorophyll *a* at the 90 m deep station, 10 km offshore the Bay of Banyuls-sur-Mer did not have any signature of the flash-flood event.

Fourteen sharp peaks of Chlorophyll *a* similar to the October 2005 peak were recorded during the eight years of long-term data, but only five of them can be directly related to low salinity events. In fact, the probability of missing low salinities associated with a flash-flood on a weekly sampling schedule is high (50% for the October 2005 flow event for example). Nonetheless, low salinity episodes are often observed in the SOMLIT long-term weekly monitoring in the Bay of Banyuls-sur-Mer and the good correlation between low salinity and high silicate concentration strongly supports a continental origin for the fresh water.

However, river inputs described only by low salinity in the SOMLIT long-term survey are not systematically followed by a Chlorophyll *a* peak (Fig. 2). Although some Chlorophyll *a* peaks may have been missed by the weekly monitoring (50% probability as well in October 2005), photosynthesis may also have been limited by other factors, including: (1) low nutrients inputs, (2) specific nutrients limitations, (3) low irradiance and (4) temperature limitations. Temperature limitations are not relevant in our NW Mediterranean example, since the temperature ranges from 12 °C to 24 °C (SOMLIT long-term data) are considered good for primary production (Jacques 1970). Both the long-term monitoring and the flash-flood data confirm DIN and silicate enrichment in nearshore waters. A limitation in phosphates could inhibit photosynthesis. However, we suggested that although dissolved phosphate is not directly transported in the flash-flood waters, it can be released at sea, through reactive processes of the suspended materials. Photosynthesis after river inputs may therefore be limited by low irradiance caused by high turbidity associated with the suspended matter in the river discharge waters and bottom sediment resuspension by swell activity. Anyway, the brevity of the river discharge and of the eventual primary production response by the ecosystem, together with specific limitations by turbidity conditions suggests that observing the primary production stimulation by local rivers requires a dedicated high frequency nearshore monitoring program.

5 Conclusion

The adaptative sampling strategy used in this study of the Baillaury River described well the discharge, nutrients and particulate loads during three flash-floods events between October 2004 and October 2005. Neither dissolved nor particulate loads correlated with the river discharge, similar to other small intermittent Mediterranean rivers (Tournoud et al. 2003). Relating flash-floods to a marine ecosystem response requires at least a daily sampling frequency during the event, as for example the October 2005 flow event signature was absent in the regular monitoring data of the long-term SOMLIT program (SOLA station).

However, the marine response to flow events in the NW Mediterranean remains difficult to study from observations only since resuspension caused by swells can interfere. Fortunately, during this study, swells were moderate and therefore mainly affected the nearshore area, allowing the offshore effect of the flood to be observed. The river flash-flood stimulated the phytoplanktonic productivity, leading to a transitory and localized Chlorophyll *a* peak. We suggest that direct dissolved inputs of nitrate and silicate, combined with phosphate release after reactive processes within the TSM inputs lead to the observed bloom seven days after the river discharge peaked. Combining these observations with numerical modeling will provide a description of the relevant forcing and discriminate dominant processes. A scenario will be tested in future modeling work of a dedicated flash-flood ecosystem functioning model for the Bay of Banyuls-sur-Mer.

Although the impact of the river flash-flood on the marine benthic ecosystem was not monitored during this study, the quantity and quality of the particulate matter in the river and at sea suggests that the immediate effect of the flash-flood inputs on nearshore benthic ecosystem remain limited in space and are likely to be inhibitory (diluted organic matter, decreasing nutritional value during the flow event). Further offshore however, post-bloom sedimentation may benefit to the benthic ecosystems. Thus, future observations of flash-floods impacts should consider the coupling between benthic and pelagic ecosystems. Finally, a complete study should include contaminant transport.

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