

Geochemical and hydrodynamic constraints on the distribution of trace metal concentrations in the lagoon of Nouméa, New Caledonia

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Abstract

Seawater samples were collected in the lagoon of Nouméa (southwest New Caledonia) along two transects from eutrophic coastal bays to the oligotrophic barrier reef. Land-based emissions to the lagoon were measured with dissolved and particulate concentrations of chromium (Cr) and nickel (Ni), used as tracers of both terrigenous and industrial (Ni ore treatment) activities, as well as dissolved and particulate concentrations of zinc (Zn), used as a tracer of urban effluents. The spatial variability of metal concentrations was related to geochemical and hydrodynamic conditions, i.e., respectively: (1) natural and anthropogenic emission sources, and chemical processes occurring in the water column; and (2) water residence times. The parameter used to describe the residence time of water masses was the local e-flushing time, i.e. the time required for a tracer mass contained within a given station to be reduced by a factor $1/e$. High metal concentrations were found in coastal areas (up to 9000 ng dissolved Ni L⁻¹), and steeply decreased with distance from the coast (down to 101 ng dissolved Ni L⁻¹ near the barrier reef) to reach levels similar to those found in remote Pacific waters, suggesting a rapid renewal of waters close to the barrier. Distributions of metals in the lagoon are controlled upstream by land-based emission sources and later chemical processes. Then hydrodynamics constrain metal distributions, as shown by the observed relationship between local e-flushing times and the spatial variability of metal concentrations. In addition, a change in the direction of prevailing winds yielded a decrease of dissolved metal concentrations at the same site by a factor of 2.5 (Cr and Ni) and 2.9 (Zn). It is suggested that the residence time is a key parameter in the control of elemental concentrations in the lagoon waters, as much as land-based emission sources.

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1. Introduction

Soils in southern New Caledonia are developed on ultramafic rocks (peridotites) that degrade into residues (laterite and saprolite layers) highly enriched by weathering in nickel (Ni) and chromium (Cr), either adsorbed onto iron oxides or incorporated into their mineral lattice (Becquer et al., 2001; Quantin et al., 2002). These enriched layers are subjected to intense mining extraction and strong soil erosion due to

tropical rainfall. The combination of these processes results in the potential mobilisation of high amounts of terrigenous fine particles, likely to affect coastal waters by aeolian and river transports.

Consequently, coastal waters are presumably enriched in trace metals, mainly cobalt, iron, Ni and Cr (Bustamante et al., 2003), which may affect the coral reef food webs (Monniot et al., 1994). The release of dissolved metals from land-based emission sources may be a significant process for coastal waters in the lagoon, particularly for the case of Ni, owing to the mineral input from New Caledonian soils (Ambatsian et al., 1997; Fernandez et al., 2006). In addition, coastal areas are subjected to anthropogenic influences in the vicinity of

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the city of Nouméa: industrial activities, chiefly linked to the treatment of lateritic and saprolitic Ni ores (Doniambo factory, Nouméa), are superimposed upon wastewater and urban effluents.

Because Ni mining plays a significant and increasing economic role in New Caledonia, a scientific program has been devoted since 1996 to the impact of its anthropogenic and terrigenous loads on the 2000 km² southwest lagoon around Nouméa, where about half of the island population lives. Several researches have been conducted on the functioning of this lagoon, including hydrodynamics and suspended matter transport modelling (Douillet et al., 2001; Ouillon et al., 2004), biogeochemical cycling modelling (Pinazo et al., 2004), hydrological variability (Ouillon et al., 2005) and geochemical analysis of the sediment (Fernandez et al., 2006). Global and local residence times of water masses were also calculated for the lagoon so as to bring additional tools in the analysis of its biological functioning (Jouon et al., 2006; Mari et al., 2007; Torréton et al., 2007).

In that context, this paper presents a complementary study devoted to the measurements of metal concentrations in the water column from the coast to the barrier reef and to their analysis against the magnitude of the incoming metal inputs and the physical forcing of the water circulation (wind, tide, residence time).

2. Study area

2.1. Characteristics of the lagoon

The lagoon of New Caledonia, located 1500 km east of Australia, covers a total area of 23,400 km² (Fig. 1). The New Caledonia Reef is the second widest tropical reef system in the world after the Australian Great Barrier Reef. The southwest lagoon of New Caledonia, around Nouméa, is a nearly enclosed, relatively shallow site (on average 17.5 m deep), surrounded by oligotrophic oceanic water and connected to the ocean by narrow passes through the reef.

Two major factors control circulation in the southwest lagoon of New Caledonia: tide and wind (Douillet, 1998). The most frequently encountered wind regime is the southeasterly trade wind (average speed 8 m s⁻¹, direction 110°, more than 2/3 of the yearly wind occurrence). A description of the resulting current regime is given in Douillet et al. (2001). Under trade wind forcing, swell penetration into the lagoon is negligible, and wind–wave growth is limited by a fetch of a few tens of kilometres.

2.2. Adjacent land use

The near-shore environment is subjected to terrestrial inputs and, especially in the bays around the city of Nouméa, to both industrial and urban inputs that increase general productivity in these areas. Industrial emission sources (treatment of Ni ores) are likely to introduce Cr and Ni in the lagoon waters. Urban emission sources presumably give off amounts of zinc (Zn), which is an ubiquitous urban tracer (Migon, 2005).

Grande Rade (from station D01) is overall characterised by urban and industrial activities (Doniambo factory). Sainte-Marie Bay (from station N04) is mostly affected by wastewater and urban effluents, but not under the influence of industrial inputs (Mari et al., 2007). Its main terrigenous Cr and Ni incoming fluxes are due to the Coulée River loads, owing to Cr and Ni ore deposits comprised in its watershed (Fernandez et al., 2006).

3. Methods

3.1. Sampling

Seawater samples (2.5 L) were collected using a Teflon pump along two transects from the coast to the barrier reef in the southwest lagoon of New Caledonia (Fig. 1). Samples were collected at 5 m depth at six stations, along the two transects, during two sampling campaigns: 22 November 2004 (D01, D08, D22, M05, M10 and M41, from Grande Rade to the outer edge of the coral reef) and 29 November 2004 (N04, N12, N33, M33, M10 and M41, from Sainte-Marie Bay to the outer edge of the coral reef). Eutrophication in the bay of Grande Rade is mainly of industrial origin, due to the close proximity of a large Ni smelt, while in the bay of Sainte-Marie, eutrophication is mostly due to wastewater outfalls from the Sainte-Marie area (i.e., urban origin). Conductivity, Temperature and Depth (CTD) profiles were recorded using a SeaBird SBE 19 probe at each sampling station.

Hydrological and chemical characteristics during the two sampling campaigns are summarised in Table 1.

3.2. Metal analysis

Seawater samples were filtered on cellulose acetate membranes (Sartorius 11107-025 N, diameter 25 mm, porosity 0.2 µm). Dissolved and particulate concentrations of Cr, Ni and Zn were measured. Exchangeable metallic forms in the dissolved phase were fixed on Chelex (Bio-Rad) resins in mini-chromatographic columns (Bio-Rad). The chemical forms fixed on the resin were eluted with 10 mL HNO₃ 2.5 M and stored in Teflon PFA bottles. The quality of the exchange on the resin was checked with 10 mL more of the same acidic solution (resin blank). Dissolved samples were UV-irradiated according to the protocol proposed by Sander and Koschinsky (2000) to turn all Cr in its oxidised form from Cr(VI): 50 µL H₂O₂ and 20 µL HCl were added to 10 mL of sample to increase the oxidation potential prior to the irradiation. The irradiation was carried out during 1 h at 85 °C using a 707 UV-Digester (Metrohm). This procedure guaranteed that all H₂O₂, likely to interfere with the voltammetric analysis of Cr, was removed. The particulate phase was mineralised as follows: the organic matrix was destroyed with an oxidizing attack (HNO₃), and mineral aluminosilicate matrixes were destroyed with HF. The sample was freeze-dried in 7 mL Teflon flasks, used for the mineralisation. The mineralisation protocol was:

- (1) Nine hundred microlitres HNO₃ 65% were added to each flask. These flasks were sealed and put into larger Teflon

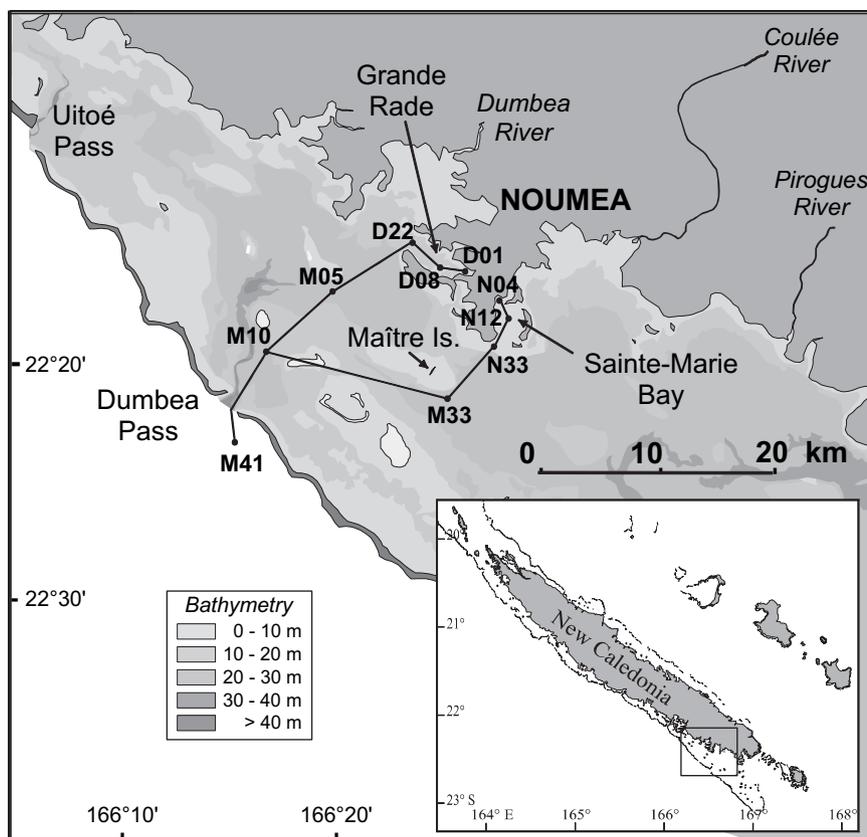


Fig. 1. Sampling stations in the southwest lagoon of New Caledonia.

bottles (60 ml) that act as expansion cells, overcome acidic evaporation by leaks and help to prevent contamination. This apparatus was left 2–3 h in an oven at 60 °C, and then 3–4 h at 150 °C, after which bottles and flasks were brought to room temperature and left open under laminar flow hood until a black dry residue remained.

- (2) Two hundred microlitres HNO₃ 65% and 200 µL HF 40% were added to the remainder. The flasks and bottles were closed and put in an oven 2–3 h at 60 °C, and then 3–4 h at 150 °C, prior to open evaporation at room temperature under laminar flow hood, until a white dry residue was obtained. This residue was ultrasonically dissolved in 1 mL HNO₃ 1 N. The samples were then made up with Milli-Q water (resistivity: 18 MΩ cm) to 10 mL.

It was assumed that Cr(III) in particulate samples was oxidised during the mineralisation procedure, due to the use of HNO₃. Blanks for voltammetric analysis were irradiated following the same protocol. Zn samples were analysed by differential pulse anodic stripping voltammetry with a hanging mercury drop electrode. The instrumental sensitivity (i.e., smallest legible signal, arbitrarily evaluated to 1 nm) was 20 ng L⁻¹, using a standard electrolysis time of 5 min. Nickel was analysed by adsorptive cathodic stripping voltammetry. Nickel measurements were performed by adding a complexing agent (dimethylglyoxime 5 × 10⁻⁴ M) and buffering at pH 9.16. The limit of detection was 3 ng L⁻¹, with a standard electrolysis time of 5 min. This analytical technique has

been described in detail by Van den Berg (1986). Chromium was analysed by adsorptive cathodic stripping voltammetry. Chromium measurements were performed by adding a complexing agent (diethylenetriaminepentaacetic acid 0.015 M) and buffering at pH 5.2. This analytical technique has been described in detail by Sander and Koschinsky (2000).

For each metal, three standard additions were used to determine the metal concentrations. Measurements were performed with an EG&G Princeton Applied Research 264A polarographic analyser in conjunction with a 303A static Hg drop electrode. A medium Hg drop electrode was used as the working electrode (1.6 mm² surface area). The auxiliary electrode was a Pt wire and the Ag/AgCl reference electrode was filled with a saturated solution of ultrapure KCl. The analytical procedure was checked using open ocean seawater reference material (NASS-4) provided by the National Research Council, Canada. The results were within the quoted standard deviation intervals. Reagent/manipulation blanks were always under the detection limits. Measurement reproducibility was always <5%. The preparatory manipulations of samples and voltammetric measurements were carried out in Class 100 laminar airflow benches located in a clean room. All reagents were provided by Merck (Darmstadt, Germany), quality Suprapur.

3.3. Dynamical and meteorological parameters

In order to gain understanding of the interaction between hydrodynamics and geochemistry, one must first identify the

Table 1
Hydrological and chemical characteristics during the two sampling campaigns. Local e-flushing times (LeFT) are given by Jouon et al. (2006)

Date	Stations	Temperature (°C)	Salinity	Tide regime	Wind speed (m s ⁻¹)	Wind direction (Degree)	Rain the week prior to sampling (mm)	LeFT (days)
22/11/2004: Between 09:00 and 10:00 AM	D01	24.8	36.1	Low tide at 10:20 AM (0.65 m), high tide at 04:29 AM (1.20 m)	8.4 ± 1.1	113.8 ± 11.3	2.2	46.9
	D08	25.1	36.1					40.8
	D22	24.6	36.0					31.0
	M05	24.1	35.8					5.6
	M10	24.1	35.8					0.4
	M41	23.6	35.7					0.0
29/11/2004: Between 09:00 and 10:00 AM	N04	24.7	36.1	High tide at 09:38 AM (1.55 m), low tide at 03:46 PM (0.70 m)	9.9 ± 0.2	118.8 ± 3.4	7.8	17.1
	N12	24.7	36.2					12.9
	N33	24.6	36.0					12.4
	M33	24.0	35.8					0.5
	M10	23.6	35.8					0.4
	M41	23.0	35.7					0.0

hydrodynamic processes likely to affect the spatio-temporal distribution of elemental concentrations in the lagoon, and define parameters to quantify these processes.

The velocity field is relevant when the same water mass is studied at different stages from a Lagrangian point of view. In that case, and in association with hydrological measurements, it can be used to study the dilution factor of dissolved elements or the transport of suspended matter (e.g., Naudin et al., 1997). The velocity field is less relevant to compare different water masses. In that case, parameters deriving from hydrodynamics enable to analyse the kinetics of biological reagents or the moving of organisms with respect to the water masses (see a review in Jouon et al., 2006).

Several global and local transport time scales have been defined (e.g., Deleersnijder et al., 2001; Monsen et al., 2002). Each of these hydrodynamic parameters is associated to a unique calculation method which involves either the computation of input and output fluxes, the computation of the transport equation for a dissolved tracer, or the computation of series of trajectories. In their paper, Jouon et al. (2006) have compared different methods and listed the names of the associated time scale parameters found in the literature.

In the present work, the concentrations of dissolved and particulate metals are analysed against a typical scale for the renewal of a given water column, namely the local e-flushing time, expressed in days, as defined by Jouon et al. (2006). This parameter indicates the time required for a tracer mass contained within a given station (control volume) to be reduced by a factor $1/e$. It is variously called in the literature “flushing time” (Monsen et al., 2002), “residence time” (Shen and Haas, 2004; Wang et al., 2004) or “e-folding time” (Delhez et al., 2004). The local e-flushing time was calculated for all the sampling stations from a 3D hydrodynamic model adapted to the topographic, tidal and meteorological constraints of the Nouméa lagoon (Jouon et al., 2006). Fig. 2 presents the resulting field of the local e-flushing times calculated for trade wind rate (constant southeastern wind 110°, 8 m s⁻¹) and a periodic tide evolution resulting from M2 and S2 harmonics that are the

major tidal constituents within the lagoon (Douillet, 1998). This modelling exercise provides estimates of the renewal rates of the water masses in the lagoon (i.e., local e-flushing times), which can be regarded as mean values, considering that the initial parameters used in the model are annual averages of wind conditions.

Wind speed and direction were continuously recorded at a meteorological station located on the Maître Island, situated between the two transects, close to the sampling station M33 (see location in Fig. 1, wind data in Fig. 3). Fig. 3 and Table 1 show that the wind conditions that prevailed during the two sampling days were trade wind conditions close to the average situation. The local e-flushing times presented in Fig. 2 are thus supposed applicable to the two sampling campaigns.

4. Results and discussion

4.1. Spatial distributions

Concentrations of dissolved and particulate Ni, Cr and Zn at all sampling stations are presented in Table 2. Two major features appear as following: (1) metal concentrations are significantly different along the transect D01–M10 and along the transect N04–M10; and (2) metal concentrations steeply decrease from the bays to the barrier reef.

The variation of metal concentrations along the two transects is shown in Fig. 4. The concentrations of dissolved metals strongly decrease from the coastal stations to the barrier reef: although the lagoon stretches over only 20 km from the bays to the barrier reef, concentrations decrease as steeply as, e.g., from 9000 down to 101 ng Ni L⁻¹ from D01 to M41. The steepest decrease is found for Ni. The decrease of particulate metal concentrations exhibits the same trend, although it is less marked than that of the dissolved phase. Similar patterns have been already observed in the superficial sediment of the lagoon, with a more important decrease from the bays to the barrier reef for Ni, compared, for example, with Cr (Ambatsian et al., 1997). Dissolved and particulate concentrations of Ni are

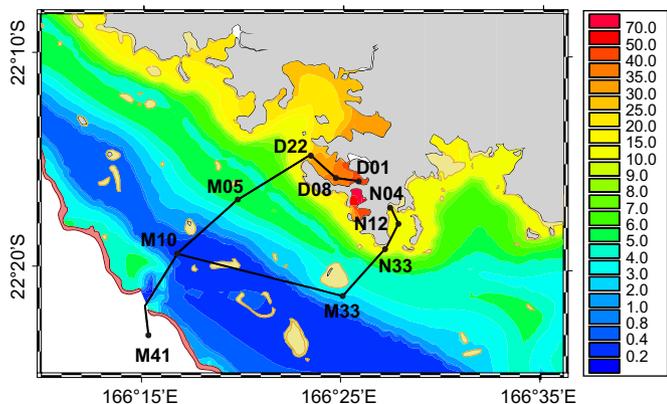


Fig. 2. Local e-flushing time distribution around Nouméa. The control volume considered for calculation is the southwest lagoon of New Caledonia as defined in Jouon et al. (2006). Local e-flushing times are expressed in days.

higher than those of Cr or Zn by a factor ranging between 2 and 45, approximately.

Dissolved Cr and Ni concentrations measured close to the barrier reef (e.g., at stations M10 and M41) are comparable to those encountered in the surface waters of the Pacific Ocean (Table 3), i.e. among the lowest values reported in the Southern Hemisphere (Apte et al., 1998).

4.2. Natural and anthropogenic emission sources

Concentrations of dissolved Ni (and, to a lesser extent, of Cr) are significantly higher in Grande Rade, under the influence of the Doniambo factory, than in Sainte-Marie Bay, where urban influences prevail (9000 ng Ni and 587 ng Cr L⁻¹ at D01 vs 1800 ng Ni and 142 ng Cr L⁻¹ at N04), while Zn exhibits very similar dissolved concentrations at the two sites D01 and N04: 538 and 522 ng L⁻¹, respectively (Table 2). Zinc is greatly enriched in urban runoff, compared with other metals transported by the sewerage network (Angelidis, 1995; Wiesner et al., 1998). For the specific case of New Caledonia, another significant source of Zn may be the weathering of Zn sheet roofs by tropical rainfall (J.M. Fernandez, personal communication). This probably explains that the Zn inputs to the two bays are very similar, contrarily to Cr and Ni.

Dissolved Zn concentrations in the barrier reef area are significantly higher than those found in remote Pacific areas (Table 2). This metal is mainly of urban origin, among which a great part is linked to motor vehicle use, owing to tyre wear (Wiesner et al., 1998; Migon, 2005) and, therefore, it is spread over the lagoon waters, to a large extent, by the atmospheric transport route. It is hypothesized that most of Zn loads are emitted from the southward region of Nouméa, relative to the transects, and atmospherically transported and spread over the lagoon. Aeolian inputs of Cr and Ni are relatively less important because under the influence of prevailing winds, plumes from the Dumbea factory do not significantly affect the transect area, which is only subjected to terrigenous aeolian inputs, therefore.

4.3. Geochemical processes

The difference between D01 (industrial) and N04 (urban) is even higher for particulate Ni concentrations (5818 and 505 ng L⁻¹, respectively, i.e. a factor of ~11.5). Nickel is significantly released from the sediment to the lagoon waters and then does not coprecipitates with ambient calcium carbonate (CaCO₃), the remaining fraction of particulate Ni being associated with iron oxides (Ambatsian et al., 1997). It is believed that the availability of iron oxides is significantly higher in the industrial loads of Grande Rade, compared with the natural inputs of the Coulée River watershed. As a result, the trapping of Ni onto iron oxides might be less efficient in Sainte-Marie Bay. Conversely, particulate Cr concentrations are slightly lower in D01 than in N04 (130 and 186 ng L⁻¹, respectively, i.e. a factor of ~0.7), despite supposedly higher emission sources of total Cr in D01. This might be due to sorption processes. Chromium is known to adsorb onto various surfaces, such as:

- (1) Iron oxides and hydroxides (Eary and Rai, 1987; Sander and Koschinsky, 2000).
- (2) Organic matter. The reduced form of Cr, Cr(III), commonly found in marine environments together with the oxidised species Cr(VI), is believed to significantly adsorb onto particulate organic matter, which process may be

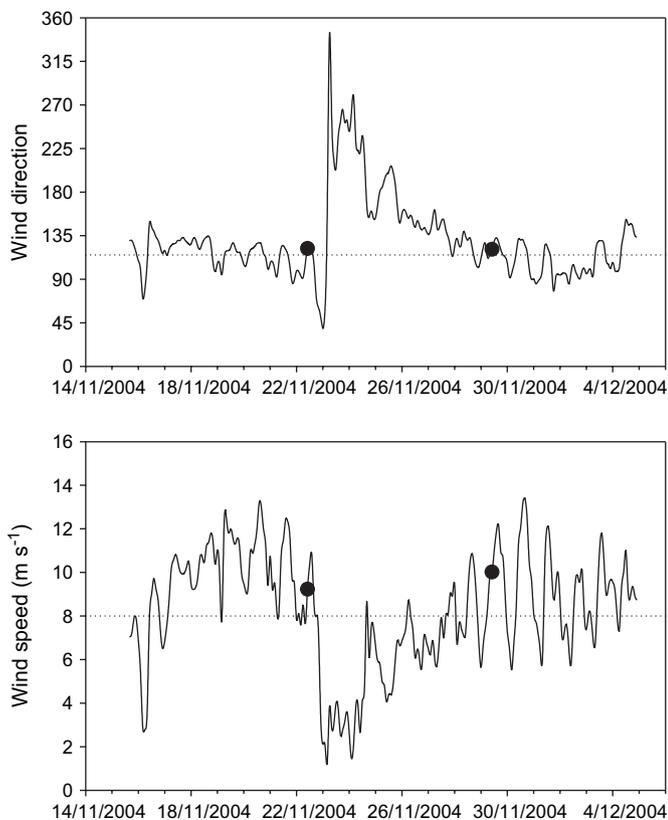


Fig. 3. Wind direction (a) and speed (b) at Maître Island during the field campaigns. Wind direction is expressed in degrees and a 0° wind comes from north.

Table 2
Dissolved and particulate concentrations of Ni, Cr and Zn at all stations, in ng L⁻¹

Sampling site	Ni		Cr		Zn	
	Dissolved	Particulate	Dissolved	Particulate	Dissolved	Particulate
M41 – 22/11/04	101		163.0	4.3		
M41 – 29/11/04	174	14.2	69.3	27.9	117.0	15.9
M10 – 22/11/04	651	50.7	166.0	4.5	370.0	33.0
M10 – 29/11/04	260	37.3	69.0	29.6	127.0	19.3
M05	470	42.0	113.5	2.2	454	95.0
D22	1800	267.4	317.0	6.0	176	64.3
D08	4000	2106.5	520.0	26.3	715	285.4
D01	9000	5818.0	587.0	129.7	538	368.0
M33	442	51.7	115.6	47.0	176	27.0
N33	755	53.8	114.0	108.0	51	34.8
N12	1300	616.1	258.0	147.6	310	149.0
N04	1800	504.5	142.0	185.8	522	226.0

enhanced in seawater because of alkaline pH (Kerndorff and Schnitzer, 1980; Poulton et al., 1988). On the one hand, in more or less oxidised surface waters, at seawater pH, the main Cr species are oxyanions in the Cr(VI) form such as CrO_4^{2-} , HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ (Sadiq, 1992) and the concentration of Cr(III) is very low. On the other hand, the oxidation of Cr(III) to Cr(VI) is very slow in natural marine environments, and Cr(III) is involved in the faster sorption processes (Richard and Bourg, 1991). Significant amounts of Cr(III) have been found in hydrothermal plumes in Pacific waters (North Fiji Basin), supposedly stabilised by organic complexation (Sander and Koschinsky, 2000), and in open surface waters (Van den Berg et al., 1994).

- (3) CaCO_3 surfaces. However, it is a common consensus that such surfaces play a minor role in the adsorption of Cr, particularly at seawater pH (Poulton et al., 1988; Zachara et al., 1988).

Taking into account the diversity of sorption processes for Cr, as well as the numerous factors that control these processes, the present data set does not enable to explain the different behaviours of particulate Cr in Grande Rade and Sainte-Marie Bay, compared with, e.g., Ni.

Concentrations of particulate Zn are comparable in D01 and in N04 (368 and 226 ng L⁻¹, respectively, i.e. a factor of ~1.6), which is consistent with the environmental characteristics of Grande Rade and Sainte-Marie Bay as well as with the ubiquitous character of Zn.

Distributions of trace metals in seawater are largely controlled by the biota (Bruland et al., 1991; Mackey et al., 2002). However, biological uptake and remineralisation at depth are not taken into account in the observed metal concentration variations in the present data. Except in the close vicinity of the barrier reef, metal concentrations are not of the same order of magnitude as the requirements of algal growth or bioaccumulation in plankton. It is assumed that such processes do not significantly affect the metal concentrations in the lagoon, where the prevailing causes of spatio-temporal variability of Cr, Ni and Zn are local geochemistry and hydrodynamics.

4.4. Role of hydrodynamics

The very low concentration levels of dissolved Ni and Cr close to the barrier reef (Table 2) indicate that the processes occurring in the coastal margin (atmospheric or riverine inputs, coastal effluents) are of negligible importance in determining Cr and Ni concentrations in the barrier reef area. Indeed, taking into account: (1) the significance of land-based emission sources of Cr and Ni derived from terrigenous erosion and mining activities; and (2) the relatively short distance from the bays to the barrier reef (~20 km), the concentrations at the barrier reef are unexpectedly low, and similar to open ocean values.

What is the specific influence of hydrodynamics on the spatio-temporal variability of metal concentrations? The low concentration of dissolved metals at the barrier reef and the strong concentration gradient from the coast to the barrier suggest a rapid renewal of waters close to the barrier reef, with the input of oceanic waters along the barrier. The relationship between the residence time of water masses (described by computed e-flushing times) and the spatial variability of metal concentrations (Fig. 5) confirms the role of hydrodynamics on the distributions of metal concentrations. A similar relationship between e-flushing times and other biogeochemical parameters has been previously evidenced at the same sampling sites (Mari et al., 2007; Torr ton et al., 2007).

Regression lines between total concentrations and residence times give the following correlation coefficients (R^2): 0.743, 0.881 and 0.553 for Ni, Cr and Zn, respectively, for the 12 sampling stations (Fig. 5). These results show that the water renewal explains a significant part of the variance of metal concentrations in the water column. This part is very significant for Ni and Cr, but much less for Zn, which is in agreement with the peculiarities of Zn emission and transport discussed above, i.e., the significance of diffuse urban sources and of medium-range aeolian transport. For total Ni and Cr concentrations, Fig. 5 clearly shows that two sub-sets of data may be distinguished, one corresponding to the enriched and slowly renewed waters that include stations D01, D08, D22,

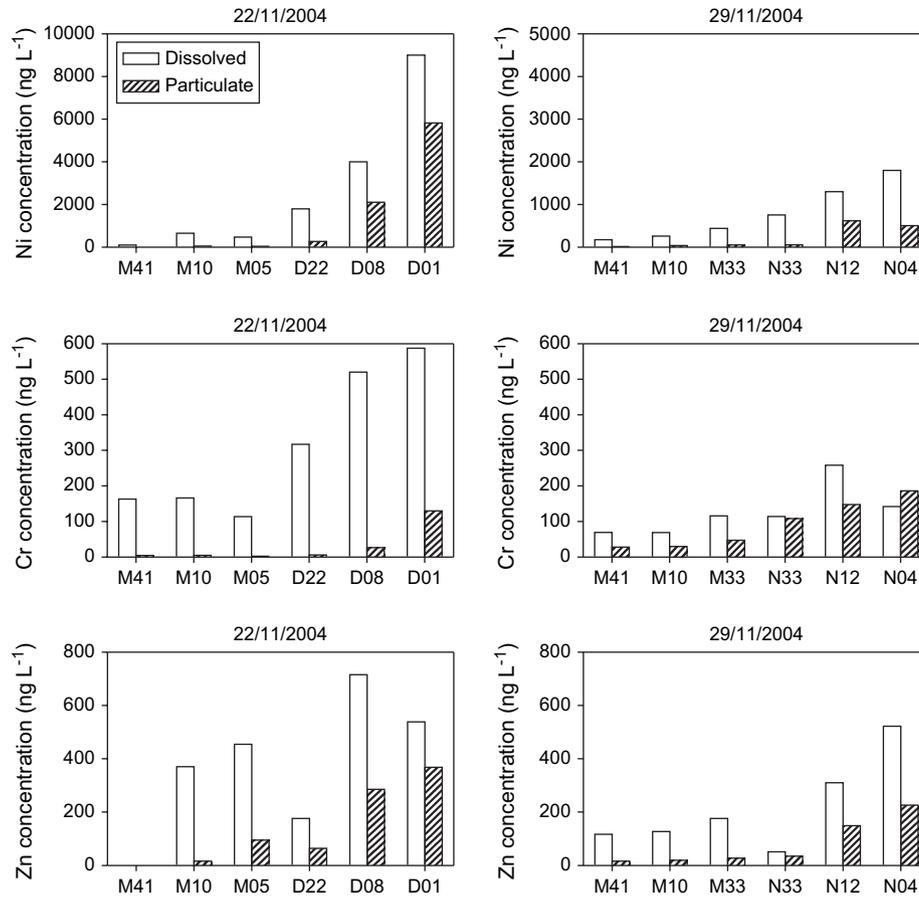


Fig. 4. Metal concentration variation from the bays to the barrier reef.

N04, N12 and N33, and the other corresponding to the rapidly renewed waters, as explained in Section 3.3.

Although no measurements of fluxes entering the bays are available, the account of local potential sources of metal emission clearly shows that the highest loads are emitted in Grande Rade, in the vicinity of the Doniambo factory and in the zone of ore ship discharge, close to the station D01. The highest residence times are found in this area. Even if it is difficult to precisely quantify the respective contributions of the intensity of

inputs and hydrodynamic processes, it is clear that the combination of these two factors controls to a large extent the distribution of metals.

A comparison of the respective contributions of residence time and distance between the stations and the emission sources showed that, although usually believed a major regulating parameter of the distribution of metal concentrations, the distance was of minor importance. Fig. 6 shows that local e-flushing times explain to a large extent the variability of

Table 3
Mean dissolved Cr, Ni and Zn concentrations at stations M10 (inside edge of the lagoon) and M41 (outside edge of the lagoon), compared with other sheltered Pacific values (all expressed in ng L⁻¹). For New South Wales coastal waters, Apte et al. (1998) have hypothesized that fluvial inputs or processes occurring in the coastal margin were of limited importance in determining trace metal concentrations

Metal	Present work	Apte et al. (1998) ^a	Mackey et al. (2002) ^b	Noriki et al. (1998) ^c	Sander et al. (2003) ^d	Ellwood (2004) ^d	Nakayama et al. (1981) ^e
Cr	M10: 116	—	—	—	<200	—	480
	M41: 116.15	—	—	—	—	—	—
Ni	M10: 260	180	117	70–622	—	—	—
	M41: 137.5	—	—	—	—	—	—
Zn	M10: 248.5	<2	—	—	—	0.4–0.9	—
	M41: 117	—	—	—	—	—	—

^a New South Wales coastal waters.

^b Western open Pacific.

^c Equatorial Pacific.

^d Sub-Antarctic Pacific (offshore New Zealand).

^e Pacific Ocean.

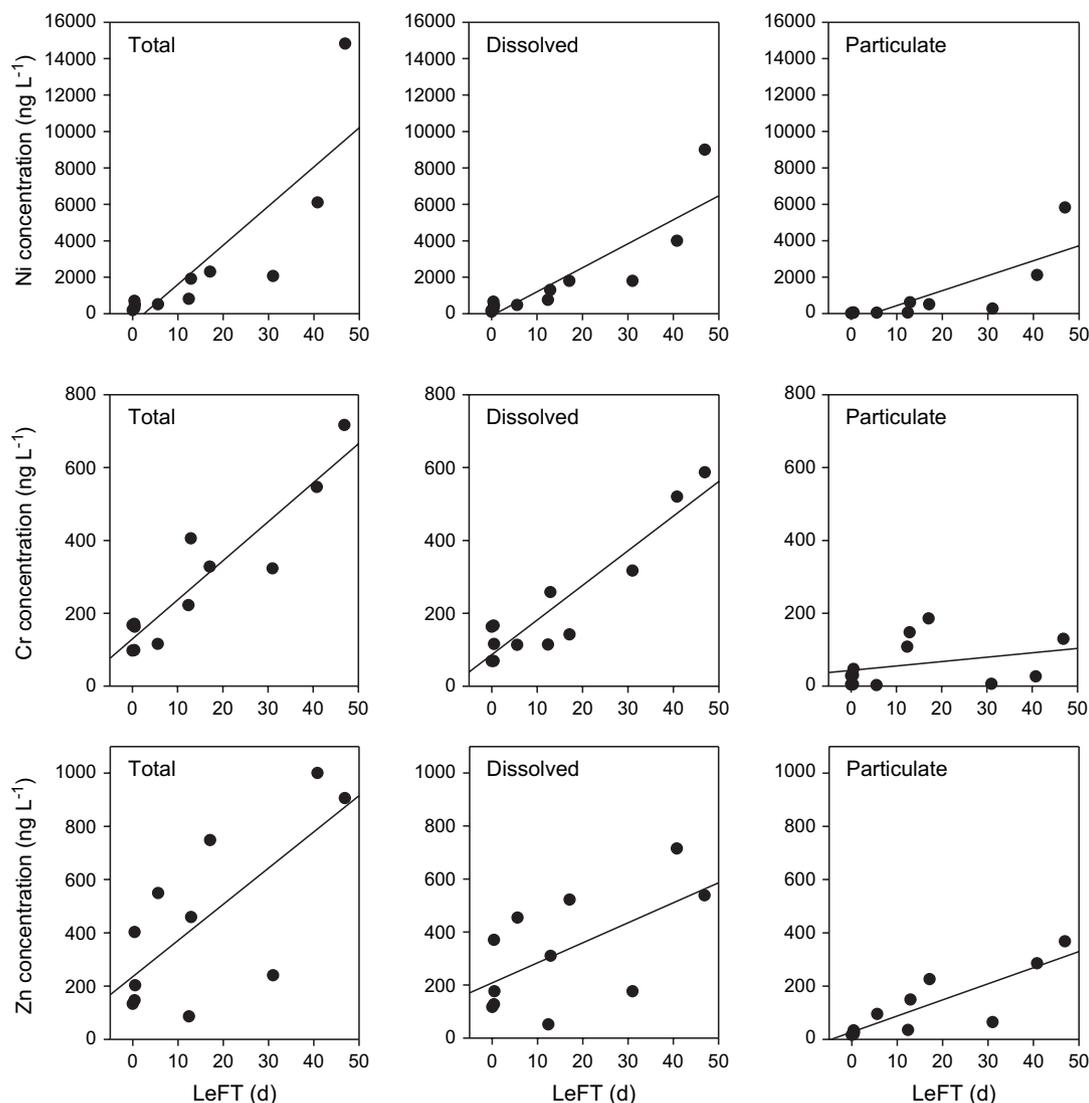


Fig. 5. Total, dissolved and particulate metal concentrations as a function of the local e-flushing time (LeFT).

metal concentrations, while the influence of the distance from the sources is very low (except for particulate Cr). This suggests that, basically, the decrease of concentrations with distance from the emission source is strongly driven by local e-flushing times. This may also explain why the decrease of Ni concentration from the bays to the barrier reef area is steeper than that of Cr: as far as one moves away from the emission source, the local e-flushing time prevails over the decreasing of metal concentrations with distance. As a result, the observed decrease of concentrations may be independent on the nature of the metal, as well as on its initial concentration level in the bays.

The correlation between concentrations and residence times is overall better for dissolved metals than for particulate metals (0.792 against 0.672 for Ni, 0.882 against 0.103 for Cr, but 0.394 against 0.749 for Zn). Dissolved concentrations are better correlated with residence times because e-flushing times are computed from the local evolution of the concentration of a dissolved tracer.

Seawater was sampled twice at two different dates at only two stations (M41 and M10), with contrasted meteorological configurations, 22 November was characterised by constant trade wind rate, while 29 November followed a change into western winds of variable strength (Fig. 3). It is likely that this change yielded an incoming flux of metal-depleted oceanic water. This flux is believed to come from west and from the outer edge of the reef. As a result, dissolved metal concentrations were significantly different at M10 between 22 and 29 November: 166–69 ng L^{-1} (Cr), 651–260 ng L^{-1} (Ni) and 370–127 ng L^{-1} (Zn). At M41, dissolved Cr concentrations fell from 163 down to 69.3 ng L^{-1} . Surprisingly, Ni dissolved concentrations increased (from 101 up to 174 ng L^{-1}). This might be the result of an analytical contamination, but the sampling station M41 is located out of the lagoon, where waters are already very depleted in metals, hence it is probably less (or not) sensitive to the impact of incoming oceanic water. Dissolved Zn concentrations were not measured at M41 on 22 November.

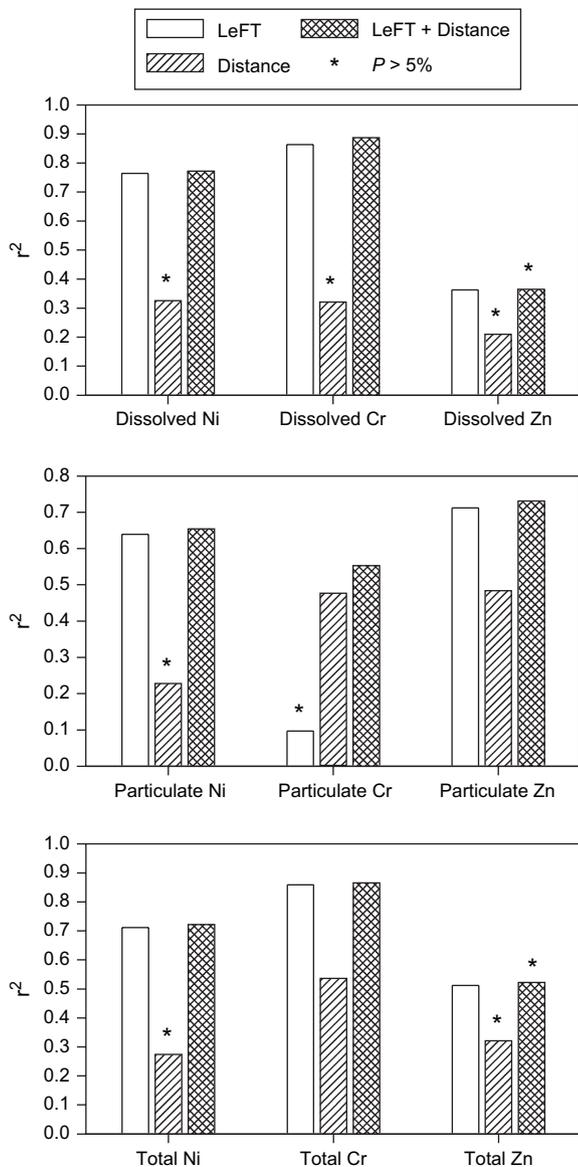


Fig. 6. Correlation coefficients of simple linear regressions for metal concentration vs local e-flushing times, and vs distance from the emission source, and multiple linear regression for metal concentration vs local e-flushing times and distance from the emission source. Taking into account the low impact of river loads, the “mean” emission source is assumed as the centre of Nouméa. LeFT means local e-flushing time.

As well, particulate Ni and Zn concentrations slightly decreased at M10 (50.7–37.3 and 33.0–19 ng L⁻¹, respectively). Particulate Cr concentrations were very low at M10 (4.5 ng L⁻¹). In trade wind rate, M10 is sheltered from wind waves by islands (Fig. 1) and from swell that does not penetrate into the lagoon. On the contrary, when western winds prevail, swell and water masses from the outer edge of the reef may contribute to local sediment remobilisation. Owing to the low metal concentrations at M10, it is likely that sediment mobilisation driven by incoming water masses became the most important process and yielded an increase of particulate Cr concentrations on 29 November (29.6 ng L⁻¹).

5. Conclusions

The magnitude and variability of Cr, Ni and Zn concentrations in the lagoon are controlled upstream by land-based emission sources: industrial (Grande Rade) and terrigenous (Sainte-Marie Bay) are superimposed upon a common urban source from the city of Nouméa. The raw metal loads then undergo a variety of chemical processes (sorption, precipitation, dissolution, release from sediment, etc.). However, owing to the specific circulation of the lagoon, the fate of dissolved and particulate metal concentrations is strongly constrained by hydrodynamics. The residence times of water masses point out their rapid renewal in the vicinity of the barrier reef. This is likely to counterbalance the high loads of Cr and Ni that enter the lagoon waters, and actually results in unexpectedly low concentration levels in waters close to the barrier reef. Except for Zn, of which the atmospheric input is believed to be spread over the whole surface of the lagoon, the peculiar combination of prevailing winds and lagoon hydrodynamics in the region of Nouméa finds here expression in a possible “cleaning” of surface waters with the rapid flushing of water masses.

As pointed out by the present data set, the fitting of metal concentrations on hydrodynamic models is difficult because of the combined influence of other parameters such as the location and strength of emission sources, and geochemical processes. The analysis may be improved by additional sampling at the same stations, for the same metals, during various episodes of wind forcing, in particular during episodes of low wind forcing. The analysis of episodes of nonsteady and aperiodic atmospheric forcing will require to adapt the methods of computation of local residence times.

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