



## Tracking trace elements into complex coral reef trophic networks



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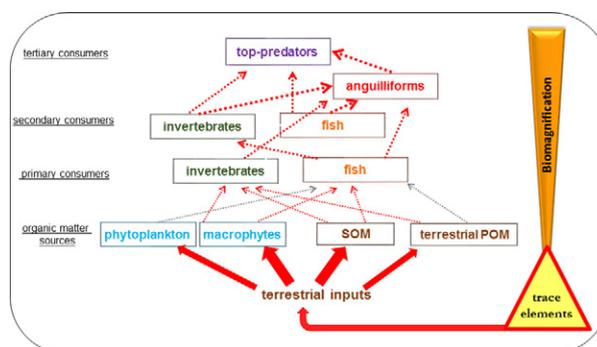
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### HIGHLIGHTS

- Trace elements were measured in various components of coral reef trophic networks.
- Organic matter sources, invertebrates and fish showed different concentrations.
- Two food webs constituted the most important transfer pathways of trace elements.
- Biomagnification along food webs was confirmed for Hg (suggested for Se and Zn).

### GRAPHICAL ABSTRACT



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### ABSTRACT

The integration, accumulation and transfer of trace elements across the main trophic levels of many food webs are poorly documented. This is notably the case for the complex trophic webs of coral reef ecosystems. Our results show that in the south-west lagoon of New Caledonia both abiotic (i.e. sediments) and biotic (i.e. primary producers, consumers and predators) compartments are contaminated by trace elements. However, our analyses revealed different contamination patterns from the sources of organic matter to the predators. The trophic levels involved in the sedimentary benthic food web (S-BFW, based on the sedimentary organic matter) and to a lesser extent in the reef benthic food web (R-BFW, based on algal turf) were mainly contaminated by trace elements that originate from mining activities like Ni and associated trace elements (Co, Cr, Fe, and Mn). Trace elements linked to agro-industrial (As, Hg, and Zn) and urban (Ag, Cd, Cu, Pb, Se, and V) activities were also integrated into the S-BFW, but preferentially into the R-BFW, and to a lesser extent into the detrital benthic food web (D-BFW, supplied by sea-grass plants). Most of the trace elements were biodegraded with increasing trophic levels along food webs. However, a marked biomagnification was observed for Hg, and suspected for Se and Zn. These results provide important baseline information to better interpret trace element contamination in the different organisms and trophic levels in a highly diversified coral reef lagoon.

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### 1. Introduction

Urbanization, agricultural, industrial and mining activities release large amounts of chemicals and trace elements into the environment (Richmond, 1993). In the ocean, substantial quantities of these products

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are directly discharged into littoral waters or indirectly transported via hydraulic and aerial flows to the sea (Holt, 2000). Overall, it has been estimated that various types of pollution negatively impact 25% of the coral reefs worldwide (Burke et al., 2011). Metallic trace elements are particularly toxic because they tend to bioaccumulate in the food webs (Eilser, 2010). They may have important physiological effects on organisms, their strong detrimental effects on coral reef ecosystems have been demonstrated (Webster et al., 2001). However, the paucity of scientific information on the environmental distribution of trace elements across the trophic webs of coral reefs raises serious difficulties for describing contamination pathways, and thus for assessing possible short-term and long-term effects.

Furthermore, the sources of contamination by trace elements are spatially and temporally heterogeneous (Holt, 2000). Contaminants can originate from both natural and anthropic sources and their transfer into aquatic environments is influenced by different factors, for example climatic conditions (e.g. flooding) or human activities (e.g. deforestation and erosion on watersheds, open-cast mining). In addition their transfer throughout trophic levels depends on the physiological characteristics of the organisms. Consequently, different contaminants are unequally distributed among the different trophic compartments in the ecosystems (Moore and Ramamoorthy, 1984). Some trace elements stay dissolved in the water or are adsorbed on suspended particles, others are stored and accumulated in the sediments (e.g. adsorbed on organic or inorganic particles), and to a lesser extent absorbed by macroalgae, seagrass and algal turf. Although trace elements show various affinities for the macromolecules that form the cell walls of micro- and macroalgae (Davis et al., 2003), concentrations detected in primary producer tissues are generally directly proportional to the concentrations that prevail in the surrounding water (Métian et al., 2008b). These compartments that involve primary producers are at the basis of the food webs; they constitute potential reservoirs for trace metal accumulation and they represent possible sources of contamination for various consumers and predators (Tsakovski et al., 2012). But only the trace elements present in a transferable form, i.e. digestible, assimilable, and therefore bioavailable after chemical transformations, can be transferred from a prey to a predator and thus can spread across food webs (Tariq et al., 1993). Monitoring the transfer of trace elements in each of the main trophic levels, additionally to the abiotic components, provides a temporal integrated assessment of the fraction really accessible across the whole food web (Danis et al., 2004). By targeting the potential bioavailable fraction, the relevant bioaccumulation and biomagnification processes can be characterized.

All consumers exposed to trace elements may bioaccumulate them into their tissues by a diffusion process of waterborne trace elements through the epithelia (Randall et al., 1998), or by the ingestion of contaminated food (e.g. Bustamante et al., 2002, 2004; Cresson et al., 2014; Baptista et al., 2016). The relative importance of each pathway varies with the organisms and with the bioavailability of trace elements (Wang and Fisher, 1999). The foraging pathway is recognized as the main source of contamination in many cases, however (e.g. Reinfelder et al., 1998; Wang, 2002; Wang and Ke, 2002; Mathews and Fisher, 2009). The resulting concentrations represent the balance between accumulation and elimination, and both vary with metabolism, tissue turnover, growth rate, animal age and reproduction (Rainbow et al., 1990). Non-essential elements, such as Cd, Hg and Pb, can rapidly become toxic with increasing bioaccumulation (Devineau and Amiard-Triquet, 1985). These elements must be detoxified and/or excreted to prevent toxic effects (Rainbow, 2002). However, below certain thresholds, many trace elements (e.g. Cu and Zn) are not eliminated or detoxified because they play essential physiological roles (Rainbow, 2002). Bioaccumulation is consequently a complex process influenced by species' life history traits, e.g. age/size, sex, metabolism, diet, habitat, reproductive period (Blackmore, 2001; Harmelin-Vivien et al., 2009). Sampling a wide range of species is thus essential to encompass this variability. An accurate assessment of the main trophic levels of the

targeted ecosystem is essential to carefully select representative organisms of each trophic level. Biomagnification is the result of the increase of tissue concentrations of a contaminant as it passes through two or more trophic levels (Macek et al., 1979). To accurately appraise biomagnification, it is essential to determine the trophic level of each of the sampled organisms, and to consider all main levels from primary producers to various consumers, and different classes of predators (Peterson and Fry, 1987).

Achieving these numerous prerequisites that are critical to track contamination in complex food webs is logistically demanding. This probably explains the scarcity of global assessments performed in coral reefs, particularly in the Pacific Ocean. Piecemeal, albeit extremely valuable, information is available however in New Caledonian waters. Different studies revealed large-scale contamination of the New Caledonian lagoon by trace elements originating from mining activities (e.g. Métian et al., 2008a; Hédouin et al., 2009; Bonnet et al., 2014). Yet precise contamination pathways remain unclear. In most studies, algae, bivalves, or a few groups of fish and predators were studied independently and thus were limited to a given trophic level (e.g. Bustamante et al., 2003; Métian et al., 2008a, 2008b, 2013; Chouvelon et al., 2009; Bonnet et al., 2014; Briand et al., 2014). A more comprehensive assessment of the contamination by trace elements is thus needed. The main trophic structures (i.e. food chains) that compose the entire food webs of most coral reefs contain a very high number of taxa and thus display a great level of complexity. In the south-west lagoon of New Caledonia, the assemblage of the main trophic structures has been recently clarified using stable isotope analyses through an extensive sampling of various organisms belonging to the main levels, from primary producers to predators (Briand et al., 2015, 2016). Two main trophic structures were identified: the reef benthic food web (R-BFW) with algal turf as a primary source of organic matter (OM), and the sedimentary benthic food web (S-BFW) supplied by sedimentary OM. A third structure, the detrital benthic food web (D-BFB) supplied by seagrass OM, occupies a secondary place in the trophic network of the lagoon. These structures are interconnected and high-level predators belonging to a given structure can use prey items from others as complementary feeding sources (Briand et al., 2016). Thus, the main structures are actually interconnected rather than independent. Nonetheless, the identification of these major trophic structures provides an important framework to track contamination in the whole ecosystem.

The aim of this study is to assess the concentrations of 14 trace elements in various organisms representative of the main trophic structures involved in the functioning of a complex reef ecosystem, the south-west lagoon of New Caledonia. Although their origins can be multiple and complex, the selected trace elements have been respectively associated with mining (Co, Cr, Fe, Mn, and Ni), agro-industrial (As, Hg, and Zn), and urban (Ag, Cd, Cu, Pb, Se, and V) activities, based on their likely main source (e.g. Sañudo-Willhelmy and Flegal, 1992; Nriagu, 1994; Callender and Rice, 2000). To assign sampled organisms into each of the main trophic levels, OM sources, intermediate consumers and higher level predators, we used stable isotope analyses (nitrogen:  $\delta^{15}\text{N}$ ). It was thus possible to integrate the contamination results into structured transfer pathways (Briand et al., 2016). Finally, possible biomagnification and/or detoxification processes occurring across the different trophic levels and structures in New Caledonian coral reefs were examined.

## 2. Material and methods

### 2.1. Study context

The reefs of New Caledonia form the second most extensive continuous coral system in the world and are one of the main biodiversity hot spots of the planet (Roberts et al., 2002). Although currently considered as generally healthy, the coral reefs of this

archipelago are subjected to various pressures (Wilkinson, 2004). Due to intensive mining activity, insufficiency of wastewater treatment plants, increasing urbanization and industrialisation, vast amounts of contaminants (including metallic trace elements) are directly discharged into the lagoon.

Mining activities (open-cast mines) are a major source of revenue in New Caledonia. Almost 15% of the mainland surface area was or is exploited for Ni ore and it has been estimated that 20% of known world accessible stocks of nickel are in the soils of New Caledonia (Dalvi et al., 2004). Extraction requires the processing of extremely large amounts of laterites and saprolites (i.e. typical ores with low Ni and Co content), involving total forest clearing (and subsequent replanting) of vast areas and huge water and energy consumption. The mining activities as a whole generate massive sediment deposits and marked metal contamination of the lagoonal waters (Hédouin et al., 2009; Bonnet et al., 2014) that may threaten coral reefs (Rogers, 1990). Many mining sites and three Ni factories are spread over New Caledonia. In this economic context, and in spite of a current nickel crisis, increasing Ni exploitation is to be expected in the future.

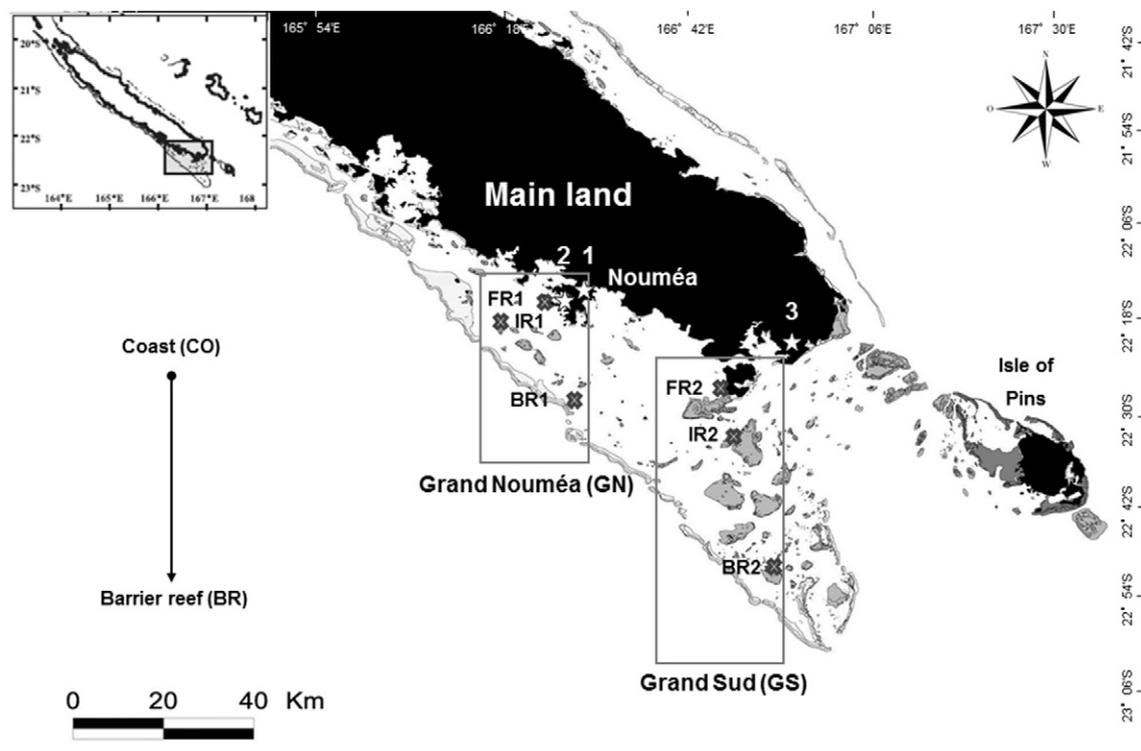
Agricultural and urban activities generate particular forms of contamination. Although probably a minor source of trace elements, 3674 tons of fertilizers and 152 tons of phytosanitary products (herbicides, insecticides and fungicides) were imported in 2011 in New Caledonia, of which, respectively, 90% and 30% were sold to industry (DAVAR, 2012). In addition, unevaluated domestic uses of various chemicals probably increase the contamination of the lagoon by trace elements and organic contaminants (IAC, 2013). Sewage-treatment plants do not collect all the wastewaters from urbanized and industrialized areas, and they are under-sized (e.g. ~65% of the sewage is processed in the city of Nouméa). Thus, huge amounts of contaminated sewage have been directly discharged into the harbours for decades; and although decreasing, this water contamination has not yet stopped.

## 2.2. Study sites and sampling

The study was carried out in the south-western lagoon of the main Island of New Caledonia (Fig. 1). Two areas were investigated. The Grand Nouméa area (GN) is close to the city of Nouméa and subjected to a wide range of anthropogenic pollution. Nouméa is a relatively large city (~180,000 inhabitants, including the suburbs) surrounded by extensive industrial and agricultural zones. In particular, a Ni factory (Société Le Nickel) implanted in the city (Fig. 1) has been in operation since 1880. In contrast, the Grand Sud area (GS) is relatively distant from any populated site and is therefore less influenced by industrial and urban pollution. Nevertheless, open-cast mines have been developed in this area since 1950 and a mining factory (Goro, Vale-NC) was set up near the Bay of Prony in 2005 (Fig. 1).

In each area, three sites (fringing reef, intermediate reef and barrier reef) located along a coast-barrier reef gradient (Fig. 1) were sampled twice, from January to April 2011 (austral summer, hot, wet season) and from August to September 2011 (austral winter, cool, dry season). At each site, the main trophic compartments were sampled: various OM sources (sediment and primary producers), several consumers (herbivorous, omnivorous and carnivorous invertebrates) and high-level predators (anguilliform fish). The sedimentary organic matter (SOM) and macro-invertebrates were directly collected during diving sessions. A light trap was used to capture micro-invertebrates.

High-level predators, different species of anguilliform fish (e.g. Muraenidae, Congridae) were collected using their main predators: the sea kraits (sea snakes of the genus *Laticauda*, *Laticauda laticaudata* and *L. saintgironsi*). Sea kraits feed intensively and almost exclusively on anguilliform fish, swallow their prey whole, and return to land to digest. These snakes are highly philopatric and they capture their prey in the vicinity of their home islet (Brischoux et al., 2007, 2009). Sea kraits were captured by hand on land and the anguilliform specimens were retrieved via gentle forced regurgitation. This cost efficient sampling



**Fig. 1.** Study site locations in the southwest lagoon of New Caledonia, SW Pacific Ocean. Six sites distributed on a coast-barrier reef gradient (fringing reef FR, intermediate reef IR and barrier reef BR) were sampled in two different areas referred to as Grand Nouméa (GN, area 1) and Grand Sud (GS, area 2). Stars indicate zones of human activities: the industrial area of Ducos (1), the Nickel factory SLN (2), and the Nickel factory Vale-NC (3). The emerged land is indicated in black; grey areas represent coral reefs; the dark grey line represents the slope of the barrier reef.

strategy provides abundant and spatially accurate information on a wide variety of anguilliform fish species (e.g. [Brischoux et al., 2007, 2011; Bonnet, 2012](#)). In this study, we selected poorly digested or intact prey to ensure that the isotopic values of the anguilliform fish were representative of each station; indeed almost intact prey at regurgitation are recently captured near the sampling site ([Brischoux et al., 2007](#)).

A total of 359 samples, identified at the lowest possible taxonomic level, were analysed ([Table 1](#)): 10 different macrophytes (pooling small filamentous algae known as 'algal turf', calcareous and non-calcareous macroalgae and seagrass), the first layer (< 3 cm) of the subsurface sediment (SOM), 31 species of micro- and macro-invertebrates (small and large crustaceans, gastropods, echinoderms and annelids) and 6 anguilliform fish species. For chemical analyses, a piece of the thallus of the macrophytes (algal turf, macroalgae and seagrass), of the soft muscles of all macro-invertebrates, and of the dorsal white muscles of the fish, were taken ([Pinnegar and Polunin, 1999](#)). For small invertebrates (crustaceans and polychaetes), whole individuals were used; in each species, several specimens (e.g. same station, season, size) were pooled to obtain a sufficient amount of material (e.g. 5 g). All samples were immediately frozen at  $-20^{\circ}\text{C}$ .

### 2.3. $\delta^{15}\text{N}$ analyses

SOM and muscle of the collected organisms were analysed. Samples were freeze-dried and ground to fine powder of which  $1.0 \pm 0.1$  mg ( $15.0\text{--}20.0 \pm 0.1$  mg for sediment) was sealed in tin capsules for analyses. Isotopic  $^{15}\text{N}/^{14}\text{N}$  ratios were determined with a continuous-flow mass spectrometer (Thermo Scientific Delta V Advantage, Bremen, Germany), coupled to an elemental analyser (Thermo Scientific Flash EA1112, Milan, Italy), as explained in [Chouvelon et al. \(2011\)](#). Results were expressed as isotope ratios  $\delta^{15}\text{N}$  (‰) relative to international standard (atmospheric  $\text{N}_2$  for nitrogen), according to the formula:

$$\delta^{15}\text{N} = [\text{Rsample}/\text{Rstandard} - 1] \times 10^3$$

where  $R = ^{15}\text{N}/^{14}\text{N}$ . Replicate measurements of internal laboratory standards (acetanilide) indicated a precision of 0.2‰ for  $\delta^{15}\text{N}$  values.

### 2.4. Trace element analyses

A total of 14 trace elements were analysed (Ag, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, V and Zn) in the same tissues. The total Hg concentration in the powder obtained from the tissues (see above  $\delta^{15}\text{N}$  analyses) was determined with an advanced mercury analyser (ALTEC AMA 254), directly on aliquots ranging from 5 to 50 mg of dry sample, weighed to the nearest 0.01 mg ([Bustamante et al., 2006](#)). To analyse the other elements, from 150 to 300 mg of each sample was digested using a 3:1 v/v nitric–hydrochloric acid mixture with 65% ultrapure  $\text{HNO}_3$  and ultrapure 37% HCl. The acidic digestion was performed overnight under ambient temperature and then samples were heated in a microwave for 30 min, increasing the temperature up to  $105^{\circ}\text{C}$ , and 15 min at  $105^{\circ}\text{C}$  (1200 W). After the mineralization process, each sample was diluted to 30 or 50 ml with milli-Q quality water, according to the volume of acid added to the mineralization (3 and 4.5 ml, respectively). These elements were analysed by inductively coupled plasma atomic emission spectrometry (Varian Vista-Pro ICP-OES) and mass spectrometry (ICP-MS II Series Thermo Fisher Scientific). Reference tissues—dogfish liver DOLT-4 (NRCC), lobster hepatopancreas TORT-2 (NRCC)—were treated and analysed in the same way as the samples. Results were in line with the certified values, and the standard deviations were low, indicating good repeatability of the method. The results for standard reference materials displayed recovery of the elements ranged from 70% to 133%. For each set of analyses, blanks were included in each analytical batch. The detection limits (micrograms per gram dry weight) were 0.005 (Hg), 0.015 (Cd), 0.017 (Ag), 0.02 (Cr, Co, Pb), 0.03 (Ni), 0.08 (Mn),

**Table 1**

List of sampled species: 10 macrophytes, the sedimentary organic matter (SOM), 31 species of micro- and macro-invertebrates and 6 anguilliform fish. Abbreviations: c: calcareous; indet.: unidentified; mix: mix of species; nc: non calcareous.

Type	Category	Species	Code	Food web	N
Source	Algal turf	mix (indet.)	AT	R-BFW	30
Source	Macroalgae c	<i>Halimeda cylindracea</i>	Hc	S-BFW	21
Source	Macroalgae c	<i>Halimeda opuntia</i>	Ho	R-BFW	27
Source	Macroalgae nc	<i>Padina australis</i>	Pa	D-BFW	11
Source	Macroalgae nc	<i>Sargassum cristaeifolium</i>	S	S-BFW	3
Source	Macroalgae nc	<i>Sargassum spinulligerum</i>	S	S-BFW	9
Source	Macroalgae nc	<i>Turbinaria conoides</i>	T	D-BFW	3
Source	Macroalgae nc	<i>Turbinaria ornata</i>	T	D-BFW	6
Source	Macroalgae nc	<i>Turbinaria</i> sp.	T	D-BFW	9
Source	Seagrass	<i>Halodule uninervis</i>	Hu	D-BFW	12
Source	SOM	SOM	SOM	S-BFW	36
Invertebrate	Echinid	<i>Echinometra mathaei</i>	Em	S-BFW	8
Invertebrate	Echinid	<i>Parasalenia gratiosa</i>	Pg	R-BFW	1
Invertebrate	Isopod	mix (indet.)	I	S-BFW	3
Invertebrate	Cone snail	<i>Conus marmoreus</i>	Co	S-BFW	6
Invertebrate	Cone snail	<i>Conus virgo</i>	Co	S-BFW	1
Invertebrate	Crab	<i>Grapsus albolineatus</i>	Ga	D-BFW	17
Invertebrate	Crab	<i>Leptodius sanguineus</i>	Cr	S-BFW	3
Invertebrate	Crab	<i>Pilumnus vespertilio</i>	Cr	S-BFW	3
Invertebrate	Crab	<i>Thalamita cf. coeruleipes</i>	Cr	S-BFW	1
Invertebrate	Crab	mix - 4 sp. (indet.)	Cr	S-BFW	6
Invertebrate	Hermit crab	<i>Clibanarius cf. eurystermus</i>	Ce	S-BFW	7
Invertebrate	Hermit crab	<i>Dardanus scutellatus</i>	Ds	D-BFW	3
Invertebrate	Hermit crab	<i>Dardanus lagopodes</i>	D1	S-BFW	2
Invertebrate	Hermit crab	<i>Dardanus setifer</i>	D1	S-BFW	1
Invertebrate	Hermit crab	<i>Dardanus cf. setifer</i>	D2	D-BFW	1
Invertebrate	Hermit crab	<i>Dardanus</i> sp1	D2	D-BFW	1
Invertebrate	Hermit crab	<i>Petrolisthes lamarckii</i>	H1	S-BFW	3
Invertebrate	Hermit crab	mix - 2 sp. (indet.)	H2	D-BFW	5
Invertebrate	Hermit crab	1 species (indet.)	H1	S-BFW	2
Invertebrate	Nerite	<i>Nerita albicilla</i>	N1	S-BFW	17
Invertebrate	Nerite	<i>Nerita plicata</i>	N1	S-BFW	15
Invertebrate	Nerite	<i>Nerita</i> sp1 (indet.)	N2	D-BFW	3
Invertebrate	Nerite	<i>Nerita</i> sp2 (indet.)	N2	D-BFW	2
Invertebrate	Nerite	<i>Nerita</i> sp3 (indet.)	N1	S-BFW	9
Invertebrate	Nerite	<i>Nerita</i> sp4 (indet.)	N1	S-BFW	3
Invertebrate	Shrimp	mix (indet.)	Sh	R-BFW	3
Invertebrate	Top snail	<i>Tectus niloticus</i>	Tn	S-BFW	11
Fish	Moray eel	<i>Gymnothorax chilospilus</i>	Gc	S-BFW	48
Fish	Moray eel	<i>Gymnothorax undulatus</i>	Gu	S-BFW	3
Fish	Moray eel	<i>Gymnothorax fimbriatus</i>	Gf	S-BFW	1
Fish	Conger eel	Conger Ls	Cs	S-BFW	9
Fish	Conger eel	Conger Ll	Cl	R-BFW	28
Fish	Moray eel	<i>Gymnothorax eurostus</i>	Ge	R-BFW	2

0.1 (Cu, Se), 0.2 (As), 0.3 (V) and 3.3 (Fe and Zn). All trace element concentrations are given on a dry weight basis (micrograms per gram dry weight).

### 2.5. Data analyses

For simplicity trace elements were categorized according to their likely origin: 'mining' (Co, Cr, Fe, Mn, and Ni), 'agro-industrial' (As, Hg, and Zn) and 'urban' (Ag, Cd, Cu, Pb, Se, and V) (e.g. [Sañudo-Willhelmy and Flegal, 1992; Nriagu, 1994; Callender and Rice, 2000](#)). Elements were considered as undetected when all or most of measured concentrations remained under the detection limit (*dl*) in a given group (e.g. individuals of a same species or samples from a given taxonomic or trophic group). In cases where under *dl* concentrations concerned only few samples, we used half of the *dl* value as a surrogate ([Helsel, 2010](#)).

Analyses of variance (ANOVA) and Tukey HSD post-hoc tests were performed to address three main issues:

- 1) Firstly, we aimed to assess the variability of trace element concentrations within each trophic compartment, i.e. between the different categories of OM sources, invertebrates and predator fish (ANOVA: category factor [5 to 8 levels]). We used categories based on important aspects that characterize each compartment: the functional

group (OM sources), the taxonomic origin (invertebrates) or the species level (anguilliform fish) (details in Table 1). We also considered correlations between body size or  $\delta^{15}\text{N}$  and trace element concentrations in fish (Briand et al., 2014); these variables were implemented as covariable(s) to perform ANCOVAs.

- 2) Secondly, the spatial and temporal variability of trace element concentrations for each species (ANOVA: interaction of area [2]  $\times$  site [3]  $\times$  season [2] factors) was examined. Comparisons were only performed between groups with a sufficient sample size (i.e.  $N \geq 3$ ), and species collected in at least two sites within each area and in both seasons.
- 3) Finally, we assessed the distribution of trace elements into OM sources and consumers belonging to three main trophic networks that constitute the whole food webs' architecture of the New Caledonian lagoon (Briand et al., 2016). We considered the detrital benthic food web (D-BFW), the sedimentary benthic food web (S-BFW) and the reef benthic food web (R-BFW) (details in Table 1). The nature of the OM preferentially targeted depends on each group of trace elements (mining vs. agro-industrial vs. urban). Consequently, consumers may bioaccumulate different levels of trace elements according to the origin of their nutritive resources (ANOVA: species [44]  $\times$  food web [3] factors).

The categorization presented above to perform ANOVAs (and ANCOVAs) was influenced by field sampling and the specific questions addressed. This explains why some groups aligned to a single genus when others combined multiple genera (see Results). Yet this pooling procedure was limited to organisms that belong to a well identified taxonomic or functional group.

Biomagnification potential of trace elements was estimated through the entire food webs by a trophic magnification factor (TMF), quantified with the equation relating trace element concentrations and trophic position ( $\delta^{15}\text{N}$  proxy) (Nfon et al., 2009):

$$\text{Log}_{10}[\text{element}] = a + b \times \delta^{15}\text{N}$$

The linear regression slope (b) represents the concentration variation per changing unit of trophic level over food webs, and (a) is a constant depending on the background trace element concentration (Rolff et al., 1993). Given that this process generally involves at least three trophic levels (Wang, 2002), accumulation levels measured in organisms belonging to the three different trophic compartments, i.e. primary producers, invertebrates and anguilliform fish, were taken into account. The SOM was removed from the data due to too great differences in

parameters compared with other OM sources, i.e. trace element concentrations and  $\delta^{15}\text{N}$  ratios.

The slope (b), also called 'biomagnification power' (Nfon et al., 2009), can be used in order to calculate the trophic magnification factor (TMF) of an element via the formula:

$$\text{TMF} = 10^b$$

A TMF value higher than 1 indicates an accumulation of trace elements with increasing trophic levels (i.e. biomagnification), while a value lower than 1 implies decreasing concentration through food chain (i.e. bioreduction or biodiminution) (Nfon et al., 2009).

### 3. Results

#### 3.1. Trace element concentrations in trophic compartments

##### 3.1.1. Organic matter sources

A few trace elements were below the detection limit (*dl*) in sediment (Ag and Cd) and none in primary producers (Table 2). ANOVA results showed that SOM accumulated significantly higher Cr and Fe concentrations than calcareous and non-calcareous macroalgae. Conversely, algal turf and most macrophytes showed higher concentrations in As, Se, and Zn than SOM (Table 2). Among primary producers, several significant differences were revealed, especially higher concentrations of several elements (Cr, Hg, Mn, Ni, and Pb) in algal turf than in macroalgae (Table 2). This trend was observed in seagrasses for Cr and Ni, but it remained not significant because of the high intraspecific variability.

##### 3.1.2. Intermediate consumers

All trace elements were detected in invertebrates' tissues, except V which was systematically below the *dl*. The main taxonomic groups of reef invertebrates showed different trace element concentrations. Gastropods, especially top snails, displayed significantly higher concentrations of Ag, Cu, Fe, and Mn compared to echinoderms (showing globally high Cd concentrations), plus higher Cr and to a lesser extent Se concentrations than crustaceans (accumulating high Hg, Pb, and Zn concentrations, Table 3). However, between those groups neither significant difference in Co nor clear distinction in accordance with their taxonomy in Hg and Ni were detected (Table 3). Within a same taxonomic group, among crustaceans for instance, crabs, shrimps and isopods showed higher concentrations of Ag, As, Cu, and Se levels than hermit crabs, which had significantly lower concentrations of Ag, As, Hg, Pb, and Se (Table 3). Among gastropods, top snails generally accumulated significantly lower concentrations compared to cone snails (Ag, As, Ni, and Se) or nerites (Cu, Mn, and Zn, Table 3).

**Table 2**

Concentrations of trace elements (Mean  $\pm$  SD; in  $\mu\text{g}\cdot\text{g}^{-1}$  dry weight) of different organic matter sources, all sites pooled. Number of samples analysed (*N*) and results of inter-group comparisons (F-statistic and degree of freedom of ANOVA test, Tukey *post-hoc*) are indicated. *ns*:  $p > 0.05$ ; \*  $p < 0.05$ ; \*\*  $p < 0.01$ ; \*\*\*  $p < 0.001$ ; (–) non tested; < *dl* concentrations under detection limit.

Trace elements	SOM	Algal turf (AT)	Macroalgae calcareous (Mc)	Macroalgae non-calcareous (Mnc)	Seagrass (S)	Intergroup variability	F-statistic (d.f.)
<i>N</i>	36	30	48	45	12		
Ag	< <i>dl</i>	0.10 $\pm$ 0.14	0.05 $\pm$ 0.09	0.15 $\pm$ 0.31	0.08 $\pm$ 0.09	Mc < Mnc**	3.79 (3)
As	4.43 $\pm$ 7.06	7.49 $\pm$ 6.39	8.98 $\pm$ 7.90	12.17 $\pm$ 10.89	11.50 $\pm$ 12.44	SOM < AT = Mc = S = Mnc***	13.75 (4)
Cd	< <i>dl</i>	0.11 $\pm$ 0.07	0.07 $\pm$ 0.06	0.13 $\pm$ 0.15	0.08 $\pm$ 0.04	<i>ns</i>	2.64 (3)
Co	1.99 $\pm$ 3.37	1.44 $\pm$ 1.26	1.14 $\pm$ 1.55	0.69 $\pm$ 0.29	1.35 $\pm$ 1.77	<i>ns</i>	0.65 (4)
Cr	12.44 $\pm$ 16.24	9.72 $\pm$ 8.18	6.88 $\pm$ 14.61	4.25 $\pm$ 5.39	18.90 $\pm$ 30.78	Mnc = Mc < AT = SOM*	6.85 (4)
Cu	2.29 $\pm$ 5.10	1.11 $\pm$ 1.01	0.54 $\pm$ 0.55	0.60 $\pm$ 0.52	0.57 $\pm$ 0.22	<i>ns</i>	1.81 (4)
Fe	2923 $\pm$ 5947	654 $\pm$ 721	416 $\pm$ 1092	183 $\pm$ 224	1092 $\pm$ 1668	Mnc = Mc < SOM*	4.55 (4)
Hg	0.005 $\pm$ 0.012	0.014 $\pm$ 0.013	0.002 $\pm$ 0.001	0.006 $\pm$ 0.003	0.004 $\pm$ 0.001	Mc < S = SOM = Mnc < AT***	55.68 (4)
Mn	35.33 $\pm$ 58.91	29.41 $\pm$ 36.95	9.59 $\pm$ 14.19	10.49 $\pm$ 13.20	18.23 $\pm$ 23.68	Mc = Mnc < AT*	3.65 (4)
Ni	9.66 $\pm$ 13.93	17.76 $\pm$ 19.55	7.97 $\pm$ 14.95	6.66 $\pm$ 7.61	18.00 $\pm$ 26.00	Mnc < AT*	2.66 (4)
Pb	0.28 $\pm$ 0.32	1.18 $\pm$ 1.96	0.13 $\pm$ 0.20	0.22 $\pm$ 0.34	0.35 $\pm$ 0.33	Mc < AT***	4.85 (4)
Se	0.12 $\pm$ 0.05	0.26 $\pm$ 0.16	0.16 $\pm$ 0.12	0.20 $\pm$ 0.14	0.18 $\pm$ 0.06	SOM = Mc < Mnc = AT*	6.82 (4)
V	9.07 $\pm$ 18.02	6.88 $\pm$ 6.74	5.77 $\pm$ 13.17	4.15 $\pm$ 4.76	4.94 $\pm$ 5.29	<i>ns</i>	1.63 (4)
Zn	5.5 $\pm$ 4.1	15.1 $\pm$ 13.8	7.3 $\pm$ 3.8	11.1 $\pm$ 8.8	13.5 $\pm$ 4.7	SOM = Mc < Mnc = S = AT*	11.88 (4)

**Table 3**  
Concentrations of trace elements (Mean  $\pm$  SD; in  $\mu\text{g}\cdot\text{g}^{-1}$  dry weight) of different reef invertebrates, all sites pooled. Number of samples analysed ( $N$ ) and results of comparisons between different taxonomic groups (F-statistic and degree of freedom of ANOVA test, Tukey post-hoc) are indicated. ns:  $p > 0.05$ ; \* $p < 0.05$ ; \*\* $p < 0.01$ ; \*\*\* $p < 0.001$ ; (–) non tested; <dl concentrations under detection limit.

Trace elements	Crustaceans				Gastropods			Echinoderms	Intergroup variability	F-statistic (d.f.)
	Hermit crabs (H)	Crabs (Cr)	Isopods (I)	Shrimps (S)	Top snails (T)	Nerites (N)	Cone snails (Co)	Echinids (E)		
$N$	32	33	3	3	11	53	13	12		
Ag	0.12 $\pm$ 0.28	0.26 $\pm$ 0.32	0.23 $\pm$ 0.09	0.17 $\pm$ 0.02	0.12 $\pm$ 0.16	0.24 $\pm$ 0.36	1.67 $\pm$ 2.95	0.06 $\pm$ 0.05	E = H < Cr < Co*	9.19 (7)
As	17.2 $\pm$ 18.8	59.0 $\pm$ 177	78.9 $\pm$ 132	21.8 $\pm$ 7.51	19.3 $\pm$ 13.3	36.6 $\pm$ 17.5	161 $\pm$ 102	38.1 $\pm$ 91.2	H < T = N = E = Cr = I < Co**	11.33 (7)
Cd	1.10 $\pm$ 4.52	1.77 $\pm$ 4.23	1.15 $\pm$ 0.14	1.62 $\pm$ 0.09	0.32 $\pm$ 0.79	0.54 $\pm$ 0.85	2.05 $\pm$ 5.33	4.00 $\pm$ 3.15	H = Cr = T = N < E***	6.08 (7)
Co	0.36 $\pm$ 0.28	0.58 $\pm$ 1.96	0.28 $\pm$ 0.21	0.15 $\pm$ 0.03	0.15 $\pm$ 0.14	0.59 $\pm$ 2.04	0.84 $\pm$ 2.26	0.42 $\pm$ 0.31	ns	2.01 (7)
Cr	7.66 $\pm$ 21.03	5.48 $\pm$ 16.88	1.71 $\pm$ 1.26	0.21 $\pm$ 0.14	1.27 $\pm$ 1.04	9.40 $\pm$ 28.71	76.14 $\pm$ 193.2	5.68 $\pm$ 17.79	H < N = Co*	3.86 (7)
Cu	19.99 $\pm$ 19.10	38.44 $\pm$ 30.97	19.92 $\pm$ 6.70	14.89 $\pm$ 3.44	8.42 $\pm$ 7.48	55.39 $\pm$ 86.33	27.28 $\pm$ 16.04	3.55 $\pm$ 6.40	E < H = Co = Cr = N***	7.60 (7)
Fe	101 $\pm$ 190	603 $\pm$ 1960	124 $\pm$ 60	27 $\pm$ 9	40 $\pm$ 23	77 $\pm$ 81	331 $\pm$ 655	39 $\pm$ 60	E < Co**	3.48 (7)
Hg	0.014 $\pm$ 0.013	0.081 $\pm$ 0.105	0.400 $\pm$ 0.347	0.041 $\pm$ 0.010	0.019 $\pm$ 0.011	0.022 $\pm$ 0.015	0.053 $\pm$ 0.060	0.041 $\pm$ 0.037	H < T = N = E < Cr = I*	11.38 (7)
Mn	13.27 $\pm$ 20.21	11.85 $\pm$ 32.37	3.82 $\pm$ 1.80	2.76 $\pm$ 0.42	2.20 $\pm$ 3.34	27.79 $\pm$ 34.68	9.01 $\pm$ 12.69	6.28 $\pm$ 10.91	E = Cr = H < N***	11.83 (7)
Ni	4.35 $\pm$ 6.48	4.63 $\pm$ 14.19	2.27 $\pm$ 1.45	1.25 $\pm$ 0.21	0.76 $\pm$ 0.62	6.30 $\pm$ 19.75	40.26 $\pm$ 103.0	4.00 $\pm$ 7.15	T < H**	3.12 (7)
Pb	0.49 $\pm$ 1.63	0.17 $\pm$ 0.40	74.01 $\pm$ 101.1	0.28 $\pm$ 0.22	0.05 $\pm$ 0.06	1.02 $\pm$ 4.02	0.43 $\pm$ 0.88	1.35 $\pm$ 2.59	T = Cr = Co = H = N = E $\leq$ I*	3.74 (7)
Se	1.11 $\pm$ 1.90	1.35 $\pm$ 0.71	1.55 $\pm$ 1.37	2.57 $\pm$ 0.61	0.76 $\pm$ 0.19	1.90 $\pm$ 0.94	2.60 $\pm$ 1.31	1.60 $\pm$ 1.78	T = H < Cr = E = S < Co*	10.63 (7)
Zn	101 $\pm$ 74	124 $\pm$ 77	72 $\pm$ 11	78 $\pm$ 4	39 $\pm$ 10	73 $\pm$ 21	68 $\pm$ 42	47 $\pm$ 19	T = E < N < H = Cr*	7.31 (7)

### 3.1.3. Predators

Several trace elements concentrations were below the  $dl$  in some anguilliform fish; Ag in three of them, Cd in one and V in all species (Table 4). We found differences in concentrations between species. For instance, *Conger* Ll and Ls and *G. chilospilus* displayed the highest Cr ( $\approx 4.28 \pm 6.25 \mu\text{g}\cdot\text{g}^{-1}$  dw) and Ni ( $\approx 1.69 \pm 2.48 \mu\text{g}\cdot\text{g}^{-1}$  dw) values, whereas *G. eurostus* and *G. undulatus* respectively showed the highest values of Cd ( $1.17 \pm 0.27 \mu\text{g}\cdot\text{g}^{-1}$  dw) and Pb ( $0.17 \pm 0.20 \mu\text{g}\cdot\text{g}^{-1}$  dw), and As ( $23.72 \pm 12.21 \mu\text{g}\cdot\text{g}^{-1}$  dw) and Hg ( $0.161 \pm 0.19 \mu\text{g}\cdot\text{g}^{-1}$  dw). Few differences were significant due to the high inter-individual variability observed (Table 4). However, significant differences were found between *Conger* Ll and Ls and *G. chilospilus* (for details see Briand et al., 2014).

## 3.2. Trace element concentrations in the different food webs

### 3.2.1. Mining elements - Co, Cr, Fe, Mn, and Ni

Significant differences were observed for Cr and Fe elements. The highest mean concentrations in Co, Cr, Fe, and Mn were measured in OM sources sustaining the S-BFW, i.e. SOM essentially (Table 5 and

Fig. 2a). A high intra- and interspecific variability of the concentrations was observed, although reef invertebrates (small crabs, cone snails, nerites) depending on the S-BFW overall accumulated higher mean concentrations for most trace elements than those involved in the two other food webs, mainly the D-BFW (Fig. 2a); differences were significant for Co, Fe and Mn but not for Cr and Ni (Table 5). Comparisons did not reveal any significant difference between the anguilliform fish species of the three food webs (Table 5).

### 3.2.2. Agro-industrial elements - As, Hg, and Zn

Both mean As and Hg concentrations were significantly higher in OM sources sustaining the D-BFW, i.e. seagrass, than in OM sources of the S-BFW, but higher in anguilliform fish depending on the S-BFW than specimens involved in the R-BFW (Table 5 and Fig. 2b). Zn concentrations did not show any significant difference between OM sources whereas results revealed higher Zn concentrations in anguilliform fish depending on the S-BFW compared to the R-BFW. In any cases, no significant difference of trace element concentrations was demonstrated in invertebrates.

**Table 4**

Concentrations of trace elements (Mean  $\pm$  SD; in  $\mu\text{g}\cdot\text{g}^{-1}$  dry weight) of different anguilliform species, all sites pooled. Given a low number of samples analysed for three species ( $N$ ), comparisons between groups (ANCOVA, Tukey post-hoc) were only performed between *Conger* Ls, *Conger* Ll and *G. chilospilus* (see results in Briand et al., 2014). <dl concentrations under detection limit.

Trace elements	<i>Conger</i> Ls	<i>Conger</i> Ll	<i>Gymnothorax chilospilus</i>	<i>Gymnothorax eurostus</i>	<i>Gymnothorax fimbriatus</i>	<i>Gymnothorax undulatus</i>
$N$	9	28	48	2	1	3
Ag	<dl	<dl	<dl	0.53 $\pm$ 0.40	0.30	0.29 $\pm$ 0.20
As	7.00 $\pm$ 5.76	31.71 $\pm$ 26.67	10.97 $\pm$ 7.42	2.22 $\pm$ 0.19	33.28	23.72 $\pm$ 12.21
Cd	0.07 $\pm$ 0.06	0.034 $\pm$ 0.04	0.41 $\pm$ 0.47	1.17 $\pm$ 0.27	0.07	<dl
Co	0.10 $\pm$ 0.17	0.14 $\pm$ 0.14	0.11 $\pm$ 0.08	0.23 $\pm$ 0.18	0.07	0.05 $\pm$ 0.01
Cr	1.80 $\pm$ 1.93	4.75 $\pm$ 5.91	4.53 $\pm$ 7.15	0.5 $\pm$ 0.01	0.87	0.56 $\pm$ 0.09
Cu	1.90 $\pm$ 0.94	1.88 $\pm$ 0.93	1.63 $\pm$ 0.65	0.88 $\pm$ 0.39	0.80	1.02 $\pm$ 0.48
Fe	24 $\pm$ 12	38 $\pm$ 35	40 $\pm$ 37	16 $\pm$ 11	19	7.2 $\pm$ 0.5
Hg	0.186 $\pm$ 0.193	0.095 $\pm$ 0.060	0.049 $\pm$ 0.028	0.143 $\pm$ 0.017	0.386	0.161 $\pm$ 0.019
Mn	3.46 $\pm$ 3.23	2.42 $\pm$ 1.89	2.28 $\pm$ 1.43	2.15 $\pm$ 0.96	4.99	3.69 $\pm$ 0.76
Ni	0.68 $\pm$ 0.79	1.69 $\pm$ 1.94	1.95 $\pm$ 3.19	0.17 $\pm$ 0.01	0.47	0.34 $\pm$ 0.06
Pb	0.04 $\pm$ 0.01	0.07 $\pm$ 0.10	0.05 $\pm$ 0.04	0.17 $\pm$ 0.20	0.03	0.04 $\pm$ 0.003
Se	1.34 $\pm$ 0.47	1.90 $\pm$ 0.85	1.18 $\pm$ 0.38	1.38 $\pm$ 0.25	1.36	1.95 $\pm$ 0.01
V	<dl	<dl	<dl	<dl	<dl	<dl
Zn	51 $\pm$ 27	43 $\pm$ 23	57 $\pm$ 16	37 $\pm$ 3.3	44	58 $\pm$ 5.3

**Table 5**

Summary of concentration variability in (a) “mining” and (b) “urban” or “agro-industrial” trace elements between different trophic compartments (OM sources and reef consumers, i.e. invertebrates and anguilliform fish, details in Table 1) of the three main benthic trophic pathways; the detrital benthic food web sustained by seagrass (D-BFW or D), the sedimentary benthic food web sustained by SOM and non-calcareous macroalgae (S-BFW or S) and the reef benthic food web sustained by algal turf and calcareous macroalgae (R-BFW or R). ANOVA and Tukey post-hoc tests were performed (d.f. = 2 for sources and invertebrates, d.f. = 1 for anguilliform fish); ns:  $p > 0.05$ ; \* $p < 0.05$ ; \*\* $p < 0.01$ ; \*\*\* $p < 0.001$ ; – untested.

	OM sources	F-statistic	Invertebrates	F-statistic	Anguilliform fish	F-statistic
(a)						
“Mining” elements						
Co	ns	1.25	D < S**	5.07	ns	3.40
Cr	D < S**	7.27	ns	0.49	ns	0.01
Fe	D < S*	3.91	D < S***	8.62	ns	0.17
Mn	ns	2.99	D < S***	12.17	ns	0.54
Ni	ns	2.88	ns	0.96	ns	0.0004
(b)						
“Agro-industrial” elements						
As	S < D*	4.22	ns	3.80	R < S***	20.16
Hg	S < D = R***	22.64	ns	1.04	R < S*	6.58
Zn	ns	3.76	ns	1.99	R < S***	17.03
“Urban” elements						
Ag	S < D = R*	8.59	ns	0.24	–	–
Cd	S < D = R*	6.46	D < S = R**	6.31	R < S***	45.63
Cu	ns	2.65	ns	1.10	ns	0.63
Pb	ns	2.20	D < R*	3.68	ns	3.64
Se	S < R*	4.34	ns	0.68	S < R***	29.41
V	ns	1.01	–	–	–	–

### 3.2.3. Urban elements - Ag, Cd, Cu, Pb, Se, and V

Significant differences were observed for Ag, Cd, and Se that were less concentrated in S-BFW sources. Conversely, invertebrates of the S-BFW preferentially accumulated Cd, whereas mean concentrations of the other elements were higher in consumers depending on R-BFW (Se) (Table 5 and Fig. 2c).

### 3.3. Biomagnification of trace elements along food webs

We observed complex and not consistent patterns. Concentrations of almost all trace elements (except Ag and Cr) varied significantly across increasing trophic levels that were revealed by specific  $\delta^{15}\text{N}$  ratio (Table S1). In many instances, e.g. for Co, Fe, Mn, Ni, and Pb, we found significant negative relationships ( $r$  varying from  $-0.03$  to  $-0.55$ , Fig. 3a) and trophic magnification factor (TMF) values of less than 1 (Table S1). For other elements, the relationship was significant and positive (Table S1); moderate for As, Cd, and Cu ( $r$  varying from 0.13 to 0.32, Fig. 3b) and stronger for Zn ( $r = 0.61$ ), Se ( $r = 0.67$ ) and Hg ( $r = 0.77$ , Fig. 3c). For the first five elements, TMF values obtained were higher than 1, varying from 1.07 to 1.32 (Table S1), with the highest values for Hg (TMF > 1.5).

### 3.4. Spatial and temporal variations of trace element concentrations

Most trace element concentrations in SOM significantly decreased from the coast to the barrier reef (Table S2.a). This spatial pattern was also observed along gradients of both GN and GS areas. However, the two areas showed different SOM concentrations in fringing reefs (e.g. GN < GS in As, Cu, Mn and Ni), intermediate (i.e. GN > GS in Fe, Pb, and V) and barrier reefs (e.g. GN > GS in As, Hg, Mn and Ni, Table S2.a). Regarding algal turf, significantly higher concentrations were also observed at fringing reefs for several elements (Co, Cu, Hg, Mn, Ni, Pb, Se and Zn, Table S2.b). Within GN and GS areas, only few spatial variations between sites were found, with often significantly higher concentrations detected at intermediate sites compared to barrier reef sites. Between the two areas (GN vs. GS), intermediate and barrier reef sites showed significantly higher concentrations of several trace elements measured in algal turf from GN (Co, Pb, Se, and Zn, Table S2.b). In macrophytes, however, trace element concentrations showed more complex patterns without any clear spatial structure (results not shown).

High concentrations of trace elements linked to mining activities (i.e., Co, Cr, Fe, Mn, and Ni) were essentially detected in anguilliform specimens from fringing reefs, with higher levels in GN than GS. A more homogeneous distribution pattern along the gradient characterized several urban elements (e.g., Cu and Pb, see Briand et al., 2014). Although invertebrates overall accumulated significantly higher concentrations in fringing reefs (Ag, Co, Fe, Mn, and Pb, all species pooled, ANOVA  $p < 0.05$ ), spatial patterns were complex with regard to each species; some elements showed higher concentrations in specimens from fringing reefs (e.g. Co, Hg, and Mn in the crab *Grapsus albolineatus*), while other elements displayed higher concentrations in specimens from intermediate and barrier reefs (e.g. As and Cu in *Echinometra mathaei*, Table S3.a). Spatial patterns also varied between the two areas. Individuals of two species, *Nerita albicilla* and *N. plicata*, from fringing and intermediate reefs in GS accumulated significantly higher Cd and Hg concentrations (Table S3.b), whereas *E. mathaei* from barrier reefs in GN showed significantly higher Co, Fe and Se concentrations (Table S3.a).

Overall, our results suggested that seasons did not or weakly influence trace element concentrations of reef organisms (Table S4). Yet few significant fluctuations with higher concentrations during the hot wet season compared to the cold dry season were observed.

## 4. Discussion

### 4.1. Contamination levels

#### 4.1.1. Sedimentary organic matter (SOM)

In the sediments, the high concentrations of Co, Cr, Fe, and Mn and intermediate Ni levels, might indicate contamination from mining activities, especially in the fringing reefs. These high sediment concentrations could be explained by more or less uncontrolled (and unknown) waste from the SLN factory and/or the erosion of lateritic soils intensified by open-cast mining over the last decades (Dalvi et al., 2004). The concentrations of other elements (i.e. As, Hg, Pb, Se, and Zn) in sediments were low or moderate, except for Cu and V. Therefore, although the influence of Ni exploitation appeared to be visible, the extensive urban development and industrialization that occurred during the last decades did not translate into major specific ‘urban’ contamination of the abiotic compartment sampled. Comparisons with other coastal areas suggest that the reef sediments of the New Caledonian lagoon exhibit moderate trace element concentrations originating from urban

activities. They were situated in between those recorded in poorly industrialized and urbanized islands (e.g. Wallis, south-central Pacific; Letourneur et al., *unpublished data*) versus areas under strong anthropogenic pressures (e.g. Hawaii, Caribbean Sea, Mediterranean Sea, Adriatic Sea, Guzmán and Jiménez, 1992; Miao et al., 2001; de Mora et al., 2004; Lafabrie et al., 2007). For several trace elements, concentrations were below the limit recommended by NOAA (Long et al., 1995) and Environment Canada (ISQG, 1995). Nevertheless, very high concentrations of Cr, Fe, Mn, and Ni have been measured in the sediments of the New Caledonian mangroves (Marchand et al., 2011). This strongly suggests that large quantities of trace metals discharged into the sea are actually sequestered in the mangroves. Further studies are needed to better assess the contamination rates caused by human activities that may impact different components of the lagoon.

#### 4.1.2. Primary producers

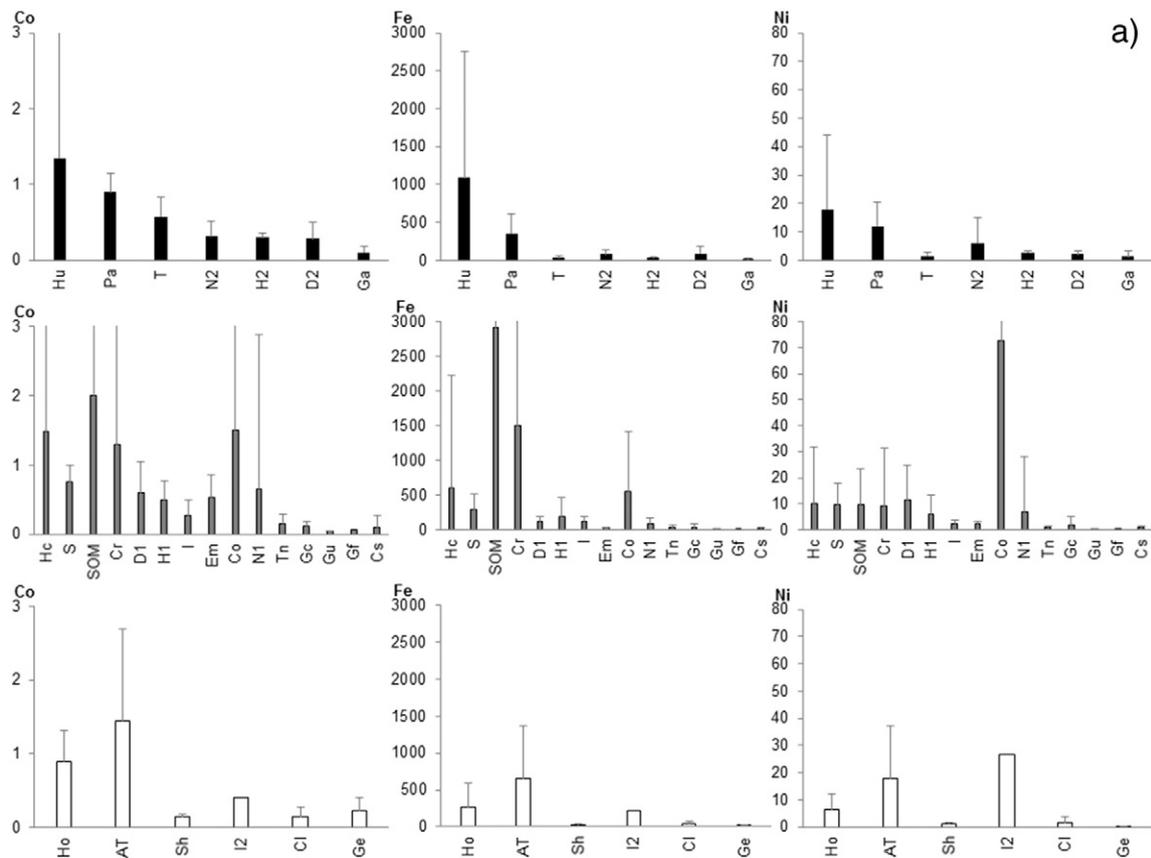
Results revealed variable values of 'urban' and 'agro-industrial' elements in macrophytes, which accumulated either higher (e.g. Ag, As, Cd, and Se) or lower (Cu and V) concentrations than SOM. The algal turf often exhibited the highest concentrations (Hg, Pb, and Zn). In addition, the algal turf and to a lesser extent the seagrasses were characterized, like SOM, by 'mining' contamination with higher concentrations of Cr, Fe, Mn, and Ni. The high accumulation levels detected in the algal turf could be explained by the influence of several intermingled factors that can influence the adsorption and/or absorption processes of trace elements. For example, the cell wall structure, surface/volume ratio or its multispecific composition (cyanobacteria, micro and macrophytes) can impact the transfer of trace elements into organisms (de Ruyter van Steveninck et al., 1988). Although the high trace element concentrations in seagrasses were almost never

statistically discriminated from the other macrophytes, their strong bioaccumulation capacity was nonetheless likely (Schlacher-Hoenlinger and Schlacher, 1998; Pergent-Martini and Pergent, 2000). Further studies are needed to assess this important issue. Compared to equivalent species sampled in other locations in the world (e.g., Wallis and the Mediterranean Sea, Lafabrie et al., 2007; Letourneur et al., *unpublished data*), macrophytes from New Caledonia revealed a moderate contamination by the 'mining' elements (Co, Cr, Fe, Mn, and Ni), and rather low (Ag, Cd, Cu, Pb, and Zn) to moderate (As, Hg, Se, and V) accumulation levels of 'urban' and 'agro-industrial' elements.

#### 4.1.3. Reef consumers

The wide variations of metallic trace element concentrations measured between the taxonomic groups and species of consumers, i.e. invertebrates and anguilliform fish, suggests that phylogeny was not the sole or the main driving factor in consumers' bioaccumulation process. Some of these differences might be due to body size and trophic status variations. Higher assimilation efficiency of trace elements in omnivorous and carnivorous invertebrates compared to herbivorous invertebrates has been documented (e.g. Fowler and Teyssié, 1997; Wang and Ke, 2002). Diet is therefore an essential parameter to consider in the assessment and interpretation of consumers' contamination (Wang and Fisher, 1999; Wang, 2002; Bustamante et al., 2002, 2004). This suggests that, in the current study, other pathways of contamination by direct contact with the sediment or from the surrounding seawater would remain minor for most trace elements.

In comparison to similar species from other geographic areas (e.g. Wallis, East Pacific, Mediterranean Sea), reef invertebrates of the New Caledonian lagoon showed respectively higher or similar concentrations of 'mining' and 'agro-industrial'/'urban' trace elements



**Fig. 2.** Mean concentrations ( $\mu\text{g}\cdot\text{g}^{-1}$  dry weight) of trace elements associated with a) 'mining' (Co, Fe, Ni), b) 'agro-industrial' (As, Hg, Zn) and c) 'urban' (Cd, Cu, Se) activities measured in reef OM sources (S), reef invertebrates (I) and anguilliform fish (A). The three main benthic trophic pathways of the neocaledonian lagoon were considered (see text); food webs mainly sustained by seagrass (black), MOS (grey) and algal turf (white). Corresponding codes are provided in Table 1.

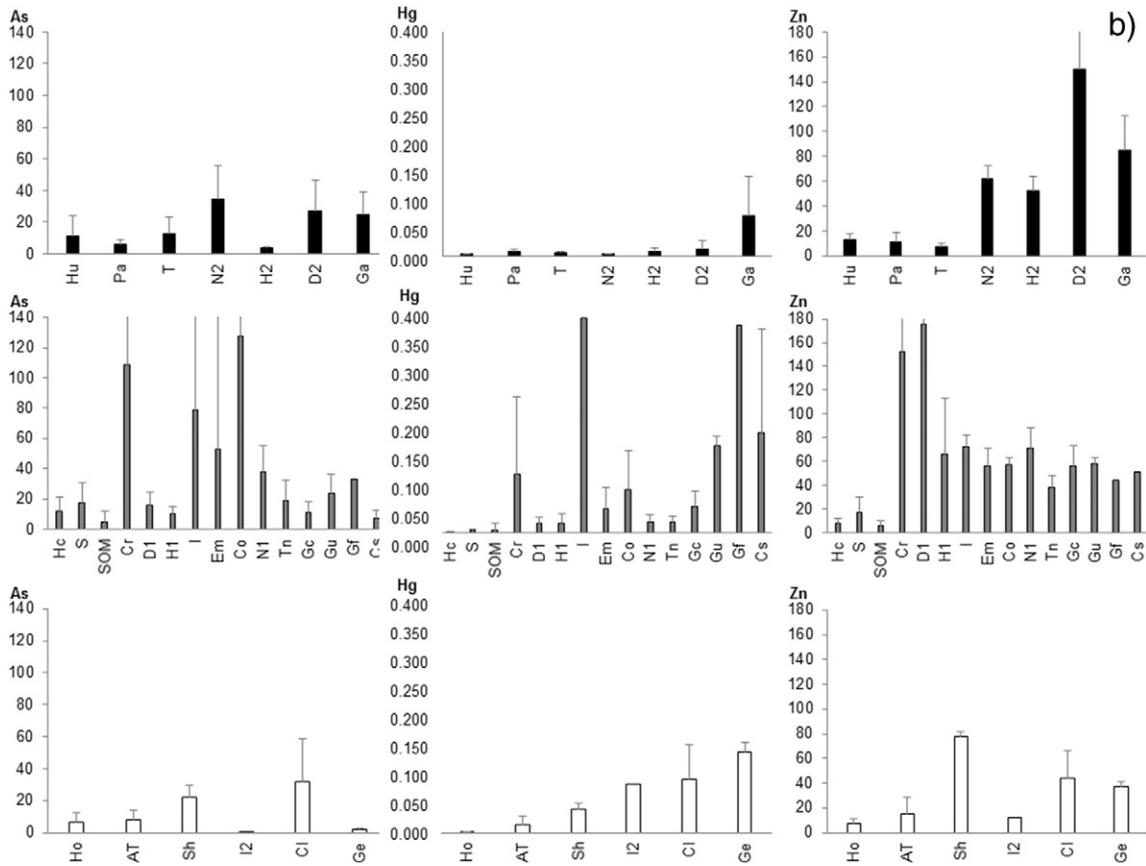


Fig. 2 (continued).

(Paez-Osuna and Ruiz-Fernandez, 1995; Firat et al., 2008; Hédouin et al., 2011; Letourneur et al., unpublished data). Concentrations for other elements such as Cu, Hg and Zn were comparable overall to the levels obtained in similar species from other areas, Fe, Mn, and Ni are strongly accumulated, with 17 to 50 times higher concentrations (Blackmore, 2001; Miao et al., 2001; Firat et al., 2008; Chouvelon et al., 2009; Métian et al., 2010; Hédouin et al., 2011). Finally, the concentrations of all trace elements were higher in our studied sedentary benthic anguilliform fish than in some more mobile fish in both the lagoon of New Caledonia and in other tropical regions (Briand et al., 2014). These results are fully consistent with previous results on anguilliform fish from New Caledonia (Bonnet et al., 2014).

4.2. Integration and transfer of contaminants through food webs

4.2.1. 'Mining' elements

Although 'mining' elements (Co, Cr, Fe, Mn, and Ni) were detected in all trophic compartments, the highest concentrations were generally found in sediment, and to a lesser extent in algal turf (Fig. 4). For instance, Fe was 7 and 73 times more concentrated in SOM than in the calcareous macroalgae *Halimeda* spp. or in the moray eel *Gymnothorax chilospilus*, respectively. Similarly, Ni concentrations were 3 to 52 times higher in algal turf than in non-calcareous macroalgae or in *G. undulatus*. Both primary compartments may therefore constitute the main storage reservoirs of this category of elements. Sediment contamination is issued from accumulation of contaminated small particles in seawater, adsorbing and transporting trace elements down into benthic substrate (Turner and Millward, 2002). It probably plays an indirect role by releasing trace elements in the water column rather than through direct contamination (Roussiez et al., 2006; Martínez-Lladó et al., 2007). The concentrations of 'mining' elements generally measured in

consumers may suggest that they have low bioavailability, and only some benthic invertebrates closely dependent on SOM for their habitat or nutritive resources, i.e. nerites, cone snails and crabs, revealed higher contamination levels than the sediment they inhabit. Overall, our results emphasized that the sedimentary benthic food web (S-BFW) might be a major direct or indirect integration pathway for 'mining' trace elements in coral reef ecosystems of New Caledonia.

4.2.2. 'Agro-industrial' and 'urban' elements

Storage role of the elements issued from multiple origin sources was apparently associated to other primary producers such as algal turf, seagrass and non-calcareous macroalgae (Fig. 4). These organisms exhibited high concentrations of Ag, As, Hg, Pb, Se, and Zn. High levels of some specific trace elements were therefore detected in reef invertebrates from the reef benthic food web (R-BFW) and the detrital benthic food web (D-BFW). For instance, isopods, cone snails and sea urchins revealed an important bioaccumulation capacity for As, Cd, and Pb. In addition, crabs and hermit crabs accumulated high concentrations of Zn. The detection in reef consumers of non-essential trace elements (e.g. Cd and Pb) emphasises the essential role played by food ingestion as a major contamination pathway (Wang, 2002; Wang and Ke, 2002; Zhang and Wang, 2006). Our results also suggested that the sedimentary benthic food web (S-BFW) may be an important integration pathway for some 'urban' and 'agro-industrial' elements into the New Caledonian reef ecosystems. Both Ag and Cd showed a preferential accumulation in SOM and consumers belonging to this trophic pathway (e.g. *Conus* spp., *Nerita* spp.), just as with As, Hg and Zn elements (e.g. small crabs, isopods, and in the fish *Gymnothorax undulatus*). This trend has been previously observed with measurements of high Hg concentrations in muscle of top-predators in close relation with sediment (Kress et al., 1998).

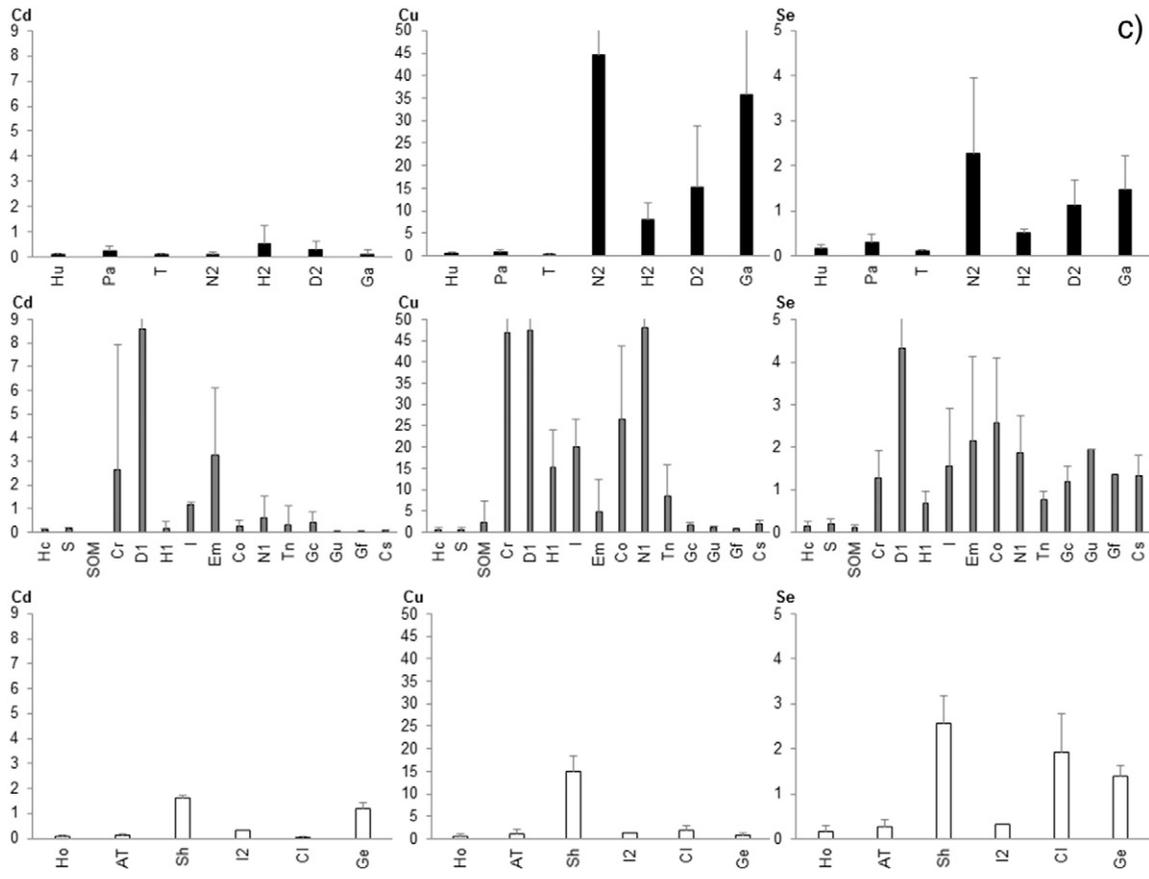


Fig. 2 (continued).

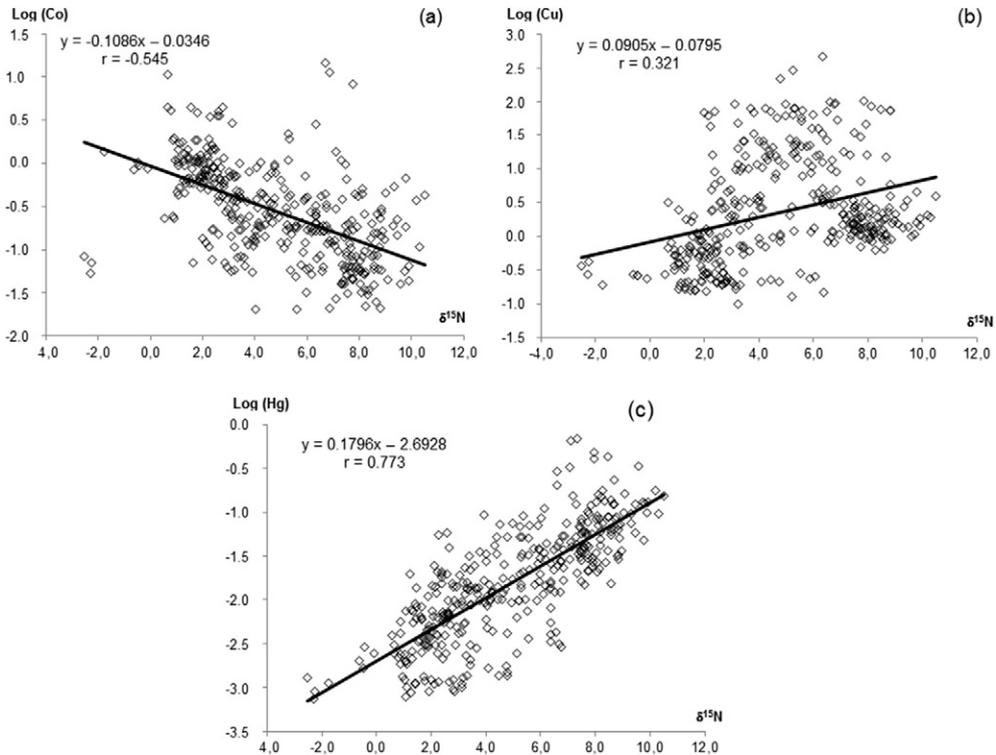
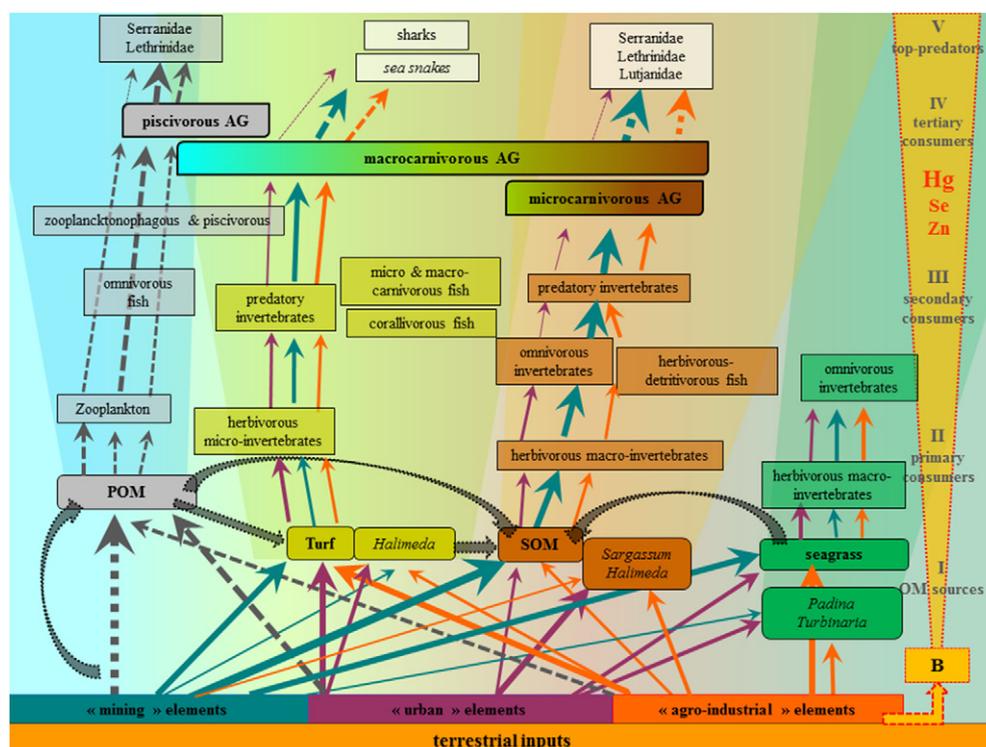


Fig. 3. Relationship between trophic level ( $\delta^{15}\text{N}$ ) and trace element concentrations (logarithm base ten) along food webs, all trophic compartments pooled. The elements presented (a) Co, (b) Cu and (c) Hg represent selected examples where significant linear regressions were found ( $p < 0.001$ ).



**Fig. 4.** Schematic representation of the integration and transfer of trace elements across the food webs of the New Caledonian lagoon up to high predator levels (anguilliform fish). The main contaminant routes are represented by arrows (dimension of the arrow provides a qualitative indication of transfer intensity), plus the biomagnification process (B) of Hg, Se, and Zn. Hypothetical and non-estimated transfers are also symbolized (dotted arrows). Color coding is used in order to differentiate trace elements from 'mining' (Co, Cr, Fe, Mn, and Ni, blue), 'urban' (Ag, Cd, Cu, Se, Pb, and V, purple) and 'agro-industrial' (As, Hg, and Zn, orange) into the reef benthic food web R-BFW (light green), the sedimentary benthic food web S-BFW (brown) and the detrital benthic food web D-BFW (dark green). An additional yet not-studied pathway, the lagoon pelagic food web L-PFW (grey), is also included to provide a more global picture. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

#### 4.3. Biomagnification of trace elements along food webs

The examination of the transfer of trace elements along the trophic levels of the New Caledonian coral reef food webs revealed different profiles, i.e. no pattern, increase or decrease (Fig. 4). A lack of biomagnification was suggested in most cases, as previously reported in other food chains (Young et al., 1980; Rainbow, 2002). Yet, a potential for biomagnification could not be excluded for several trace elements for which we obtained a positive relationship between their concentrations and trophic levels. Moderate positive relationships (TMF values < 1.25) were obtained with As, Cd, and Cu, resulting from the strong bioaccumulation capacity of several high trophic level organisms (e.g. cone snails, crabs, sea urchins, anguilliform fish), that show suitable physiological characteristics through both exposure pathways, i.e. food ingestion or diffusion process. This hypothesis fits with the fact that most of these organisms depend on the S-BFW and R-BFW, two important integration pathways for some 'urban' and 'agro-industrial' elements. The remarkable situation of Se and Zn ( $1.25 < \text{TMF values} < 1.5$ ) may reveal a biomagnification capacity, as suggested in previous studies (e.g. Barwick and Maher, 2003; Campbell et al., 2005; Cheung and Wang, 2008). Essential trace elements such as Zn may biomagnify along food webs, especially networks integrally constituted of invertebrates, which are in most cases known to efficiently accumulate this element (Dalinger, 1994). Finally, the strong relationship (TMF values > 1.5) obtained with Hg is very likely linked to a biomagnification process (e.g. Rainbow, 2002; Blackmore and Wang, 2004; Chouvelon et al., 2009) of the methylated form of Hg (methylmercury MeHg) demonstrating the high mobility, bioavailability and accumulation efficiency of MeHg (Ullrich et al., 2001). Although a stronger magnification has already been reported in low productive ecosystems associated with low dilution process in OM (Lavoie et al., 2013), the TMF value calculated in

this study for Hg (1.52) is equivalent to those obtained in the food webs of the Baltic Sea (1.50 for Hg, Nfon et al., 2009) or Mediterranean Sea (1.68 for Hg, Harmelin-Vivien et al., 2012). However, it would be premature to conclude on a similarity of functioning between those food webs; TMFs vary according to many factors, such as type, structure and length of food webs (Rasmussen et al., 1990). For instance, the food chain length strongly influences TMF values, since the longer the trophic network is, the higher the TMF (Harmelin-Vivien et al., 2012).

Rather than an increase in their concentrations with trophic levels, several elements such as Ag, Co, Fe, Mn, Ni, and Pb showed a decreasing pattern. This "trophic dilution" or biodiminution through food webs could result from several combined effects: low bioavailability of the element from prey to predator (Nfon et al., 2009), enhanced excretion rates, low assimilation efficiency (Newman and Unger, 2003) and/or again dilution effect by larger organisms (Newman and Heagler, 1991; Campbell et al., 2005).

#### 4.4. Influences of sites and seasons

The food webs of the SW New Caledonian coral reefs, especially in coastal fringing reefs, are directly subjected to high inputs such as natural soil erosion, intensive mining activities, urban development and a lack of sewage treatment facilities (e.g. Ambastian et al., 1997; Fernandez et al., 2006; Hédouin et al., 2006; Métian et al., 2008b). Although contamination decreases along the coast-ocean gradient, it is not limited to coastal zones and is spread over the whole lagoon (Bonnet et al., 2014).

The sedimentary reservoir is the best integrator of the spatial variations. It revealed the clearest decreasing gradient from the coast to the barrier reef, even if it was more visible for 'mining' than for 'agro-industrial' and 'urban' elements. The accumulation process is essentially

affected by the specific characteristics of the abiotic compartment, i.e. size of particles and organic carbon content (Luoma, 1990). Thus, SOM is a good indicator of local specificities. It showed, for example, a higher level of contamination of fringing sites in Grand Sud by all 'mining' and some 'agro-industrial' or 'urban' trace elements (i.e. As, Cr, V, and Zn), that could be explained by the strong soil erosion and mining activity in this area. On the other hand, the higher contamination of fringing sites in Grand Nouméa by some 'urban' trace elements (i.e. Cu, Hg, Pb, and Se) highlights the influence of industrial activities and urban development. The Grand Nouméa notably displayed extensive 'urban' pollution, with high concentration levels detected in sediments at the barrier reef sites. This difference with Grand Sud could be explained by the smaller surface area of this lagoon, associated with the efficient dispersion of those elements by local currents (Fichez et al., 2008), or by the previous use of islets as garbage dumps over a period of several years, mostly following WW2 (e.g. Amédée island in Nouméa offshore, Bonnet et al., 2014). Considering living organisms, spatial patterns become complex and are influenced by intermingled factors, e.g. diet and intrinsic parameters of organisms (e.g. body size). General trends and local specificities can be congruent (e.g. *Halimeda cylindracea*, anguilliform fish, Bonnet et al., 2014; Briand et al., 2014), minimized (e.g. algal turf), or divergent (e.g. *H. opuntia* or *Padina australis*) with results obtained in SOM. However, in spite of the significant spatial variations detected, broad contamination patterns through food webs were conserved at each site of the coast-barrier reef gradient and in each area. Further studies based on broader sampling design including additional areas and covering the entire archipelago would allow a more complete characterization of this spatial heterogeneity.

Seasons weakly and seldom influenced the contamination of food webs, and the rare variations found were compartment-dependent. In sediment, higher concentrations of 'mining' (Co, Fe, and Mn) and 'urban' (Cu, Hg, and Pb) elements in summer could be attributed to the intensification of terrestrial inputs during tropical rainfalls as well as other ecological factors, e.g. dissolved oxygen, salinity and detritus (Zayed et al., 1994). The observed complexity in spatial patterns of primary benthic producers and consumers probably results from the combined effects of the intrinsic traits of each species (diet, body size, and metabolism) with the local characteristics of each site (hydrology, current systems). Environmental parameters can sometimes influence bioaccumulation process; for example, turbidity, nutrient availability, light intensity and temperature are factors influencing the growth rate of producers (Farías et al., 2002), and thus indirectly affect concentrations of trace elements through dilution, especially for elements not subjected to biomagnification (Canli and Atli, 2003; Farkas et al., 2003). Nevertheless, the low temporal fluctuations observed are clearly not integrated within higher trophic levels such as the anguilliform fish that revealed very similar concentrations between seasons (Briand et al., 2014). Our temporal sampling design was appropriate considering the climate of New Caledonia, with a cold and a warm season. However, the assessment of the temporal heterogeneity of trace element sources within this complex coral reef ecosystem could be improved with a broader temporal scale, including inter-annual variability of meteorological events (rainfall, cyclones) or increasing human activities.

## 5. Conclusion

Variations in trace element concentrations were observed among compartments. SOM and algal turf are of great interest as indicators of reef food web contamination in New Caledonia because they supply respectively the sedimentary benthic food web (S-BFW) and reef benthic food web (R-BFW). These trophic chains contain the most important integration compartments and transfer pathways of most trace elements of 'mining', 'urban' and 'agro-industrial' origin. Trace elements are differently accumulated into primary producers, consumers and predatory fish, but only few exhibited biomagnification along trophic levels (Hg, and supposedly Se, and Zn). Major spatial and minor temporal

variations were mainly detected in the abiotic reservoir, i.e. SOM, revealing a higher accumulation of trace elements at coastal sites and during summer. For most organisms, the identification of simple clear patterns was impeded by marked variations of their intrinsic characteristics combined with space and time fluctuations. Instead, our complex results likely reflect the underlying complexity of coral reef functioning.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2017.08.257>.

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