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Abstract: The integration, accumulation and transfer of trace elements across the main tropic levels of many food webs are poorly documented. This is notably the case for the complex trophic webs of coral reef ecosystems. Our results concerning the south-west lagoon of New Caledonia show that both abiotic (i.e. sediments) and biotic (i.e. primary producers, consumers and predators) compartments are generally contaminated by trace elements. However, our analyses revealed specific contamination patterns from the sources of organic matter to 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: Ni and associated trace elements (Co, Cr, Fe, and Mn) were preferentially integrated into these trophic structures. 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 biodiminished with increasing trophic levels along trophic networks. 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.

Keywords: metallic contamination; food webs; trophic compartments; bioaccumulation; Biomagnification; New Caledonia

1. Introduction

Urbanisation, 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 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 (Eisler 2010), may have important physiological effects on organisms and 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 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 macro-algae (Davis *et al.* 2003), concentrations detected in primary producer tissues are generally directly proportional to the concentrations that prevail in the surrounding water (Metian *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 spread across food chains (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 determined.

All consumers exposed to trace elements may bioaccumulate them in 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. Wang 2002; Wang and Ke 2002; Burger *et al.* 2007). 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 tropic level (e.g. Bustamante *et al.* 2003; Métian *et al.* 2008a, b, 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 (i.e. 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: $\delta^{15}N$). 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 seawaters (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, 3,674 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 (Figure 1). Two areas were investigated. The Grand Nouméa area (GN) is close to the city of Nouméa, it is subjected to a 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 (Figure 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 (Figure 1).

In each area, three sites (fringing reef, intermediate reef and barrier reef) located along a coast-barrier reef gradient (Figure 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). 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, were indirectly obtained through their main predators, the amphibious sea kraits (*Laticauda laticaudata* and *L. saintgironsi*). Sea snakes resting on the beach of the surrounding island were captured and the anguilliform specimens were retrieved via gentle forced regurgitation. A widely tested sampling strategy, for which the spatial accuracy of sea snake sampling and their use as sentinels was described in previous studies (e.g. Brischoux *et al.* 2007, 2011; Bonnet 2012). In this study, we selected poorly digested prey to ensure that the isotopic values of the anguilliform fish were representative of each station; recently captured prey are almost intact at regurgitation and are found 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 (a mix of small filamentous algae known as 'algal

turf', calcareous and non-calcareous macroalgae and seagrass), the first layer (< 3 cm) of the subsurface sediment (SOM, sedimentary organic matter), 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, was 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°C.

2.3. ***$\delta^{15}N$ analyses***

SOM and muscle of the collected organisms were analysed. Samples were freeze-dried and ground to fine powder of which 1.0 ± 0.1 mg (15.0-20.0 ± 0.1 mg for sediment) was sealed in tin capsules for analyses. Isotopic $^{15}N/^{14}N$ 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, Bremen, Germany), as explained in Chouvelon *et al.* (2011). Results were expressed as isotope ratios $\delta^{15}N$ (‰) relative to international standard (atmospheric N_2 for nitrogen), according to the formula:

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

where $R = {}^{15}N/{}^{14}N$. Replicate measurements of internal laboratory standards

(acetanilide) indicated a precision of 0.2‰ for $\delta^{15}N$ 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 *$\delta^{15}N$ 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 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°C, and 15 min at 105°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, proving good repeatability of the method. The results for standard reference materials displayed recovery of the elements ranging 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), 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

In the interests of 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 in individuals of a same species or a same group (taxonomic or trophic) were under the detection limit (*dl*). In cases where these concentrations concerned only few samples, we used half of the *dl* values (Helsel 2010). Analyses of variance (ANOVA) and Tukey HSD post-hoc tests were performed so as 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 (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 the size or $\delta^{15}N$ 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 (interaction: area [2] x site [3] x 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 of the New Caledonian lagoon as presented in Briand *et al.* 2016 (species [44] x food web [3] factors). Based on this study which reconstructed the food webs' architecture from isotopic analyses, 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). Indeed, 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.

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 ($\delta^{15}N$ proxy) (Nfon *et al.* 2009):

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

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 $\delta^{15}N$ 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:

$$TMF = 10^{b}$$

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 is 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, demonstrated significantly higher concentrations of Ag, Cu, Fe, and Mn compared to echinoderms (showing globally high Cd concentrations and high Pb values in isopods), plus higher Cr and to a lesser extent Se concentrations than crustaceans (accumulating high 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).

3.1.3. Predators. Several trace elements concentrations were below the *dl* in some anguilliforms; 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* revealed the highest Cr (≈ 4.28 ± 6.25 $\mu g.g^{-1}$ dw) and Ni (≈ 1.69 ± 2.48) values, whereas *G. eurostus* and *G. undulatus* respectively showed the highest values in Cd

(1.17 ± 0.27) and Pb (0.17 ± 0.20), and As (23.72 ± 12.21) and Hg (0.161 ± 019). However, few differences were considered as clearly significant considering the high inter-individual variability observed (Table 4). However, significant differences were found between *Conger* Ll and Ls and *G. chilospilus* and detailed in the study 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 Figure 2.a). 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 (Figure 2.a); differences were significant for Co, Fe and Mn but not for Cr and Ni (Table 5). Comparisons did not confirm 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 Figure 2.b). 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 compare to the

R-BFW. In any cases, no significant difference of trace element concentrations was demonstrated in invertebrates.

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 Figure 2.c).

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 $\delta^{15}N$ ratio (Table S1). In many instances, i.e. for Co, Fe, Mn, Ni, and Pb, we found significant negative relationships (r varying from -0.03 to -0.55, Figure 3.a) and trophic magnification factor (TMF) values of less than 1 (Table S1). For other elements, the relation was significant and positive (Table S1); moderate for As, Cd, and Cu (r varying from 0.13 to 0.32, Figure 3.b) and stronger for Zn (r = 0.61), Se (r = 0.67) and Hg (r = 0.77, Figure 3.c). 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 individuals from fringing reefs (e.g. Co, Hg, and Mn in the crab *Grapsus albolineatus*), while other elements displayed higher concentrations in individuals 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 *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 influenced 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 lagoons of New Caledonia exhibit moderate trace element concentrations originating from urban activities. They were situated in between those recorded in poorly

industrialized and urbanised 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, Guzman and Jimenez 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 characterised, like SOM, by 'mining' contamination with higher concentrations in 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), justifying their consideration in further studies. 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 remained 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 (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 lagoons 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 in algal turf to a lesser extent. For instance, Fe is 7 and 73 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; Martinez-Llado *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 caused by other primary producers such as algal turf, seagrass and non-calcareous macroalgae. These organisms exhibited high concentrations of Ag, As, Hg, Pb, Se, and Zn in this study. High concentrations of some specific trace elements were therefore detected in reef invertebrates depending on 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) recalls the essential role played by food as a major contamination pathway (Wang 2002; Wang and Ke 2002; Zhang and Wang 2006). 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).

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. An inability to biomagnify 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 ($1.25 <$ 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 taller 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 there is a decrease of the contamination 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 clearer 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 differences. 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 heavy soil erosion in this area and the additional mining activity. Conversely, the higher contamination of fringing sites in Grand Nouméa by some 'urban' trace elements (i.e. Cu, Hg, Pb, and Se) highlights the intensity of industrial activities and urban development in this area. 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). Complexity in spatial patterns of primary benthic producers and consumers is probably the result of the combined effect of species' intrinsic characteristics (diet, size, and metabolism) and the local specificities of sites (hydrology, current systems). Environmental parameters can sometimes directly play on the organism's 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 quite 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 webs contamination in New Caledonia because they supply respectively the sedimentary benthic food web (S-BFW) and reef benthic food webs (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 organisms, the determination of simple clear patterns was impeded by 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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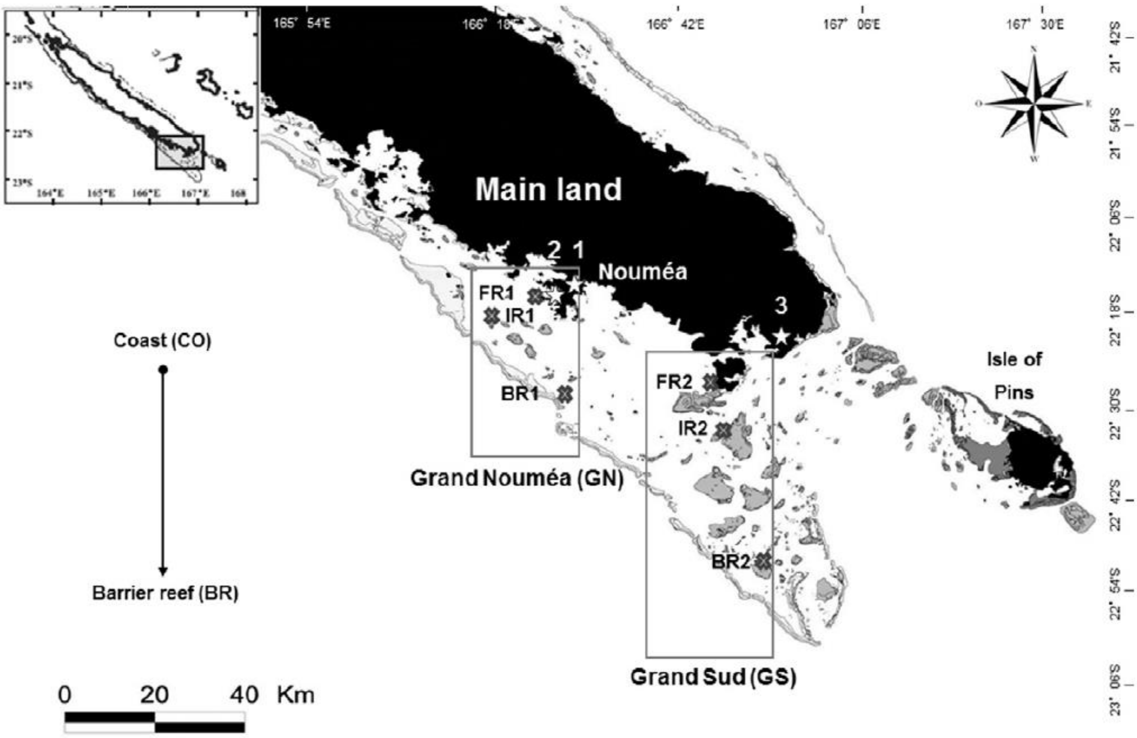


Figure 1. Study site locations in the southwest lagoon of New Caledonia, SW Pacific Ocean. Six sites distributed on a coast-barrier reef gradient (fringing reef FR, intermediate reef IR and barrier reef BR) were sampled in two different areas referred to as Grand Nouméa (GN, area 1) and Grand Sud (GS, 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.

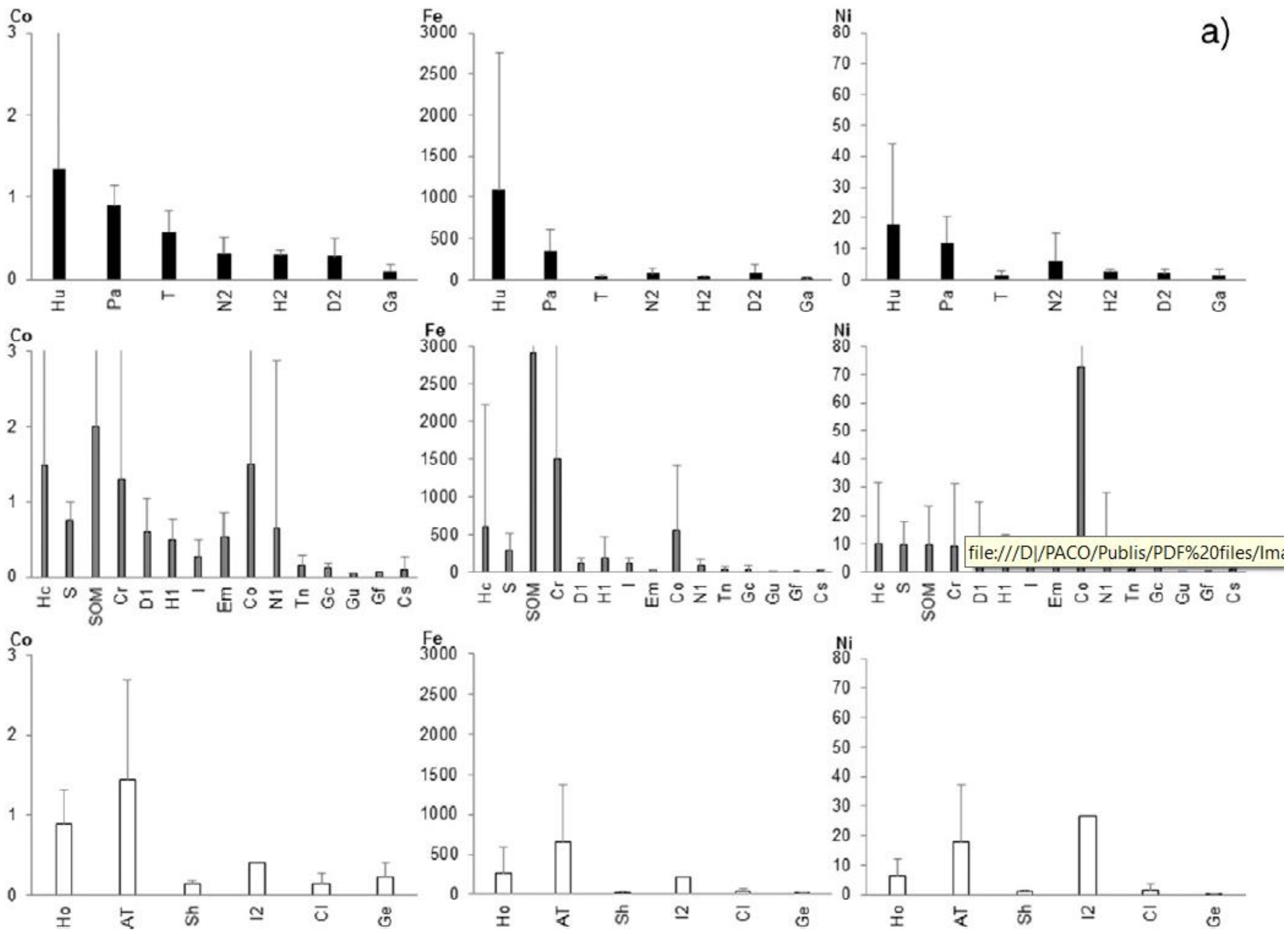
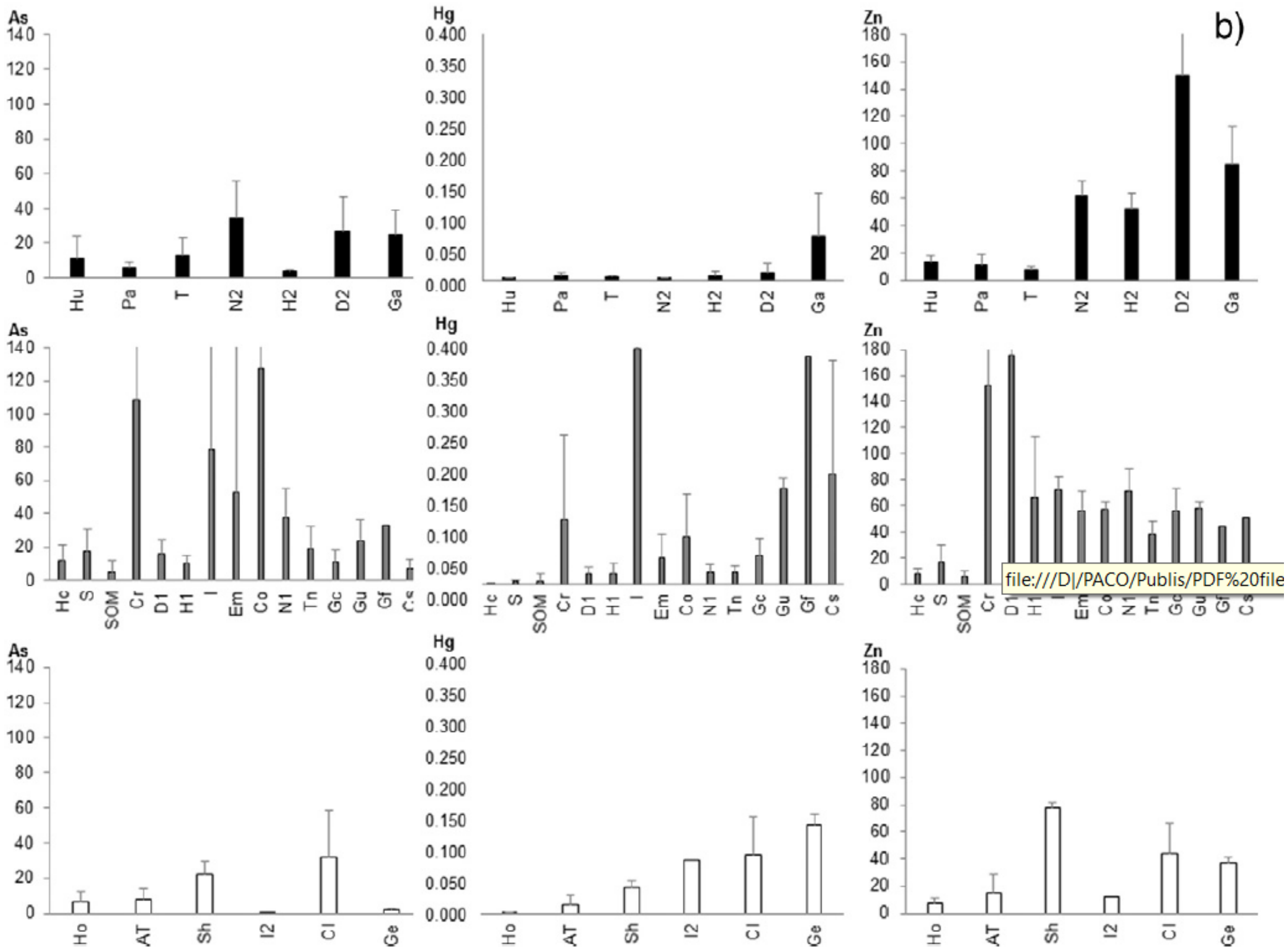


Figure 2. Mean concentrations (µg.g^{-1} dry weight) in a) 'mining' trace elements (Co, Fe, Ni), b) 'agro-industrial' trace elements (As, Hg, Zn) and c) 'urban' trace elements (Cd, Cu, Se) between reef OM sources (S), reef invertebrates (I) and anguilliform fish (A), into the three main benthic trophic pathways of the neocaledonian lagoon; food webs mainly sustained by seagrass (black), MOS (grey) and algal turf (white). Corresponding codes in Table 1.



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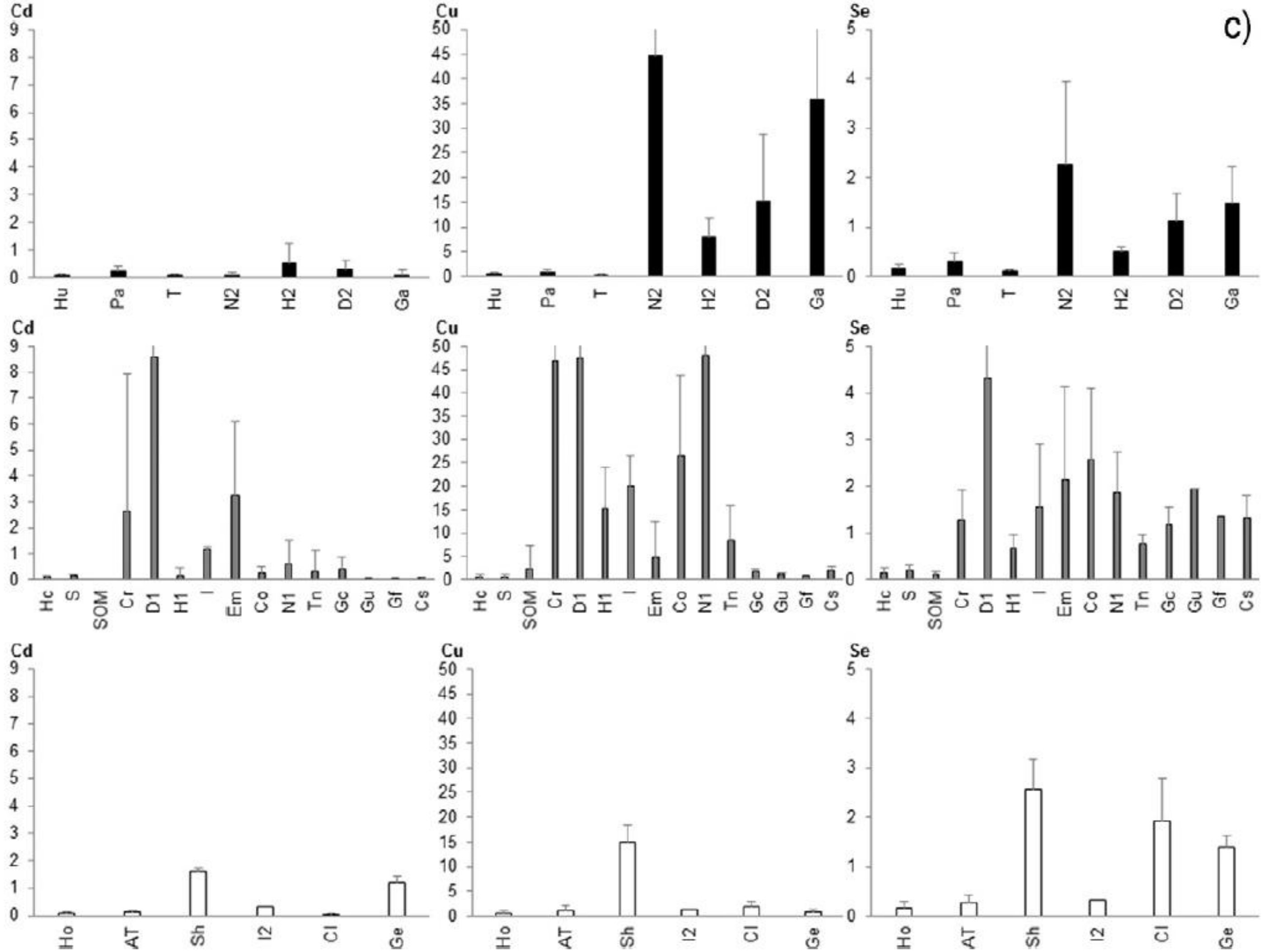

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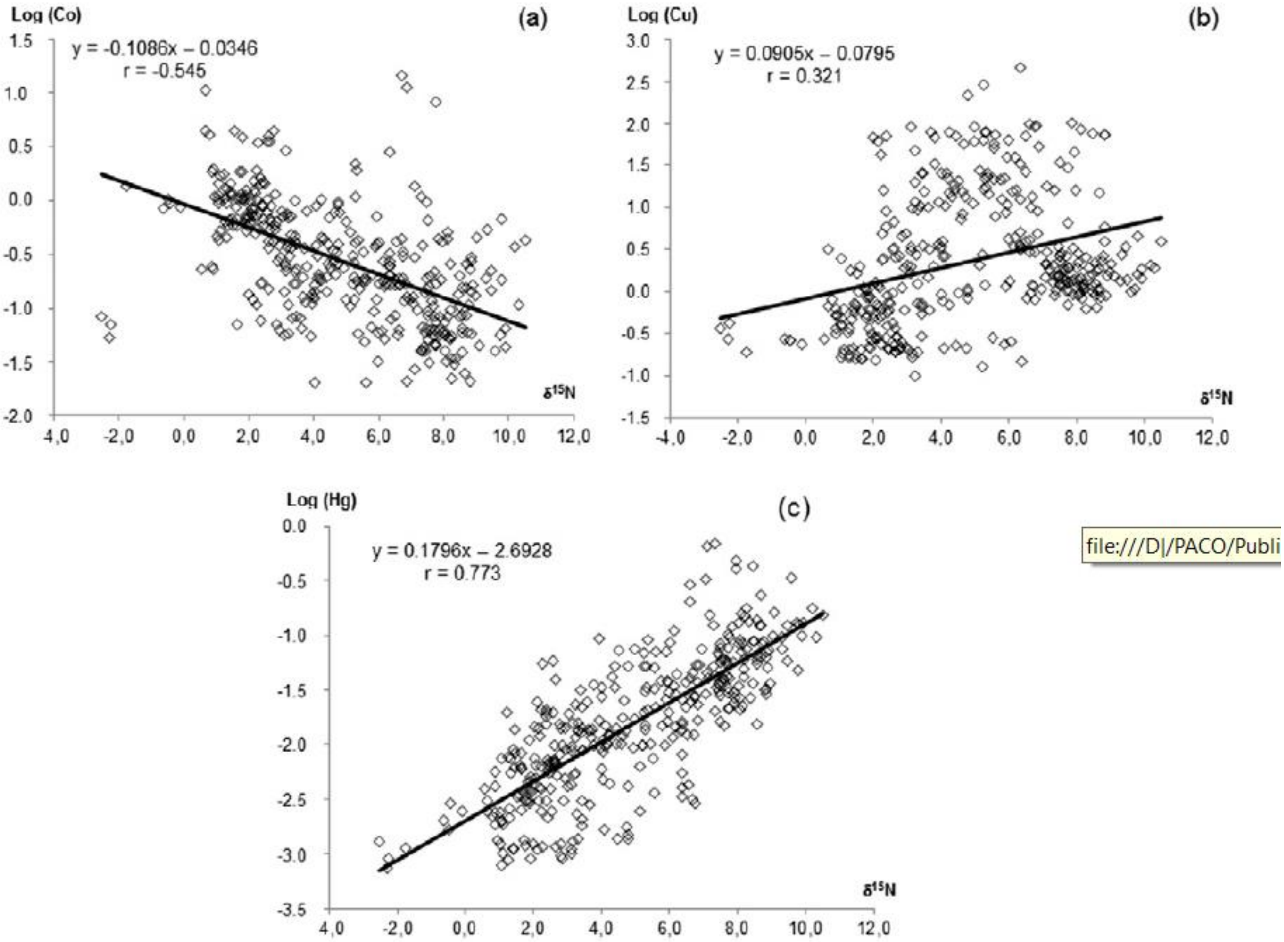

Figure 3. Relation between trophic level ($\delta^{15}N$) and trace element concentrations (logarithm base ten) along food webs, all trophic compartments pooled. The elements (a) Co, (b) Cu and (c) Hg are presented as examples, all demonstrating significant linear regressions ($p < 0.001$).

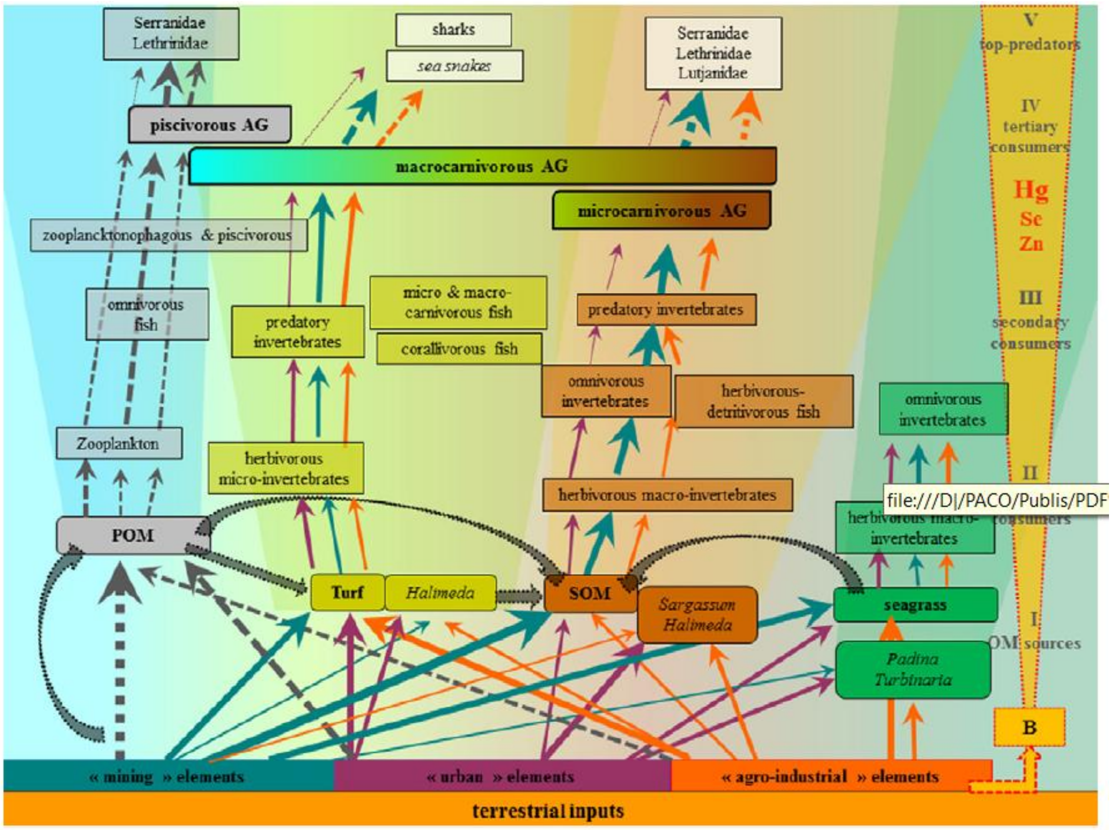

Figure 4. Schematic representation of the integration and transfer of trace elements across the food webs of the New Caledonian lagoon up to high predator levels (anguilliformfish). The main contaminant routes are represented by arrows (dimension of the arrow provides a qualitative indication of transfer 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.)

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	*Halimeda cylindracea*	Hc	S-BFW	*21*
Source	Macroalgae c	*Halimeda opuntia*	Ho	R-BFW	*27*
Source	Macroalgae nc	*Padina australis*	Pa	D-BFW	*11*
Source	Macroalgae nc	*Sargassum cristaefolium*	S	S-BFW	*3*
Source	Macroalgae nc	*Sargassum spinulligerum*	S	S-BFW	*9*
Source	Macroalgae nc	*Turbinaria conoïdes*	T	D-BFW	*3*
Source	Macroalgae nc	*Turbinaria ornata*	T	D-BFW	*6*
Source	Macroalgae nc	*Turbinaria* sp.	T	D-BFW	*9*
Source	Seagrass	*Halodule uninervis*	Hu	D-BFW	*12*
Source	SOM	SOM	SOM	S-BFW	*36*
Invertebrate	Echinid	*Echinometra mathaei*	Em	S-BFW	*8*
Invertebrate	Echinid	*Parasalenia gratiosa*	Pg	R-BFW	*1*
Invertebrate	Isopod	mix (indet.)	I	S-BFW	*3*
Invertebrate	Cone snail	*Conus marmoreus*	Co	S-BFW	*6*
Invertebrate	Cone snail	*Conus virgo*	Co	S-BFW	*1*
Invertebrate	Crab	*Grapsus albolineatus*	Ga	D-BFW	*17*
Invertebrate	Crab	*Leptodius sanguineus*	Cr	S-BFW	*3*
Invertebrate	Crab	*Pilumnus vespertilio*	Cr	S-BFW	*3*
Invertebrate	Crab	*Thalamita* cf. *coeruleipes*	Cr	S-BFW	*1*
Invertebrate	Crab	mix - 4 sp. (indet.)	Cr	S-BFW	*6*
Invertebrate	Hermit crab	*Clibanarius* cf. *eurysternus*	Ce	S-BFW	*7*
Invertebrate	Hermit crab	*Dardanus scutellatus*	Ds	D-BFW	*3*
Invertebrate	Hermit crab	*Dardanus lagopodes*	D1	S-BFW	*2*
Invertebrate	Hermit crab	*Dardanus setifer*	D1	S-BFW	*1*
Invertebrate	Hermit crab	*Dardanus* cf. *setifer*	D2	D-BFW	*1*
Invertebrate	Hermit crab	*Dardanus* sp1	D2	D-BFW	*1*
Invertebrate	Hermit crab	*Petrolisthes lamarckii*	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	*Nerita albicilla*	N1	S-BFW	*17*
Invertebrate	Nerite	*Nerita plicata*	N1	S-BFW	*15*
Invertebrate	Nerite	*Nerita* sp1 (indet.)	N2	D-BFW	*3*
Invertebrate	Nerite	*Nerita* sp2 (indet.)	N2	D-BFW	*2*
Invertebrate	Nerite	*Nerita* sp3 (indet.)	N1	S-BFW	*9*
Invertebrate	Nerite	*Nerita* sp4 (indet.)	N1	S-BFW	*3*
Invertebrate	Shrimp	mix (indet.)	Sh	R-BFW	*3*
Invertebrate	Top snail	*Tectus niloticus*	Tn	S-BFW	*11*
Fish	Moray eel	*Gymnothorax chilospilus*	Gc	S-BFW	*48*
Fish	Moray eel	*Gymnothorax undulatus*	Gu	S-BFW	*3*
Fish	Moray eel	*Gymnothorax fimbriatus*	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	*Gymnothorax eurostus*	Ge	R-BFW	*2*

Table 2. Concentrations of trace elements (Mean ± SD; in µg·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 freedomof ANOVA test, Tukey post-hoc) are indicated. ns: $p > 0.05$;* $p < 0.05$;** $p < 0.01$;*** $p < 0.001$; (−) non tested; bdl 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.)
N	*36*	*30*	*48*	*45*	*12*		
Ag	<*dl*	0.10 ± 0.14	0.05 ± 0.09	0.15 ± 0.31	0.08 ± 0.09	Mc < Mnc**	3.79 (3)
As	4.43 ± 7.06	7.49 ± 6.39	8.98 ± 7.90	12.17 ± 10.89	11.50 ± 12.44	SOM < AT = Mc = S = Mnc***	13.75 (4)
Cd	<*dl*	0.11 ± 0.07	0.07 ± 0.06	0.13 ± 0.15	0.08 ± 0.04	*ns*	2.64 (3)
Co	1.99 ± 3.37	1.44 ± 1.26	1.14 ± 1.55	0.69 ± 0.29	1.35 ± 1.77	*ns*	0.65 (4)
Cr	12.44 ± 16.24	9.72 ± 8.18	6.88 ± 14.61	4.25 ± 5.39	18.90 ± 30.78	Mnc = Mc < AT = SOM*	6.85 (4)
Cu	2.29 ± 5.10	1.11 ± 1.01	0.54 ± 0.55	0.60 ± 0.52	0.57 ± 0.22	*ns*	1.81 (4)
Fe	2923 ± 5947	654 ± 721	416 ± 1092	183 ± 224	1092 ± 1668	Mnc = Mc < SOM*	4.55 (4)
Hg	0.005 ± 0.012	0.014 ± 0.013	0.002 ± 0.001	0.006 ± 0.003	0.004 ± 0.001	Mc < S = SOM = Mnc < AT***	55.68 (4)
Mn	35.33 ± 58.91	29.41 ± 36.95	9.59 ± 14.19	10.49 ± 13.20	18.23 ± 23.68	Mc = Mnc < AT*	3.65 (4)
Ni	9.66 ± 13.93	17.76 ± 19.55	7.97 ± 14.95	6.66 ± 7.61	18.00 ± 26.00	Mnc < AT*	2.66 (4)
Pb	0.28 ± 0.32	1.18 ± 1.96	0.13 ± 0.20	0.22 ± 0.34	0.35 ± 0.33	Mc < AT***	4.85 (4)
Se	0.12 ± 0.05	0.26 ± 0.16	0.16 ± 0.12	0.20 ± 0.14	0.18 ± 0.06	SOM = Mc < Mnc = AT*	6.82 (4)
V	9.07 ± 18.02	6.88 ± 6.74	5.77 ± 13.17	4.15 ± 4.76	4.94 ± 5.29	*ns*	1.63 (4)
Zn	5.5 ± 4.1	15.1 ± 13.8	7.3 ± 3.8	11.1 ± 8.8	13.5 ± 4.7	SOM = Mc < Mnc = S = AT*	11.88 (4)

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

Table 4. Concentrations of trace elements (Mean ± SD; in µg·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). bdl concentrations under detection limit.

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

Supplementary material

Table S1. Linear regressions between trace element concentrations (in *log_{10}*, µg.g^{-1} dw) and nitrogen signature ($\delta^{15}N$, ‰) of reef organisms, all compartments and species pooled. The regression parameters (*p*, *r* and *b*), the trophic magnification factor (TMF), and the number of samples *N* are indicated. Significant positive regressions are in bold. *ns:* p > 0.05; * p < 0.05; ** p < 0.01; *** p < 0.001; untested regression for V due to undetected concentrations in several trophic levels.

Trace elements	*r*	TMF	*N*
Ag	-0.090	0.96	*274*
As	**0.276**	**1.11**	*359*
Cd	**0.132**	**1.07**	*359*
Co	-0.545	0.78	*359*
Cr	-0.029	0.98	*359*
Cu	**0.321**	**1.23**	*359*
Fe	-0.358	0.83	*359*
Hg	**0.773**	**1.52**	*355*
Mn	-0.232	0.89	*359*
Ni	-0.359	0.83	*359*
Pb	-0.183	0.90	*359*
Se	**0.668**	**1.32**	*359*
Zn	**0.610**	**1.28**	*225*

Table S2. Spatial variability of mean trace element concentrations in a) SOM and b) algal turf. Differences between fringing (FR), intermediate (IR) and barrier reefs (BR) of the general gradient, Grand Nouméa (GN; "1") and Grand Sud (GS; "2") gradients were tested (ANOVA and Tukey *post-hoc*, *ns:* p > 0.05; * p < 0.05; ** p < 0.01; *** p < 0.001; - untested).

a)

Trace elements	**General gradient**	**GN Gradient**	**GS Gradient**	**GN *vs.* GS**
As	IR = BR < FR ***	IR1 < FR1 = BR1 ***	BR2 < IR2 < FR2 **	FR1 < FR2 ***; BR2 < BR1 ***
Co	BR < IR < FR **	IR1 = BR1 < FR1 ***	BR2 < IR2 < FR2 **	FR1 < FR2 ***
Cr	BR < IR < FR ***	IR1 = BR1 < FR1 *	BR2 < IR2 < FR2 ***	FR1 < FR2 ***; IR1 < IR2 **; BR2 < BR1 ***
Cu	BR < IR < FR ***	BR1 < IR1 < FR1 ***	BR2 < IR2 < FR2 **	FR2 < FR1 ***
Fe	BR < IR < FR ***	BR1 < IR1 < FR1 ***	BR2 < IR2 < FR2 ***	FR1 < FR2 ***; IR2 < IR1 **; BR2 < BR1 ***
Hg	BR < IR < FR ***	BR1 < IR1 < FR1 ***	BR2 < IR2 < FR2 ***	FR2 < FR1 ***; BR2 < BR1 **
Mn	BR < IR < FR ***	BR1 < IR1 < FR1 ***	BR2 < IR2 < FR2 ***	FR1 < FR2 ***; BR2 < BR1 ***
Ni	BR < IR < FR ***	BR1 < IR1 < FR1 ***	BR2 < IR2 < FR2 ***	FR1 < FR2 ***; BR2 < BR1 **
Pb	BR < IR < FR ***	IR1 < FR1 = BR1 ***	BR2 = IR2 < FR2 ***	FR2 < FR1 ***; IR2 < IR1 *; BR2 < BR1 ***
Se	IR = BR < FR ***	FR1 < BR1 = IR1 ***	BR2 = IR2 < FR2 ***	FR2 < FR1 ***; BR2 < BR1 ***
V	BR < IR < FR ***	BR1 < IR1 < FR1 ***	BR2 < IR2 < FR2 ***	FR1 < FR2 ***; IR2 < IR1 *; BR2 < BR1 ***
Zn	IR = BR < FR ***	ns	BR2 = IR2 < FR2 ***	FR1 < FR2 ***

b)

Trace elements	**General gradient**	**GN Gradient**	**GS Gradient**	**GN *vs.* GS**

Ag	*ns*	*ns*	*ns*	*ns*
As	*ns*	*ns*	*ns*	*ns*
Cd	FR < BR < IR **	*ns*	*ns*	*ns*
Co	BR < IR = FR *	*ns*	BR2 < IR2 *	BR2 < BR1 ***
Cr	*ns*	*ns*	*ns*	*ns*
Cu	BR = IR < FR **	*ns*	*ns*	*ns*
Fe	*ns*	*ns*	*ns*	*ns*
Hg	IR < BR < FR ***	*ns*	*ns*	*ns*
Mn	IR = BR < FR ***	*ns*	*ns*	*ns*
Ni	BR = IR < FR ***	*ns*	*ns*	*ns*
Pb	IR = BR < FR ***	IR1 < FR1 < BR1 *	*ns*	IR2 < IR1 ***; BR2 < BR1 ***
Se	BR < IR = FR *	BR1 < IR1 < FR1 *	*ns*	IR2 < IR1 ***; BR2 < BR1 ***
V	BR < IR ***	BR1 < IR1 **	*ns*	IR2 < IR1 ***; BR2 < BR1 *
Zn	BR = IR < FR **	*ns*	*ns*	*ns*

Table S3. Spatial variability of mean trace element concentrations in two invertebrates, a) *Echinometra mathaei* and b) *Nerita albicilla*. Differences between fringing (FR), intermediate (IR) and barrier reefs (BR) of the general gradient, Grand Nouméa (GN) and Grand Sud (GS) gradients were tested (ANOVA and Tukey *post-hoc*, *ns*:p > 0.05; * p < 0.05; ** p < 0.01; *** p < 0.001; - untested).

a)

Trace elements	**General gradient**	**GN gradient**	**GS gradient**	**GN *vs.* GS**
Ag	*ns*	*ns*	-	*ns*
As	FR = IR < BR **	ns	-	*ns*
Cd	IR < FR = BR ***	IR1 < FR1 = BR1 *	-	*ns*
Co	IR < FR *	IR1 < FR1 **	-	BR2 < BR1 *
Cr	*ns*	*ns*	-	*ns*
Cu	FR < BR < IR **	*ns*	-	*ns*
Fe	*ns*	*ns*	-	BR2 < BR1 *
Hg	IR = BR < FR *	BR1 < IR1 < FR1 *	-	*ns*
Mn	IR = BR < FR *	BR1 < FR1 *	-	*ns*
Ni	*ns*	BR1 < FR1 *	-	*ns*
Pb	*ns*	*ns*	-	*ns*
Se	*ns*	*ns*	-	BR2 < BR1 *
V	-	-	-	-
Zn	*ns*	*ns*	-	*ns*

b)

Trace elements	**General gradient**	**GN gradient**	**GS gradient**	**GN *vs.* GS**
Ag	IR < BR = FR *	IR1 < BR1 = FR1 *	*ns*	FR2 < FR1 ***
As	*ns*	*ns*	*ns*	*ns*
Cd	*ns*	*ns*	*ns*	*ns*
Co	*ns*	*ns*	*ns*	*ns*
Cr	*ns*	*ns*	*ns*	*ns*
Cu	IR < FR **	IR1 < FR1 **	*ns*	*ns*
Fe	*ns*	*ns*	*ns*	*ns*
Hg	IR < FR ***	IR1 < BR1 < FR1 **	FR2 < IR2 ***	FR1 < FR2 ***; IR1 < IR2 ***
Mn	*ns*	*ns*	*ns*	*ns*
Ni	*ns*	*ns*	*ns*	*ns*
Pb	*ns*	*ns*	*ns*	*ns*
Se	BR < FR *	*ns*	*ns*	*ns*
V	-	-	-	-
Zn	*ns*	*ns*	*ns*	*ns*

Table S4. Summary of temporal variability of mean trace element concentrations in several reef invertebrates. Differences between the summer (S) and winter (W) seasons were tested at each site of the general gradient (FR, IR and BR), Grand Nouméa (FR1, IR1 and BR1) and Grand Sud (FR2, IR2 and BR2) gradients (ANOVA and Tukey *post-hoc*, *ns:* p > 0.05; * p < 0.05; ** p < 0.01; *** p < 0.001; - untested).

	Trace elements	Sites	Variations
OM Sources			
SOM	Co, Cu	FR2	W < S ***
	Fe	FR, BR	W < S *
	Hg	FR, FR1, BR2 ; IR, IR2, BR1	W < S *** ; S < W ***
	Mn, V	IR, IR1	W < S *
	Pb	BR2 ; BR1	W < S ** ; S < W *
Algal turf	Ag, Cu	BR	W < S **
	As	BR, BR2 ; IR, IR2	W < S *** ; S < W **
	Cd, Hg	FR ; IR	W < S * ; S < W ***
	Pb, Se	BR, BR1	W < S ***
	V	BR ; IR	W < S * ; S < W ***
	Zn	BR1 ; IR, IR1	W < S * ; S < W *
Invertebrates			
Grapsus albolineatus	Ni	IR1	W < S *
	Pb	BR, BR1	S < W ***
Echinometra mathaei	Ag, As, Cu	BR2	W < S ***
	Cd	BR1	S < W ***
Nerita albicilla	Hg	IR2	W < S *
Nerita plicata	Hg	IR, IR2	W < S *