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Trace element bioaccumulation in reef fish from New Caledonia: Influence of trophic groups and risk assessment for consumers

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ABSTRACT

Fourteen trace elements (Ag, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, V, and Zn) were analyzed in livers and muscles from 22 fish species from the New Caledonia lagoon, which is subjected to important chemical inputs due to intense land-based mining activities (New Caledonia is the third largest world producer of Ni). The results of this baseline research indicated that livers generally concentrated trace elements to a greater extent than muscles. Nevertheless, the overall trace element concentrations in both tissues were barely above the levels reported in fish and thus contamination at the local scale was poorly discriminated. Although these levels were low, preliminary risk assessment from a global health standpoint suggests that As would be an element potentially leading to exposure of concern for fish consumers. Based on the trace element concentrations in livers and the fish trophic preferences, some trends have been observed among trophic groups: Ag, Cu, Fe, Hg, and Zn concentrations were generally higher in liver of fish with the highest trophic position whereas Cd concentrations were lower in these groups. The use of the leopard coral grouper *Plectropomus leopardus* as a resident top predator allowed determining the geographical variations in contamination levels with significant differences for six out of the fourteen elements investigated. The sampling sites influenced by anthropogenic inputs were revealed by high Ag, Cd, Cu, Hg, and Pb concentrations. Such geographic differences also applied to Zn but surprisingly not for the typical elements associated with Ni mining, i.e., Co, Cr, Mn and Ni.

1. Introduction

New Caledonia is the third largest producer of nickel (Ni) in the world (Dalvi et al., 2004) and this activity constitutes a threat for the marine environment through metal contamination: it mainly concerns Ni and its mining by-products such as cobalt (Co), chromium (Cr) and manganese (Mn) which occur at elevated concentrations in Ni ores. However, it has been shown that other elements, such As or Hg, are also of toxicological concern in this environment (Chouvelon et al., 2009; Hédouin et al., 2009; Metian et al., 2008a).

In this specific context, metal and metalloid bioaccumulation in many taxa such as crustaceans, molluscs, ascidians or marine mammals have been investigated (Bustamante et al., 2000, 2003; Hédouin et al., 2009; Metian et al., 2008a, 2010; Monniot et al., 1994; Pernice et al., 2009), with most of the studies having been dedicated to molluscs, particularly to bivalves (e.g. Hédouin et al., 2009, 2010; Metian et al., 2008a). With the exception of Hg (Chouvelon et al., 2009), there is a considerable lack of information concerning trace element contamination in fish from New Caledonia.

Given the importance of fish as a staple food in Pacific island countries and territories (PICTs) such as in New Caledonia (an annual per capita fish consumption up to 55 kg in rural communities; Bell et al., 2009), it is crucial to fill the gap of knowledge concerning metal content in edible fish: a large consumption of fish may lead to an ingestion of a cumulative amount of metals putting local consumers' health at risk.

The main objective of the present study was to provide baseline information on trace element contamination status of the New Caledonia coastal marine environment. For this purpose, a wide

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range of fish species, collected from different locations previously characterized for their degree of contamination (Chouvelon et al., 2009; Hédouin et al., 2009), were analyzed for their trace element contents. Special emphasis was given to two body compartments: the liver which is involved in the detoxification processes of several trace elements and the muscle which is the main part that is eaten, in order to establish a preliminary risk assessment for the consumers. In addition, the variation of trace element concentrations was investigated in the tissues of the leopard coral grouper *Plectropomus leopardus* collected in various sites and the variation of trace element concentrations according to trophic groups was studied for the entire samples set.

2. Materials and methods

2.1. Sampling and sample preparation

Fish belonging to 22 species were collected in March and October 2007 along the South coast of New Caledonia (Fig. 1, Table 1), either by scuba diving or bought to local fishermen. The sampling sites were selected based on their reported contrasting contamination status (Chouvelon et al., 2009; Hédouin et al., 2009; Metian et al., 2008a): Grande Rade, Koutio Bay, Sainte Marie Bay, Ouano Bay, Maa Bay, Prony Bay (Fig. 1, Table 1). The organisms bought from fishermen were caught in the Southern lagoon (Fig. 1, Table 1).

Due to anthropogenic inputs (industry and extractive metallurgical activities), Grande Rade sediments displayed high concentrations for several trace elements (Hédouin et al., 2009). Koutio Bay is also characterised by an important rubbish dump and is influenced by inputs of domestic wastes from the city of Noumea whereas Sainte Marie Bay receives important sewage sludge from Nouméa and terrigenous inputs from the Coulée River. In contrast, Maa Bay and Ouano Bay are preserved from important anthropogenic inputs (Hédouin et al., 2009).

All collected organisms were weighed (wet wt) and measured (total length; up to the base of the caudal fork) upon return to the laboratory. The characteristics (number of individuals, length and weight, sampling period and location) of each of the 22 species collected are given in Table 1. Fish were then dissected in order to collect the liver and a piece of dorsal muscle (standardised cut on dorsal muscle just behind the head). The total number of samples was 124 (details provided in Annex 1). Each tissue sample was weighed (wet wt) and immediately placed in individual plastic bags and frozen at −25 °C. Samples were then freeze-dried and weighed again (dry wt). Freeze-dried tissues were ground and stored in individual plastic vials until further elemental analysis.

Table 1 also indicates the diet habits (through the "trophic group" column) of each species in order to assess, if any, the influence of trophic specificity on bioaccumulation of the studied elements. Diet data have been gathered in Fishbase dataset (Froese and Pauly, 2011) and they are in good agreement with fish diet analyses performed in New Caledonia by Kulbicki et al. (2005). The collected species were arranged into 4 groups in order to observe possible specific range of element concentrations for each trophic group. The groups were the following ones: grazer/scavenger (GS); predator of invertebrates (PI); predator of invertebrates and small fish (PISM); and predator of small fish (PSM). In addition, trophic levels were also gathered in Fishbase dataset (Froese and Pauly, 2011).

2.2. Trace element analysis

The analysis of Ag, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V and Zn in the tissues required the mineralization of the samples. Aliquots of liver and muscle ranging from 50 to 300 mg were digested using 3–5 ml of a 3:1 (v:v) mixture of 65% HNO_3 and 37% HCl (both from Merck and suprapur quality). Acidic mineralization was performed at room temperature overnight, then in a microwave during 30 min

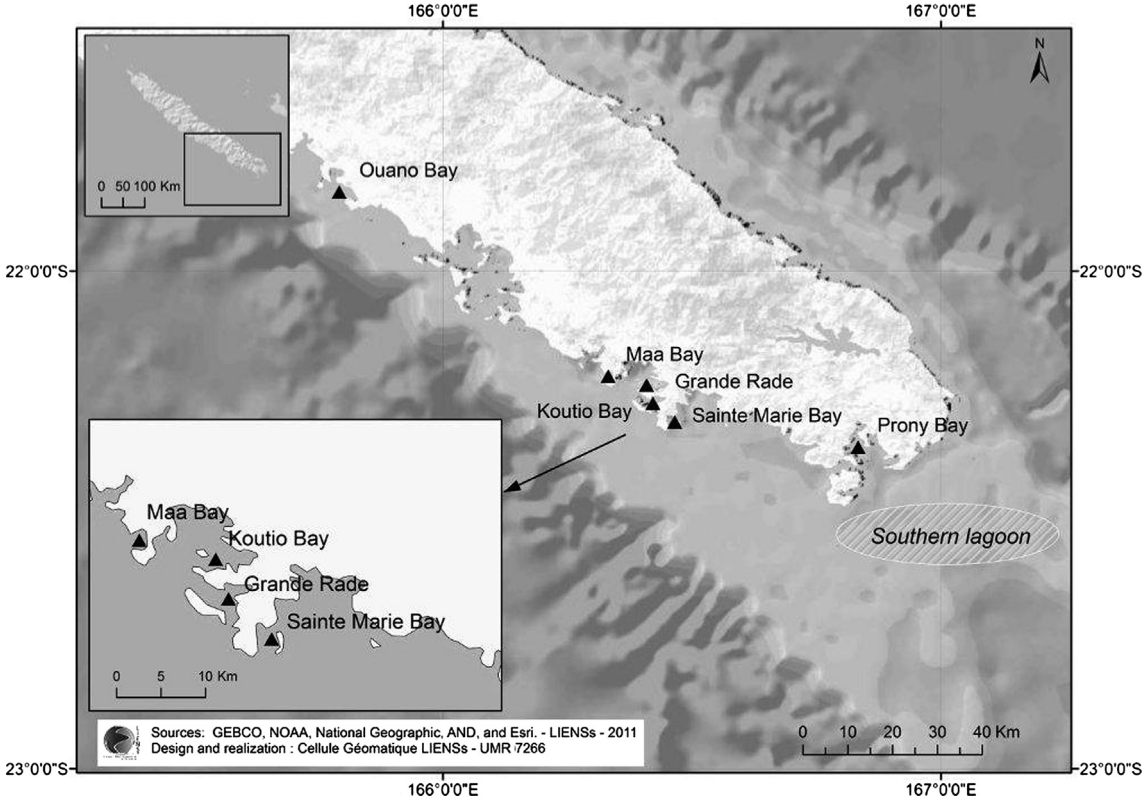

Fig. 1. Map of the sampling sites along the South coast of New Caledonia and in the vicinity of Noumea City (their positions are indicated by black triangles).

Table 1
Characteristics of the fish collected in the New Caledonia lagoon.

Family and species	*N*	Length (mm) mean ± SD (Range)	Wet weight (g) mean ± SD (Range)	Sampling site(s) (date[a])	Trophic group	Life style
Acanthuridae						
Bluespine unicornfish (*Naso unicornis*)	1	435	1600	Ouano Bay	Grazer/Scavenger	Neritic
Haemulidae						
Two-striped sweetlips (*Plectorhinchus albovittatus*)	1	405	1300	Ouano Bay	Predator (invertebrates)	Neritic
Harlequin sweetlips (*P. chaetodonoides*)	1	351	900	Grande Rade	Predator (invertebrates and small fish)	Neritic
Lemon sweetlips (*P. flavomaculatus*)	1	485	1600	Grande Rade	Predator (crustaceans and small fish)	Neritic
Painted sweetlips (*Diagramma pictum*)	1	451	1160	Ouano Bay (O)	Predator (invertebrates and small fish)	Neritic
Kyphosidae						
Brassy chub (*Kyphosus vaigiensis*)	5	317 ± 50 (260–370)	718 ± 330 (380–1100)	Ouano Bay	Grazer/Scavenger	Neritic
Labridae						
Golden-spot hogfish (*Bodianus perditio*)	1	343	800	Grande Rade	Predator (invertebrates)	Neritic
Floral wrasse (*Cheilinus chlorourus*)	1	290	450	Koutio Bay	Predator (invertebrates)	Neritic
Lethrinidae						
Grass emperor (*Lethrinus laticaudis*)	3	266 ± 11 (256–277)	376 ± 45 (331–420)	Southern Lagoon	Predator (crustaceans and small fish)	Neritic
Humpnose big-eye bream (*Monotaxis grandoculis*)	2	261 ± 7 (256–266)	420 ± 21 (405–434)	Southern Lagoon	Predator (invertebrates)	Neritic
Lutjanidae						
Mangrove red snapper (*Lutjanus argentimaculatus*)	5	449 ± 63 (348–510)	1345 ± 494 (625–1900)	Grande Rade (M&O), Ouano Bay, Maa Bay	Predator (crustaceans and small fish)	Neritic
Onespot snapper (*L. monostigma*)	2	249 ± 37 (223–275)	475 ± 177 (350–600)	Ouano Bay, Maa Bay	Predator (crustaceans and small fish)	Neritic
Platycephalidae						
Crocodile fish (*Cymbacephalus beauforti*)	2	510 ± 99 (440–580)	1425 ± 530 (1050–1800)	Prony (O)	Predator (small fish)	Benthic
Priacanthidae						
Moontail bullseye (*Priacanthus hamrur*)	7	307 ± 21 (285–340)	454 ± 96 (360–600)	Ouano Bay	Predator (invertebrates and small fish)	Neritic
Scaridae						
Blue-barred parrotfish (*Scarus ghobban*)	1	247	245	Koutio Bay	Grazer/Scavenger	Neritic
Blunt-head parrotfish (*S. microrhinos*)	1	508	3000	Ouano Bay	Grazer/Scavenger	Neritic
Rivulated parrotfish (*S. rivulatus*)	1	355	900	Ouano Bay	Grazer/Scavenger	Neritic
Yellowband parrotfish (*S. schlegeli*)	1	249	400	Ouano Bay	Grazer/Scavenger	Neritic
Serranidae						
Leopard coral grouper (*Plectropomus leopardus*)	21	413 ± 110 (265–615)	1294 ± 1051 (300–3800)	Grande Rade (M&O), Koutio Bay, Ouano Bay (M&O), Maa Bay, Sainte Marie Bay, Prony (O)	Predator (small fish)	Neritic
Highfin grouper (*Epinephelus maculates*)	1	340	480	Ouano Bay	Predator (invertebrates and small fish)	Neritic
Whitespotted grouper (*Epinephelus coeruleopunctatus*)	1	470	1500	Prony (O)	Predator (crustaceans and small fish)	Neritic
Sparidae						
Goldsilk seabream (*Acanthopagrus berda*)	2	275 ± 5 (271–278)	550 ± 71 (500–600)	Ouano Bay, Maa Bay	Predator (invertebrates and small fish)	Neritic

[a] Sampling date was mainly done in March 2007 but also in October 2007, O or M&O are indicated under brackets when sampling was realized in October and in March and October, respectively.

with increasing temperature until 105 °C, and 15 min at 105 °C (1200 W). After the mineralization process, each sample was diluted to 30–50 ml with milli-Q quality water, according to the volume of acid added to the mineralization. Elements were analyzed using a Varian Vista-Pro ICP-OES (As, Cr, Cu, Fe, Mn, Ni, Se and Zn) or a Varian ICP-MS Ultra Mass 700 (Ag, Cd, Co, Pb and V).

Hg was directly analyzed on the dried samples by atomic absorption spectrometry with an Advanced Mercury Analyser (ALTEC AMA 254). Only livers were analyzed since Hg concentrations in muscles have been reported previously (Chouvelon et al., 2009).

Reference materials (dogfish liver DOLT-4 and lobster hepatopancreas TORT-2; NRCC) were treated and analyzed in the same way as the samples. The results were in good agreement with the certified values, and the relative standard deviations were always below 15%, proving good repeatability of the method. The results for reference materials displayed element recoveries ranging from 72% to 134%. Blanks were included in each analytical batch. The detection limits (μg g^{-1} dry wt) were 0.007 (Hg), 0.02 (Ag, Cd, Co), 0.06 (Pb), 0.63 (Cr, Cu, Mn), 1.09 (Ni, V), 2.69 (Fe, Zn), 5.46 (As), and 10.9 (Se) for livers and 0.02 (Ag, Cd, Co), 0.06 (Pb), 0.53 (Cr, Cu, Mn), 0.92 (Ni, V), 2.78 (Fe, Zn), 5.49 (As), and 9.22 (Se) for muscles. All element concentrations are given on a dry weight basis (μg g^{-1} dry wt).

2.3. Data analyses

All data submitted to statistical tests were first checked for normality (Shapiro–Wilk test) and for homogeneity of variances (homoscedasticity, Bartlett test). When these conditions were satisfied, parametric tests were used in the subsequent analyses; otherwise, non-parametric analogues were used. Spearman and Pearson correlation coefficient tests were used to analyze the correlations between size or weight and trace element concentration in liver of the leopard coral grouper *P. leopardus* (according to the normality and the homoscedasticity of the data). Correlation tests were also used to analyze the correlations between trophic level values of the different species (TL; Froese and Pauly, 2011) and their concentration of metals and metalloids in the liver.

The relationships among the concentration of all the elements in fish liver were investigated using a principal component analysis (PCA); the PCA was based on the correlation matrix and normalised data for each variable (i.e., centred and divided by the standard deviation). When the major components were determined, projection of the points was realized and relevant characteristics (sampling sites and feeding/trophic groups) were taken into account.

Species/groups of species with a minimum of three individuals/replicates were considered to test differences in trace element concentrations among sampling locations (in the case of *P. leopardus*) or trophic groups, using a one-way analysis of variance (ANOVA) followed by the post-hoc Tukey test. In case correlation between size or weight and trace element concentrations was previously revealed for *P. leopardus*, ANCOVA was performed instead of ANOVA, using size or weight as covariable. Normality and homoscedasticity of residuals were also checked. When appropriate, the variability explained by each factor and their interaction was derived from the sum of squares. When required, the Kruskal–Wallis (KW) test was performed as a non-parametric analogue to ANOVA. The KW tests were followed by a multiple comparison test with Holm adjustment method (Chouvelon et al., 2011). The levels of significance for statistical analyses was always set at $\alpha = 0.05$.

2.4. Risk assessment for human consumers

A maximum safe consumption of fish was evaluated on the basis of the Provisional Maximum Tolerable Daily Intake (PMTDI) or Provisional Tolerable Weekly Intake (PTWI) given by the Joint Expert Committee on Food Additives (JECFA; http://www.inchem.org/pages/jecfa.html). In this calculation, metal sources supplied by other meals or by drinking water on the same day or week were not taken into account, i.e., only metal intake coming from the fish has been considered. The PMTDIs for Cu, Fe, and Zn are respectively 500, 800 and 1000 μg kg^{-1} d^{-1} and PTWI for inorganic As, Cd and Pb are 15, 7 and 25 μg kg^{-1} wk^{-1} (JECFA, 2006; WHO, 1989, 2003). In order to assess a "Maximum Safe Consumption" for As, Cd, Cu, Pb, Zn and Fe (per week or day, depending of the studied element: PMTDI or PTWI), mean concentrations in μg g^{-1} dry wt measured for each muscle sample were first converted to wet wt, taking into account a conventional dry wt/wet wt ratios (75%; Chouvelon et al., 2009). Then, the respective PMTDI or PTWI multiplied by a consumer average body weight (viz. 50 and 80 kg for female and male humans, respectively) was divided by the element concentration in the considered fish muscle to obtain the "Maximum Safe Consumption". It can be summarized with the following equation (Eqn. (1)):

$$\mathbf{MSC_A} = (\mathbf{W_{ind}} * \mathbf{JL_A}) / \mathbf{X_A} \quad (1)$$

Where $\mathbf{MSC_A}$ is the Maximum Safe Consumption (g wet wt d^{-1} or wk^{-1}) of a food item in relation with a contaminant A, $\mathbf{X_A}$ is the mean concentration of A in μg g^{-1} wet wt, $\mathbf{W_{ind}}$ is the body weight (kg) of the human for whom the assessment of the MSC_A is carried out.

$\mathbf{JL_A}$ represents either PTWI or PMTDI of A. MSC_A will thus provide a mass of fish (in g) that is the maximum amount allowed per day or per week (depending on whether PMTDI or PTWI were used) for the considered human.

3. Results

3.1. Tissue concentrations

The trace element concentrations in the liver of the different fish species collected from the different sampling sites are given in Table 2. The ranges of detected concentrations for each element among fish livers were as follows: 0.02–6.55 μg Ag g^{-1} dry wt, 8.53–43.8 μg As g^{-1} dry wt, 0.06–16.7 μg Cd g^{-1} dry wt, 0.13–6.68 μg Co g^{-1} dry wt, 0.78–5.33 μg Cr g^{-1} dry wt, 1.11–642 μg Cu g^{-1} dry wt, 240–8770 μg Fe g^{-1} dry wt, 0.03–6.44 μg Hg g^{-1} dry wt, 0.93–8.77 μg Mn g^{-1} dry wt, 1.47–5.02 μg Ni g^{-1} dry wt, 0.06–1.82 μg Pb g^{-1} dry wt, 16.1–21.3 μg Se g^{-1} dry wt, 1.20–8.36 μg V g^{-1} dry wt, and 19.6–1662 μg Zn g^{-1} dry wt.

Concentrations of trace elements in fish muscle are presented in Table 3. This table does not contain data for Ag, Cd and Ni (which concentrations were always below the detection limits of the analytical method) nor for Se (which was above the detection limit only in the muscle of *Epinephelus maculates in Ouano*: 21.3 μg g^{-1} dry wt; $n = 1$) or Mn (muscle of *Scarus microrhinos* reaching 1.06 μg g^{-1} dry wt; $n = 1$). The ranges of concentrations for the other elements (As, Co, Cr, Cu, Fe, Pb, V, and Zn) in the fish muscles were: 6.83–38.4 μg As g^{-1} dry wt, 0.02–0.35 μg Co g^{-1} dry wt, 0.88–1.39 μg Cr g^{-1} dry wt, 0.46–1.51 μg Cu g^{-1} dry wt, 5.38–37.1 μg Fe g^{-1} dry wt, 0.07–0.15 μg Pb g^{-1} dry wt, and 8.59–38.2 μg Zn g^{-1} dry wt.

When data was available in both livers and muscles, the liver to muscle ratio was calculated. This ratio was over 1 in most cases and reached up to 742 for Fe in *Cymbacephalus beauforti* from Prony Bay. The only few exceptions to this "enrichment" factor were found for As in Haemulidae species (0.53, 0.82, 0.76 in *Plectorhinchus albovittatus*, *Plectorhinchus chaetodonoides*, *Plectorhinchus flavomaculatus*, respectively).

Table 2
Trace element concentrations (mean ± SD and range, μg g^{-1} dry wt) in the liver of fish collected, and the mention of their trophic group (TG; GS: grazer/scavenger; PI: predator of invertebrates; PISM: predator of invertebrates and small fish; and PSM: predator of small fish).

Scientific name and location	TG	*N*	Ag	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	V	Zn
Kyphosus vaigiensis	GS	5	0.05 ± 0.02	<8.15	8.12 ± 2.38	1.55 ± 0.70	1.10 ± 0.38	23.1 ± 12.5	910 ± 390	0.25 ± 0.03	2.29 ± 0.77	1.60 ± 0.08	<0.08	<16.3	<1.63	97.6 ± 12.2
			0.02–0.08	–	5.92–11.4	0.66–2.28	0.81–1.56	10.1–39.9	260–1280	0.21–0.29	1.45–3.33	1.47–1.67	–	–	–	76.2–107
Naso unicornis	GS	1	0.07	10.2	8.92	5.62	0.82	9.44	4620	0.31	3.92	<1.64	<0.08	<16.4	7.22	110
Scarus ghobban	GS	1	0.04	<9.41	0.06	1.24	0.94	1.51	250	0.06	2.63	<1.88	0.14	<18.8	<1.88	19.6
S. microrhinos	GS	1	0.03	<7.74	0.88	1.34	<0.77	1.11	240	0.03	0.93	<1.55	<0.08	<15.5	<1.55	23.4
S. rivulatus	GS	1	0.04	<9.88	2.64	0.53	0.99	2.00	540	0.04	1.14	<1.98	<0.08	<19.8	1.98	21.7
S. schlegeli	GS	1	0.04	<8.77	0.63	0.24	0.88	3.97	250	0.04	1.45	<1.75	<0.08	<17.5	<1.75	46.0
Bodianus perditio	PI	1	0.05	43.8	0.25	0.80	0.83	8.78	1600	5.04	2.42	<1.65	0.21	<16.5	<1.65	63.5
Cheilinus chlorourus	PI	1	1.96	10.4	3.39	6.25	0.80	53.0	7080	2.69	4.27	1.62	0.24	19.1	3.83	122
Monotaxis grandoculis	PI	2	0.05–0.10	9.80–17.1	1.91–4.51	0.42–0.46	<0.80–0.84	9.87–24.4	1270–1300	0.11-0.11	2.95–3.06	<1.60	0.07–0.08	16.8–17.3	<1.60	134–175
Plectorhinchus albovittatus	PI	1	0.04	13.4	0.35	0.78	0.82	16.9	1860	0.73	2.27	<1.64	0.10	<16.4	<1.64	330
Acanthopagrus berda																
Maa	PISM	1	0.08	<7.42	1.21	4.89	<0.74	22.4	1120	0.48	7.02	<1.48	<0.07	<14.8	<1.48	131
Ouano	PISM	1	0.14	17.9	5.13	0.71	<0.75	174	1200	0.25	7.11	<1.51	0.14	<15.1	2.09	344
Diagramma pictum	PISM	1	0.13	9.54	0.92	1.36	<0.65	50.1	2340	0.28	3.81	3.15	0.49	17.7	<1.30	199
Epinephelus maculates	PISM	1	0.56	<8.15	2.89	1.98	0.82	167	3530	1.00	5.46	<1.63	<0.08	21.3	<1.63	1153
E. coeruleopunctatus	PISM	1	0.54	<6.31	0.18	0.42	<0.63	55.7	2240	0.88	1.52	<1.26	<0.06	<12.6	<1.26	1034
Lethrinus laticaudis	PISM	3	0.08 ± 0.02	16.9 ± 5.75	5.46 ± 3.56	0.50 ± 0.14	1.38 ± 0.79	26.1 ± 8.59	2130 ± 760	0.25 ± 0.14	3.75 ± 0.59	1.67	0.11 ± 0.07	17.1 ± 1.27	1.65	261 ± 15.5
			0.06–0.11	10.4–21.4	3.33–9.57	0.34–0.61	<0.81–1.94	17.2–34.4	1270–2690	0.15–0.41	3.34–4.42	<1.62–1.67	0.06–0.19	16.2–18.5	–	243–270
Lutjanus argentimaculatus																
Grande Rade	PISM	2	0.60–3.32	<6.82	0.19–0.21	0.61–2.51	<0.68	67.9–160	1450–4110	1.10–1.40	3.23–5.97	<1.36	0.16–0.33	<13.6	<1.36–1.46	349–648
Maa	PISM	1	0.03	<8.18	0.06	6.68	0.82	28.0	4400	1.57	5.22	<1.63	0.09	<16.4	3.92	332
Ouano	PISM	2	0.09–0.13	<8.10	1.47–1.77	1.07–1.41	0.81	17.7–40.4	1520–3450	0.42–0.43	5.05–5.79	<1.62	<0.08	<16.2	1.93–4.83	456–543
L. monostigma																
Maa	PISM	1	0.03	<7.78	5.94	6.22	<0.78	14.3	8770	1.51	8.77	3.34	1.37	<15.6	1.77	663
Ouano	PISM	1	0.04	<7.95	2.49	1.95	<0.79	12.5	1910	0.63	5.20	<1.59	0.26	<15.9	<1.59	214
Plectorhinchus chaetodonoides	PISM	1	0.11	20.1	0.95	5.86	0.83	17.9	3660	1.72	8.30	5.02	1.68	18.7	1.72	156
P. flavomaculatus	PISM	1	0.21	29.3	0.63	2.79	<0.70	21.1	1930	1.61	3.48	4.17	1.82	20.8	<1.40	109
Priacanthus hamrur	PISM	7	0.05 ± 0.02	10.1 ± 2.22	6.20 ± 5.36	0.25 ± 0.05	2.06 ± 1.79	22.8 ± 12.2	1870 ± 710	0.38 ± 0.26	6.07 ± 0.71	1.79 ± 0.45	<0.08	16.1	<1.61	282 ± 143
			0.03–0.08	<7.93–11.7	1.40–16.7	0.17–0.31	<0.79–5.33	8.64–39.5	960–2870	0.15–0.76	5.44–7.22	1.59–2.79	–	<16.1–16.1	–	109–535
Cymbacephalus beauforti	PSM	2	0.17–0.18	<6.01–11.5	1.24–1.82	0.36–0.40	<0.55	16.7–45.8	3370–5640	3.19–4.09	1.31–2.55	<1.20	<0.06	<12.0	1.20–2.07	48.4–71.0
Plectropomus leopardus																
Grande Rade (M)	PSM	3	3.47 ± 1.24	<8.10	0.24 ± 0.01	1.18 ± 0.58	0.81 ± 0.00	111 ± 27.0	2500 ± 350	5.25 ± 0.73	2.91 ± 0.37	<1.62	0.24 ± 0.05	<16.2	5.66 ± 2.40	393 ± 167
			2.08–4.47	–	0.24–0.25	0.81–1.84	<0.77–0.81	80.3–128	2130–2820	4.68–6.07	2.63–3.33	–	0.20–0.29	–	3.76–8.36	282–585
Grande Rade (O)	PSM	2	0.28–0.57	<11.4	0.07–0.12	0.22–0.50	<0.65	63.1–69.2	820–1730	0.64–1.71	4.69–5.66	<2.29	0.11–0.16	<22.9	<2.29	126–214
Koutio	PSM	4	5.39 ± 1.02	<8.27	0.10 ± 0.02	0.30 ± 0.05	0.83 ± 0.01	316 ± 100	2100 ± 640	0.33 ± 0.06	3.24 ± 0.37	2.80	0.10 ± 0.02	<16.5	<1.65	666 ± 250
			3.87–6.05	–	0.08–0.12	0.24–0.36	<0.53–0.83	222–424	1320–2780	0.26–0.38	2.74–3.62	<1.65–2.80	0.08–0.12	–	–	498–1029
Maa	PSM	4	1.86 ± 0.63	<8.23	0.54 ± 0.19	0.73 ± 0.32	0.82 ± 0.01	467 ± 155	4090 ± 2070	0.43 ± 0.19	3.30 ± 0.38	<1.65	<0.08	<16.5	4.00	735 ± 147
			1.11–2.57	–	0.36–0.77	0.48–1.18	<0.74–0.82	322–642	2660–7140	0.26–0.71	2.83–3.69	–	–	–	<1.48–4.00	539–883
Ouano (M)	PSM	2	0.19–0.25	<8.20	3.30–4.98	0.42–1.20	<0.76–0.82	37.8–135	3100–7840	3.06–6.44	3.54–5.74	<1.64	0.08–0.13	<16.4	2.99–5.47	866–1052
Ouano (O)	PSM	2	0.09–0.14	<5.97	0.31–0.75	0.13–0.28	<0.60	22.1–55.2	1200–2650	0.27–0.41	1.57–1.85	<1.19	<0.06	<11.9	<1.19	656–702
Prony	PSM	1	0.16	<5.46	0.33	0.32	<0.55	90.9	1120	0.09	3.57	<1.09	<0.05	<10.9	<1.09	678
Sainte Marie	PSM	3	5.36 ± 1.04	<8.07	0.15 ± 0.09	0.70 ± 0.26	0.92 ± 0.22	366 ± 207	3730 ± 2290	1.02 ± 0.43	3.16 ± 1.19	<1.61	0.09 ± 0.02	<16.1	2.53 ± 1.58	1079 ± 505
			4.61–6.55	–	0.09–0.26	0.50–0.99	0.78–1.18	185–591	2090–6350	0.53–1.34	2.22–4.50	–	0.08–0.12	–	1.56–4.35	760–1662

Table 3
Trace element concentrations (mean ± SD and range, μg g^{-1} dry wt) in the muscle of fish collected, and the mention of their trophic group (TG; GS: grazer/scavenger; PI: predator of invertebrates; PISM: predator of invertebrates and small fish; and PSM: predator of small fish).

Scientific name and location	TG	*N*	As	Co	Cr	Cu	Fe	Pb	Zn
Kyphosus vaigiensis	GS	5	<8.26	0.20 ± 0.07	<0.83	<0.83	8.69 ± 1.06	<0.08	24.1 ± 8.51
			–	0.11–0.30	–	–	7.60–10.2	–	17.3–38.2
Naso unicornis	GS	1	<7.99	0.13	<0.80	<0.80	10.0	<0.08	8.59
Scarus ghobban	GS	1	<8.16	0.30	<0.82	<0.82	10.7	<0.08	9.83
S. microrhinos	GS	1	<8.18	0.26	<0.82	<0.82	7.88	<0.08	10.4
S. rivulatus	GS	1	<8.17	0.12	<0.82	<0.82	11.7	<0.08	9.29
S. schlegeli	GS	1	<8.03	0.07	<0.80	<0.80	13.6	<0.08	11.7
Bodianus perditio	PI	1	18.3	0.04	<0.82	<0.82	13.4	<0.08	16.6
Cheilinus chlorourus	PI	1	<7.85	0.07	<0.78	<0.78	9.70	<0.08	12.2
Monotaxis grandoculis	PI	2	<8.12	<0.03	<0.81	<0.81	6.60–7.14	<0.08	10.5–12.1
Plectorhinchus albovittatus	PI	1	25.4	<0.03	<0.83	<0.83	15.5	0.10	12.7
Acanthopagrus berda									
Maa	PISM	1	10.3	0.05	<0.78	<0.78	8.16	<0.08	14.9
Ouano	PISM	1	21.0	<0.03	<0.80	<0.80	8.06	0.14	14.0
Diagramma pictum	PISM	1	6.83	0.02	<0.61	0.64	12.7	<0.06	12.8
Epinephelus coeruleopunctatus	PISM	1	8.38	<0.02	<0.59	<0.59	6.19	<0.06	13.2
E. maculates	PISM	1	<7.99	<0.03	<0.80	<0.80	22.7	<0.08	13.7
Lethrinus laticaudis	PISM	3	13.8 ± 7.57	<0.03	<0.79	<0.79	9.19 ± 1.42	<0.08	11.8 ± 0.23
			<7.87–19.1	–	–	–	7.56–10.1	–	11.6–12.0
Lutjanus argentimaculatus									
Grande Rade	PISM	2	<8.19	<0.02–0.03	<0.82	<0.82	8.87–9.72	<0.08–0.11	12.0–12.8
Maa	PISM	1	<8.25	<0.03	<0.82	<0.82	15.7	0.09	12.2
Ouano	PISM	2	<8.05	<0.03	<0.81	<0.81	11.2–11.8	<0.08	11.6–12.5
L. monostigma									
Maa	PISM	1	<7.60	0.35	<0.76	<0.76	14.5	<0.08	10.3
Ouano	PISM	1	<8.08	0.08	<0.81	<0.81	11.8	<0.08	10.5
Plectorhinchus chaetodonoides	PISM	1	24.6	0.12	<0.78	1.51	22.6	<0.08	15.3
P. flavomaculatus	PISM	1	38.4	0.10	<0.82	1.08	17.0	<0.08	16.2
Priacanthus hamrur	PISM	7	9.47 ± 1.47	<0.03	1.39	<0.83	10.4 ± 3.56	0.09	11.3 ± 0.61
			<7.85–10.8	–	<0.70–1.39	–	7.82–16.9	<0.07–0.09	10.6–12.4
Cymbacephalus beauforti	PSM	2	<6.01–7.77	<0.02	<0.60	<0.53–0.64	7.01–7.60	<0.05–0.07	11.8–14.11
Plectropomus leopardus									
Grande Rade (March)	PSM	3	<8.02	<0.03	<0.80	<0.80	8.48 ± 1.59	<0.08	13.0 ± 1.96
			–	–	–	–	6.89–10.1	–	11.2–15.1
Grande Rade (October)		2	<5.89	<0.02	<0.59	<0.59–0.71	8.00–18.3	0.12–0.15	12.5–15.6
Koutio		4	<8.25	<0.03	<0.83	<0.83	9.73 ± 1.41	<0.08	11.3 ± 0.63
			–	–	–	–	8.41–11.5	–	11.3–12.7
Maa		4	<8.26	<0.03	<0.83	<0.83	11.1 ± 5.39	<0.08	11.4 ± 0.35
			–	–	–	–	8.23–19.2	–	10.9–11.7
Ouano (March)		2	<8.18	<0.03	<0.82	<0.82	6.98–14.8	<0.08	12.9–13.0
Ouano (October)		2	<5.49	<0.02–0.02	<0.55–0.88	<0.55–0.64	6.76–37.1	<0.08	14.7–16.4
Prony		1	<5.90	<0.02	<0.59	<0.59	8.51	<0.06	10.9
Sainte Marie		3	<7.73	<0.03	<0.77	<0.77	6.43 ± 1.55	<0.08	12.8 ± 1.33
			–	–	–	–	5.38–8.21	–	11.5–14.1

The trace element concentrations in fish livers were combined in a PCA (Fig. 2). The first two principal components accounted for 44% of the total variation present in the data set (24% and 20% for axes 1 and 2, respectively). Co, Fe, Mn, V, and Zn concentrations were the variables contributing the most to the first axis (contribution of each variable >10%), whereas Ag, Cu, Ni, Pb, Zn, and Se concentrations mostly contributed to the second one (contribution of each variable > 10%). The major components 1 and 2 showed that liver Cd concentrations were highly correlated with Cr concentrations (Fig. 2A) and negatively correlated to Ag, Cu and Zn concentrations. When individuals were grouped by locations or by trophic groups (Fig. 2C and D), no clear segregation emerged from the PCA. Nevertheless, Sainte-Marie Bay and predators of small fish (PSM) seem to be related to elevated concentrations of Ag, Cu and Zn.

3.2. Element concentrations among sampling locations

Fig. 3 displays the concentrations of trace elements in the liver of the leopard coral grouper *P. leopardus* from different sites of the lagoon of New Caledonia. A significant, positive correlation was found between Ag, Cd, Co, Cu, Hg and Ni concentrations and fish size or weight. The appropriate factor (weight for Ag, Cu and Ni; size for Cd, Co and Hg) was then used as covariable in the ANCOVA performed to test the differences among sites when normality and homogeneity of variances was verified.

Ag, Cd, Cu, Hg, Pb and Zn concentrations in the liver displayed significant differences among sampling sites (p_{ANCOVA} or $p_{Krustal–Wallis}$ or $p_{ANOVA} < 0.0001$ for Ag, Cu and Pb; <0.05 for Hg, Cd and Zn). Multiple comparison tests (or post-hoc Tukey test) also showed that the highest trace element concentrations were not always measured in the liver of fish from the same location. For example, the Ag concentrations in the liver of the leopard coral grouper *P. leopardus* were significantly higher in Sainte-Marie and Koutio Bays whereas the highest Pb concentrations were found in Grande Rade. Nevertheless, the highest mean concentration in liver were found in Grande Rade for seven out of the fourteen elements examined (i.e., As, Co, Hg, Mn, Pb, Se, and V) whereas the lowest mean concentrations of Fe and Zn were found in fish from this site. Relatively homogeneous concentrations of trace elements related to Ni mining ores (Co, Cr, Mn and Ni) were found in *P. leopardus* livers collected from the different sampling locations.

3.3. Element concentrations and trophic position

Fig. 4 depicts the trace element concentrations in liver by groups through bar plots (mean ± standard deviation). Regardless the site,

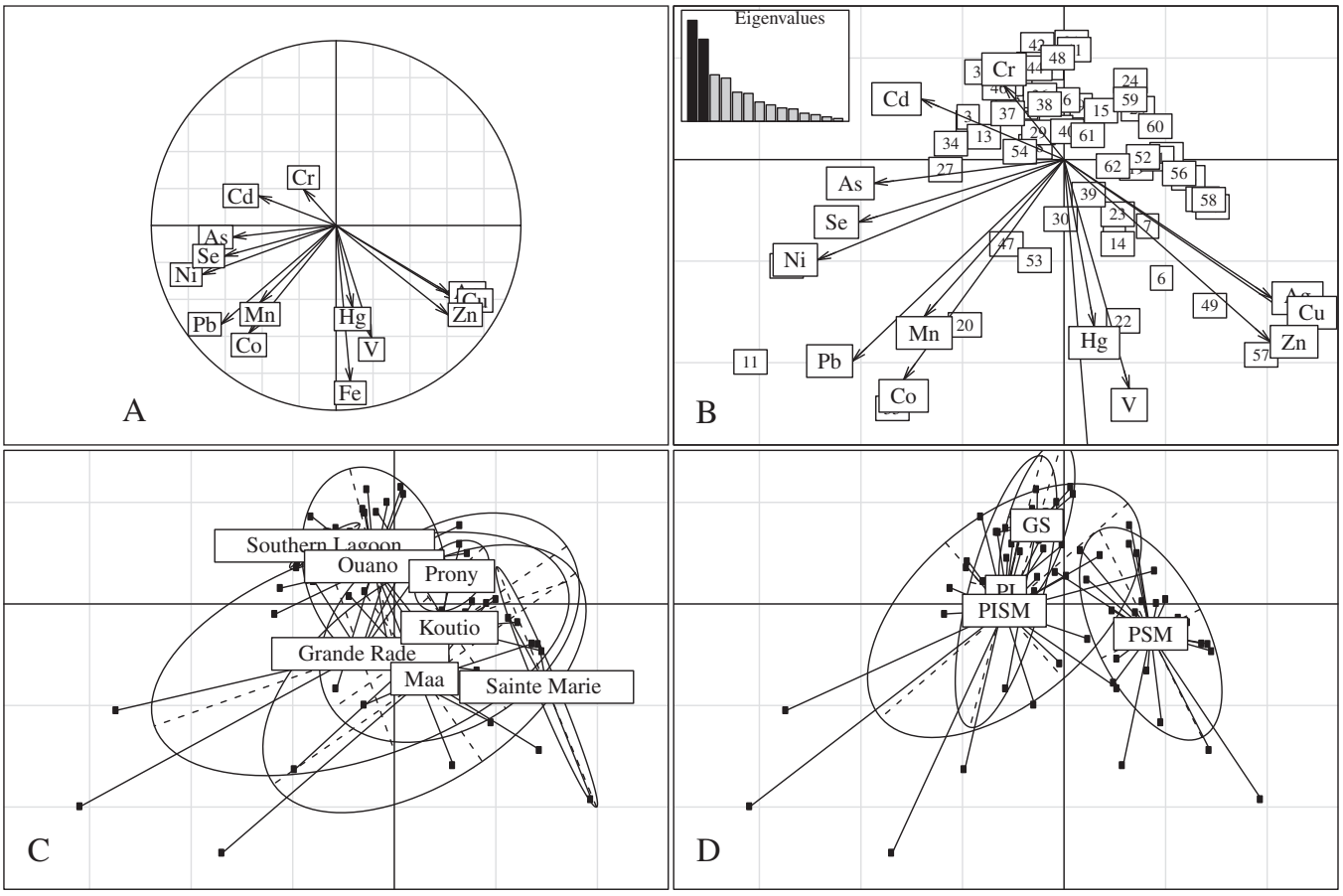

Fig. 2. Projection of variables and individuals on the first two components resulting from the principal component analysis (PCA). A) Correlation bi-plot showing the distribution of the variables. The length of the line for a variable shows how well it is represented by the two-dimensional approximation, and reflects its contribution to the first two principal components. Horizontal axis: principal component 1 (24%); vertical axis: principal component 2 (20%). Variables pointing in the same direction display a high positive correlation. Variables pointing in the opposite direction have a high negative correlation. Variables with an angle of 90° have a correlation close to 0. B) Projection of individuals on the correlation bi-plot with eigenvalue of the first two components. C) Grouping of individuals by sampling sites. D) Grouping of individuals by trophic groups.

liver concentrations of most elements (i.e., Ag, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Se and Zn) displayed significant differences among trophic groups (Kruskal–Wallis rank sum test <0.001 for Ag, Cd, Cu, Zn; Kruskal–Wallis rank sum test <0.01 for As, Cr, Fe, Hg, Ni, Se; ANOVA <0.001 for Mn). A multiple comparison test also showed that top predator group (PSM) showed the highest concentrations of Ag and Cu (Fig. 4). In addition, liver Zn concentrations also increased with higher trophic position although this trend was not significant for all the selected groups. Similarly, Fe and Hg concentrations in PSM groups were the highest (significantly higher than GS for Fe and GS and PISM for Hg). However, the group of predators of invertebrates (PI) had relatively high concentrations for both metals.

In contrast, Cd concentrations showed a significant decrease with increasing trophic position. The highest liver concentrations of Mn and Ni were found in the group of predator of invertebrates and small fish (PISM) and the group of predator of invertebrates (PI) displayed greater liver concentrations of As and Se than the other groups.

Significant correlation ($p < 0.05$) between liver element concentrations and trophic level values (TL; determined by Froese and Pauly, 2011) was observed for all elements except Mn, Pb and V. With the increase of TL, a significant increase of the concentrations of Ag ($r = 0.66$), Cu (0.62), Fe (0.47), Hg (0.46) and Zn (0.59) was observed and confirmed the higher concentrations of these metals also displayed in top predator group (PSM). In contrast, concentrations of Cd, Co, Cr, Ni and Se decreased with the increase of TL ($r = -0.44$, -0.34, -0.40, -0.41 and -0.33, respectively).

3.4. Risk assessment for human consumers

The Maximum Safe Consumption (MSC) of fish was calculated based on the mean concentration of element in edible flesh (viz. muscle) of each species per site. MSC can be calculated on a daily basis or on weekly basis and it depends on the recommended intake for each contaminant by JECFA (WHO, 2003): either PTWI or PMTDI.

The "Maximum Safe Daily Consumption" (MSDC, in g wet wt d^{-1}) of edible flesh for Cu, Fe and Zn was above 800 g for a 50-kg person (12,420 g, 810 g and 980 g, respectively) and above 1290 g for an 80-kg person (19,870 g, 1290 g and 1570 g, respectively).

The "Maximum Safe Weekly Consumption" (MSWC, in g wet wt wk^{-1}) of edible flesh for inorganic As and Pb values was estimated taking into account the "Provisional Tolerable Weekly Intake" (PTWI) recommended by JECFA (WHO, 2003). The maximum amount of fish that should be eaten by a 50-kg person to reach the PTWI for Pb is about 6250 g over a week (ca. 10,000 g for an 80-kg person). Overall, As appears as the only element of concern regarding the consumption of New Caledonian fish: its MSWC for a

Element	Locations
Ag **	Ouano Maa GR SM Koutio
Ag	Ouano Koutio SM Maa GR
Cd *	Koutio GR SM Maa Ouano
Co	Koutio Ouano SM Maa GR
Cr	Ouano GR Koutio Maa SM
Cu **	Ouano GR Koutio SM Maa
Fe	GR Koutio Ouano SM Maa
Hg *	Koutio Maa SM Ouano GR
Mn	SM Ouano Koutio Maa GR
Ni	Ouano SM Maa GR Koutio
Pb ***	Ouano Maa SM Koutio GR
Se	Ouano Koutio SM Maa GR
V	Koutio Maa Ouano SM GR
Zn *	GR Koutio Maa Ouano SM

Fig. 3. Comparison of trace element concentrations in the liver of leopard coral grouper *Plectropomus leopardus* among sampling sites. Tukey multiple comparison tests were performed after one-way ANOVA or ANCOVA (Weight as covariable for Co, Hg, V and Length for Cu). Mean concentrations are ranked from the left to the right by increasing order. Underlines (_) indicate locations among which concentrations are not significantly different ($\alpha = 0.05$). Sampling locations are: Ouano Bay (Ouano), Grande Rade (GR), Maa Bay (Maa), Koutio Bay (Koutio) and Sainte-Marie Bay (SM). Significant differences: * for $p < 0.05$; ** for $p < 0.01$; *** for $p < 0.001$.

50-kg person is ranging between 14.6 and 82.4 g (23.4–132 g for an 80-kg person). The consumption of *Bodianus perditio*, *P. albovittatus*, *P. chaetodonoides* and *P. flavomaculatus* should be limited the most (max ca. 14–23 g for 50-kg persons and ca. 23–37 g for 80-kg persons).

4. Discussion

4.1. Tissue-specific trace element concentrations and related risk for consumers

Most studies carried out so far on metal bioconcentration in the New Caledonia waters have investigated macroalgae, invertebrates (crustaceans, molluscs, and ascidians) and marine mammals (Bustamante et al., 2000, 2003; Hédouin et al., 2009; Metian et al., 2008a, 2008b; Metian and Warnau, 2008; Monniot et al., 1994; Pernice et al., 2009) whereas only one study focussed on fish in which muscular concentrations of Hg were examined (Chouvelon et al., 2009). In this respect, the dataset of the present study provides substantial baseline information on trace element contamination status of fish from the New Caledonia lagoon. Our dataset is also a good tool to assess the risk related to local fish consumption in a tropical lagoon subjected to high metal inputs (Ambastian et al., 1997). In general, trace element concentrations measured in edible tissues (viz. muscles) did not reveal excessive risk for consumers in New Caledonia. Nevertheless, As and to a very lesser extend Zn (only for the consumption of the Moontail bullseye *P. hamrur*) might pose some hazard for human consumers. However these data are probably somewhat overestimated as one has to keep in mind that only 10 out of 22 species were concentrating measurable levels of total As and that the MSWC calculation is based on a 100%

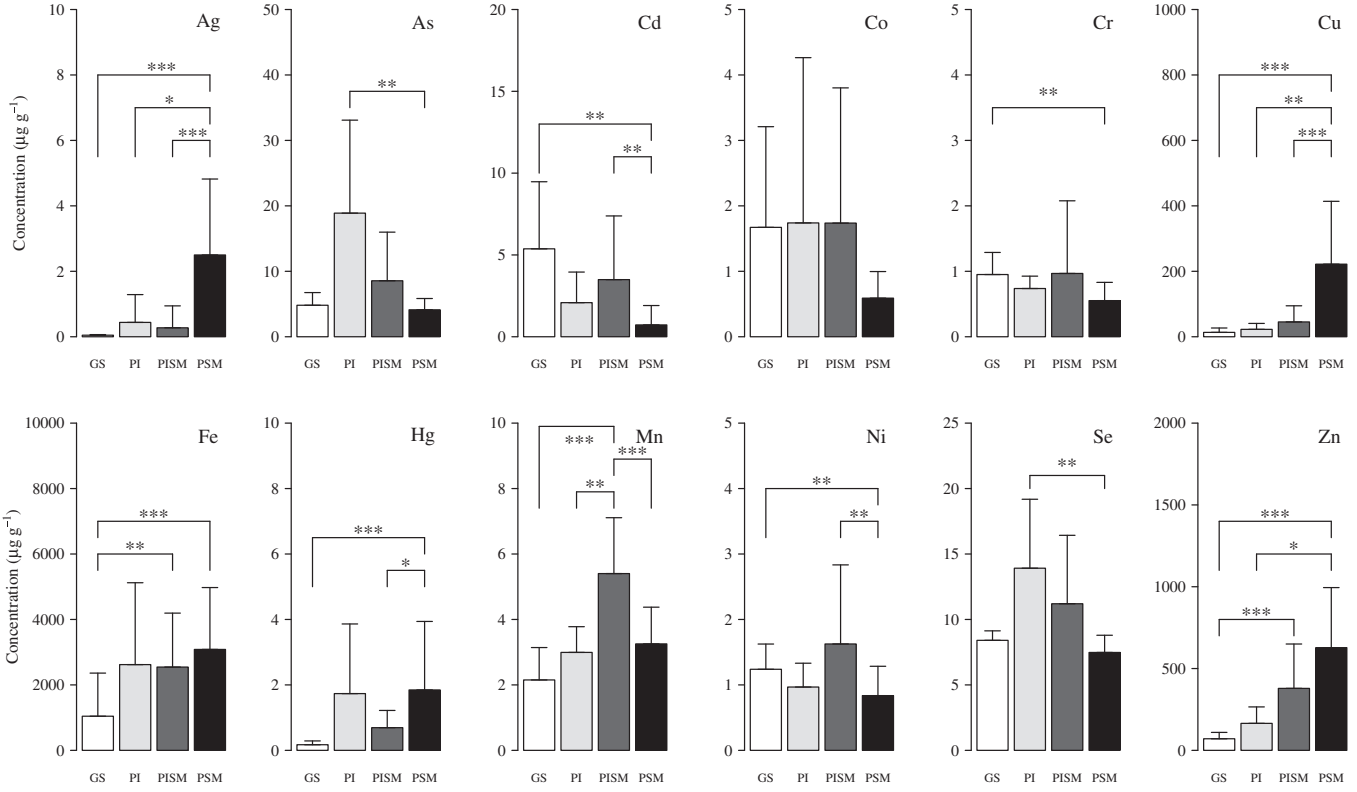

Fig. 4. Global comparison of trace element concentrations (μg g^{-1} dry wt) in the liver of fish from New Caledonia according to their trophic group. GS: grazer/scavenger ($n = 10$); PI: predator of invertebrates ($n = 5$); PISM: predator of invertebrates and small fish ($n = 23$); and PSM: predator of small fish ($n = 24$). Significant differences: * for $p < 0.05$; ** for $p < 0.01$; *** for $p < 0.001$.

proportion of inorganic As which is not the case in fish (EFSA, 2009).

To better assess the extent of this risk, speciation of As in fish flesh should be investigated as it may be mainly under organic forms, which are generally assumed to be of no toxicological concern (EFSA, 2009). The latter subject is however a matter of debate as many organo-arsenicals undergo biotransformation, and consumers can therefore be exposed to their toxic intermediates (Buchet et al., 1996; Le et al., 1994; Moore et al., 1994). In seafood, it is generally considered that approximately 10% of the total As is under inorganic form (Tao and Bolger, 1998). Hence, when applying a factor of 10 to our risk assessment computation, As concentration found in some species of fish (e.g. *P. flavomaculatus*) might still be a health risk for the consumers since their MSWC (week dose) for a 50 kg person would still range between realistic values of 141 and 824 g (230 g–1.3 kg for a 80 kg person). Muscles of New Caledonian fish displayed generally low concentrations of trace elements, whether they came from locations impacted or not by mining activities. The comparison with the data available in the literature indicated that trace element concentrations found in the muscle of New Caledonian fish were generally similar or, in most cases, lower than the values reported for fish from other tropical regions (e.g. Eisler, 2010; Neff, 2002). Only As displayed similar or slightly higher levels than average concentrations in muscle of comparable tropical fish. Indeed, the concentrations of this metalloid measured during the present study ranged from 6.83 to 38.4 μg g^{-1} dry wt corresponding to 1.4–7.7 μg g^{-1} wet wt whereas its range in fish muscle is generally from 2 to 5 μg g^{-1} wet wt (Eisler, 1981). However, high As concentrations have already been reported in fish muscles, reaching up to 52.3 and 77.6 μg g^{-1} dry wt, respectively in *Hippoglossoides elassodon* and in *Parupeneus multifasciatus* (Denton et al., 2006; Meador et al., 1998). Eisler (2010) noted that As muscular concentrations were generally lower than liver ones. Our data are generally in agreement with this observation. Nevertheless, the As liver/muscle concentration ratio was equal to 0.53, 0.82, 0.76 in *P. albovittatus*, *P. chaetodonoides*, *P. flavomaculatus*, respectively (all belonging to the Haemulidae Family). To our knowledge such ratios below 1 have never been highlighted although examination of the literature data regarding fish from both pristine and contaminated areas reveals that As concentrations higher in the muscles than in the liver have already been reported (Denton et al., 2006; Meador et al., 2004). This preferential accumulation of As in fish muscles is not well understood and therefore deserves additional investigations.

The liver, which may be the largest organ after the muscles in a fish body, is not directly involved in digestion, but assimilates nutrients, produces bile, and detoxifies toxins from both endogenous (metabolic) and exogenous sources (Bone and Moore, 2008). With the exception of As, the liver accumulates higher concentrations of trace elements than the muscle in fish from New Caledonia (Tables 1 and 2). This observation is consistent with data previously reported (Eisler, 2010; Neff, 2002) and likely results from the detoxification processes occurring in the liver to cope with the potential toxicity of trace elements. The resulting bioaccumulation also closely relates to the metabolism of essential elements in fish, which leads to their storage and mobilization for vital requirements.

Although many studies have been conducted on trace elements in fish, some elements such as Co, Cr, Mn, Ni, Se, and V have rarely been investigated (Eisler, 2010). These elements were analyzed in the present study to generate a baseline dataset for various tropical fish species. In addition, Co, Cr, Mn and Ni are closely related to the mining activities occurring in New Caledonia and can be of concern to fish from the New Caledonia lagoon and to their consumers. As opposed to the low concentrations of these elements in muscle, their content is relatively high in liver, thereby confirming the role of the latter organ in the detoxification and storage of these trace elements as well. Overall, the range of liver Co, Cr, Mn and V concentrations was similar to the values generally reported in fish (Table 4). Ni concentrations were somewhat higher than those reported for tropical fish, which is in agreement with the fact that Ni concentrations in fish tissues are frequently elevated in the vicinity of Ni smelters and refineries, Ni–Cd battery plants, sewage outfalls, and coal ash disposal basins (Eisler, 2010). Nevertheless, Ni was accumulated significantly in the liver only by few species (several species remained under the detection limit), with the highest Ni level measured in *P. chaetodonoides* from Grande Rade subjected to important releases of Ni mining products and by-products (e.g. Hédouin et al., 2009).

Although Cu is less accumulated in fish than in algae or invertebrates (Eisler, 2010), high levels were reported in fish from tropical areas (Eisler, 2010) and the range of liver Cu concentrations (e.g. 1.61–319 μg g^{-1} dry wt in Guam harbours fish; Denton et al., 2006) is wider and higher than in fish from temperate areas (Eisler, 2010). The range of liver Cu concentrations in New Caledonia fish is even wider and maximum value is higher (1.11–642 μg g^{-1} dry wt) than previously reported in Guam harbours fish.

Zn is an essential element that is also well studied in fish (e.g. Bury et al., 2003) and tends to be highly bioaccumulated in liver of some New Caledonian fish (up to 1662 μg Zn g^{-1} dry wt). Our results showed however considerable inter- and intra- specific variability with values ranging between 19.6 and 1662 μg Zn g^{-1} dry wt. These results are consistent with previously reported liver concentrations of Zn for other tropical fish, ranging between 12 and 2284 μg Zn g^{-1} dry wt (Denton and Burdon-Jones, 1986; Denton et al., 2006).

4.2. Variation of trace element concentrations among sampling sites

In order to evaluate the bioavailability of metals along the New Caledonian coast, bivalves have been previously used (Hédouin et al., 2009). However, fish can also be good bioindicators

Table 4
Co, Cr, Mn, Ni, Se, and V concentrations (mean ± SD or range; μg g^{-1} dwt) in liver of fish from various geographical areas.

Species	Location	Co	Cr	Mn	Ni	Se	V	References
Parupeneus multifasciatus	Maui, Hawaii, USA	1.98 ± 0.79	1.44 ± 1.05	7.42 ± 1.76	0.53 ± 0.38	nd	5.11 ± 2.38	Hédouin et al., 2011a
15 species	Townsville Coastal Waters, Australia	nd	<0.6–2.8	nd	<0.2–7.4	nd	nd	Burdon-Jones et al., 1975
32 species	Guam harbours, Guam	nd	<0.15–1.58	nd	<0.16–<1.35	nd	nd	Denton et al., 2006
50 species	Great Barrier Reef, Australia	nd	nd	nd	All <0.5	nd	nd	Denton and Burdon-Jones, 1986
22 species	Lagoon of New Caledonia	0.13–6.68	0.78–5.33	0.93–8.77	1.47–5.02	16.1–21.3	1.20–8.36	Present study
Compendium data[a]	–	0.05–4.8	<0.04–3.6	Up to 1.1	Up to 7.6	Up to 6.7	0.024	Eisler, 2010

nd = no data.
[a] Since the water contents of fish livers vary widely only values reported in dry weight were included.

considering their biological and life cycle specificities. For instance, the restricted mobility of fish species (characterizing thus a limited living area) is a suitable characteristic for a marine fish providing a site-specific record of the contamination; it fulfils one of the general prerequisite of bioindicator species (Phillips and Rainbow, 1994). Here, we considered the leopard coral grouper *P. leopardus* as a potential bioindicator species in order to compare different locations as this fish is resident species and an apex predator (St. John, 1999; Zeller, 1997). To this end, the liver was used to establish the comparisons as it has been shown as the target organ for most of the trace elements examined (Table 2). Leopard coral groupers caught in Koutio and Sainte-Marie Bays showed the highest Ag and Cu concentrations among sampling sites. Koutio Bay is influenced by the inputs of domestic wastes from Noumea City and by the occurrence of an important rubbish dump. Sainte-Marie Bay receives urban wastewaters from the Sainte-Marie area (district of Nouméa). For Ag, results on leopard coral groupers are in agreement with previous works on algae and invertebrates collected in urban areas such as Sainte-Marie Bay (Hédouin et al., 2009; Metian et al., 2008a). On the other hand, the liver of *P. leopardus* did not show significant difference among sites for metals related to the mining activities (viz. Co, Cr, Mn, Ni). This result deserves particular attention as in Grande Rade, that is subjected to important inputs of mining products and by-products as confirmed by recent sediment analyses (Hédouin et al., 2009), invertebrates showed clearly higher Co, Cr and Ni concentrations compared to the other stations (Hédouin et al., 2011b). In contrast, our observations suggest that these metals are not readily bioavailable for fish from the dissolved phase and/or that they are poorly transferred through the food chain up to leopard coral groupers. Similarly limited contaminations by trace metals have been previously observed in tissues of fish exposed to mine waste disposal (Brewer et al., 2007). Among the trace elements considered, only Hg and Pb were significantly more bioaccumulated in fish from Grande Rade than from the other sampling stations, likely resulting from the releases from human activities in this site. In contrast to the other metals, Cd was significantly higher in Ouano, Maa and Sainte Marie Bays than in the other sites (Fig. 3). As it was for mining-related elements, these observations are not in accordance with the Cd contamination status of the sediment (Hédouin et al., 2009), which confirms the importance to work directly on the organism in order to better estimate the biological significance of reported contamination levels.

4.3. Variation of element concentrations according to trophic groups

Diet is generally considered as the major route for trace element bioaccumulation in fish (Wang, 2002; Willis and Sunda, 1984; Xu and Wang, 2002; Zhang and Wang, 2006). Bioavailability of metals from ingested food is strongly influenced by the nature of the food and varies considerably among species (e.g. Luoma et al., 2002). The present study revealed a strong relationship between the concentrations of several elements (Ag, As, Cu, Cd, Hg, Mn, Se and Zn) in storage tissues and the fish feeding preferences/regimes. The best example was Zn for which liver concentrations increased with both trophic level and trophic groups (Fig. 4). However, this positive relationship is contrasting with the results of Ting (1971) who did not find any significant difference in the content of Zn in the muscle, skin, viscera, or bones of 7 species of fish representing various feeding regimes. Moreover an inverse relationship between Zn concentrations and trophic position has even been suggested in some earlier studies on global food webs (Schafer et al., 1982; Young and Mearns, 1979; Young et al., 1980). Therefore, these controversial observations deserve further attention and research.

As for Zn, the liver concentrations of Ag and Cu were generally higher in high trophic level fish. The highest liver concentrations of Cu were displayed by the leopard coral grouper *P. leopardus*, which also exhibited high concentrations of Ag, Hg, and Zn (Table 2). These observations are probably related to the induction of metallothionein-like proteins that have a high affinity for these elements (Hamilton and Mehrle, 1986).

The behaviour of Cd and to a lesser extent of Cr, tended to be opposite to Ag, Cu and Zn in fish liver in terms of variation of concentrations among trophic groups defined in the present study (Figs. 2 and 3). Indeed, the liver Cd concentration was the lowest in the highest trophic group (PSM $= 0.72 \pm 1.18$ μg g^{-1} dwt) and the highest in grazers/scavengers (5.37 ± 4.10 μg g^{-1} dwt). Even though the considerable inter-specific variability observed previously (Denton and Burdon-Jones, 1986) and in the present study (Table 1) prevents concluding that liver Cd concentrations are decreasing with the increasing trophic level of fish, the trend is supported by the variation of Cd concentrations along with the variation in food regime (TL in function of Cd concentrations; Froese and Pauly, 2011).

Intermediate feeding regimes (omnivorous or PI and PISM groups) tended to display significantly high levels of As, Mn and Se. PI and PISM fish with elevated As concentrations in their tissues (Fig. 3) usually came from sites where As concentrations in invertebrates were relatively high too (Hédouin et al., 2009). Previous studies carried out in New Caledonia have shown the capacity of invertebrates to highly accumulate As in their tissues (Metian et al., 2008a; Hédouin et al., 2009). For example, very high As concentrations were found in the clam *Gafrarium tumidum* from Ouano Beach (441 ± 84 μg g^{-1} dry wt; Hédouin et al., 2009). These observations are further confirming the importance of the dietary route for As uptake (Meador et al., 2004).

In the case of Mn, liver concentrations were systematically higher in the trophic group "PISM" than in other groups, confirming the importance of food pathway for the accumulation of this element (Eisler, 2010). Nevertheless, further investigations and a larger sampling set are required to explain the reasons why this group consuming invertebrates and small fish accumulated more Mn than groups eating exclusively invertebrates or fish.

5. Conclusion

The present paper indicated that metal concentrations in fish tissues does not clearly reflect the specific contaminated environment where they live in the context of Ni mining activity in New Caledonia. Some metals such as Ag, Cd, Cu, Hg and Zn are nevertheless differentially bioaccumulated in fish in different locations demonstrating the capability of *P. leopardus* to be used as bioindicator species to evaluate the contamination status of its environment, especially the urban disturbances. Food preferences seem to play a key role in the accumulation of several trace elements (Ag, As, Cd, Cu, Mn and Zn) in fish from New Caledonia. Dedicated investigations should be carried out on this issue in future field studies to complement laboratories studies of trace element bioaccumulation in fish. Finally, risk of potential As poisoning through the consumption of fish should be further assessed through specific determination of the inorganic As content in fish tissues.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.marenvres.2013.03.001.

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