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Comparative bioaccumulation of trace elements between *Nautilus pompilius* and *Nautilus macromphalus* (Cephalopoda: Nautiloidea) from Vanuatu and New Caledonia

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ABSTRACT

The concentrations of 16 trace elements were investigated and compared for the first time in the digestive and excreting tissues of two *Nautilus* species (Cephalopoda: Nautiloidea) from two geologically contrasted areas: (1) *N. macromphalus* from New Caledonia, a region characterized by its richness in nickel ores and its lack of tectonic activities and (2) *N. pompilius* from the Vanuatu archipelago showing high volcanic and tectonic activities. In both *Nautilus* species, results clearly highlighted that the digestive gland played a key role in the bioaccumulation and storage of Ag, Cd, Ce, Co, Cu, Fe, La, Nd, V, and Zn whereas As, Cr, Mn, Ni, Pb, and Se were accumulated in a greater extent in the excreting tissues (i.e. pericardial and renal appendages). Despite contrasting environments, no significant difference ($p<0.05$) was found between the two *Nautilus* species in the concentrations of most of the essential and non-essential elements, including Ni and associated metals in Ni ores (i.e. Co and Mn). As nautilus lives on the outer shelf of barrier reefs, these results strongly support the hypothesis that the New Caledonian lagoon traps the major amount of the trace elements derived from natural erosion and the intense mining activities conducted on land. In contrast, the concentrations of the rare earth elements (Ce, La, and Nd) were significantly higher in *N. pompilius* than in *N. macromphalus*, probably as a result of the local enrichment of Vanuatu waters by specific environmental processes, such as volcanism or upwelling.

1. Introduction

Marine organisms are exposed to trace elements that are present in their diet and dissolved in seawater. This double exposure results in element accumulation in their different tissues whether or not these elements are essential to the metabolism (Rainbow, 2002). This process, widely described as bioaccumulation can vary greatly according to the specificities of the organisms such as age/size, sex, and lifestyle, and according to the relative bioavailability of the metal in diet and seawater (Rainbow and Wang, 2001). Comparative analysis of trace element concentrations between closely related species living in different geographical areas can therefore allow at assessing the influence of the environment on their bioaccumulation.

Among the marine species, cephalopods belong to a molluscan group comprising ca. 700 species (Boyle and Rodhouse, 2005), in which high concentrations of trace elements such as Ag, Cd, Cu or Zn have generally been recorded (Martin and Flegal, 1975; Finger and Smith, 1987; Miramand and Bentley, 1992; Yamada et al., 1997; Bustamante et al., 1998; Dorneles et al., 2007). Indeed, several studies have demonstrated that the digestive and the excretory organs of cephalopods play a major role in the bioaccumulation of trace elements, as these organs are deeply involved in the assimilation processes, detoxification, and storage of both essential and non-essential metals (Miramand and Guary, 1980; Miramand and Bentley, 1992; Bustamante et al., 2000, 2002a, b, 2004).

In the present work, we focused on the bioaccumulation of trace elements in the *Nautilus* genus. Nautiluses are scavenger cephalopods, inhabiting the outer shelf of barrier reefs in the Indo–Pacific area, generally at a depth of 300–500 m (O'Dor et al., 1993; Norman, 2000). In spite of its evolutionary interest (Nautilus is the last representative of ectocochleate cephalopods, i.e. considered as a "living fossil"; Boyle and Rodhouse, 2005) and its physiological specificities (slow digestion and most of the excretory processes taking place in the pericardial appendages;

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Schipp et al., 1985; Westermann et al., 2002), only very few studies deal with the bioaccumulation of trace elements in this ancestral genus. High concentrations of several metals and metalloids were reported in the digestive and excretory tissues of *Nautilus macromphalus* (Bustamante et al., 2000), a species endemic to the New Caledonian waters. These authors suggested that the high metal concentrations may be due to a high exposure in the metal-rich conditions in the surrounding New Caledonian waters. Indeed, the largest resources of Ni as laterites in the world are present in New Caledonia where open-cast mining is conducted since the 20th century, leading to a dramatic increase of metal concentrations in coastal waters and, subsequently, the metal burdens in marine biota (Labrosse et al., 2000; Metian et al., 2008). However, it is not clear whether metal accumulation observed in *N. macromphalus* reflected the impact of metal contamination through human activities on the outer shelf waters of New Caledonia or either if it is more due to a natural progressive bioaccumulation during nautilus long life span (*viz.* 10–15 yr).

The aim of the present study was therefore to determine the bioaccumulation of a large range of elements in the genus *Nautilus* comparing two species from geologically contrasted areas: (1) *N. macromphalus* from New Caledonia which is characterized by its richness in nickel ores and its lack of tectonic activities and (2) *N. pompilius* from the Vanuatu archipelago which shows high volcanic and tectonic activities (Harrison et al., 1996). The analysed elements comprised 11 metals (Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn), two metalloids (As and Se) and three rare earth elements (Ce, La, and Nd). These elements were selected for comparison with other species and other published works concerning Nautilus (e.g. Miramand and Bentley, 1992; Bustamante et al., 2000; Ichihashi et al., 2001). The concentrations and relative contents of these different trace elements were determined in the digestive and the excretory tissues (i.e. pericardial and renal appendages) and compared between both nautilus species. The specificities and the potential influence of the environment on bioaccumulation of these trace elements in the *Nautilus* genus are discussed.

2. Materials and methods

2.1. Biological material

Three *N. pompilius* and five *N. macromphalus* specimens were collected, respectively, off Santo island coast (Vanuatu, 15°40′522″S, 167°02′838″E, depth: 334 m) and on the outer shelf of New Caledonia (22°20′500″S, 166°13′400″E, depth: 300 m) in May 2006 (Fig. 1). Each individual was measured and weighted prior to dissection. The main features of the eight specimens sampled are reported in Table 1.

All specimens were dissected aseptically and for each specimen one pericardial appendage, one renal appendage and a fraction of the digestive gland were immediately frozen in liquid nitrogen and stored at −80 °C for metal analyses.

2.2. Analytical procedure

Tissue samples were freeze-dried. Aliquots of the samples ranging from 20 to 300 mg were 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 heated in a microwave during 30 min, with increasing temperature until 105 °C, and 15 min at 105 °C (1200 W). After the mineralisation process, each sample was diluted to 30 or 50 ml with milli-Q quality water, according to the volume of acid added to the mineralisation (3 and 4.5 ml, respectively).

Ag, As, Cd, Ce, Co, Cr, Cu, Fe, La, Mn, Nd, Ni, Pb, Se, V, and Zn were analysed either by ICP-OES (Varian® Vista-Pro) and ICP-MS (Varian® Ultra Mass 700). Reference tissues, dogfish liver DOLT-3 (NRCC), lobster hepatopancreas TORT-2 (NRCC) and bush branches and leaves (GBW 07602) were treated and analysed in the same way as the samples. Results were in good agreement with the certified values, and the standard deviations were low, proving good repeatability of the method. The results for standard reference materials displayed recoveries of the elements ranging from 81% to 119% ($n = 10$). For each set of analyses, blanks were included in each analytical batch. The detection limits ($\mu g\, g^{-1}$ dry wt) for ICP-OES were 8.3 (As, Fe, Zn), 3.3 (Ag, Se), 1.67 (Pb, V), 0.83 (Cd, Co, Cr, Cu, Mn, Ni), and for ICP-MS, they were 0.150 (Ni, V), 0.065 (Cd, Co, Cr, Cu, Mn, Pb), 0.033 (Ag), 0.017 (Nd), 0.008 (Ce, La). Average element concentrations are presented with standard deviations. All trace element concentrations are given on a dry weight basis ($\mu g\, g^{-1}$ dry wt).

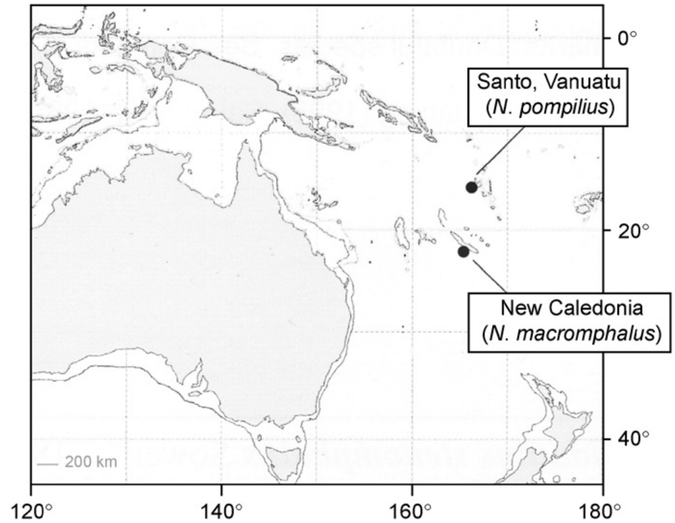

Fig. 1. Location of *Nautilus pompilius* and *N. macromphalus* specimens' collection.

Table 1
Characteristics of the sampled specimens of *Nautilus pompilius* and *N. macromphalus*

Species	Sex	Length (mm)	Weight (g)
N. pompilius			
1	Male	177	825
2	Male	151	660
3	Male	171	796
N. macromphalus			
1	Male	164	766
2	Female	162	676
3	Male	173	870
4	Male	160	758
5	Male	140	480

2.2.1. Data analyses

Statistical analyses were performed using MINITAB 13.2 Software. Comparison of trace element concentrations in nautilus tissues between sites was tested by 1-way ANOVA. Hypothesis of normal distribution was tested using the Anderson–-Darling test and equality of variance by the Bartlett test. Pearson coefficients were calculated between trace elements in each tissue. The significance level for statistical analyses was always set at $\alpha = 0.05$.

3. Results

3.1. Trace element concentrations in the tissues

Metal concentrations in the digestive gland, the renal appendages and the pericardial appendages of *N. macromphalus* and *N. pompilius* are reported in Table 2. La, Ce, and Nd concentrations fell below the detection limit in the renal appendages. Among the three tissues analysed, the digestive gland was the major site of accumulation for Ag, Cd, Ce, Co, Cu, Fe, La, Nd, V, and Zn (Table 2). The digestive gland also concentrated As and Ni at concentrations close to the highest ones recorded in the other tissues. As, Cr, Mn,