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Metal and metalloid concentrations in the giant squid *Architeuthis dux* from Iberian waters

Bustamante P[1*], González AF[2], Rocha F[3], Miramand P[1], Guerra A[2]

1. Littoral, Environnement et Sociétés (LIENSs), UMR 6250, CNRS-Université de La Rochelle, 2 rue Olympe de Gouges, F-17042 La Rochelle cedex 01, France

2. Instituto de Investigaciones Marinas (CSIC), ECOBIOMAR, Eduardo Cabello 6, 36208 Vigo, Spain

3. Departamento de Ecología y Biología Animal, Facultad de Ciencias, Campus As Lagoas-Marcosende, Universidad de Vigo, 36310 Vigo, Spain

[*] Corresponding author; Phone : +33 546 507 625 ; Fax : +33 546 458 264; E-mail : pbustama@univ-lr.fr

Abstract: This study investigated 14 trace elements (Ag, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, V and Zn) in the tissues of the giant squid *Architeuthis dux* from the Mediterranean and Atlantic Spanish waters. As for other families of cephalopods, the digestive gland and the branchial hearts of *Architeuthis* showed the highest concentrations of Ag, Cd, Co, Cu, Fe, Ni, Se, V and Zn, highlighting their major role in the bioaccumulation and detoxification processes. With the exception of Hg, the muscles showed relatively low trace element concentrations. Nevertheless, this tissue contained the main proportion of the total As, Cr, Hg, Mn, Ni, and Zn body burden because muscles represent the main proportion of the squid mass. These findings suggest that the metal metabolism is overall the same as other cephalopod families from neritic waters. In females, Zn concentrations increased in the digestive gland with the squid's weight likely reflecting physiological changes during sexual maturation. Comparing the trace element concentrations in the tissues of *Architeuthis*, higher Ag, Cu, Hg and Zn concentrations in the squid from the Mediterranean reflected different exposure conditions. In comparison to other meso-pelagic squids from the Bay of Biscay, Cd concentrations recorded in the digestive gland suggest that *Architeuthis* might feed on more contaminated prey or that it displays a longer life span that other cephalopods.

Key words: trace element; bioaccumulation; cephalopod; giant squid, *Architeuthis*

1. Introduction

Cephalopods play a key role in marine ecosystems both as predators and prey. They constitute a class of marine molluscs which are found in a great variety of habitats from coastal waters to very deep-ocean environments (Boyle and Rodhouse, 2005). Independently of the species, the habitat or the life span they display, cephalopods share the ability to accumulate inorganic and organic pollutants such as metals, PCBs or organochlorine pesticides (e.g. Martin and Flegal, 1975; Tanabe et al., 1984; Miramand and Bentley, 1992; Yamada et al., 1997; Bustamante et al., 2000, 2006a; Ueno et al., 2003; Storelli et al., 2006). Consequently, they were reported to constitute a significant vector of contaminants to the species feeding on them, in particular seabirds and marine mammals (e.g. Honda et al., 1983; Muirhead and Furness 1988; Bustamante et al., 1998; Lahaye et al., 2005). However, most studies focused on commercially targeted species which are 1) easy to sample and 2) of high economic and health interest concerning human consumption. Many of these cephalopod species are also consumed by top marine predators, but there is a gap in the information concerning non-targeted species. This lack of data on bioaccumulation of contaminants is particularly obvious for oceanic and deep-sea species, like the giant squid *Architeuthis*.

Overall, the biology, behaviour and life cycle of *Architeuthis* are still poorly known in many aspects even if this squid has received considerable attention over the last decade (see González et al., 2002; Guerra et al., 2004, 2006; Kubodera and Mori 2005). Most of the information available on this squid comes from dead stranded animals and from predator trophic ecology studies. Indeed, squid flesh and beaks are often recorded in the stomach of sperm whales, but also of seabirds and sharks (Roper and Boss 1982; Clarke 1996; Santos et al., 2002; Cherel and Hobson 2005). Giant squids are also increasingly captured by trawling

nets because of the development of deep-sea fisheries (Guerra et al., 2006). In deep water conditions, the giant squid would have a particular diet and exposure conditions to trace elements and metals. For example, Hg bioavailability seems to be enhanced in these deep environments because the absence of solar radiation and the low oxygen concentrations in the deep environment favors a high methylation rate by bacteria (Monteiro et al., 1996). Also, Cd is enriched in mesopelagic waters while depleted in the surface ocean because of its regeneration from sinking biological debris from epipelagic zone and its uptake by organisms at the surface (Boyle et al., 1976).

In this framework, the objectives of this study were to provide baseline data on a wide range of trace elements in the giant squid *Architeuthis dux* from the Spanish waters. To this end, the concentrations and tissue distribution of 12 metals (Ag, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, V and Zn) and 2 metalloids (As and Se) were determined in the tissues and organs of fished and stranded specimens. The recorded values were then compared to the data from the current literature for other cephalopod species.

2. Material and methods

2.1. Sampling and sample preparation

Six specimens of giant squid were collected between 2001 and 2005. Table 1 shows the main data of the specimens as well as the sampling site, date, and mode of capture. Five specimens were caught in the Bay of Biscay (Asturias, North Spain) and one in the western Mediterranean Sea. Two of them were mature males and four were immature or maturing females.

Collected specimens were immediately frozen prior to dissection. In the laboratory, each individual was weighed and measured (mantle length ML, total length TL), and the sex and maturity stage determined. The digestive gland, gills, ink sack, branchial hearts and their appendages, systemic heart and brain were totally removed. In addition, pieces of muscle, skin, digestive and genital tissues (i.e. oviduct gland, ovary and testis), were sampled to determine trace element concentrations. As it was not possible to separate the different tissues and to weigh them, the total concentrations in the whole *Architeuthis* specimens were estimated according to the measured concentrations in the different tissues and to their relative weight in fishery targeted squids.

2.2. Analytical procedure

All samples were freeze-dried for several days then grounded. Aliquots of the samples ranging from 50 to 300 mg were digested using a 3:1 v:v nitric-hydrochloric acid mixture with 65% HNO_3 (Merck, suprapur quality) and 70% HCl (Merck, suprapur quality). 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 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 (3.0 ml or 4.5 ml).

Ag, As, Cd, Co, Cr, Cu, Fe, Mn, Ni Pb, Se, V and Zn were analysed either by Inductively Coupled Plasma-Optical Emission Spectrometry (Varian® Vista-Pro) or Inductively Coupled Plasma-Mass Spectrometry (Varian® Ultra Mass 700). For Hg, two aliquots ranging from 10 to 50 mg of dried material were directly analysed in an Advanced Mercury Analyser spectrophotometer (Altec® AMA 254).

Reference tissues (dogfish liver DOLT-3, NRCC, and lobster hepatopancreas TORT-2, NRCC) 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 (Table 2). The results for standard reference materials displayed recoveries of the elements ranging from 88% to 116% (n=10).

The detection limits (µg.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 were 0.167 (Ni, V), 0.083 (Cd, Co, Cr, Cu, Mn, Pb), 0.033 (Ag) for ICP-MS. Trace element concentrations are given relative to the dry weight (µg.g^{-1} dry wt) while the distribution percentages are calculated for wet weight.

3. Results

3.1. Trace element concentrations in soft tissues

Trace element concentrations in the tissues and organs of *Architeuthis* are reported in Figure 1. Among the sampled tissues, the digestive gland was the major site of concentration for Ag, Cd, Co, Cu, Fe and Se with 1.13-14.0 µg Ag.g^{-1}, 27.2-134 µg Cd.g^{-1}, 2.0-4.8 µg Co.g^{-1}, 64-1218 µg Cu.g^{-1}, 52-1862 µg Fe.g^{-1} and 9.7-19.5 µg Se.g^{-1} (Figure 1). The digestive gland also concentrated Ni, V and Zn at concentrations closed to the highest concentrations recorded in the other tissues with 0.11-1.42 µg Ni.g^{-1}, 0.60-4.34 µg V.g^{-1}, and 34-219 µg Zn.g^{-1}. Interestingly, the digestive gland also exhibited the lowest concentrations of As, Cr and Hg with 31-65 µg As.g^{-1}, 0.41-1.40 µg Cr.g^{-1}, and 0.32-1.56 µg Hg.g^{-1} (Figure 1).

The concentrations of As, Co, Hg, Ni, Se and V were also remarkable in branchial hearts, which play an important excretory role in cephalopods. In this tissue, the concentrations of trace elements were the highest for Ni or very close to the highest for As, Co, Hg, Se and V. Branchial hearts concentrated As from 86 to 111 µg.g^{-1}, Co from 3.15 to 3.22 µg.g^{-1}, Hg

from 0.71 to 4.37 µg.g^{-1}, Ni from 0.74 to 2.60 µg.g^{-1}, Se from 8.2 to 9.3 µg.g^{-1} and V from 1.50 to 2.46 µg.g^{-1} (Figure 1).

Muscles exhibited generally among the lowest concentrations for all trace elements except for Hg which exhibited the highest values in this tissue (1.86-3.32 µg Hg.g^{-1} dry weight; Figure 1). Cr and Zn were highly concentrated in the ovary with concentrations ranging from 0.65 to 6.12 µg.g^{-1} and 131 to 149 µg.g^{-1}, respectively. The oviduct gland also displayed high concentrations of As and Mn as well as the digestive gland appendages had high concentrations of Cr and Pb (Figure 1).

3.2. Distribution of the trace elements in soft tissues

The proportions of the whole body burden of the trace elements contained in each organ and tissue are shown in Figure 2. With the exception of As, Cr, Hg and Mn which were mainly found in the body muscular parts (69 ± 9%, 68 ± 20%, 87 ± 5%, and 55 ± 22%, respectively), the digestive gland contained the largest quantities of all trace elements : 98 ± 1% of Ag, 99 ± 1% of Cd, 97 ± 2% of Co, 92 ± 5% of Cu, 85 ± 16 % of Fe, 53 ± 28% of Ni, 69 ± 22% of Pb, 77 ± 5% of Se, 71 ± 19% of V, and 53 ± 17% of Zn (Figure 2).

Although the concentrations of some trace elements were high in the branchial hearts or in the gills, these tissues contained in fact low amounts of the considered elements because of their small masses relative to the whole body weight (Figure 2).

3.3. Influence of the size/weight and origin

The size/weight only influenced Zn concentrations in the digestive gland (R^2=0.934, p=0.020) and Cr and Ni concentrations in the gills (R^2=0.968 p=0.007 and R^2=0.969 p=0.007).

No statistical tests were performed to compare the influence of the origin on the accumulated trace elements because our sampling only included one specimen from the Mediterranean.

However, this giant squid clearly displayed higher concentrations of Hg than any of those from the Bay of Biscay with 1.56 *vs* 0.47 ± 0.13 µg.g^{-1} in the digestive gland (see Table 3), 2.97 *vs* 1.38 ± 0.34 µg.g^{-1} in the gills, and 3.32 *vs* 2.07 ± 0.19 µg.g^{-1} in the mantle muscle (data not shown). Important differences also appeared for Ag, Cu and Zn with 14.0 *vs* 1.90 ± 0.47 µg Ag.g^{-1}, 1218 *vs* 108 ± 83 µg Cu.g^{-1}, and 219 *vs* 103 ± 51 µg Zn.g^{-1} in the digestive gland (Table 3), and 4.80 *vs* 0.31 ± 0.11 µg Ag.g^{-1}, 206 *vs* 31 ± 24 µg Cu.g^{-1} and 111 *vs* 60 ± 35 µg Zn.g^{-1} in the gills (data not shown).

4. Discussion

Previous studies have demonstrated the ability of cephalopods to accumulate high concentrations of trace elements in their tissues but very little data is available in the current literature for non-targeted and/or deep-waters species such as the giant squid *Architeuthis*. Although globally poorly documented, metal and metalloid concentrations in cephalopod tissues have received increasing interest over the last decades, particularly in Europe and Japan, as these molluscs play a major role both as predators and food items in marine ecosystems (see the reviews by Clarke 1996; Croxall and Prince 1996; Klages 1996; Smale 1996; Boyle and Rodhouse, 2005). The central role of the digestive gland in trace element bioaccumulation and detoxification has been highlighted many times, particularly for toxic metals such as Ag and Cd (e.g. Martin and Flegal 1975; Miramand and Bentley 1992; Bustamante et al., 2002, 2004; Ichiashi et al., 2001a; Miramand et al., 2006). Beside the digestive gland, which also plays a major role in the energetic metabolism of cephalopods (e.g. Rosa et al., 2005; Moltschaniwskyj and Johnston 2006), the branchial hearts and their appendages are involved in trace element excretion processes, allowing the depuration and/or the storage of various metals and radionuclides (e.g. Nardi and Steinberg 1974; Miramand

and Guary 1980; Guary et al., 1981; Miramand and Bentley 1992; González et al., 1998; Bustamante et al., 2002, 2006b). As for coastal and/or oceanic targeted cephalopods, the digestive gland and the branchial hearts of *Architeuthis* generally contained the highest concentrations of most of the considered elements, i.e. Ag, Cd, Co, Cu, Fe, Ni, Se, V and Zn (Figure 1). This finding strongly suggests that the metabolism of trace elements in *Architeuthis* is very close to, or even the same as other families of cephalopods. This is supported by the fact that trace element concentrations in the digestive gland of *Architeuthis* closely fall within the same range than for other cephalopod species (Table 3), indicating that the potential of *Architeuthis* for their bioaccumulation is relatively similar. Moreover, according to the elevated proportions of the total element body burden, the digestive gland of *Architeuthis* might play a central role in the detoxification and storage of most of the analysed elements, i.e. Ag, Cd, Co, Cu, Fe, Ni, Pb, Se, V and Zn (Figure 2). It would be a great interest to investigate the detoxification strategies in the digestive gland of *Architeuthis* in comparison to that of other families of cephalopods.

Besides the digestive gland, muscles contained very high proportions of total body burdens of As, Cr, Hg, Mn, Ni, and Zn (Figure 2). With the exception of Hg, trace element concentrations in *Architeuthis* muscles were relatively low and these high proportions resulted from the elevated muscular mass respective to the whole body weight. For Hg, the concentrations recorded in the muscles were the highest among the different organs and tissues (Figure 1). Previous studies have reported relatively similar Hg concentrations between the different tissues of different squid species from the Northern Atlantic waters (Bustamante et al., 2006a; Pierce et al., 2008). It is therefore noteworthy that muscular Hg concentrations in *Architeuthis* were 2 to 4 times higher than in the digestive gland. In comparison with Ag, Cd, Co, Cu, Fe, Ni, Pb, Se, V and Zn, the role of the digestive gland in the storage of Hg appeared to be relatively limited in *Architeuthis*. This may be due to an

excretion function of Hg by the digestive gland, and/or a preferential redistribution of Hg to muscular tissues where it binds to the sulphydryl groups of proteins (Bloom, 1992; Bustamante et al., 2006a). Such a redistribution might indicate that most of the Hg ingested from the prey would be in the organic form such as fish in which Hg content is virtually 100% in the methylated form (Bloom, 1992). Little is known about the diet of *Architeuthis*, it includes other cephalopods (Pérez-Gándaras and Guerra, 1978, 1989), crustaceans (e.g. *Nephros norvergicus*) as well as a large proportion of fish of different families accordingly to the available prey in the area (for instance *Trachurus trachurus, Maurolicus muelleri* and *Micromesistius poutassou* in Ireland waters and equivalent species from Namibia and New Zealand) (see Guerra et al., 2006 for a review). Further studies therefore should focus on trace elements in the typical prey of *Architeuthis* to provide insights on this aspect.

As in other cephalopod species, trace element concentrations in *Architeuthis* may vary with biological and environmental factors such as age (size/weight), sex, and geographical origin (e.g. Monteiro et al., 1992; Bustamante et al., 1998; Raimundo et al., 2004; Pierce et al., 2008). Our limited sampling did not allow making comparisons for all these factors. However, considering the 5 specimens from the Bay of Biscay, it appears that size/weight poorly influenced trace element concentrations in *Architeuthis* tissues. The increase of Zn concentrations from 34 to 160 $\mu g.g^{-1}$ dwt in the digestive gland might be related to metal physiological changes related to the sexual maturation as reported for other cephalopod species like *Sepia officinalis* from the English Channel (Miramand et al., 2006). In females, high concentrations of Zn in the ovary of *Architeuthis* (120 ± 38 $\mu g.g^{-1}$ dwt) were close to that in the genital tract of *Sepia officinalis* (123 ± 3 $\mu g.g^{-1}$ dwt; Miramand and Bentley, 1992). Within the ovary, essential elements such as Zn are stored in metal-containing enzymes and metalloproteins (Gerpe et al., 2000) and transferred to the yolk of the eggs (Villanueva and Bustamante, 2006, Lacoue-Labarthe et al., 2008). Cr and Ni in the gills also

displayed a significant increase with size/weight. In the current literature, very little data is available on the variation of Cr and Ni concentrations in cephalopod tissues. For example, in the squid *Sthenoteuthis oualaniensis* Cr concentrations were higher in juveniles than in adults, whereas juveniles displayed lower Ni concentrations than adults (Ichihashi et al., 2001a). Such a difference for *S. oualaniensis* was explained by the evolution of food habits between the juvenile and adult stages, juvenile feeding more on crustaceans while adults primarily preyed on fish. According to the lack of significant variation in the digestive gland, such a switch is not likely to occur in the size range of *Architeuthis* we analysed. Furthermore, even if the diet could represent the main pathway for many elements - as experimentally shown for Am, Cd, Co and Zn (Koyama et al., 2000; Bustamante et al., 2002, 2004, 2006b) - seawater could also be an important uptake pathway, as elements pass through the skin and through the gills. For instance, seawater represents the main pathway for Ag in *Sepia officinalis* (Bustamante et al., 2004). Therefore, Cr and Ni bioaccumulation in gills might also result from a direct uptake from seawater all along the lifespan of *Architeuthis*.

Trace element concentrations in cephalopods could also vary according the location where individuals were captured (Bustamante et al., 1998; Seixas et al., 2005ab; Pierce et al., 2008). In the case of *Architeuthis*, this is clearly exemplified by the much higher Hg concentrations in the tissue of the specimen from the Mediterranean. Higher Hg concentrations in Mediterranean organisms have been highlighted many times and are typically explained by high temperatures and absence of solar radiation in the deep environment. These conditions favor a high methylation rate of the metal, methyl-Hg being highly bioavailable for marine biota, which consistently biomagnifies through the food chain. Moreover, natural sources of Hg in the Mediterranean Sea may contribute to Hg enrichment through the benthic food webs, as it constitutes the richest natural reserve of this element (Bacci, 1989). Higher Ag, Cu and

Zn concentrations in the digestive gland and in the gills also indicated different exposure conditions of this specimen compared to those from the Bay of Biscay. In cephalopods, Ag bioaccumulation in the digestive gland might reflect the global contamination of the surrounding waters (e.g. Martin and Flegal, 1975; Miramand et al., 2006), seawater being the main pathway of exposure and Ag having a fast turn-over in the tissues (Bustamante et al., 2004). Interestingly, Ag, Cu, Hg and Zn are metals that bind to metallothionein proteins (MTs), which play a role in the homeostasis of the essential metals (i.e. Cu and Zn) and in the detoxification of non-essential metals (i.e. Ag, Cd and Hg) (Roesijadi, 1992, 1996; Viarengo and Nott, 1993). The role of MTs in metal sequestration in cephalopods is not completely clear (Bustamante et al., 2006c) and this issue clearly deserves further investigation.

Even though trace elements are generally considered for their potential toxicity in ecotoxicological studies and biomonitoring surveys, there is increasing interest in their use for providing information on life history and trophic ecology of cephalopods (Jackson et al., 2007). Thus, Cd is of particular interest because it is highly bioaccumulated by cephalopods. Indeed, Cd is efficiently absorbed and strongly retained in the digestive gland (Bustamante et al., 1998, 2002). Even if most of cephalopod species display short life spans i.e. typically less than 2 years, they can accumulate very high Cd concentrations in their digestive gland reaching up 1000 $\mu g\ g^{-1}$ wet wt in the squid *Illex argentinus* (Dorneles et al., 2007). Because of Cd incorporation by organisms in epipelagic waters and its regeneration from sinking biological debris in the mesopelagic environment (Boyle et al., 1976), deep-water cephalopods might show relatively high Cd concentrations. In the Bay of Biscay, Cd concentrations reached 9.1 and 33.1 $\mu g.g^{-1}$ dry wt in the digestive gland of the mesopelagic squids *Histioteuthis reversa* and *Teuthowenia megalops*, respectively (unpublished data) and would be due to the consumption of prey highly contaminated with Cd. Even elevated

compared to neritic squid species (Bustamante et al., 1998), these concentrations are lower than those measured in the digestive gland of *Architeuthis*, suggesting that 1) the giant squid feed on more contaminated prey than Histioteuthidae and Cranchidae, or 2) it displays a much longer life span that other cephalopods. Age estimation and growth rates of giant squids are still open questions. Indeed, isotopic analysis indicated that the age for the giant squid *Architeuthis sanctipauli* from Tasmania was 14 years for specimens ranging from 191 to 240 cm ML (Landman et al., 2004). This completely disagrees with the age estimated from growth increment counts in statoliths of *Architeuthis dux* and *Architeuthis* sp. from the Atlantic and caught off New Zealand. Specimens ranging from 43 to 161 cm ML had between 153 and 435 increments (Jackson et al., 1991; Gauldie et al., 1994; Lordan et al., 1998; González et al., 2002). If the increments were daily deposited, as it occurs in other cephalopods, the age of these animals will not exceed two years. This finding implies that *Architeuthis* would have a very fast growth rate with intense food intakes that in turn would lead to the bioaccumulation of relatively high Cd concentrations in its digestive gland.

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Table 1. Sampling information and squid biological characteristics. T: trawling; S: Stranded; F: Floating at the surface; ML: Dorsal mantle length; TL: Total length.

N°	Sampling site	Sampling date	Mode of capture	Weight (kg)	ML (cm)	TL (cm)	Sex / Maturation
1	Off Luarca (Asturias, North Spain)	12 September 2001	T	90	127	710	F / Immature
2	Ribadesella (Asturias, North Spain)	23 October 2001	S	104	150	800	F / Maturing
3	Colunga (Asturias, North Spain)	15 September 2003	S	80	152	1200	F / Immature
4	Off Gijón (Asturias, North Spain)	16 September 2003	F	66	122	620	M / Mature
5	Off Gandía (Valencia, Western Mediterranean)	19 July 2005	T	50	107	600	M / Mature
6	Off Gijón (Asturias, North Spain)	22 July 2005	T	139	146	820	F/ Maturing

Table 2. Comparison of certified trace elements concentrations (µg g^{-1} dry weight) in reference materials (n=10) with the values determined in the present study (nc: not certified value, nd: not determined). ICP-MS - Inductively Coupled Plasma Mass Spectrometry; ICP-OES - Inductively Coupled Plasma Optical Emission Spectrometry; AMA – Advanced Mercury Analyser.

Element	Method	TORT-2			DOLT-3		
		Measured	Certified	Recovery	Measured	Certified	Recovery
		Mean ± SD	Mean ± SD		Mean ± SD	Mean ± SD	
Ag	ICP-MS	6.21 ± 1.69	nc	-	1.21 ± 0.10	1.20 ± 0.07	101
As	ICP-OES	21.8 ± 2.4	21.6 ± 1.8	101	9.9 ± 0.3	10.2 ± 0.5	97
Cd	ICP-MS	26.4 ± 2.2	26.7 ± 0.6	99	19.3 ± 0.7	19.4 ± 0.6	99
Co	ICP-MS	0.45 ± 0.09	0.51 ± 0.09	88	0.29 ± 0.05	nc	-
Cr	ICP-OES	0.69 ± 0.18	0.77 ± 0.15	90	4.02 ± 0.93	nc	-
Cu	ICP-OES	95 ± 15	106 ± 10	90	31.9 ± 0.7	31.2 ± 1.0	99
Fe	ICP-OES	100 ± 10	105 ± 13	95	1349 ± 76	1484 ± 57	91
Hg	AMA	0.27 ± 0.01	0.27 ± 0.06	100	3.36 ± 0.08	3.37 ± 0.14	100
Mn	ICP-OES	13.5 ± 2.0	13.6 ± 1.2	99	9.73 ± 0.14	nc	-
Ni	ICP-OES	2.44 ± 0.56	2.50 ± 0.19	98	2.46 ± 0.45	2.72 ± 0.35	90
Pb	ICP-MS	0.32 ± 0.17	0.35 ± 0.13	91	0.294 ± 0.056	0.319 ± 0.045	92
Se	ICP-MS	6.48 ± 0.48	5.63 ± 0.67	115	7.56 ± 0.65	7.06 ± 0.48	107
V	ICP-MS	1.55 ± 0.24	1.64 ± 0.19	95	nd	nc	-
Zn	ICP-OES	188 ± 20	180 ± 6	104	97.3 ± 1.4	86.6 ± 2.4	116

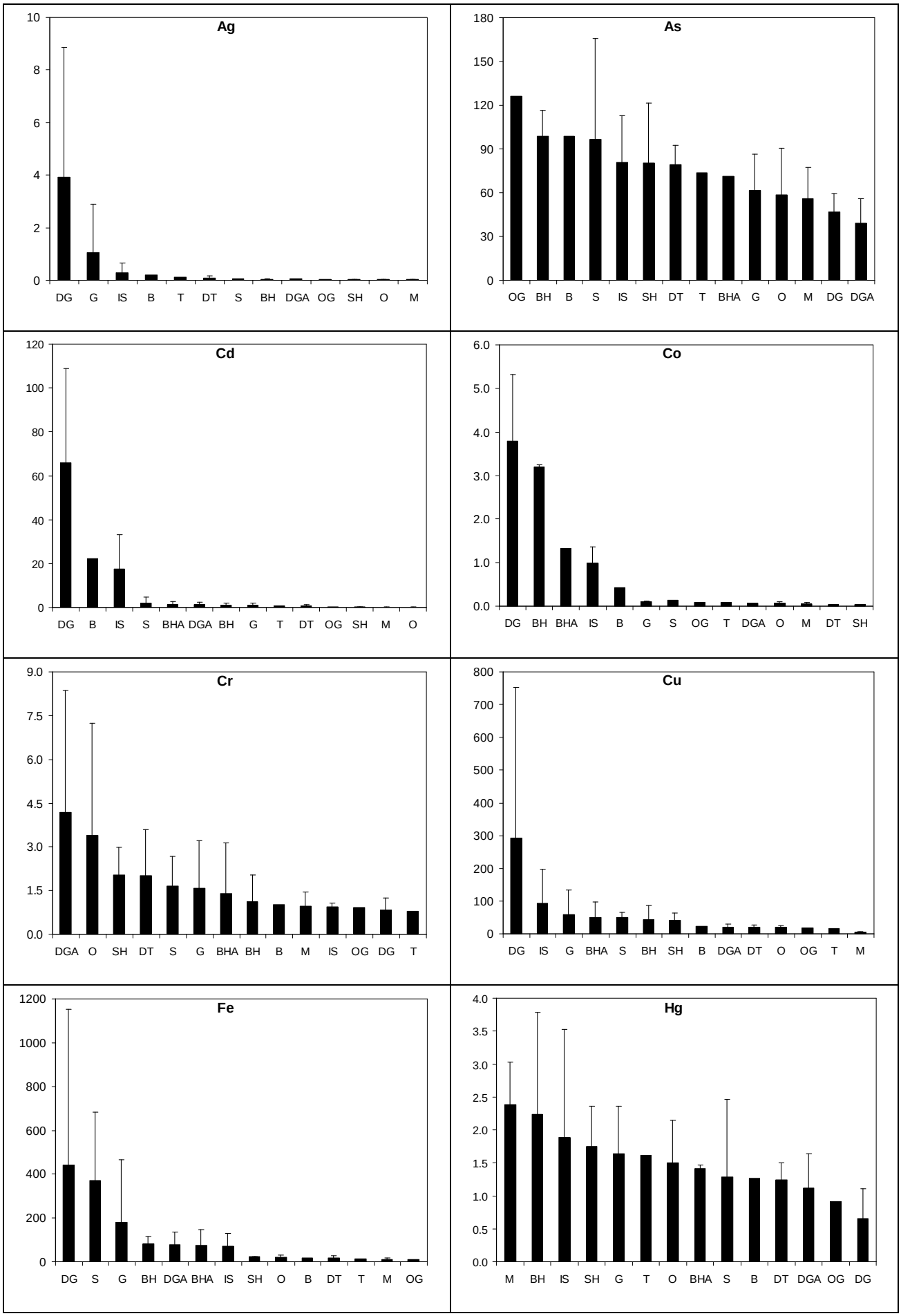
Table 3. Reported metal concentrations (Mean ± SD, µg g^{-1} dry weight) in the digestive gland of different cephalopod species.

Species	Ag	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	V	Zn	Reference
Architeuthidae														
Architeuthis dux	1.90 ± 0.47	48 ± 14	60.8 ± 46.2	3.27 ± 1.76	0.93 ± 0.41	108 ± 83	497 ± 779	0.47 ± 0.13	2.72 ± 2.12	0.62 ± 0.54	0.41 ± 0.33	2.24 ± 1.91	103 ± 51	a
A. dux	14	44	90.7	4.8	0.49	1218	158	1.56	2.26	1.37	0.85	1.72	219	b
Nautilidae														
Nautilus macromphalus	4.43 ± 1.95	185 ± 64	45 ± 13	5.9 ± 3.6	4.2 ± 0.8	106 ± 46	554 ± 238	-	8.9 ± 2.0	11.9 ± 7.8	-	8.0 ± 2.3	672 ± 208	c
Sepiidae														
Sepia officinalis	6.15 ± 1.75	-	12.7 ± 0.4	3.3 ± 0.6	1.1 ± 0.1	315 ± 3	244 ± 28	-	3.3 ± 0.1	1.3±0.4	1.14 ± 0.06	5.0 ± 1.3	571 ± 47	d
S. officinalis	13 ± 2	-	25 ± 5	10 ± 2	-	600 ± 10	390 ± 10	-	-	-	2.2 ± 0.5	3.3 ± 0.1	1400 ± 500	e
Loliginidae														
Loligo opalescens	25.1 ± 12.6	-	85.0 ± 51.6	-	-	5350 ± 3210	111 ± 73	-	-	-	-	-	247 ± 131	f
L. opalescens	45.9 ± 19.0	-	122 ± 58	-	-	8370 ± 3130	87 ± 49	-	-	-	-	-	449 ± 201	f
Ommastrephidae														
Nototodarus gouldi	-	-	33 ± 30	-	-	363 ± 238	-	-	-	-	-	-	830 ± 355	g
N. gouldi	3.3 ± 1.4	-	50 ± 25	-	-	246 ± 298	745 ± 440	-	4.2 ± 1.1	-	-	-	696 ± 295	h
Ommastrephes bartrami	12.1 ± 8.6	-	287 ± 202	-	-	195 ± 212	399 ± 204	-	-	-	-	-	163 ± 55	f
Stenoteuthis oualaniensis	24.1 ± 10.9	-	782 ± 255	-	-	1720 ± 151	319 ± 67	-	-	-	-	-	513 ± 288	f
*S. oualaniensis**	14.0	22.4	199	3.28	0.163	558	293	0.125	1.36	1.91	1.10	1.85	128	i
*Todarodes pacificus**	*3.5*	*7.5*	*60*	*0.78*	*0.375*	*27.5*	*325*	*0.133*	*3.5*	*7.0*	*0.60*	*13.8*	*195*	j
Octopodidae														
Eledone cirrhosa	3.20 ± 1.74	-	24.0 ± 1.8	2.06 ± 0.08	0.8 ± 0.1	456 ± 11	287 ± 13	-	4.2 ± 1.6	2.5 ± 0.1	1.17 ± 0.09	3.3 ± 0.5	646 ± 86	d
Octopus vulgaris	-	-	-	8.8	-	275	275	-	2.7	-	-	-	1300	k
O. vulgaris	-	-	50 ± 10	-	-	2500 ± 700	700 ± 130	-	7.0 ± 0.5	-	-	4.5 ± 1.0	1450 ± 400	l
O. vulgaris								0.58 ± 0.08			4.9 ± 1.9	7.2 ± 6.9		m

a: Present study (Bay of Biscay); b: Present study (Mediterranean); c: Bustamante et al., (2000); d: Miramand and Bentley (1992); e: Miramand et al., (2006); f: Martin and Flegal (1975); g: Finger and Smith (1987); h: Smith et al., (1984); i: Ichihashi et al., (2001a); j: Ichihashi et al., (2001b); k: Ueda et al., (1979); l: Miramand and Guary (1980); m: Seixas and Pierce (2005ab) and Seixas et al., (2005a)

* converted to dwt using a factor of 2.5

in italics: median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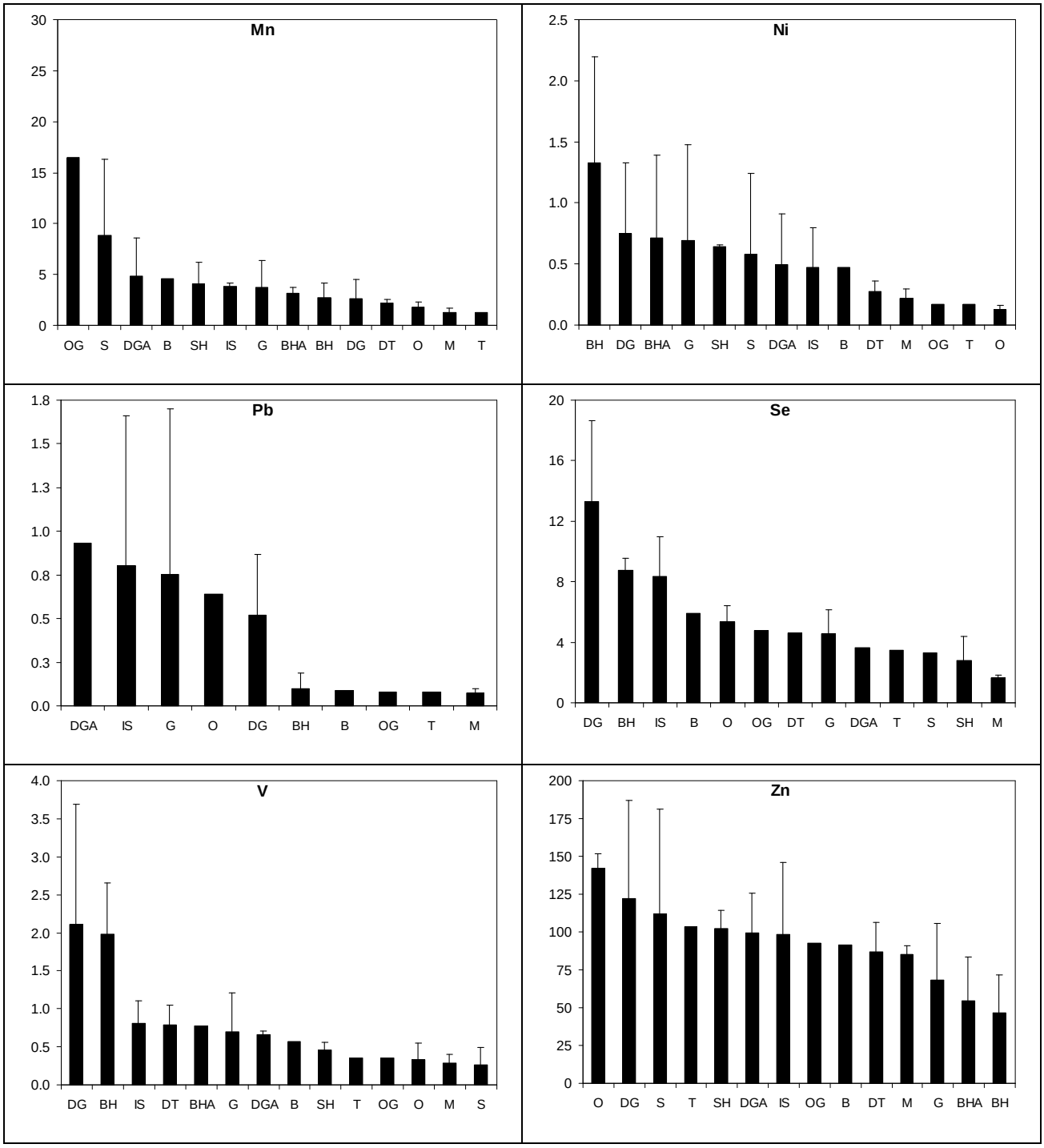
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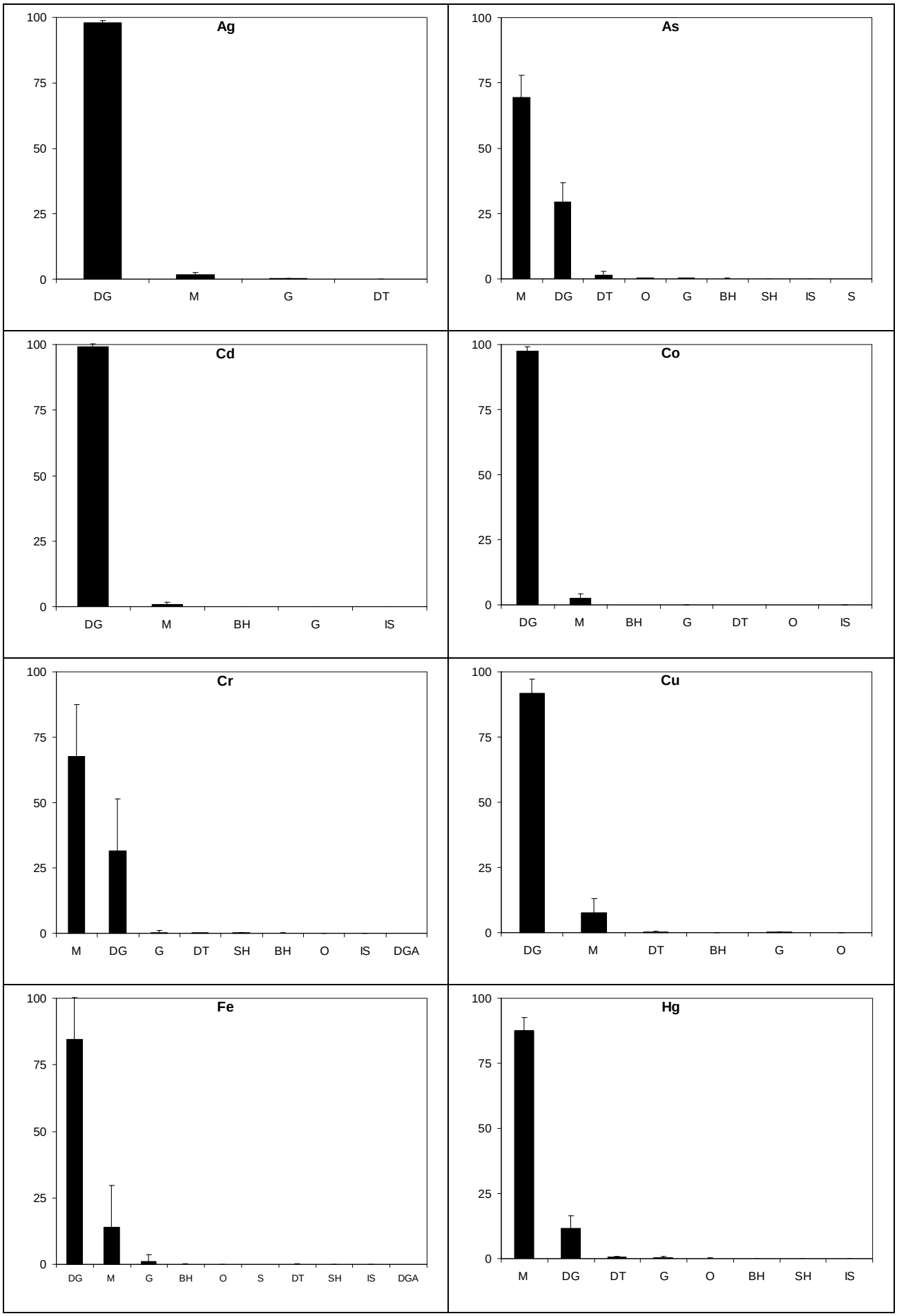
Figure 1.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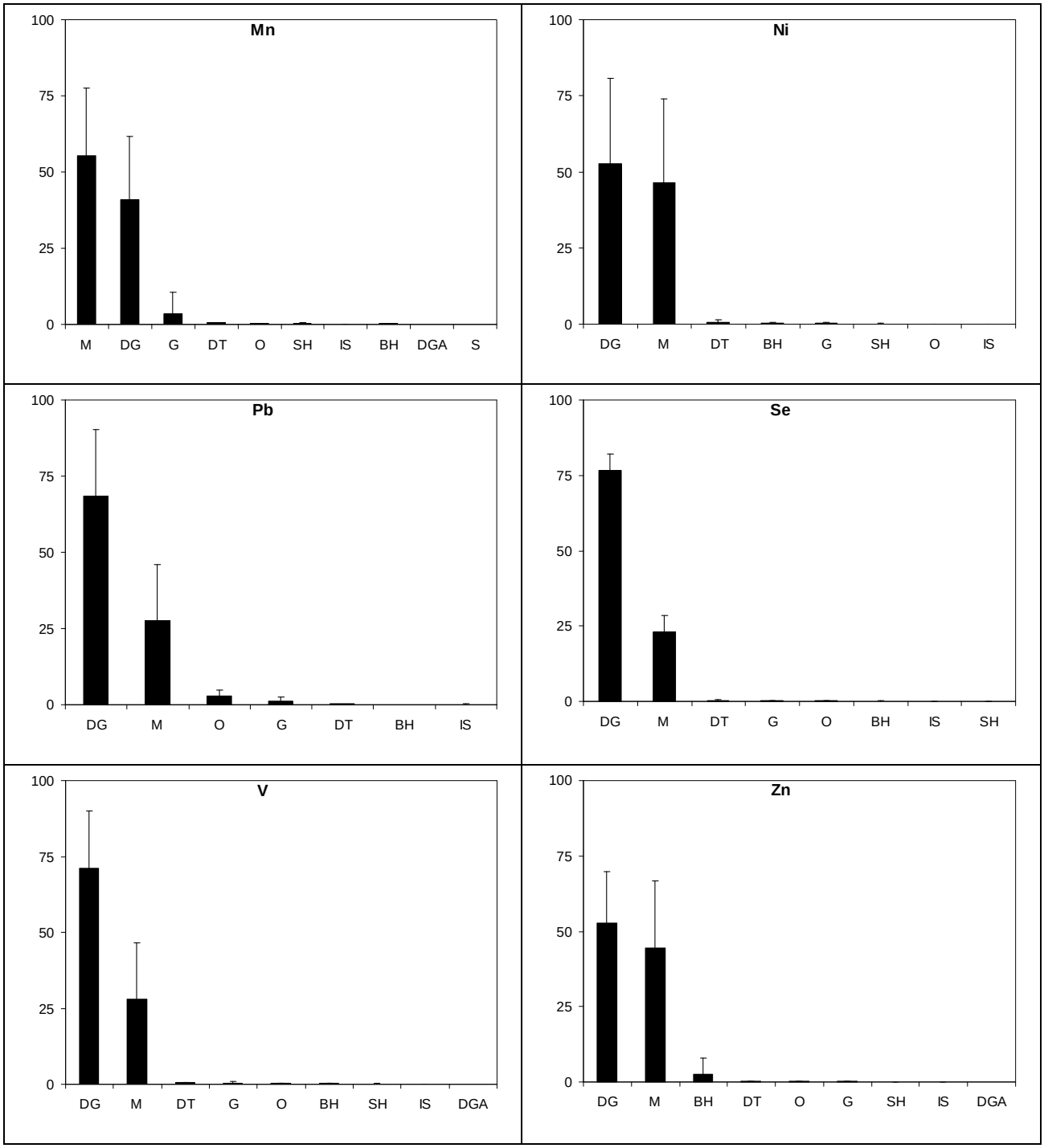
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Figure 2.