Age, sex and spatial dependent variations in heavy metals levels in the Glaucous Gulls (*Larus hyperboreus*) from the Bjørnøya and Jan Mayen, Arctic

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Abstract Heavy metals (Cd, Cu, Fe, Mn and Zn) concentrations were determined in different tissues (muscle, kidney, liver, brain, gonads, heart and feathers) of Glaucous Gulls (Larus hyperboreus) from Bjørnøya and Jan Mayen. The age and spatial dependent variations in heavy metals were quantified and interpreted in view of the three chemometric techniques, i.e. nonparametric Mann-Whitney U test, redundancy gradient analysis and detrended correspondence analysis. The Glaucous Gulls from Bjørnøya contained significantly higher (p < 0.05) levels of Cd, Cu and Zn than those inhabited Jan Mayen. Adult birds were characterized by greater (p < 0.01)concentration of muscle, hepatic and renal heavy metals in comparison to chicks. Insignificantly higher slope constant Zn/Cd for the liver than for

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G. W. Gabrielsen The Polar Environmental Centre, Norwegian Polar Institute, 9296 Tromsø, Norway the kidney may reflect insignificant Cd exposure. Estimate of transfer factor (TF) allows us to assess variations in heavy metal concentrations during the individual development of Glaucous Gulls. It may be stated that there is a distinct increase of bioaccumulation of all the studied metals during subsequent stages of the bird life.

Keywords Heavy metals • Glaucous gulls (*Larus hyperboreus*) • Individual development and growth • Bioaccumulation • Arctic

Introduction

Due to the wide distribution and relatively high position in the trophic chain, seabirds are widely used as bioindicators or biomonitors of heavy metals (Kim et al. 1996; Furness and Camphuysen 1997; Thompson et al. 1998; Dietz et al. 2000; Riget et al. 2000; Savinov et al. 2003). The pathways of heavy metals transportation from industrialised Europe to the remote places in the Arctic have been well distinguished (AMAP 1997, 2004). Nevertheless, our knowledge of trace elements in seabirds from the Norwegian and Barents Seas is still insufficient (Savinov et al. 2003). Heavy metal contaminants are widely distributed in the European as well as in the Arctic environment. The distinguishing between natural, background and anthropogenic levels of heavy metals in the

Arctic is difficult to establish due to complex atmospheric and sea current transport of these pollutants (AMAP 2004). The Arctic Monitoring and Assessment Programme (AMAP) has provided some basic data on heavy metals levels in Arctic biota. Studies performed within AMAP have shown possible influence of heavy metals on some organisms, especially on those that are food specialised and/or top predators. The Glaucous Gull (Larus hyperboreus) is one of the most common seabirds in the Arctic (Cramp and Simmons 1983; Anker-Nilssen et al. 2000). The population status of this species in the Arctic environment is unknown until nowadays, but the available data show that the Glaucous Gull can play an important role of the top predator in the European Arctic, where true predators are abundant (Løvenskiold 1964; Anker-Nilssen et al. 2000). As a migratory bird, Glaucous Gulls may be exposed to various contaminants along their migrating routes as well as at wintering and breeding grounds. According to Savinov et al. (2003), geographical differences in heavy metal levels were found for Glaucous Gulls breeding in different colonies in the Barents Sea.

The Bjørnøya and Jan Mayen are two breeding sites of the Glaucous Gull within the Atlantic sector of Arctic. Although the Bjørnøya population has been recently studied, including population number and food sources (Theisen 1997; Malinga 1999; Bustnes et al. 2000), information about the Jan Mayen population of the Glaucous Gulls is scarce. The Bjørnøya population breeds all over the coast line of the island in the number of approximately 2,000 breeding pairs (Mehlum and Bakken 1994). Data on food composition (Bustnes et al. 2000; Malinga 1999) show that the Glaucous Gull is a top predator in the Bjørnøya area with a wide spectrum of food sources (seabird, fish, sea invertebrates). It migrates mainly to the wintering grounds in the Western Europe, but some data (Salomonsen 1971) showed other possible migration routes—to Iceland and Southern Greenland. Little is known about the migration route for the Jan Mayen population. We presume that, similar to gulls from the Bjørnøva and Svalbard, these birds feed on local seabirds and fish.

The aim of the present study was to study the possible difference in heavy metals in birds breeding in two different areas of the European Arctic as well as to find relationship between metals, if any exists, dependent on sex and age of the gulls. The present study was also projected to estimate bioaccumulation trends during lifetime of Glaucous Gulls breeding on Bjørnøya.

Materials and methods

Sampling and chemical analysis

Collection of birds took place during the summer seasons in 1995, 1996 and 1997 on the Bjørnøya and in 1995 on Jan Mayen (Fig. 1). A total of seven and 48 Glaucous Gulls were collected on Jan Mayen and Bjørnøya, respectively (Table 1). Glaucous Gulls from Bjørnøya were shot in 1995 on the southern coast (n = 5) and on the southwestern coast in 1996 (n = 25). In 1997, a total of eight birds were found dead on the south-eastern coast and on the south-western coast of Bjørnøya.



Fig. 1 Localizations of Glaucous Gull sampling: Bjørnøya and Jan Mayen, Arctic

Table 1 Number of eggs, chicks and adult birds collectedon Bjørnøya and Jan Mayen areas

		Bjørnøya	Jan Mayen
Eggs		$8 + 1^{a}$	0
Chicks		7	0
Adults		48	7 ^b
	Females shot	13	4
	Males shot	27	1
	Females found dead	8	0
	Males found dead	0	0

^aOne egg with embryo analysed separately

^bIncludes birds of unknown sex: one shot and one found dead

Additionally, eight eggs from abandoned nests were collected in this area. One egg contained an embryo which was analysed separately. Chick concentrations were compared with shot adult ones. All chicks collected in 1997 were found dead in the northern west part of island. Based on own experience, we classified all of them to the age category of first week of life. Chicks were stored in separate bags and stored in freezer.

The specimens shot on both the islands were dissected, and tissue samples were stored in the laboratory at the Norwegian Polar Institute in Tromsø. Specimens found dead on the Bjørnøya were dissected immediately after their finding, and all the collected samples were stored in freezers. Sex was determined in all the adult birds except for two specimens from Jan Mayen. The body weight was also recorded. Liver, kidney, muscle (pectoral), heart, brain, gonads and feathers (plucked from breast) were dissected and stored separately in polyethylene bags at -20° C. The collected eight abandoned eggs were divided into sub-parts, i.e. egg-shell and contents. Embryo was homogenised as whole and treated as one sample. The tissue samples were dried to a constant weight at 60°C. Feathers were washed off from blood and some physical remains, e.g. sand using deionised water (Millipore ®) alternately with acetone (Burger and Gochfeld 1995). The samples were homogenized and up to four replicate sub-samples of each were prepared. One gram of sub-samples was transferred to the teflon bombs, and after the addition of 9 ml of 65% HNO₃, the material was mineralised in MILESTONE® 409

microwave digestion system including blank samples.

Analyses were carried out by flame AAS (Philips PU 9100 Atomic Absorption Spectrophotometer) using deuterium-background correction. All samples were processed and analysed for a particular metal on the same day. To check for contamination, blank samples were also analysed using the same procedure. The quality of the method used was checked and confirmed in a separate comparative study of metals in a standard reference material, i.e. Fish Flesh MA-B-3/TM (IAEA, Monaco) The agreement between the data obtained for the standard reference material and the declared values was satisfactory based on the estimated accuracy and precision expressed as the recoveries (87.4–101.8%) and the standard deviations (1.1–6.9%), respectively (Szefer et al. 2002).

The limits of detection for Zn, Cu, Cd, Mn and Fe were as follows: 0.01, 0.20, 0.15, 0.15 and 0.30 μ g/g, respectively.

In case of some samples (e.g. brain, gonads) represented in very small amount, we decided to analyse pooled samples, i.e. the same amount of tissue (dried up to a constant weight) was taken from 2–4 individuals (up to 1 g) and proceeded according to the procedure described above.

Expressing concentrations of the analysed metals on a dry weight enables overcoming difficulties connected with precise determination of the initial wet weight of the tissue just after its taking from an organism. The samples collected by the Norwegian expedition were frozen and delivered to Poland by the air transport and frozen again until the first stage of their analytical processing began.

Statistical analysis

The primary data on metal concentration were stored in a database under individually identified numbers. Data from replicate sub-samples were recalculated into the mean value and the standard deviation for each metal concentration. The samples were assigned to different categories, i.e. shot and found dead. Since muscle, kidney and liver samples were highly representative, we decided to make statistical comparison of concentration data with respect to sex, age, way of bird sampling (shot, found dead) and sampling site (Bjørnøya, Jan Mayen).

Due to a small number of birds collected on Jan Mayen (N = 7), it was decided to reject them and make intercomparison studies relative to sex considering exclusive data obtained for the Bjørnøya specimens. Spatial comparison was firstly done for all 48 adult specimens and next for females only (the Jan Mayen group was represented by four females). Therefore, the number of measurements taken into account varied in each comparison. Since the number of birds collected in both the localities (Bjørnøya and Jan Mayen), as well as sex and age class representation of samples, were incomparable, concentration data were processed statistically by non-parametric Mann-Whitney U test (MWU). All statistical analyses were performed using the STATISTICA 6.0 software package.

We used detrended correspondence analysis due to an appropriate gradient length (1.303) in the data collected. To study the effect of several environmental variables on a composition of metal roots, direct redundancy gradient analysis (RDA) was performed. The statistical significance of the relationship between metal roots and the whole set of environmental variables was tested by a Monte Carlo (MC) permutation test using 'the global permutation test' in the CANOCO[®]package (Ter Braak and Smilauer 2002).

The formula proposed by Szefer (1991) was adapted to calculate transfer factor (TF) with respect to age (comparison between young and older birds) as follows:

$$TF = C_c/C_p$$

where:

 $C_{\rm c}$ —mean level of particular metal in older specimens; $C_{\rm p}$ —mean level of particular metal in younger specimens or eggs.

In the case of estimate of metal bioaccumulation along the relation female–egg (albumen with yolk or egg shell), the following ratio was used:

 $TF = C_{(Egg)}/C_{(Female)}$

The results obtained only for shot adults were used in TF calculations.

Results

Intra- and inter-tissue associations of metals

A total of 14 significant positive intra-tissue correlations were found between individual metal concentrations and tissues. The concentrations of the analysed metals, i.e. Cd, Cu, Fe, Mn and Zn in tissues of Glaucous Gull, are presented in Table 2.

Altogether, eight associations between metals in muscle and liver, seven between metals in muscle and kidney and nine between metals in liver and muscle were detected. Similar to the intratissue correlations, all the inter-tissue associations were positive (Table 3).

Age-, sex- and spatial-dependent variations in metal concentrations

Based on RDA analysis, we found that chicks differed significantly from adult birds with respect to the levels of Mn, Cu and Fe in muscle; Zn, Mn, Cd and Cu in kidney and Cd and Cu in liver. It should be emphasised that the abovementioned variations are highly significant at p < 0.006 (Table 4).

Muscle and renal concentrations of Cu differed significantly between the sexes with higher levels occurred in females (Table 2). MC permutation test of RDA analyses and MWU show different types of results/analyses. Whilst the MC indicates the "amount" of variability within the analysed samples described by results of chemical analyses, the MWU shows "direct" differences between the compared groups. Based on the MC, we may say that sex does not influence on the total variability of the analysed samples, but in the light of the MWU, there are two "direct" differences between males and females, concerning Cu in kidney and muscle (Table 2).

Shot birds differed from those found dead with respect to muscle levels of Cd, Cu and Fe as well as hepatic Zn and renal Cu. In all the cases, levels of these metals were higher in specimens found dead.

Table 2 Metal concentrations [μg^{-1} dw; mean \pm standard deviation] in egg shells, glair with yolk, chicks, and adults of Glaucous Gulls from Bjørnøya and Jan Mayen and their statistical differences between sex, sampling, and area groups

Samples/tissues	$W\%^a$	Parameter ^b	Cu	Zn	Mn	Fe	Cd
Bjørnøya							
Eggs							
Egg shells	_	8	3.01 ± 0.99	9.04 ± 9.31	1.59 ± 0.78	22.8 ± 36.5	0.67 ± 0.35
Glair with yolk	70	8	3.82 ± 1.44	42.1 ± 4.23	1.83 ± 0.56	68.5 ± 19.6	nd
Chick embryo	_	1	4.25	58.1	1.41	90.7	nd
Chick							
Muscle	75	5 (3)	4.30 ± 0.62	53.3 ± 8.96	1.03 ± 0.30	9.6 ± 15.9	0.41 ± 0.22
Kidney	73	5 (3)	12.8 ± 0.8	73.7 ± 1.83	4.20 ± 0.23	254 ± 124	0.90 ± 0.36
Liver	72	8	11.5 ± 2.06	64.7 ± 12.1	7.97 ± 1.93	310 ± 175	0.28 ± 0.10
Heart	70	7 (3)	11.3 ± 1.49	76.6 ± 7.28	2.76 ± 0.10	253 ± 53.1	nd
Adults shot							
Males							
Muscle	69	27	$15.3 \pm 1.45^{d, *, ***}$	68.1 ± 18.1	1.60 ± 0.42	$191 \pm 31^{***}$	$0.41 \pm 0.25^{***}$
Kidney	72	26	19.7 ± 3.79 ***, ***	$159 \pm 45.8^{*****}$	9.36 ± 2.63	331 ± 114	43.4 ± 15.8
Liver	69	26	18.5 ± 2.59	$87.2 \pm 18.2^{***}$	11.4 ± 2.27	742 ± 252	6.23 ± 5.39
Feather	_	12	9.54 ± 2.92	71.5 ± 16.2	0.43 ± 0.29	31.1 ± 19.3	nd
Females							
Muscle	69	13	$16.6\pm1.81^*$	62.7 ± 13.6	1.69 ± 0.42	$192 \pm 26.4^{*****}$	0.52 ± 0.31
Kidney	72	13	$22.1\pm3.29^{**,*****}$	164 ± 31.8	10.5 ± 2.29	283 ± 85.0	$44.4 \pm 14.1^{*****}$
Liver	69	12	20.3 ± 4.43	93.8 ± 23.4	12.3 ± 3.20	775 ± 306	$5.46 \pm 3.50^{****}$
Feather	_	2	7.56	68.2	0.29	4.21	nd
Gonads	77	14 (5)	5.84 ± 1.64	86.9 ± 12.5	2.06 ± 0.36	274 ± 133	4.89 ± 2.97
Adults found dea	de						
Muscle	69	8	$18.3 \pm 3.99^{***}$	75.5 ± 29.6	1.21 ± 0.47	$281 \pm 99.3^{***}$	0.64 ± 0.54
Kidney	72	5	27.8 ± 6.84	183 ± 65.7	9.55 ± 2.13	336 ± 112	42.1 ± 15.2
Liver	69	8	16.9 ± 5.99	$113 \pm 44.4^{***}$	9.27 ± 4.58	1137 ± 458	5.71 ± 3.93
Heart	73	6	13.7 ± 6.15	55.5 ± 15.2	1.82 ± 0.55	753 ± 214	0.36 ± 0.27
Jan Mayen							
Adult shot ^c							
Muscle	68	7	16.0 ± 2.43	68.2 ± 11.8	2.07 ± 0.91	$168 \pm 59.2^{*****}$	0.26 ± 0.03
Kidney	69	7	$15.9 \pm 2.63^{*****}$	$113 \pm 21.3^{*****}$	20.1 ± 34.7	668 ± 802	$26.2 \pm 13.0^{*****}$
Liver	65	7	16.3 ± 3.79	79.7 ± 14.2	20.3 ± 27.3	1120 ± 524	$6.40 \pm 2.64^{****}$
Feather	_	7	9.77 ± 5.30	90.7 ± 15.1	2.47 ± 4.33	144 ± 249	nd
Gonads	70	5 (3)	6.38 ± 3.58	65.4 ± 19.2	13.4 ± 18.1	1095 ± 1120	16.2 ± 16.5
Brain	80	6	7.85 ± 1.87	44.4 ± 8.70	1.68 ± 0.34	143 ± 47.1	0.31 ± 0.19

^a Mean percentage of water in tissue

^b Number of specimens and pooled samples in parentheses

^c One specimen found dead included

^d Mann–Whitney's U test

^eFemales only

*p < 0.01, **p < 0.05, statistical differences in metal concentration between sexes (Bjørnøya birds only); ***p < 0.05, statistical differences in metal concentration between sampling groups (shot vs. dead, Bjørnøya birds only); ****p < 0.01, *****p < 0.05, statistical differences in metal concentration between area groups (Bjørnøya vs. Jan Mayen, females only)

Spatial differences in renal concentrations of Zn, Cd and Cu and muscle and hepatic concentrations of Fe were observed with generally lower levels of these metals in Jan Mayen birds with the exception of higher concentration of hepatic Fe. The metal distribution in the gull tissue was predicted by nominal (age, sex, geographical position) and interval (body weight) variables which cumulatively explained 33% of the total metal roots variability (RDA; Table 4).

	Liver	Kidney	Muscle	M vs L	M vs K	L vs K
	(N = 46)	(N = 44)	(N = 48)	(N = 46)	(N = 44)	(N = 44)
Cu	(+)Mn*, (+)Fe**	(+)Zn*, (+)Cd*	(+)Zn**, (+)Fe*	(+)Zn*, (+)Cu*	(+)Cu*	(+)Cu*
Zn	(+)Cd*, (+)Fe*	(+)Cd*, (+)Cu*	(+)Fe*, (+)Cd**,	-	-	(+)Zn*, (+)Cd**,
			(+)Cu**			(+)Cu*
Mn	(+)Cu*, (+)Fe*	(+)Fe*	-	(+)Mn*, (+)Fe*	(+)Zn**, (+)Mn*, (+)Fe*	(+)Mn*, (+)Fe*
Fe	(+)Zn*, (+)Cu**, (+)Mn*	(+)Mn*	(+)Zn*, (+)Cd*, (+)Cu*	(+)Zn*, (+)Mn**, (+)Cu*, (+)Fe*	(+)Mn**, (+)Cu*	(+)Mn*, (+)Fe*
Cd	(+)Zn*	(+)Zn*, (+)Cu*	(+)Zn**, (+)Fe*	_	(+)Cu**	(+)Cd*

Table 3 Intra- and inter-tissue association of metals in liver, kidney and muscle of Glaucous Gull from Bjørnøya at p < 0.01 and p < 0.05

(+) positive correlation

p < 0.01, p < 0.05

Individual development and growth

In the case of individual development, low TF values were observed at early stages of life-time, i.e. egg-embryo (unhatched chick)-nestlings in their first week of life (Table 5). At this stage of development, particularly interesting are: over five-fold increase of Mn concentration in liver, almost three-fold increase of Cd concentration in muscle and nearly three-fold increase of Cu concentration in kidney. Additionally, a remarkable increase of Fe concentration was recorded in both kidney and liver. In the next stage of individual growth, TF was estimated for adult individuals (males and females) with respect to chicks. In this case (compared with nestlings in first week of life), a rapid increase of Cd concentrations in adults was noted, reaching TFs up to ca. 50 for kidney of males and females. In the case of the remaining metals. TF values varied from 1.11 to 3.85. TFs were also calculated for the breeding stage, i.e. female–egg. A somewhat higher level of Cd in egg shells as compared to that noted for muscle of females was observed.

Discussion

The relatively high standard deviations obtained for mean concentration values in the present study (Table 2) reflect the inter-specimen variations, reported earlier for many animals, including seabirds (AMAP 1997; Joiris 1997; Norheim 1987; Prestrud et al. 1994; Savinov et al. 2003).

The tissue concentrations are within the ranges of concentrations reported elsewhere for other species of seabirds, including the Glaucous Gull (Dietz et al. 2000; Kim et al. 1996; Mallory et al. 2004; Nielsen and Dietz 1989; Norheim 1987;

Table 4 Results of Monte Carlo permutation test (F) for analysed variables

Variables	Conditional effects				
	Lambda A	P value	F		
Area	0.12	0.016	7.17		
Shot/dead	0.06	0.042	4.12		
Age	0.13	0.006	9.75		
Body weight	0.02	0.318	1.19		
Sex	0.00	0.910	0.10		

Area-Bjørnøya/Jan Mayen; shot/dead specimens, age-chicks, adults; body weight; sex-male, female

Table 5 Transfer factors (TFs) of heavy metals estimated for selected steps in Glaucous Gull life-time nested on Bjørnøya <i>M</i> muscle, <i>K</i> kidney, <i>L</i> liver	Relation	Cu	Zn	Mn	Fe	Cd
	Glair with yolk \rightarrow embryo	1.11	1.38	0.77	1.32	1.00
	Embryo \rightarrow chick (M)	1.01	0.92	0.73	0.98	2.73
	Embryo \rightarrow chick (K)	3.01	1.27	2.98	2.80	6.00
	Embryo \rightarrow chick (L)	2.71	1.11	5.64	3.42	1.87
	Chick \rightarrow female (M)	3.85	1.18	1.64	2.14	1.27
	Chick \rightarrow female (K)	1.73	2.23	2.50	1.11	49.3
	Chick \rightarrow female (L)	1.77	1.45	1.54	2.50	19.5
	Chick \rightarrow male (M)	3.56	1.28	1.55	2.13	1.00
	Chick \rightarrow male (K)	1.54	2.16	2.23	1.30	48.2
	Chick \rightarrow male (L)	1.60	1.35	1.43	2.39	22.3
	Female (M) \rightarrow egg shell	0.18	0.14	0.94	0.12	1.29
	Female (K) \rightarrow egg shell	0.14	0.06	0.15	0.08	0.02
	Female (L) \rightarrow egg shell	0.15	0.10	0.12	0.03	0.12
	Female (M) \rightarrow glair with yolk	0.23	0.67	1.09	0.36	0.29
	Female (K) \rightarrow glair with yolk	0.17	0.26	0.18	0.24	0.00
	Female (L) \rightarrow glair with yolk	0.19	0.45	0.14	0.09	0.03

Thompson et al. 1998; Riget et al. 2000; Savinov et al. 2003).

The lack of significant sex-dependent variations in metal levels except renal and muscle Cu in adult individuals (Table 2) indicates that generally, no differentiation in metal levels between the sexes took place during growth. This finding is confirmed by RDA (Table 4), and inter-comparison study of literature data, e.g. reported for gulls (in the case of Cd; Burger and Gochfeld 1995) and water birds (Mateo and Guitart 2003). This finding may also reflect similar feeding/foraging behaviour of both sexes which has not been previously studied so far in the case of Glaucous Gulls.

The significant spatial differences found between tissue concentrations indicate that some environmental factors are responsible for higher accumulation of heavy metals in birds from the Bjørnøya. Two explanations are most probable. The first is that birds from Jan Mayen have a different food spectrum or the concentration of accumulated metals in food taxa is lower in this region. However, the lack of data concerning the diet of gulls from Jan Mayen region impedes a reliable confirmation of this hypothesis. The second explanation considers bird migration after the breeding season. Gulls from the Svalbard region migrate towards the south, i.e. in the direction of the Northern Europe where they overwinter, while birds from Jan Mayen could head for southern Greenland (much less polluted than Europe), where this species occurs also in the winter season. Some part of the population from the Spitsbergen and the Iceland region migrates in this direction as well (Salomonsen 1967).

The revealed differences between birds shot and found dead concern four out of 15 analysed parameters. Differences were found in the case of all metals (except Mn) in muscle, kidney and liver. Probably, birds found dead were sick and/or may suffer from starvation. Previous research on seabirds' heavy metal contamination showed that body condition is one of the important factors influencing metal absorption—especially in the case of Cu and Zn (Debacker et al. 2000).

Considering the concentration of heavy metals during the individual development of Glaucous Gulls, it may be stated that there is a distinct increase of concentrations of all the studied metals during subsequent stages of life. Although at early stages (egg-unhatched chick), this enhancement is small or does not occur at all (see the "Results" section), but at the stage of a several-week-old nestling, we can observe a several-fold increase of concentration of Cd. Due to a lack of samples coming from birds at the intermediate stage (1-3 years), the next stage of development cycle considered adult birds (4 years old or older). In comparison with nestlings, in this case, a strong increase of concentrations of the metals analysed took place. Concentrations of Zn, Fe, Cu and Mn increased in birds' tissues many times, especially Fig. 2 Relationship between renal concentrations ($\mu g g^{-1} d.w.$) of Cd and Zn in all the specimens studied of Glaucous Gull from Bjørnøya and Jan Mayen, Arctic



in the case of renal Cd (TF \sim 50). Such agedependent variation in metal concentrations was reported for Glaucous Gull (and other Laridae from the Arctic area) from Greenland (Riget et al. 2000). In case of the relation females–eggs (both albumen with yolk and egg shell), very low values of TF were generally noted except for Cd. The TF for Cd in the egg shell (1.29), calculated relative to muscle of a female, suggests a possibility of transfer of heavy metals at the stage of egg production

(formation). The fact that this refers only to the egg shell could be the starting point for further studies on mechanisms of heavy metal transfer at this stage.

There is a significant positive correlation between hepatic Zn and renal Zn, Cu and Cd. Moreover, hepatic Cd is highly correlated with renal Cd (Table 3). These co-associations are in agreement with those reported for seals of the Antarctic (Szefer et al. 1994). Both intra- and

Fig. 3 Relationship between hepatic concentrations of Cd and Zn (μ g g⁻¹ d.w.) in all the specimens studied of Glaucous Gull from Bjørnøya and Jan Mayen, Arctic



inter-associations of the analysed metals found in the present study show, with special consideration of Zn-Cd correlation (Figs. 2 and 3), the possible effect of metallothionein synthesis caused by high Cd accumulation. Such 'overproduction' can lead to increase of Zn uptake stated in previous works for marine mammals (Honda et al. 1987; Szefer et al. 1994, 2002) as well as in the case of seabirds (Norheim 1987; Kim et al. 1996; Honda et al. 1990). It has been reported that excessive concentrations of hepatic Zn reveal a high Cd exposure in marine vertebrates, such as birds and sea mammals. According to Doyle and Pfander (1975), lower slope constants (Zn/Cd) for liver than those for kidney have been observed in the case of animals unexposed to high concentrations of Cd.

A somewhat higher slope constant Zn/Cd for the liver (2.5) than for the kidney (1.97) may reflect not too high Cd exposure (Figs. 2 and 3). According to Honda and Tatsukawa (1983), such difference between bioaccumulation rates of Zn and Cd in the liver and kidney may be used as an indicator of the Cd exposure. A higher increase of hepatic Zn relative to Cd suggests the formation of metallothioneins corresponding to a higher molar ratio of Zn/Cd. Intercepts calculated from equations related to renal and hepatic the Zn-Cd correlations are 75.4 and 77.4 $\mu g g^{-1}$ d.w., respectively (Figs. 2 and 3). It means that these values may correspond to the physiological concentrations of Zn in the kidney and liver of the gulls studied. In principle, it is in an agreement with the renal and hepatic concentrations of Zn in chicks containing the average 73.7 and 64.7 μ g g⁻¹ d.w., respectively (Table 2).

Summing up, it can be stated that the Glaucous Gull, as a predator inhabiting the Arctic ecosystem (Verreault et al. 2007), can play a role in the transport of Cd. However, a somewhat higher slope constant Zn/Cd for the liver than for the kidney may reflect insignificant Cd exposure. Considering concentration of heavy metals during the individual development of Glaucous Gulls, it may be stated that there is a distinct increase of bioaccumulation of all the studied metals during subsequent stages of life.

Based on TFs, especially estimated for the female-egg shell relation corresponding to the

stage of formation of eggs, it may be said that several mechanisms of detoxification could take place, at least during formation of egg shell.

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