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Metals and Selenium in Sand Martin's Plumage

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Birds are affected by environmental pollution directly or through the food chain. Once heavy metals or selenium are in the body, they can move from tissue to tissue, be excreted, or be sequestered in bones, feathers or other tissues (Braune and Gaskin 1987).

Previous work investigated heavy metals and selenium in feathers and showed that feathers produce equally informative material as other organs of the bird (Pilastro et al. 1993). The sampling of feathers is ideal for monitoring heavy metals' bioavailability in birds because feathers can be easily collected, can be removed without harm to the bird, and can then be analyzed to give an indication of the exposure of a particular species to environmental heavy metals. Studies have begun which compare the element concentration characteristic of birds' habitat with the data found from bird feathers. This makes the herring gull suitable for indirect measurement of the pollution of the German North Sea Coast region (Thomson et al. 1993). As a result of their overall sensitivity and ability to accumulate high levels of contaminants, ospreys (*Pandion haliactus*) have been used as bioindicators of environmental contamination (Furness 1993). Studies have also shown that insectivorous pied flycatcher (*Ficedula hypoleuca*) nestlings and black-crowned night heron (*Nycticorax nycticorax*) pre-fledglings, both show heavy metal body burdens that correlate well with the distance of their nests from a heavy metal source (Custer and Mulhern 1983).

In several publications (Brothers and Brown 1987, Walsh 1990) it has been suggested that the analysis of bird feathers may be a non-invasive and reliable way of identifying contaminants in a birds environment. Migration patterns may also influence metal distribution (Norheim and Kjos-Hanssen 1984). These studies have led to an increased interest in the use of birds as monitors of geographical, historical and global patterns of heavy metal pollution within the environment, and as a consequence, to a growing database of metal levels in bird populations. The identification of wintering areas of migratory colonies is a very complicated work. The analysis of feathers as a new method could simplify the question by representing the area where the feather was produced. This project needed some preliminary investigations. The aim of this study is to compare the element content

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of Sand Martin feathers to human hairs, to carry out the correlation element-element in the feathers, and to investigate the age of Sand Martins on the element content of its feather.

MATERIALS AND METHODS

For the experiments we used feathers of Sand Martins. The feathers were examined by permission of the nature conservation authorities. In the case of such protected birds, we had to make the analysis from a single feather, to avoid killing the bird, and to enable us to take samples again from the same bird for monitoring investigations.

In sample preparation (Vallner et al. 1999) ultrasonic washing was used at 44 kHz frequency applied to each individual feather for 4 x 1 minutes. Feathers were placed in quartz tubes and washed with ultra-pure water (purified using a Milli-Q water-filtering system), to remove any surface contaminants. They were then oven-dried at 50 °C for about 24 h, until of constant mass.

In order to dissolve the feather samples, following a pre-digestion period, microwave digestion system Milestone MLS 1200 Mega was applied. Pre-digestion period: for 40 hours at room temperature and atmospheric pressure the samples were kept in test-tube with a mixture of HNO_3 (A.R., 68 %, Prolabo, Manchester, EEC) and H_2O_2 (A.R., 35 %, Reanal; Hungary). The applied digestion program was: 1 min. 250 W, 2 min. 0 W, 5 min. 250 W, 2 min. 400 W, 2 min. 600 W. To eliminate the "memory effect" of the PTFE-bombs of the microwave system, we used one quartz test-tube for each feather during the digestion, three test-tubes in each bomb (Vallner et al. 1999). The feather-solutions were dried out on a 95 °C-hot quartz-sand-bath for three hours and then each taken up in 120 µl nitric-acid (2 mol/dm^3).

The element content of these small volume samples was determined partly by a Spectroflame-type inductively coupled plasma atomic emission spectrophotometer (ICP-AES) (Spectro GmbH, Kleve, Germany) with the following parameters: plasma gas 1.6 dm^3 min^{-1}, coolant gas 15 dm^3 min^{-1}, nebulizer gas 0.6 dm^3 min^{-1}, excitation 27 MHz, 1.05 kW, and a cross flow nebulizer for Ca, Fe, Mg, Mn, Sr and Zn. An Unicam 939 QZ graphite furnace atomic absorption spectrometer (GF-AAS) was used for As, Cd, Co, Mo and Se. Feathers were analysed only once due to low sample volumes. The coefficient of variation for the measurements on replicate samples from a large sample (Merck, Germany) of known metal concentrations ranged from 3-10 %.

RESULTS AND DISCUSSION

The use of feathers for biomonitoring has several advantages over other tissues, because collection of feathers is less stressful than collection of blood, and feathers can be easily stored without refrigeration. Metals accumulate in feathers. Once the feathers are formed in the bird, the metal concentrations remain the same over time, unlike metal concentrations in other tissues (Walsh 1990).

In general, there are two categories of skin appendages, characterised by either protrusion out of or invagination into the body surface. The skin appendages that protrude out of the body surface are hair, feather, scale, nail, claw, etc. They provide a variety of functions to individuals, ranging from environmental protection to ritual mating displays. Sequestering heavy metals (and selenium) in feathers may be an important route for eliminating pollutants. Thus, it seems to be obvious to find similar heavy metal content in hair and feathers (Widelitz et al. 1997).

To determine the average content of different elements, we analyzed a homogenised feather powder sample prepared from more than 100 Sand Martins' feathers. The human scalp hair matrix was investigated by Suzuki et al. (1985) from approximates 20 kg hair - used for reference material preparation in 2 g units. The feather and hair element concentrations are compared in Fig. 1. Only in the content of Mn, Co and As, there is more than one order difference. We measured ten-times higher values in the feather than were given for hair. These Co- and As-data regarding hair element contents are in agreement with the results of other authors (Valkovic 1988). Due to the fact that the lower limit of normal Mn-status in bristles is 8 ppm (Régiusz-Mőcsényi et al. 1990) Japanese reference hair-matrix seems to be poor in Mn, rather than feathers too rich (Fig. 1.). Except for the mentioned differences, the data are in accordance with our hypothesis. As the Fig. 1. shows, while the feather and hair data are almost always similar, the total body element contents presented (Katz and Chatt 1988) are quite different from those.

There is no evidence that the trace element concentrations measured in the present study were at toxic levels, since all values were lower than those regarded as toxic in the literature.

Several studies have been carried out to investigate the toxic relevance of trace element accumulation in birds by focusing on correlation between essential and non-essential elements. These correlation appear to indicate the existence of detoxifying mechanisms. Correlation could be also explained by assuming that uptake and pathways of metabolism and storage are similar for certain pair of elements. Muirhead and Furness (1988) found significant positive correlation between cadmium and zinc in seabirds. They concluded that seabirds use storage of bound metals for detoxification and therefore they are not able to adequately regulate the concentrations of these metals. Similar interactions were observed between copper and cadmium, but the biochemical mechanism of this relationship is not yet fully understood. Significant correlations between elements were quite rare in egrets, whereas positive correlation were established between Se and Pb, Se and Cd, Se and Hg, Cd and Hg, Cd and Zn, and Cu and Zn in several organs of flamingos (Cosson et al. 1988).

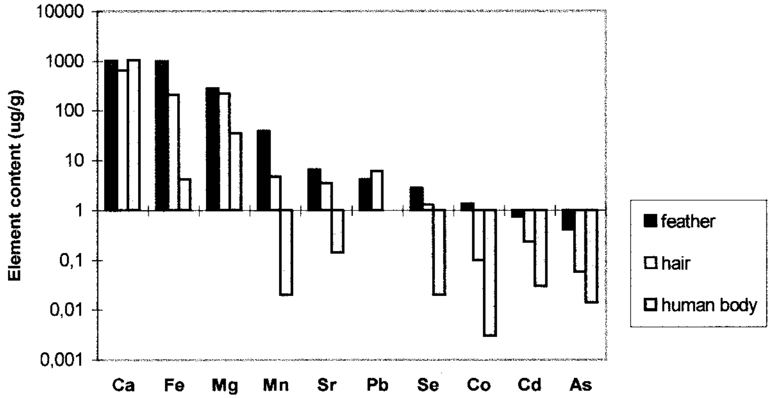

Fig 1. The average of element content [$\mu g\ g^{-1}$] of Sand Martin feathers, human hair and total body.

Table 1. Correlation of element versus element in Sand Martin feathers.
Note: N.S: no strong correlation
+ strong positive correlation ($0.70 < r$),
- strong negative correlation ($r < -0.70$).

	Fe	Mg	Mn	Sr	Co	Se	Cd	Mo	As	Zn
Ca	N.S.	+	+	+	N.S.	N.S.	N.S.	N.S.	N.S.	+
	Fe	+	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	-
		Mg	+	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	+
			Mn	N.S.	N.S.	N.S.	+	N.S.	N.S.	+
				Sr	N.S.	+	N.S.	N.S.	N.S.	-
					Co	N.S.	N.S.	N.S.	N.S.	N.S.
						Se	N.S.	N.S.	N.S.	N.S.
							Cd	N.S.	N.S.	+
								Mo	N.S.	N.S.
									As	N.S.

In the case of Sand Martins, correlations were carried out in order to compare different metal contents in feathers. Linear correlation coefficients were determined for feather samples (Table 1).

In the present study there are revealed positive correlation between Mn and Cd, Sr and Se and Cd and Zn in adult Sand Martins, indicating that detoxification mechanisms also play an important role in these birds. Although the similar chemical properties of Zn an Cd (like atomic size and electronic structure) explain the competition of their ions for biological binding sites in many zinc enzymes, there are data (Elinder 1987) showing that at low Cd-concentrations the Zn-metallothionein was the main chemical form in the animal body, and the Cd-toxicity is high only when the metallothionein-bound sites are already occupied by other metals. The Cd-Zn positive correlation may be a result of "too low" Cd-levels.

Cd and Mn give positive correlation. As it was published earlier (Chowdhury and Chandra 1987), the Cd and Mn are in a synergistic correlation. This is in agreement with our findings.

The earlier analysis of bound showed, that the Sr/Zn ratio depends on feeding habitats. A lower ratio is seen in animal-based food, and higher ratio in plant-based food (Pais 1996). Since Sand Martins feed on insects, the negative correlation between Sr and Zn can be explained.

Comparism of the element content of juvenile and adult Sand Martins. The effect of age on metal contaminant levels have been documented in a variety of organisms. Age-dependent levels of metals have also been described in birds. According to Burger (1993), there are three explanations for age differences in pollutant residues in birds: 1. adults accumulate pollutants over a longer time period, and therefore a bigger secretion of heavy metals through the feather, 2. adult and young birds differ in their feeding habits, and 3. there may also be age differences in intestinal absorption or in toxicokinetics. The second explanation can be extended to the eventual different environment as breeding area, with its influence on the element content of growing feathers.

We studied the age of Sand Martin as a factor in element content variation in feathers. In the case of most of the elements the concentrations for the adult is higher, indeed. The increase of trace element concentrations in adult Sand Martins compared to juvenile bird is consistent with the findings of other investigations. Higher levels of selenium, mercury and cadmium were found in adult kittiwakes than in their fledglings (Wenzel and Gabrielsen 1995). Similar findings were described for Cd and Hg in common murres. Furness and Tasker (1992) reported that cadmium concentrations in samples of Great Skuas, Laughing Gulls, Royal Terns, and Sandwich Terns increased with age. Consequently, the age-dependent accumulation of the Cd, Co, Mn, Mo and Sr in Sand Martins found in this study supports the hypothesis that bioaccumulation from chick development to adult stage is a widespread phenomenon in birds in general. In our investigation, the only exception was the selenium with higher values for juvenile birds.

There are some topics (Lock et al. 1992, Honda et al. 1986), which found higher metal levels in juvenile birds: in some bird species either copper or zinc levels were higher in juvenile birds than in adults. But zinc is one of the elements believed to be required for feather development. Thus it is incorporated in this tissue during feather growth. In our investigations no significant differences were found in zinc concentrations between adult and juvenile Sand Martins. Pronounced differences between adult and juvenile birds for selenium were found. The age-dependent increase of selenium levels in liver and feather samples of kittiwakes (Wenzel and Gabrielsen 1995) is consistent with the findings of Furness and Hutton (1979). Goede (1985) found rapidly decreasing selenium concentrations in the Dunlin (*Calidris alpina*) after departure from more polluted winter quarters in the Wadden Sea compared to less polluted breeding grounds in northern Norway and attributed this decline to the short biological half-life of selenium.

In the case of Sand Martins, the inversion occurred probably because of a selenium-poor African wintering area where the adults feather was produced, compared by the Hungarian Upper Tisza selenium-rich region. To generalise this inversion for selenium in the case of Sand Martins, needs more investigation.

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