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Metals and trace elements in feathers: A geochemical approach to avoid misinterpretation of analytical responses

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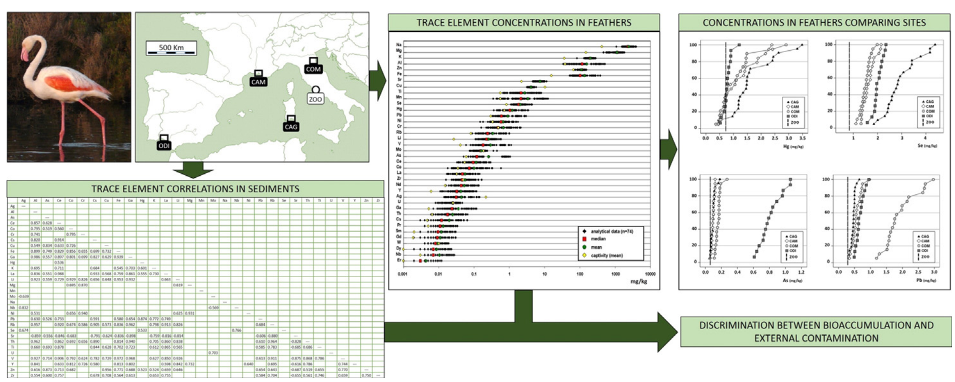
HIGHLIGHTS

- Feathers are confirmed as an important tool for non-destructive biomonitoring.
- A geochemistry approach is helpful to assess external contaminants in feathers.
- Birds living in a defined area, as chicks, are more suitable for studies on feathers.
- External contamination should be cautiously discussed in studies on feather analysis.
- Washing methods should be ameliorated to reduce external contamination in feathers.

GRAPHICAL ABSTRACT



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ABSTRACT

Assessing trace metal pollution using feathers has long attracted the attention of ecotoxicologists as a cost-effective and non-invasive biomonitoring method. In order to interpret the concentrations in feathers considering the external contamination due to lithic residue particles, we adopted a novel geochemical approach. We analysed 58 element concentrations in feathers of wild Eurasian Greater Flamingo *Phoenicopterus roseus* fledglings, from 4 colonies in Western Europe (Spain, France, Sardinia, and North-eastern Italy) and one group of adults from zoo. In addition, 53 elements were assessed in soil collected close to the nesting islets. This enabled to compare a wide selection of metals among the colonies, highlighting environmental anomalies and tackling possible causes of misinterpretation of feather results. Most trace elements in feathers (Al, Ce, Co, Cs, Fe, Ga, Li, Mn, Nb, Pb, Rb, Ti, V, Zr, and REEs) were of external origin. Some elements could be constitutive (Cu, Zn) or significantly bioaccumulated (Hg, Se) in flamingos. For As, Cr, and to a lesser extent Pb, it seems that bioaccumulation potentially could be revealed by highly exposed birds, provided feathers are well cleaned. This comprehensive study provides a new dataset and confirms that Hg has been accumulated in feathers in all sites to some extent, with particular concern for the Sardinian colony, which should be studied further including Cr. The Spanish colony appears critical for As pollution

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and should be urgently investigated in depth. Feathers collected from North-eastern Italy were the hardest to clean, but our methods allowed biological interpretation of Cr and Pb. Our study highlights the importance of external contamination when analysing trace elements in feathers and advances methodological recommendations in order to reduce the presence of residual particles carrying elements of external origin. Geochemical data, when available, can represent a valuable tool for a correct interpretation of the analytical results.

1. Introduction

As a consequence of human activities, coastal aquatic ecosystems are now polluted by a large diversity of contaminants which may have a considerable impact on the ecohealth of these habitats (Calow, 1993; Halpern et al., 2008). However, trace element inputs may derive also from natural processes such as rock weathering, volcanism, and water discharge (Garrett, 2000).

Many elements (e.g. Fe, Co, Cu, Mn, Mo, Zn) are essential to life, but toxic in excessive quantities (Singh et al., 2011). Similarly, Se exerts a protective action against Hg in the marine environment, but Hg can biomagnify in the food chain with detrimental effects on organisms (Beijer and Jernelöv, 1978; Cuvin-Aralar and Furness, 1991). Other elements that are normally toxic, turn beneficial under certain conditions (e.g. V, W, and even Cd) (Lane et al., 2005; Singh et al., 2011). On the other hand, As, Sb, and few others (e.g. Pb, Hg, Ni, Pu, Tl) seem to be toxic irrespective of quantities, without known beneficial effects on organisms (Hargreaves et al., 2010). Most of Rare Earth Elements (REEs) have been so far thought to be non-essential, but toxicological effects in humans are demonstrated for some (Pałasz and Czekaj, 2000). The accumulation of persistent contaminants in sediments exposes wildlife living in coastal wetlands to the adverse effects of such pollutants (Furness and Rainbow, 1990) even for many years after the polluting event (Hill, 2010). All this considered, many researchers point out that urgent and persistent monitoring studies on biogeochemical behaviour of practically all trace elements should be undertaken.

In waterbirds, the ingestion of food, soil or sediment is the most important intake pathway (Beyer et al., 1994; Burger and Gochfeld, 2002). Acute poisoning can occur, causing death of fully developed birds (Pain and Rattner, 1988), but more often chronic exposure at low concentrations occurs, especially in long-lived birds (Scheuhammer, 1987). Possible consequences are impaired growth, development, reproduction, behaviour, resistance to diseases and disorder in other physiological mechanisms contributing to population decline (Burger, 1993; Dauwe et al., 2005; Eeva and Lehikoinen, 1995; Frederick and Jayasena, 2011; Gangoso et al., 2009; Koller, 1980; Nam and Lee, 2006; Scheuhammer, 1987; Scheuhammer and Norris, 1996; Snoeijs et al., 2004; Talloen et al., 2008).

Waterbirds have been extensively used as sentinels of environmental pollution, in particular for trace elements (e.g. Burger and Gochfeld, 2004; Furness, 1993; Lewis and Furness, 1991; Nygard et al., 2001; Peakall, 1992; Sanpera et al., 2000, 2007; Tavares et al., 2009; Walsh, 1990). Colonial species are considered more suitable for that purpose (Fox and Weseloh, 1987). The fidelity to the breeding sites and relative abundance in a limited area imply several advantages (Kushlan, 1993). On the other hand, colonial waterbirds are often protected by environmental legislation and therefore the use of a non-invasive technique is preferable or the only possible solutions.

Potentially, feathers are good bioindicators since they are simple to collect, store and use (Furness, 1993; García-Fernández et al., 2013). Birds sequester some metals in growing feathers proportionally to blood levels (Barbieri et al., 2009; Burger and Gochfeld, 2009a; Golden et al., 2003) and a relatively high proportion of the body burden of certain metals is stored in feathers (e.g. Hg, Furness et al., 1986; As, Smith et al., 2008).

Metal accumulation in feathers may vary in relation to trophic levels, foods, and moult (Braune, 1987; Dauwe et al., 2003; Nygard et al., 2001; Stewart et al., 1999, 1997). Within species, age (Burger, 1995; Burger and Gochfeld, 2000), reproductive stage (Wayland et al., 2005), location, physiological condition, and clutch (Rumbold et al., 2001) can also have an effect. However, a lot of previous investigations on pollutants in feathers were conducted on adults of unknown age, foraging areas, moulting stage and migratory status patterns.

Chick feathers appear more suitable for assessing metal bioaccumulation because the weight of variability factors such as age, moult, and exposition to atmospheric deposition is minimized (Burger, 1993). However, relatively few studies have focused on chicks comparing different colonies. Such studies mainly referred to herons and ibises (Abdennadher et al., 2011; Abdullah et al., 2015; Burger, 2013; Clarckson et al., 2012; Cotìn et al., 2012; Golden et al., 2003; Goutner et al., 2001; Herring et al., 2009; Kim and Oh, 2014a; Rubio et al., in press; Rumbold et al., 2001; Sepulveda et al., 1999; Spahn and Sherry, 1999), terns and gulls (Burger, 1996; García-Tarrasón et al., 2013; Kim and Oh, 2014b; Ramos et al., 2013; Sanpera et al., 2007), and pelagic birds (Blévin et al., 2013) and focused especially on Hg.

Feathers are subjected to external contamination to some extent (Ek et al., 2004; Fasola et al., 1998; Hahn et al., 1993; Hollamby et al., 2006; Valladares et al., 2010). It can occur from direct atmospheric deposition, contact with soil, dust or water, or from the deposition of contaminants on feathers during preening (Dauwe et al., 2002). Waterfowls and seabirds may also secrete metals through salt gland and embrocate them on their feathers (Dmowski, 1999). The extent of the external contamination is element-related (Jaspers et al., 2004): for Hg, it is considered negligible (e.g. Appelquist et al., 1984; Dauwe et al., 2003; Dmowski, 1999; Ek et al., 2004; Goede and De Bruin, 1984), but for most elements this is not true or not clear (Cardiel et al., 2011; Dmowski, 1999).

Nevertheless, very few studies have highlighted the problem of external contamination (Scheifler et al., 2006) or aimed to solve it, and therefore the analytical results cannot always can be easily interpreted, with the possible exception of Hg (Dauwe et al., 2003). In most studies, feathers were washed before analysis. A thorough alternate washing with deionized water and acetone was frequently adopted (e.g. Ansara-Ross et al., 2013; Carvalho et al., 2013; Costa et al., 2013). In some studies, instead of acetone, other solutions based on NaOH (e.g. Cotìn et al., 2012; Ramos et al., 2013), or a chloroform-methanol mixture were applied (e.g. Lucia et al., 2013). These methods were occasionally followed by an ultrasonic bath. Less frequently, feathers were simply rinsed with deionized water (Markowski et al., 2013), sometimes preceded by a washing with a mild-metal free detergent (Bryan et al., 2012). In some cases feathers were not washed at all (Abdennadher et al., 2011; Kim and Oh, 2014a, 2014b). In any case, it was demonstrated that no washing procedure is able to ensure the total removal of the surface contamination from feathers (Cardiel et al., 2011; Espín et al., 2014).

The Greater flamingo (*Phoenicopterus roseus*) is a potential sentinel of the health of coastal ecosystems since it is large, wide-ranging, abundant, long-living, as well as easily observed and monitored. The breeding ecology of the Greater flamingo is well known, as well as its biology (Johnson and Cézilly, 2007), as is desirable when a sound interpretation of the contamination level in the study areas is the main objective (Burger and Gochfeld, 2009a, 2009b). This species feeds in flock, on small benthonic invertebrates and occasionally seeds of aquatic plants by filtering mud, typically in brackish wetlands and