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Arsenic and mercury in bird feathers: Identification and quantification of inorganic pesticide residues in natural history collections using multiple analytical and imaging techniques

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ABSTRACT

Life science collections and their curated metadata are now seen as potential archives of environmental levels of trace elements. Bird feathers are especially promising material, but surface contamination might present a significant issue. The suitability of preserved specimens for environmental studies may be further limited by historical application of inorganic pesticides in the collections. Arsenic (As) and mercury (Hg) are the most significant inorganic contaminants in natural history collections since they were widely applied as pesticides from the late 18th century until the 1980s. Potential presence of As- and Hg-containing pesticide residues has also to be taken into account when members of the public are allowed to handle specimens. Even though the testing of taxidermy and anthropology museum collections for pesticide residues is becoming a common practice, it is generally done qualitatively rather than quantitatively. In this study, the concentrations of As and Hg were determined in feathers of eleven bird specimens considered for an interactive display and were found to range from 1.1 to 15,183 μg g^{-1} and from <1 to 26,960 μg g^{-1}, respectively. The study shows how the quantitative information can be obtained and the history of the pesticide treatment reconstructed using a combination of analytical techniques including bulk analysis by inductively coupled plasma mass spectrometry (ICP-MS) following destructive or non-destructive sampling, and spatially resolved techniques such as laser ablation (LA)-ICP-MS and scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS). Inorganic As speciation by squarewave anodic stripping voltammetry (SWASV) and localisation of pesticide residues by X-ray micro-computed tomography (μCT) can provide additional information. It is found that As is not only present as micron-sized particulate residues, but becomes incorporated into the keratin matrix of the feathers. Mercury is probably nano-particulate and fully incorporated into keratin. The history of pesticide treatment might be complicated with mixtures of chemicals involving both As and Hg compounds and more than one way of pesticide application used on the same specimen.

1. Introduction

Life science collections and their curated metadata are now seen as potential archives of environmental levels of trace elements [1–3]. Trace metal concentrations in bird tissues and feathers are studied in context of their relationship with the environmental contamination (e.g. [4]). An active discussion is taking place on how to exclude surface contamination in determining metal contents of bird feathers [5]. Changes in metal concentrations (e.g., in feathers) induced by conservation treatment have also been discussed [6]. The suitability of preserved specimens for environmental studies may be further limited by historical application of inorganic pesticides in the collections [3,7]. Arsenic (III) oxide (As_2O_3) historically known as 'white arsenic' and mercury (II) chloride ($HgCl_2$) known as 'corrosive sublimate' were first used for the preservation of natural history specimens probably in the 17th century [8] and widely applied since the 1770s.

Natural history collections that include specimens prepared before the 1980s are likely to contain historical pesticide residues [9]. In the 1970s, As compounds were still recommended for skin treatment of taxidermy specimens [10]. The National Park Service (USA) used As compounds until at least 1976 and mercuric chloride until at least 1980 [11]. Elevated concentrations of As in dust were found in

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museums' zoology and anthropology departments [12,13], so untreated specimens may also be contaminated. Inorganic compounds of As and Hg are toxic, and As is a known carcinogen [14]. Pesticide residues in taxidermy and anthropology collections are an occupational hazard for museum workers and external researchers using the collections. The exposure of general public to pesticide residues is generally minimised by barriers such as glass cases and cupboards. However, the general public, especially children, can also be at risk of exposure in settings such as interactive ('touch and feel') displays. In assessing chemical risks for children, behavioural factors must be considered. The normal hand-to-mouth activity of young children may result in an increase in toxic metal intake from pesticide particles potentially present at the surface of taxidermy specimens. While non-invasive methods such as X-ray fluorescence spectroscopy (XRF) are preferred for screening collections for elevated concentrations of toxic elements [15], due to the nature of specimens and heterogeneity of contaminant distribution, the results are generally qualitative [16].

Unfortunately, there is very little data available that provide quantitative information on the content and distribution of pesticides in individual specimens. Information of this type is critical for the assessment of the suitability of natural history collections for environmental research. Quantitative data on concentrations of toxic elements in taxidermy specimens combined with spatially resolved chemical information can also provide an insight into the history of pesticide treatment and behaviour of toxic elements in treated objects, which can in turn be used in forensic [17] and environmental [2] studies and for assessing the risks of handling specimens with an unknown conservation history [18].

In this study, we attempt to reconstruct the history of specimen treatment with inorganic pesticides using a combination of bulk chemical analysis, spatially resolved methods, speciation analysis and 3D imaging. Inductively coupled plasma mass spectrometry (ICP-MS), albeit a technique generally requiring destructive sample preparation, has an advantage of very low detection limits for most elements in a single multi-elemental analysis. Its use in combination with micro-destructive sample introduction such as laser ablation (LA-ICP-MS) provides an opportunity to acquire spatially resolved data from a single feather [19] for which additional information can be obtained by other analytical techniques.

2. Materials and methods

2.1. Specimens

Eleven bird specimens (mounted birds, wings and a study skin), representing species widespread in the UK, were selected for testing with a view of using them in educational displays and were consequently used for further research constituting this study. None of the bird specimens contained any background information on the pesticide treatment; most of them did not have any detailed record associated with them, and only two specimens were dated.

2.2. Inductively coupled plasma mass spectrometry (ICP-MS)

A single feather was collected from each specimen with a minimum damage to the specimen. Additional feathers were collected in triplicate from different parts of the two specimens, significantly contaminated with As and Hg (kingfisher and kestrel wing), in order to confirm variations in pesticide concentrations across the specimen. Feathers (0.6–11.5 mg) were weighed using an MC6 Sartorius microbalance ($d = 0.001$ mg) and transferred into 60 ml Savillex® fluoropolymer vessels. 2.5 ml HCl, 0.5 ml HNO_3 (both acids Romil® SpA™ grade) and some ultrapure water (18.2 MOhm cm^{-1}) were added, and the vessels were kept heated at 70 °C overnight. Samples were diluted with ultrapure water to 50 ml and further diluted for ICP-MS analysis, when necessary, using ca. 0.25 M HCl.

Swab tests for bulk concentrations were conducted by running commercial cotton swabs on wooden sticks (WA 7, Heinz Herenz Hamburg, Germany), moistened with ultrapure (18.2 MOhm cm^{-1}) water, 10 times over the area about 10 × 10 cm in the direction of the feathers. Swabs were then put into 20-mm sterile Sartorius® tubes and 5 ml of 0.25 M HCl was added to each tube. The swabs were left to soak for 3 h before vortexing and removal, and the solution were analysed within 24 h.

ICP-MS analysis was conducted using an Agilent 7700x instrument. To minimise polyatomic interferences, the instrument was run with 5 ml min^{-1} He (99.9995% purity) in the collision-reaction octopole cell (CRC) as well as with no collision gas entering the CRC. Lead (Pb; average of ^{206}Pb, ^{207}Pb and ^{208}Pb) and Hg (^{202}Hg) were determined in the 'no gas' mode while As (^{75}As) was determined in the 'He mode'. 0.5 M HCl was used to rinse the system for 80 s between the samples. The limit of quantification (LOQ) for As in 0.25 M HCl was only 0.02 μg l^{-1} and the LOQ for Hg and Pb were 0.006 and 0.003 μg l^{-1} respectively. The use of CRC technology for the simultaneous determination of As and Hg is critical because $^{75}As^{+}$ detection is severely affected by molecular interference from $^{40}Ar^{35}Cl^{+}$ in the presence of chlorine, but Hg requires the presence of HCl for stability in solution [20]. The suitability of the sample digestion protocol and the analytical accuracy were checked by analysing a reference material TORT-2 (Lobster hepatopancreas; National Research Council Canada), which was digested using the same protocol. The concentrations obtained for As, Hg and Pb were within the uncertainty of the reference values. The reproducibility of analysis (1sd, $n = 3$) was within 3% for As and within 1% for Hg and Pb.

2.3. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

Complete feathers of the two specimens containing the highest levels of As and Hg (kingfisher and kestrel wing) were sampled for the LA-ICP-MS study. Feathers were covered with stretched pieces of Parafilm M® material to prevent contamination of the laser ablation system and cross-contamination during analysis.

A New Wave Research 193 nm UV excimer laser system was used in conjunction with an Agilent 7700x ICP-MS. A 'two-volume' cell was used with a floating stage, which was flushed with He to collect the analyte. A pellet of NIST SRM 1566a (Oyster) was prepared by placing the powder between the layers of Parafilm M® and pressing it with a hydraulic press at 10 bars, and used to assess the stability of the ICP-MS signal throughout the analyses. The laser was pulsed at 10 Hz with a fluence of 3.2 mJ cm^{-2}. Gas blanks of 30 s were used with each analysis. Each sweep lasted 0.23 s and 60 s of ablation was recorded for each analysis. Ablation spots were 50 μm in diameter.

Data were reduced using in-house software. No attempt is made to quantify the data and produce concentrations due to a lack of matrix-matched reference materials. Data are presented as ^{43}Ca-normalised intensities [21] derived from the mean counts per second of the ablation minus the mean counts per second of the gas blank [22] and used for comparison with other analyses of the same feather, as the matrix and ablation conditions are the same, and calcium is assumed to be homogenously distributed in feathers [19].

Each 60 s ablation included a signature of the Parafilm® layer in addition to the feather keratin and then the glass slide. A uniform slice containing 25 sweeps (5.7 s) was used for all analyses beginning from the first stabilised part of the keratin signature (Fig. 1), with no used signal passing into the signature of the glass slide.

2.4. Squarewave anodic stripping voltammetry

Swab tests for As speciation were conducted by running commercial cotton swabs on wooden sticks (WA 7, Heinz Herenz Hamburg, Germany), moistened with ultrapure (18.2 MOhm cm^{-1}) water, over three different areas on each specimen. Swabs were then put into