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Hg and Se Speciation in Liver Tissue of Marine Birds

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Abstract. X-ray fluorescence microprobe maps of Hg and Se distribution were made on liver tissue slices from marine birds (Cormorants) from Florida's Everglades. The birds bio-concentrate these toxic pollutants that are ingested from their diet of fish. The fluorescence maps show strong localization of Mercury and Selenium into "hot spots" less than 100 microns in size. XAFS measurements were made on hot spots to demonstrate that the Hg and Se are indeed are chemically bound, supporting the idea that moderate levels of Se may have a protective effect against Hg through its complexation.

1. Introduction

Hg pollution and toxicity is a serious health concern. Environmental Hg is generated from both natural and anthropogenic sources, commonly as an airborne pollutant from the burning of coal and municipal waste, volcanic eruptions, and as a water pollutant from natural and industrial emissions. Recent reviews can be found in [1,2].   It has been observed that elevated Hg concentrations in tissues are often accompanied by elevated Se concentrations. This work is an investigation into the speciation of Hg and Se in tissues using x-ray fluorescence mapping and XAFS. Previous electron microscopic/x-ray microprobe studies by Martoja and Viale [3] on liver tissue from marine mammals has shown that Hg and Se are present in small particles which appeared to have the approximate stoichiometry HgSe; these were proposed to be the mineral Tiemannite. Subsequent XAFS studies by Arai et al [4] were done on liver tissue *extracts* from fur seals and albatrosses that indicated coordination of Se by Hg in a manner consistent with HgSe deposition. Together these studies suggest that Hg is complexed by Se (and perhaps S) into an inorganic form that renders the Hg immobile and less toxic, as proposed by Martoja and Viale [3]. However, those measurements were made on different samples, from different species, with different techniques, and the only successful XAFS measurements were on tissue *extracts*, not whole tissues.

Here we report spatially resolved x-ray fluorescence and XAFS measurements on the *same* sample consisting of *whole* liver tissue sections (rather than extracts) from a cormorant (a fish-eating marine bird) obtained from Florida's Everglades.

2. Materials and Methods

Initial investigations were made on the speciation of Hg in liver tissues from cormorants known to have high Hg exposure. Focussed x-ray beams were used on the BioCAT undulator beamline at the APS, using a multilayer array analyzer. Initially these measurements were done on bulk tissue specimens, but the average concentration was too low to obtain good XAFS data. However, in one measurement, at a particular location, a surprisingly large signal was obtained, suggesting that there were "hot spots" of high Hg concentration. Subsequently, spatial maps of x-ray fluorescence were made on 20 micrometer thick liver tissues slices using the BioCAT undulator beamline at the APS with a Vortex silicon drift detector. The step size is 0.14 mm in the short direction (x) and 0.10 in the long direction (y). Because statistical correlations between the bulk Hg and Se contents were known from the literature, Hg and Se maps were measured, as were Fe and elastic scatter as controls. Hg and Se XAFS measurements were made on selected regions of high concentration. More than 300 one-minute long continuous scans were summed together to obtain sufficient signal to noise. Here we report Se K-edge results.

3. Results

Fluorescence maps are shown in Figure 1. The Hg and Se evidently are mostly concentrated in "hot spots" that are smaller than the spatial resolution of approximately 100 micrometers.
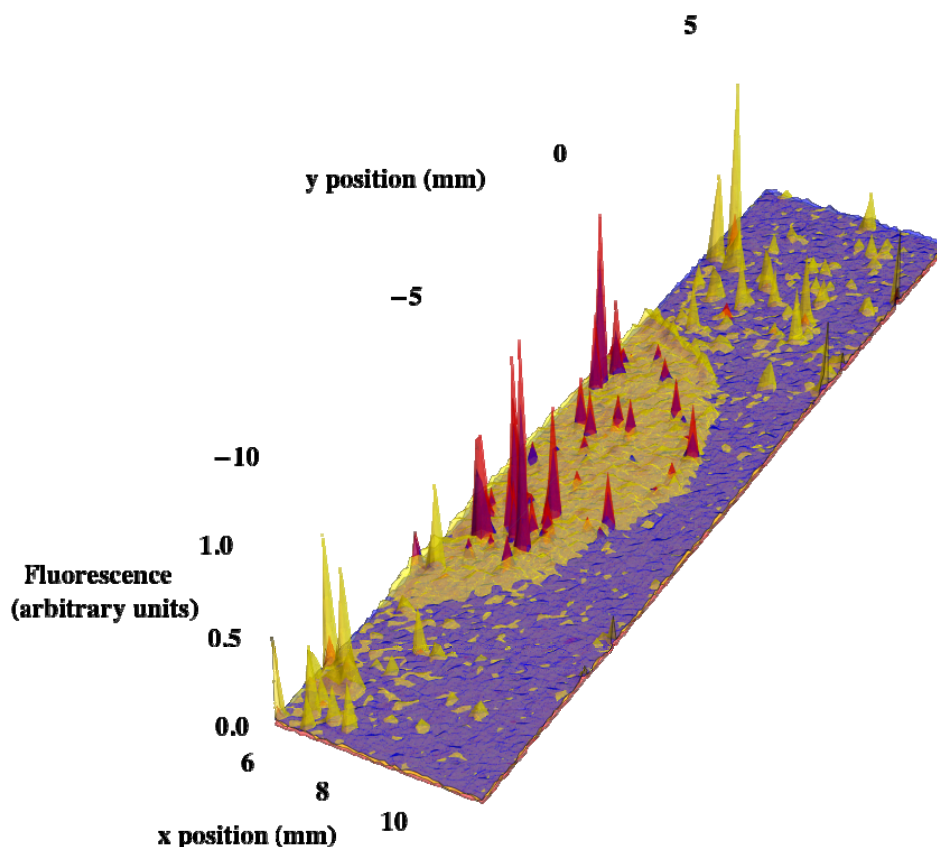

Figure 1: Spatial maps of fluorescence of Hg (red), Se (blue), and Fe (yellow). This shows the existence of "hot spots" of high concentration of both Hg and Se. The peaks corresponding to Hg and Se overlap so that they appear purple. The yellow Fe peaks are not spatially well-correlated with Hg and Se. The spatial resolution is approximately 100 micrometer.

XAFS measurements were subsequently made on one of the hot spots. Several hundred quick-XAFS scans of one-minute duration were summed together to obtain sufficient signal to noise.   We report results on first shell Se edge EXAFS analysis.   The Hg L_1 edge is several hundred eV below the Se K-edge, which complicates the EXAFS analysis for the Se edge, because of the limited data range. Although the Hg L_1 edge EXAFS overlaps the Se EXAFS range, it varies more slowly there because of the quadratic dependence of E on k. It varies sufficiently slowly that it appears as a background that is spectrally distinct from the Se edge EXAFS. Therefore conventional methods of analysis are sufficient for this purpose. Only the first shell was analyzed because the limited information content in the data restricts the number of parameters.

The data were reduced using Mathematica 8 and Athena [5], and then fit using Artemis [5], using the mineral HgSe (Tiemannite) as a theoretical standard (see Figure 2).   Tiemannite is of the Zincblende structure, with each Hg and Se tetrahedrally surrounded by atoms of the other type.   Fourier transforms of the Se K-edge data from k=2 to 10.5 Å^{-1} are shown in figure 3; no phase correction was done, so the true distances are approximately 0.4 Angstrom longer than it appears.   The background peak at R~1.0 Å is primarily due to the Hg L_1 edge EXAFS extending into the Se transform range, but it is of no consequence because it is spectrally isolated at low-R.

The first shell Fourier transform peak is split because of a Ramsauer-Townsend resonance in Hg's backscattering amplitude, which has a minimum at about k=6 Å, giving the appearance of a beat. A value of $S_0^2 = 0.85$ was used, and delta E_0 was 4.10 ± 1.43 eV. The first shell distribution of atoms is well fit as 4 ± 1 Hg atoms at 2.61 ± 0.02 Å   and $\sigma^2 = 0.010 ± .003$ Å^2. This large value of σ^2 is presumably due to structural disorder.   The number of independent points was 7, variables 4, reduced chi square 15.1, R-Factor .056.   Error estimates presented are fitting errors estimated by Artemis.
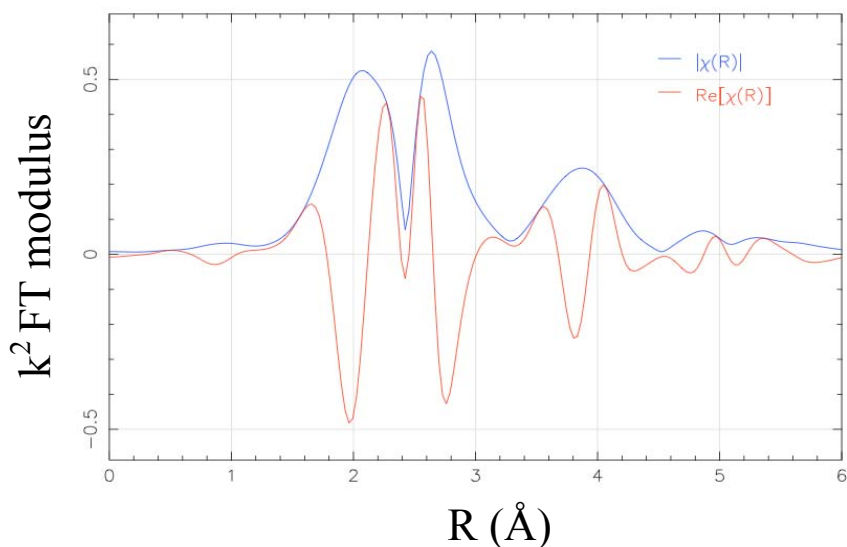

Figure 2: Fourier Transform of theoretical spectrum of Tiemannite, with DWFs calculated by FEFF8 in Debye approximation at sample temp 300K and Debye temperature 200K.   The nearest neighbor peaks are due to 4 Hg atoms at 2.63 Å, and the peak at 3.8 Å is Se.   The first shell peak splitting is due to a Ramsauer-Townsend-type resonance in the backscattering amplitude of Hg.
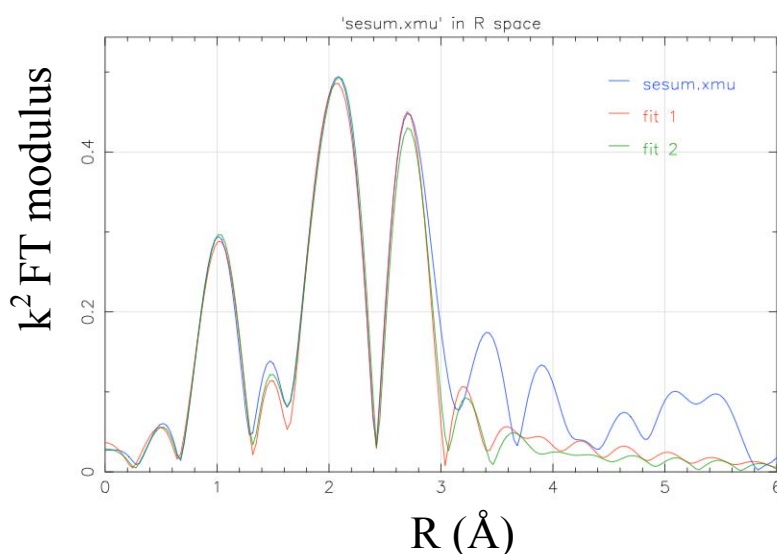
Figure 3: Magnitude of k^2 Fourier transform of summed Se data and two R-space fits to data fit between R=1.6-3.2 Å. The (background-fitted) peak at R=1.0 Å is due to Hg EXAFS extending into the Se transform range, and is of no consequence. The data within the fit range correspond to a single shell of 4 Hg at 2.61 Å; the peak splitting is due to the shape of the Hg scattering amplitude function.

4. Discussion and Conclusions

Electron microscopic studies in marine mammals previously have shown evidence for nanoparticles containing Hg and Se which were assumed to be HgSe [3]. Although the nearest neighbor environment of the Se is indeed similar to that in the mineral Tiemannite, the second and higher shells appear to differ from this simple picture. In Tiemannite there is also a well ordered set of Se atoms in the second coordination shell, and such a shell is not evident in the sample Fourier transforms. The observed suppressed second shell signal could be due to several factors: large structural disorder; reduced number of neighbors, if the particles are nano-scale; or mixed Se and S coordination, which would tend to cause cancellations of the EXAFS contributions through interference.

Direct evidence is presented here for chemical bonding between the Hg and Se that is contained in small particles in liver tissue of cormorants. This is consistent with the proposal [1] that Se may offer a protective effect against Hg through its complexation into inorganic particles.

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