Distribution and Speciation of Arsenic in Poultry Particulate Emissions

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The use of organo-arsenicals such as roxarsone in poultry production is quite common. These compounds are primarily used as anticoccidials, as growth promoters, and to increase feed efficiency. Such usage has raised a variety of environmental concerns such as the accumulation of arsenic in poultry excrement and the release of arsenic into air, soil and water resources. Confined animal feeding operations (CAFOs), such as broiler poultry houses, are sources for airborne particulate matter (PM) emissions and have become major environmental and human health concerns. Many growers and their families are the primary operators of these CAFO facilities, and can spend anywhere from 25-45 hours per week working on the farm. Farm workers who average as little as two hours per day inside of a CAFO may develop acute and chronic respiratory diseases associated with the long term exposure to the particulate matter. Studies have indicated that there is a presence of toxic metals and metalloids, such as arsenic found in the poultry litter; however, it is not well known whether the re-suspended PM from these poultry houses carries such toxic contaminants, which could be harmful to human health. This presentation will focus on the chemistry and metal(loid) speciation of airborne emissions of both $PM_{2.5}$ and PM_{10} from confined broiler operations. The samples were analyzed using traditional wet chemistry techniques, such as inductively coupled plasma-mass spectrometry (ICP-MS) to determine total heavy metal and metalloid concentrations. More advanced, state-of-the-art, synchrotron-based spectroscopic and microscopic techniques, such as SEM-EDX were applied to determine arsenic and other metal speciation and distribution, and thus shed light on the potential toxicity. The results of this research suggest that arsenic concentrations vary depending upon location, size fraction, and period of growout cycle. In addition, u-XANES results suggest that the arsenic present in both PM_{10} and $PM_{2.5}$ fractions can be in organic and inorganic forms, and is widely distributed across the filtered samples of the particulate matter.
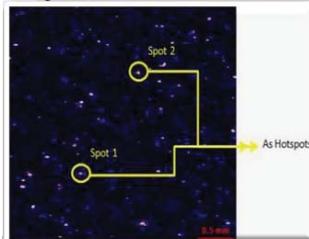

Figure: 3mm x 3mm micro X-ray fluorescence (m-XRF) map of As from a PM10 sample. The bright "hot" spots indicate an area where there is higher intensity of As present.

On overview of the deep carbon cycle and its isotope heterogeneity

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Carbon is massively exchanged between the Earth's surface and the deepest part of the mantle so that, on billion years time-scales, is at, or close to, steady state (= amounts and isotope compositions of C being degassed and subducted being balanced). This is best evidenced by constant C-isotope compositions, over nearly 3.5 Gy, in both sediments (typically 20% organic matter, 80% carbonates with $\delta^{13}C$-values of -25 and 0‰ respectively) and mantle-derived samples (MORB, OIB, diamonds, carbonatites, carbonates from kimberlite) averaging $\delta^{13}C \sim -4 \pm 1$‰. This can also be inferred from the short modern residence time of surface carbon, close to 1.5 Gy. The implication is that modern recycled carbon flux equals degassed carbon flux at about 2×10^{12} mol/y.

Owing to mantle carbon steady-state, it is unlikely that mantle (= *cycled*) and primordial (= *uncycled yet*) carbon would display distinct isotopic, although longer residence time of mantle carbon, ca. 4-6 Gy, suggests that such a primordial C-reservoir might exist. Our best estimate, based upon diamonds having the most primordial (= *lowest*) N-isotope compositions, indicates a primordial C-isotope composition close to -3.5‰. The size of the primordial carbon reservoir remains however elusive.

If subducted carbon has a $\delta^{13}C_{average} \sim -4$‰, it is originally both chemically and isotopically heterogeneous; so there is some chance that some deep mantle domains would record a subduction-related heterogeneity. Such a heterogeneity cannot however be inferred from mid-ocean ridge or ocean island basalts; the C-isotope variability mostly reflect degassing processes (= lowering residual $\delta^{13}C$). This is best illustrated by relationships with degassing proxies (e.g. $^{40}He/^{40}Ar^*$) but not with those tracing mantle volatile heterogeneity (e.g. H_2O/Ce, D/H or $\delta^{34}S$-ratios). So, if any, mid-ocean ridge or ocean-island basalts bear very small C-isotope heterogeneity.

Many authors ascribe low $\delta^{13}C$-diamonds (typically in the range of -15 to -25‰) to mantle carbon isotopic *heterogeneity* related either to subduction or to be primordial. Coupled $^{34,33}S$, N and C-isotope systematics suggest however that most relate to high-temperature fractionation, occurring at depths (typically 250-150 km), prior to diamond precipitation.

Yet, several diamond populations (from komatiites in French Guyana and from Jericho kimberlite in Northern Slave with $\delta^{13}C$-modes $\sim$-28 ‰ and -38‰ respectively) are unique and difficult to interpret in the light of heterogeneity being either primordial, subducted or mantle-related (i.e. there are only rare sediments with $\delta^{13}C$ as low as -40‰). Together with diamonds from the transition-zone (from 300 to 660 km depth), there is still the possibility that mantle domains with odd C-isotope characteristics indeed exist. If correct, this would have very strong implications when considering sedimentary C-isotope excursions associated with the emplacement of large igneous provinces: their C-budget would not need to be close to the *canonical* mantle $\delta^{13}C$ of -4‰.