

## Mercury stable isotope time trends in cryogenically archived ringed seal livers from the Alaskan Arctic

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Because of its long residence time in the atmosphere, gaseous mercury (Hg) emitted from distant anthropogenic sources reaches high latitude regions carried by air flow [1]. Springtime atmospheric Hg depletion events (AMDEs) were early on recognized as a potential key control on Hg entering the Arctic ecosystem. Even if a large amount of AMDE Hg deposited is immediately re-emitted to the atmosphere, the remainder is mobilized by meltwater [2] and transformed by bacteria into methyl-Hg. This neurotoxic form is able to bio-accumulate along the trophic chain and high concentrations are observed in top predators. Global emission Hg trends and AMDEs alone are however unable to explain observed temporal trends in biota Hg in Western and Eastern Arctic sectors [4]. Marine mammal's exposure to MeHg therefore needs additional consideration of physiological, ecological and climate change factors such as feeding behavior, habitat utilization, and sea-ice disappearance. Recent work on arctic seabird eggs [5] has shown a possible link between sea-ice cover and biota Hg isotope signatures. It was inferred that by blocking UV radiation the sea-ice diminishes photochemical breakdown of bioavailable surface ocean MeHg. Here we further explore the potential influence of climate change on Arctic Hg biogeochemistry. We focus on ringed seals, a sea-ice dependent species considered as appropriate Hg biomonitors in the Arctic region. Indeed, their high degree of site fidelity allows spatio-temporal analysis of biomarkers. Hg speciation (inorganic Hg, MMHg) and stable isotopic composition (C, N, Hg) measurements were made on 53 ringed seal liver samples archived at the US Marine Environmental Specimen Bank. Sampling covers a period of 14 years (1988-2002), allowing an accurate time trend analysis. The isotopic signature  $\Delta^{199}\text{Hg}$ , which is a tracer for inorganic or methyl Hg photochemistry in surface waters, varied from 0.05 to 1.04 ‰. This variation was not related to in-vivo metabolic effects or ecological effects such as feeding habitat ( $\delta^{13}\text{C}$ ) and trophic level ( $\delta^{15}\text{N}$ ).  $\Delta^{199}\text{Hg}$  shift from  $+0.37 \pm 0.08\%$  (SE, n=5) in 1988 to  $+0.59 \pm 0.07\%$  (SE, n=7) in 2002, and show a significant increase of 4.8% yearly ( $R^2=0.70$ ,  $p^* < 0.05$ ) in this period. We suggest that this reflect the progressive decrease in sea-ice cover between 1988 and 2002. This is coherent with our previous study [5].

[1] Macdonald et al. (2005) *Sci Total Environ*, **342**, 5-86

[2] Steffen et al. (2002) *Atmos Environ*, **36**, 2653-2661.

[3] Loseto et al. (2004) *ES&T*, **38**, 3004-3010.

[4] Gaden et al. (2009) *ES&T*, **43**, 3646-3651

[5] Point et al. (2011) *NGS*, **4**, 188-194.

## Characterization of combustion products from biomass pellets

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Two different types of biomass pellets (a DIN+ wood pellet and a new pellet made of the *Miscanthus* grass) and their combustion products (bottom ash and fly ash) were investigated by Atomic Absorption Spectroscopy (AAS), Scanning Electron Microscopy (SEM), Electron Microprobe Analysis (EMPA), and X-ray diffraction (XRD). Also, an attempt was made to characterize combustion-derived particles in the exhaust gas by using SEM images and EDX spectra.

The fuels were combusted in a glass tube reactor using a heating ramp (20-820°C @ 20°C/min). The particles were collected by an Electrical Low Pressure Impactor (ELPI) on twelve stages depending on their aerodynamic diameter. The main focus was put on the alkali, alkaline earth and silicon contents as these compounds commonly lead to the formation of corrosive deposits in biomass power plants and may also contribute to hazardous primary and secondary particulate matter in the atmosphere.

The results reveal relatively higher potassium and calcium contents in the *Miscanthus* fuel and its combustion products. On the other hand, the silicon contents of the fuel and the combustion products are almost identical for the two pellet types. The unexpected high silicon content in the wood pellet is inferred to result from contamination during harvesting and pellet production, a hypothesis supported by the presence of extraneous quartz grains observed by SEM. In the *Miscanthus* pellet potassium and silicon were also found inside the cells, and thus represent inherent inorganic material. In the bottom ash of the *Miscanthus* pellet, a multitude of mineral phases, predominantly lime, have been identified by XRD, and evidence for ash melting was obtained from SEM observations. In the bottom ash of the DIN+ wood pellet, only quartz and calcite were detected, with no indication for ash melting.

The inorganic particles collected from the flue gas were classified on the basis of their chemical composition and shape in order to assign them to a probable mineral phase. In the *Miscanthus* particulate matter samples, twelve different inorganic particle types with mean diameters from 1-20 µm were identified. In the DIN+ particulate matter sample, a total of seven different particle types were found, but the main fraction (~80%) is represented by quartz grains with mean diameters > 10 µm.

The major part of the inorganic (ash-forming) fraction of the DIN+ pellet is represented by extraneous material, whereas significant amounts of the inorganic constituents of the *Miscanthus* pellet are located inside the biostructures. This may lead to higher reactivity during combustion and the formation of secondary phases such as lime and melilite, and the formation of a wide variety of particle types.