## Speciation and bioavailability of iron in anthropogenic aerosol emissions

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The majority of current atmosphere/ocean models assume that windborne mineral dust is the source of >90% of the iron deposited to the surface of the world's oceans<sup>[11]</sup>. While anthropogenic combustion aerosols account for a small percentage of deposited iron by mass, the greater solubility of iron compounds in these particles<sup>[2]</sup> compared to mineral dust<sup>[3]</sup> suggests that they may be more significant than their total concentration would indicate. These aerosols may be major sources of bioavailable iron to High Nutrient Low Chlorophyll oceanic regions<sup>[4]</sup>, and atmospheric processing by acidic gases may further increase the soluble iron content of the particles<sup>[5]</sup>.

The speciation of iron compounds in fly ash particles from ship emissions, coal and biomass burning were determined using X-ray Absorbance Near Edge Spectroscopy and XRF mapping at the ANKA synchrotron in Karlsruhe and the Diamond facility in Harwell. Coal fly ash samples from four sources were subjected to simulated atmospheric processing with SO<sub>2</sub>, NO<sub>x</sub>, ozone and artificial sunlight followed by extraction to monitor any changes in iron solubility.

XANES analysis shows that iron is mostly present in coal fly ash as Fe(III) in hematite, with some magnetite and ferrihydrite while ship emissions mostly resemble ferric sulfate. Most iron present in ash from biomass burning was found to result from iron-rich "hotspots" likely to be particulate contamination from dust or soil rather than the biomass itself. The influence of atmospheric processing varies across coal fly ash samples, ranging from no discernible impact to a ~50% increase in iron solubility depending on the source of the ash and UV irradiation.

[1]Hajima et al. Prog. in Earth & Planetary Sci. (2014) pp 1-29 [2] Chen et al. Environ. Sci. & Tech. (2012) 46, pp 2112-2120 [3] Shi et al. (2012) Aeolian Research 5, pp 21-42 [4] Ito (2013) Global Geochem. Cyc. 27, 1-10 [5] Ito, Environ. Sci & Tech (2013) pp 70-75