

## Assessing the importance of ab- and adsorption to the gas-particle partitioning of different POPs

RAINER LOHMANN<sup>1</sup>, KEVIN C. JONES<sup>2</sup>,  
STEVEN J. EISENREICH<sup>3</sup> AND GERHARD LAMMEL<sup>4</sup>

<sup>1</sup>Graduate School of Oceanography, University of Rhode Island, Narragansett, RI, 02882, U.S.A.  
(lohmanna@gso.uri.edu)

<sup>2</sup>Department of Environmental Science and Centre for Chemicals Management, Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, UK  
(k.c.jones@lancaster.ac.uk)

<sup>3</sup>European Chemicals Bureau, Joint Research Centre, European Commission, ISPRA, Italy 21020  
(steven.eisenreich@jrc.it)

<sup>4</sup>Max Planck Institute for Meteorology, Bundesstrasse 55, 20146 Hamburg, Germany (lammel@recetox.muni.cz)

The gas-particle partitioning of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) was examined (i) by re-interpreting results from controlled field experiments and (ii) in diurnal samples taken in the New Jersey - New York City (NJ) region. In the controlled field experiments, aerosol-laden filters were exposed to elevated concentrations of PCDD/Fs. Gas-particle partitioning coefficients,  $K_{ps}$ , were significantly correlated with octanol-air partitioning coefficients,  $\log K_{oa}$ s. The regression of all individual datapoints resulted in the following best fit ( $r^2 = 0.74$ ,  $n = 87$ ):  $\log K_{p, meas} = 1.00 (\pm 0.13) \log (10^{-12} f_{om} K_{oa} / \rho_{oct}) - 0.15 (\pm 0.48)$ . We interpret this as showing that the ability of organic matter (OM) to absorb PCDD/Fs is generally well described by the octanol-air partitioning model ( $f_{om} K_{oa}$ ). Results will be compared to previous observations of the gas-particle partitioning of PAHs.

At the NJ land-based sites, samples were taken and analyzed for organic (OC) and elemental carbon (EC), gaseous and particulate PCDD/Fs.  $K_{ps}$  were significantly correlated with the  $f_{om} K_{oa}$  approach. Adsorption to the GFF and possibly to BC will have contributed to the observed  $K_p$  values. Gas-particle predictions based on BC adsorption and OM absorption, with  $K_p = f_{om} K_{oa} / (10^{12} \rho_{oct}) + f_{BC} K_{BC-air} / (10^{12} \rho_{BC})$  resulted in  $K_p$  predictions that were close to measured values. In favour of adsorption to the GFF being the major reason is that NB displayed highest  $K_p$  values, which was also most prone to this sampling artefact based on relatively low sampling volumes and TSP concentrations. In addition, while adsorption to BC would result in better prediction of  $K_p$  values, no influence of  $f_{BC}$  or  $f_{BC}/f_{om}$  ratios was seen, suggesting that it was of lesser importance in our sample set.

## Fe<sup>3+</sup>/ΣFe in lower mantle (Mg,Fe)O: Calibration of the “flank method”

M. LONGO AND C. MCCAMMON

Bayerisches Geoinstitut (michaela.longo@uni-bayreuth.de;  
catherine.mccammon@uni-bayreuth.de)

The lower mantle, which represents more than half the Earth by volume, is dominated by (Mg,Fe)(Si,Al)O<sub>3</sub> perovskite and ferropicriole (Mg,Fe)O. Studying these phases are therefore critical to determining redox conditions and their consequences for mantle properties and dynamics. Studies have shown that the Fe<sup>3+</sup> concentration in (Mg,Fe)(Si,Al)O<sub>3</sub> perovskite is essentially insensitive to oxygen fugacity; hence our attention is turned to (Mg,Fe)O. Our goal is to calibrate the “flank method” [1] on synthetic (Mg,Fe)O using the electron microprobe, and then apply the method to determine Fe<sup>3+</sup>/ΣFe in ferropicriole inclusions from lower mantle diamonds.

Initial experiments focused on synthesis of polycrystalline (Mg,Fe)O with varying Fe/Mg and Fe<sup>3+</sup> concentrations with run product characterisation using transmission electron microscopy, X-ray diffraction and Mössbauer spectroscopy. However electron microprobe measurements of the X-ray emission Lβ/Lα ratios showed up to 10% variation, likely due to the porous nature of the sample surfaces, so further synthesis was performed using a multianvil press to obtain single crystals. The reproducibility of Lβ/Lα measurements showed dramatic improvement, and experiments are continuing in order to generate a suite of high quality crystals over a wide composition range. The use of enriched <sup>57</sup>Fe enables Mössbauer measurements to be carried out on the same sample used for the electron microprobe measurements, and an ongoing parallel study on natural garnets shows promising results for this approach.

### References

[1] Höfer, H.E. and Brey, G.P. (2007) *Am. Min.*, in press