Hg isotopic composition in lichens: A new tool to monitor air quality and pollution sources

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Lichens are filters of atmospheric particulate and gaseous matter and well-known passive bio-monitors of air quality. Trace metal concentrations and isotopic ratios (Pb) contained in lichens were widely used to quantify, discriminate and monitor atmospheric emissions or depositions. Hg is an emerging isotope system and promising for our understanding of its biogeochemical cycle. Moreover, mass dependent (MDF) and non-mass dependent fractionation (NMF) of Hg isotopes can be used for source tracing of atmospheric mercury. Our goal is to show the potential of Hg isotopes measured in lichens to assess atmospheric sources and depositions, and the overall air quality at the local and global scale.

Lichens (43 samples from 20 sampling points) were sampled over a 7 year time span (2001-03-06-08) within and around a 300 000 inhabitants city in NE of France in a 15 km radius. The main wind directions are SW and NE. Except for one sampling point (see below), all lichens show a range of Hg concentrations from 80 to 200 ng.g^{-1} and of δ^{202}Hg (relative to NIST 3133) from -2 to -0.6 %, both homogeneous from year to year at a given locality. The isotopic composition varies systematically along a SW-NE section across the studied area, with δ^{202}Hg lower in rural sites (-2‰) and reaching -0.6‰ in the city centre.

We measured significant NMF in all samples, with negative $\Delta^{199\text{-}201}$Hg (-0.6 to -0.2‰). These cap-delta values also show a gradient along the SW-NE section, the more negative anomalies being in the outer part of the city. The data suggest a progressive contribution of direct anthropogenic sources from rural/sub-urban to urban sites. Lichens sampled in the SE corner of the area display a uniform isotopic composition (δ^{202}Hg = -1.00 ± 0.25‰, 2SD n=5 and $\Delta^{199\text{-}201}$Hg = -0.45 ± 0.20‰, 2SD n=5), within the overall measured range. In contrast, all lichens sampled in one locality of the NW corner (15 Km from downtown) have higher [Hg] (400 ng.g^{-1}) and positive δ^{202}Hg (+1.4 ± 0.2‰ 2SD, n=4). This could be attributable to the presence a nearby iron mining sites.

Present emission of methane, ethane and propane from Earth's degassing

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Contemporary geological sources of methane, including gas manifestations and microseepage from petroliferous (sedimentary) and geothermal areas, are the second most important natural emission of this gas to the troposphere (~53 Tg/y; [1]), after wetlands. It represents almost 10% of total methane emission into the atmosphere. Geo-methane emissions are now considered as a new class of greenhouse-gas source for the European (EMEP/COIRINAIR) and US (EPA) emission inventories. Global geo-methane emission estimates have recently been supported by top-down analysis based on the newly derived atmospheric fossil methane (radiocarbon-free) fraction of ~30% [1]. Six source categories must be considered: mud volcanoes, gas seeps (independent of mud volcanism), microseepage (diffuse exhalation from soil in petroleum basins), submarine seepage, geothermal (non-volcanic) manifestations and volcanoes. Marine seepage and microseepage are the largest sources (~20 and 10-25 Tg/y, respectively) and their uncertainties need to be reduced.

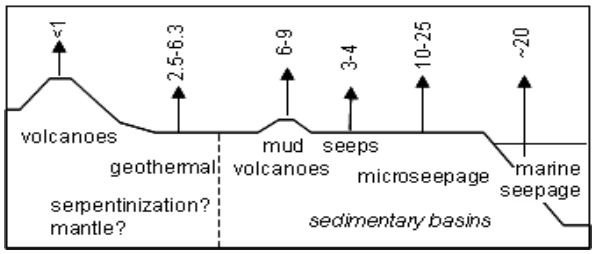

Figure 1: Global geo-CH_4 emission estimates (Tg CH_4/y).

Recently, a robust data-set consisting of methane, ethane and propane concentration in surface gas manifestations from 238 sites throughout the world, allowed to estimate a global geological output of ethane and propane in the order of 2-4 Tg y^{-1} and 1-2.4 Tg y^{-1}, respectively [2], i.e., Earth's degassing accounts for at least 17% and 10% of total ethane and propane emissions. Geologic seepage is therefore important not only for the greenhouse gas budget but also for emission of ozone precursors and photochemical pollutants. The atmospheric budget of hydrocarbons is not independent of geophysical processes of the solid Earth and planet degassing.

[1] Etiope *et al.* (2008) *Res. Geoph Lett.* **35**, L09307.
[2] Etiope & Ciccioli (2009) *Science* **323**, 5913, 478.