

## The stable isotope signature of CH<sub>4</sub> emissions from northern wetlands

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Stable isotope ratios of carbon and hydrogen from individual CH<sub>4</sub> sources have proven useful for interpreting the atmospheric CH<sub>4</sub> budget. However, effective use of isotope data for this purpose relies upon the accurate characterisation of isotope signatures from different sources and an understanding of processes that alter primary isotope ratios.

Natural wetlands contribute c. 20% of global CH<sub>4</sub> emissions per annum to the atmosphere and exhibit a wide range of stable isotope values. The purpose of this study was to determine the influence of methanogenic pathways on the <sup>13</sup>C value of CH<sub>4</sub> emissions from a range of wetland types. Flux rate and the <sup>13</sup>C value of CH<sub>4</sub> emissions were determined using sealed chambers. High resolution depth profiles of CH<sub>4</sub> and SCO<sub>2</sub> concentrations and δ<sup>13</sup>C values were measured in pore water collected using an in situ gas-water equilibration technique. Changes in the prevalence of the two main methanogenic pathways (acetate fermentation and CO<sub>2</sub> reduction) with depth in each wetland were determined by injection of <sup>14</sup>CH<sub>3</sub>COO<sup>-</sup> or H<sub>4</sub>CO<sub>3</sub><sup>2-</sup> into intact peat mini-cores, which were then incubated at in situ temperatures. High resolution profiles of SO<sub>4</sub><sup>2-</sup> in pore water also were measured to establish the depth at which secondary alteration of <sup>13</sup>C-CH<sub>4</sub> by methanotrophy could be considered negligible.

Data were collected from six wetlands located in England and Wales, consisting of raised, basin and blanket bogs, a valley mire and an intermediate fen. Initial sampling during spring months under high water-table level conditions yielded CH<sub>4</sub> emissions with highly <sup>13</sup>C-depleted signatures (δ<sup>13</sup>C = -94.2 to -74.8‰) and low emission rates (22 to 115 mg CH<sub>4</sub>/ m<sup>2</sup> day). The pore water concentration of CH<sub>4</sub> increased with depth at all sites; however, rates of methanogenesis determined using <sup>14</sup>C-labelled tracers were highest in shallow peat collected from just below the depth at which SO<sub>4</sub><sup>2-</sup> was largely removed from pore water by sulphate-reducing bacteria. The unusually low δ<sup>13</sup>C values of the CH<sub>4</sub> emissions appears to result from fractionation during transport through vascular flora because CH<sub>4</sub> in pore water to 75 cm depth was <sup>13</sup>C-enriched relative to CH<sub>4</sub> in surficial flux. Methane emissions typically were more <sup>13</sup>C-enriched in areas of each wetland where Sphagnum mosses comprised a greater proportion of groundcover relative to vascular flora.

## Mercury speciation in an estuary influenced by past mercury mining activities

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The tailings and contaminated soil in the Idrija region, the world's second largest mercury mining area, are continuously eroded and serve as a source for the river, the flood plain, and the Gulf of Trieste, Northern Adriatic Sea (Horvat et al. 1999, Covelli et al. 1999, Sirca et al. 1999, Hines et al. 2000). An assessment of the extent of contamination in the Gulf of Trieste after the closure of the Hg mine was made and mass balance calculated. Investigations in 2002 were focused on the biogeochemical cycling of mercury in the estuary of the river Sosa and the presentation will combine these results obtained with measurements performed in upstream areas and in the Gulf of Trieste.

### Discussion and results

The results in the estuary indicated that inorganic mercury was mostly bound to particulate matter, while monomethylmercury (MeHg) was present in the dissolved form, showing highest values in August (low water flow) and lowest in May (spring high water flow). Dissolved elemental Hg (DGM) in waters was highest in February (winter, low water flow). Bottom water layers were always higher, while the mixing layer low total Hg and MeHg was found. The presence of dimethyl-mercury (DMM) was also confirmed in bottom water layers. All forms of Hg except MeHg increased downstream.

### Conclusions

Seasonal and spatial variations in mercury speciation in the catchment, estuary and the marine environment indicate various biogeochemical factors responsible for Hg transport and transformations. Modeling of these processes remains very challenging tasks accompanied with large uncertainties, which can only be resolved with well planned research.

### References

- Covelli, S., Faganeli, J., Horvat, M., Brambati, A.: *Estuar. Coast. Shelf Sci.*, 48(4): 415-428 (1999).  
Hines, M.E., Horvat, M., Faganeli, J., Bonzongo, et al.: *Env. Res.* 83, 129-139. (2000)  
Horvat, M., Covelli, S., Faganeli, J., Logar, M. et al. *Sci. Tot. Environ.*, 237/238, 43-56 (1999).  
Sirca A, Horvat M, Rajar R, Covelli S, Zagar D, Faganeli J (1999) *Acta Adriat.* 40/2, 75-85.