

## Summary

Methane emissions from landfills are an important source of greenhouse gases. Landfill emissions are point emissions and in contrast to other sources, such as rice fields and cattle, they can be controlled more easily. Biological CH<sub>4</sub> oxidation in the aerobic cover layer can be a good alternative for gas collection and recovery systems, especially for old landfills where large investments are not feasible. The quantification of CH<sub>4</sub> oxidation is not an easy task because the emissions are not homogeneous and any disturbance of the cover layer changes the emission. Isotope measurements enable to make an estimate of the CH<sub>4</sub> oxidation efficiency without disturbing the soil but current isotope methods contain simplifications that result in large uncertainties.

For good quantification an accurate determination of the isotope fractionation factor ( $\alpha_{\text{ox}}$ ) of CH<sub>4</sub> oxidation, or the preference of the bacteria for lighter isotopes, is required. The calculation of  $\alpha_{\text{ox}}$  is based on independent batch experiments with soil samples from the landfill cover. Most studies so far used data analysis methods based on approximations of the Rayleigh model to determine  $\alpha_{\text{ox}}$ . In this study, the two most common approximations were tested, the simplified Rayleigh approach and the Coleman method. To do this, the original model of Rayleigh was described in measurable variables, CH<sub>4</sub> concentration and isotopic abundances, and fitted to batch oxidation data by means of a weighted non-linear errors-in-variables regression technique. The results of this fit were used as a benchmark to which the results of the two conventional approximations were compared. The Coleman approximation was shown to be acceptable but not recommended for C fractionation (error on  $\alpha_{\text{ox}} - 1$  up to 5%) and unacceptable for H fractionation (error up to 20%). The difference between the simplified Rayleigh approach and the exact Rayleigh model is much smaller for both C and H fractionation (error on  $\alpha_{\text{ox}} - 1 < 0.05\%$ ). There is also a small difference when errors in both variables (CH<sub>4</sub> concentration and isotope abundance) are accounted for instead of assuming an error-free independent variable. By means of theoretical calculations general criteria, not limited to CH<sub>4</sub>, <sup>13</sup>C, or D, were developed for the validity of the simplified Rayleigh approach when using labelled compounds.

It is usually assumed that the only fractionating process in landfill cover soils is the CH<sub>4</sub> oxidation itself. Recently it was shown that neglecting the isotope fractionation by diffusion results in underestimation of the CH<sub>4</sub> oxidation. In this study a simulation model was developed that describes gas transport and CH<sub>4</sub> oxidation in landfill cover soils. The model

distinguishes between  $^{12}\text{CH}_4$ ,  $^{13}\text{CH}_4$ , and  $^{12}\text{CH}_3\text{D}$  explicitly, and includes isotope fractionation by diffusion and oxidation. To evaluate the model, the simulations were compared with column experiments from previous studies. The predicted concentration profiles and isotopic profiles match the measured ones very well. Simulations with and without fractionation by transport show that fractionation by diffusive transport in this setup has a profound influence on the isotope profiles. Diffusion hides the oxidation and must therefore be accounted for in the calculation of  $\text{CH}_4$  oxidation based on isotopes. The classical isotope method does not account for that. Overall, the comparison shows that a model-based isotope approach for the determination of  $\text{CH}_4$  oxidation efficiencies is feasible and superior to existing isotope methods.

This research has spurred interest in dispersion at low gas velocities. In the model evaluation a significant dispersion effect was found in the stable isotope profile of  $\text{CH}_4$  in a landfill cover soil simulated in the lab. Current techniques to determine dispersivity of gas flow in porous media require multiple experiments and are restricted to flow velocities sufficiently high to observe significant mechanical dispersion effects. However, the difference between molecular diffusion and mechanical dispersion can have a significant influence on stable isotope signatures at low velocities as well because molecular diffusion leads to isotope fractionation, whereas mechanical dispersion does not. In this study a new method to determine the dispersivity of gas flow in porous media is developed using a single steady-state experiment. The determination is possible even at low gas velocity. The dispersivity was shown to be constant at approximately 1 mm at interstitial gas velocities of  $10^{-4}$  to  $10^{-3}$   $\text{m s}^{-1}$  but increases rapidly at lower velocities, and can be as high as 7 cm. It was shown that Fick's law with constant diffusion coefficients is not adequate for analyzing these data and that the Stefan-Maxwell equations must be used.

The  $\text{CH}_4$  oxidation and transport model was also tested on field data. Also in real landfill covers the model was able to fit the concentration profiles and isotopic profiles. Simulations indicate that the open system equation, which does not take into account diffusion fractionation, should give a better estimate for  $\text{CH}_4$  oxidation when applied on  $\delta\text{D}$  measurements instead of  $\delta^{13}\text{C}$  because the fractionation factor for oxidation is 10 times larger for deuterium than for carbon.

While current isotope method has shortcomings, it can still be used as a rough estimate with an underestimation of the oxidation percentage. If possible, D isotopes should be used and in

this case the fractionation factor should be calculated with the Rayleigh model and not the approximation by Coleman et al. (1981).