Reassessing reaction rates for TSR by experiments and modelling

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The large uncertainties in published kinetic rate data for the thermochemical reduction of sulfate (TSR) hamper the development of detailed geochemical modelling approaches to be included in e.g. basin modeling software for risk assessment. The scatter in of the reported activation energies or rate constants for TSR has several reasons:

Many experimental approaches suffer from a lack of control of crucial system parameters, such as pH and hydrogen fugacity during the experiment. In most studies the temperatures are above 320°C, which allows additional parallel reactions as e.g. thermal cracking of hydrocarbons. In addition, ignoring disproportionation reactions of initially added elemental sulfur inparts some published reaction rates based on sulphate concentrations.

In molecular modeling studies the calculated kinetic rate constants mainly depend on the choice of the interacting molecules, e.g. sulfate or bisulfate or contact-ion pairs of sulfate with different organic molecules.

We performed geochemical modeling, using Geochemist's Workbench® with a modified thermodynamic database and published kinetic data for several relevant sulfate-reducing reactions. Published experimental studies have been reinvestigated for the aforementioned effects (e.g. initial S).

Additionally, experiments in Dickson-type flexible gold bags and seald gold capsules have been carried out to test some commonly made assumptions about the order of the reaction with regard to hydrogen, sulfate, elemental sulfur and different organic compounds.

We find that the following parameter are critical in controlling the rate of TSR in addition to pH: levels of dissolved molecular hydrogen, presence of CH_3^* radicals produced during cracking, and the presence of S^* radicals.

A key question is whether there is one initial step of the TSR reaction – as assumed in the modeling studies – or whether there are several possible reducing agents for the hexavalent sulfur that are important in natural settings and hence have to be included in the geochemical modeling.

Isotopologue data reveal denitrification as the primary source of nitrous oxide at nitrogen fertilization gradient in a temperate agricultural field

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The microbial origin of nitrous oxide (N_2O) production in terrestrial ecosystems has long been debated. Both nitrification and denitrification produce N_2O but their relative importance remains uncertain. Here we apply site preference (SP – the difference in $\delta^{15}N$ between the central and outer nitrogen [N] atoms in N_2O), to estimate the proportion of N_2O from bacterial denitrification. Soil flux chambers were deployed at a N fertility gradient planted to winter wheat in a corn–soybean–winter wheat rotation at the Kellogg Biological Station Long-term Ecological Research site in SW Michigan. Fertilizer (28% urea ammonium nitrate) was applied to plots along the gradient in the spring of 2007 to obtain levels of 0, 134, and 246 kg N ha^{-1}. The average flux weighted $\delta^{15}N$-N_2O increased with increasing N fertilizer rate (-14.7, -12.3 and -9.1 ‰, for the 0, 134, and 246 kg N ha^{-1}treatments, respectively), whereas the $\delta^{18}O$ values decreased (33.2, 28.7 and 25.3 ‰, respectively). Weighted SP values for N_2O were low at all N rates (0.7, 4.0, and 3.8 ‰, respectively), which is consistent with a source of N_2O predominantly from denitrification. Consequently, we find that denitrification was the principal pathway of N_2O production in row–crop agricultural fields, irrespective of the rate of N fertilizer applied.