The effect of sorption on chlorine stable isotopes of TCE

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Chlorinated solvents are one of the most common groundwater contaminants, occupying 12 out of the top 20 places of the most hazardous organic compounds encountered in groundwater. Accidental spills that occur during production, storage or transportation activities along with their chemical stability made them one of the most ubiquitous and recalcitrant pollutants of groundwater and soil [1].

In the last 10 years, compound-specific carbon stable isotopes have been increasingly used as an indicator of chemical and biological degradations of chlorinated solvents in groundwater [e.g. 2, 3, 4]. More recently, compound-specific chlorine stable isotopes are being used to investigate the behavior of these compounds [5, 6].

In order to accurately interpret isotopic data obtained for chlorinated solvents in groundwater systems, the isotopic effects of subsurface processes must be well understood. The majority of the previous studies that used compound-specific stable isotopes (mainly carbon isotopes) to distinguish different plumes (i.e., fingerprinting) and trace them back to the release source point [e.g. 7, 8] assumed that isotopic fractionations associated with physical processes such as sorption and diffusion are negligible. These assumptions were based on studies conducted on carbon stable isotopes such as [e.g., 9]. During this study, the effect of sorption on chlorine stable isotopes of TCE on various media was investigated by conducting batch experiments. The preliminary data obtained from the experiments showed that sorption is often associated with a measurable isotopic fractionation of chlorine stable isotopes unlike the negligible fractionation of carbon stable isotopes reported previously and confirmed during the recent study.

[1] Alvarez & Illman (2006) *Bioremediation and Natural Attenuation*, John Wiley & Sons, 609 pp. [2] Hunkeler *et al.* (1999) *ES&T* **33**, 2733-2738. [3] Sherwood Lollar *et al.* (1999) *Org Geochem*. **30**, 813-820. [4] Elsner *et al*., (2007) *ES&T* **41**, 4111-4117. [5] Shouakar-Stash *et al.* (2006) *Appl Geochem* **21** 6-781. [6] Aby *et al.* (2009) *ES&T* **43**, 101-107. [7] Hunkeler *et al.* (2004) *J Contam Hydrol* **74**, 265- 282. [8] Chartrand *et al*. (2005) *ES&T* **39**, 1064-1070. [9] Slater *et al.* (2000) *Analyt Chem* **72**, 5669-5672.

How to feed the deep biosphere in a continental sedimentation basin

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The Sanhu Depression of Qaidam Basin lies in western China and is a prolific region of biogenic gases with a proved reserve of 300 bil steres. The microbiological survey demonstrates that abundance microbes occur unlimitedly from surface to depths of 2400 m. The origin of the nutrient for such a deep biosphere is still unclear. Whatever the origin of the substrate is, they should be solved in the water before microbial metabolism. Therefore, as an alternative nutrient, the distribution of soluble (reactive) organic matter should be important in the investigation of nutrient origin.

The ROC (reactive organic carbon) content was investigated by ultrasonic extraction of sedimental samples in the 6 N HCl solution. To understand the effect of early diagenesis, a part of samples were heated at 80°C before extraction. Three phenomena were clearly observed: (1) ROC content at a constant temperature decreases with the increasing depths of samples. The lower part should be attributed to the microbial consume; (2) For a same sample, ROC content of the sample heated at 80°C is dramatically higher than that without heated. For some samples, the increments are twice as much as the value of samples without heated in our experiment condition; (3) Prolonging heating time at 80°C could enhance the ROC content.

Two conclusions could be drawn: (1) The dramatically increasing ROC content by thermal action to organic matter should be the major nutrient substrate for deep biosphere in most continental basins [1]; (2) The nutrient supplied during early diagenesis could be kinetic modelled. That could help us to understand how and when the biogenic gases formed in a special geological condition.

[1] Horsfield B. *et al*. (2006) *EPSL*, **246**, 55-69.