

## Isotopic evidence for TCE co-metabolism stimulated by electron donor addition to groundwater

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For more than 10 years, electron donor has been injected into the Snake River aquifer beneath the Test Area North site of the Idaho National Laboratory of eastern Idaho for the purpose of stimulating microbial reductive dechlorination of the trichloroethene (TCE) in the groundwater. This has resulted in significant removal of TCE from the source area of the contaminant plume. It has also led to highly elevated concentrations of dissolved CH<sub>4</sub> in the groundwater extending for more than 200 m down gradient from the injection well. The δ<sup>13</sup>C values of dissolved CH<sub>4</sub> in the groundwater increase from -55‰ in the source area to -18‰ with distance from the injection well whereas the δ<sup>13</sup>C values of dissolved inorganic carbon decrease from 8‰ to -13‰, indicating a shift from methanogenesis to methane oxidation in the plume. This change in microbial activity is confirmed by PhyloChip microarray analyses of the 16S rRNA genes obtained from microbial communities within the groundwater. Accompanying this change in microbial populations is also a decrease in the abundance of dechlorinating microorganisms (e.g., *Dehalococcoides ethenogenes*) and an increase in organisms known to be capable of aerobic cometabolism of TCE (e.g., *Methylosinus trichosporium*). Incubation experiments with <sup>13</sup>C-labeled TCE introduced into microcosms containing basalt and groundwater from the aquifer confirm that co-metabolism of TCE is occurring. The capacity of this system to degrade TCE determined from these experiments is estimated at approximately 7.5 μg of TCE per liter of water. The results of this study suggest that the change from anaerobic to aerobic microbial activity in the distal portions of groundwater TCE plumes undergoing electron donor addition to stimulate reductive dechlorination of TCE could lead to co-metabolism of TCE, further limiting the spread of the plume.

## Atomistic simulation of the crystallisation and growth of calcium carbonate nano-particles

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Atomistic simulation of nano-particles is important because it allows the size and shape-dependence of their structure and thermodynamic properties to be studied directly. In this paper we report on four broad areas of work modelling the stability, aggregation and nucleation of CaCO<sub>3</sub> nano-particles.

We have simulated nano-particles of sizes ranging from 18 to 324 formula units, in vacuum and in water [1], from which it is clear that the breakdown of structural order in the smaller particles is caused by the rotation of CO<sub>3</sub><sup>2-</sup> groups on the surface when there is little bulk mineral to stabilise the structure. When water is present, the surface ions bond to the water in the first hydration layer and thus are prevented from rotating to the same extent. The structure of the water close to the particle is strikingly similar to that previously seen when considering infinite planar surfaces.

In an attempt to extend this initial work we have begun to consider how such nano-particles aggregate to form macro-sized particles. Initially we have considered eight particles consisting of 75CaCO<sub>3</sub> units, both in vacuo and in solution, using a combination of potential of mean force and conventional molecular dynamics. Initial results suggest that if one face each particle is doped with Mg<sup>2+</sup> the particles aggregate so as to maximise the amount of Mg<sup>2+</sup> on the surface of the resulting combined particle.

At the other end of the scale it is also possible to use molecular dynamics to investigate the processes of cluster formation and growth of CaCO<sub>3</sub> from aqueous solution [2].

The influence of both temperature and concentration have been studied and, using a combination of order parameters we can relate the clusters that form to the structure of the larger nano particles, considered in our earlier work.

Finally we have begun to use meta-dynamic methods to study these systems over longer time-scales than can be accessed via standard simulation methodologies.

[1] Cooke & Elliott (2007) *J Chem. Phys.* **127**, 104706.

[2] Hamad, Cristol & Catlo (2005) *J. Am. Chem. Soc.* **127**, 2580.