Abiotic transformation of perchloroethylene by manganese oxide

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Perchloroethylene (PCE) is an important contaminant of world soil, air, and water systems with effects on aquatic life and humans. Thus, its reactivity with soil minerals is an important issue. Batch experiments were performed to examine the synergistic effect of sorbed hexanes on the degradation of PCE by MnO_2. The amount of PCE adsorption on the surface of synthetic hydrous (10% water) MnO_2 was estimated from the rapid initial loss of PCE from the headspace. Analysis of head space gases was by GC-FID and GC. In the absence of hexanes, no reaction was observed, however in the presence of hexanes, a reaction took place at ambient temperature. The products are mainly methane, ethylene, vinyl chloride and CO_2, all in trace amounts. PCE disappearance is rapid ($t_{1/2}$~10 min at 30°C), independent of whether O_2 is present or not. The reactivity depended on both the amount of hexanes present and MnO_2. The activation energy of the reaction was measured to be 16.04 KJ mol^{-1}, low enough to indicate that the reaction might be diffusion controlled. Manganese oxide reduction is a minor reaction, and the hexane appears be consumed in the process. The reaction by PCE with MnO_2 proceeds via a redox mechanism that is currently under investigation. Thus, synthetic crystalline MnO_2, which is similar in structure to a common soil constituent, is found to promote degradation of PCE at 30°C, via possibly a redox mechanism. Furthermost, the reaction shows degradation under ambient environmental conditions. We are currently fine tuning the catalyst (by surface engineering) to increase product yield and provide the basic data necessary to develop new strategies for abiotic remediation of PCE-contaminated soil and sediments.

CH_4 emission, production and their $\delta^{13}C$ values in submerged rice soil as influenced by elevated atmospheric CO_2 concentration

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An experiment was carried out in six controlled-environment chambers to study the effects of elevated CO_2 on CH_4 emission from a submerged rice soil. In three chambers, CO_2 concentration was maintained at 350 µmol mol^{-1} (ambient CO_2), while in another three, CO_2 was controlled at 650 µmol mol^{-1} (elevated CO_2) throughout a rice growing season from May 15 to September 30, 2002. At the tiller, panicle formation and early grain filling rice growth stages, 413‰ $\delta^{13}C$-CO_2 was fed to all chambers for each 3 days. The samples of plant, soil, soil solution, emitted CH_4 and dissolved CH_4 and CO_2 in flooding water and soil solution were sampled before and after the feeding. The $\delta^{13}C$ values of all samples were measured by an IRMS (MAT 252, ThermoFinnigan) interfaced with GC-C (HP 5890), PreCon/GC-C and EA (EA1108, Fisons).

Elevated CO_2 significantly decreased CH_4 concentration in the submerged paddy soil during early rice growth stage (from June to July) where the most CH_4 originated in soil organic matter and applied rice straw. However, elevated CO_2 increased CH_4 concentration in the soil and CH_4 emission to the atmosphere during the later rice growth stage (from August to September) where the most CH_4 originated in rice. Elevated CO_2 increased bubble volume in the submerged paddy soil, the concentration and amount of CH_4 also increased by elevated CO_2. The changes in $\delta^{13}C$ values between before and after 413‰ $\delta^{13}C$-CO_2 feeding indicated that rice roots exudates are the dominant substrate for CH_4 production in the submerged rice soil.

The increase in CH_4 emission by elevated CO_2 was significant during later rice growth stage, regardless of transport pathways, either plant mediated or ebullition-diffusion, in the pot experiment. The CH_4 dissolved in flooding and soil solution also showed same trend with CH_4 emission. The emitted CH_4 by ebullition-diffusion accounted for 7.5 and 6.7 % of total emission under ambient and elevated CO_2 conditions respectively. The results of enriched ^{13}C-CO_2 feeding indicated that a large proportion of emitted CH_4 was supplied from plant exudates in the case without rice straw application.