Potential Atmospheric Contributions of Methane From Fractured Bedrock Aquifers

Along with carbon dioxide (CO_2), nitrous oxide (N_2O), and chlorofluorocarbons (CFCs), methane (CH_4) concentrations in the atmosphere have increased markedly since the industrial revolution *[Ledley et al., 1999]*. These so-called greenhouse gases, along with water vapor, are generally considered to be the major players in the current global warming trend. Just how much of the global warming is due to anthropogenic contributions has not been resolved; however, recent increases in the atmospheric concentration of methane are undeniable. The bulk of the atmospheric methane increase has been attributed to [i] burning of fossil fuels and biomass, [ii] wetlands and flooded crops, [iii] natural gas seeps, and [iv] emissions from domesticated animals and landfills.

The presence of methane in groundwater is due to either thermogenic or biogenic sources. Thermogenic methane is generally confined to very deep aquifers that contact oil/gas reservoirs, and is eventually released into the overlying geologic or aqueous (e.g., marine) environments *[Cramer et al., 1999]*. Biogenic sources result from the anaerobic degradation of organic matter that either is lain down with the geologic strata or infiltrates through overlying soils. Methane released from groundwater is not usually considered to be an important atmospheric contributor because of its oxidation within near-surface aerobic soils. Of course, this truism does not apply to groundwater that is pumped to the surface and used for irrigation or other purposes, permit-ting the direct volatilization of methane from water to air *[Watanabe et al., 1994]*.

In this short research communication, I will confine my comments to unconfined groundwater aquifers. Methane produced in unconfined groundwater must partition into the overlying soil gas and diffuse through the unsaturated zone toward the atmosphere. If the soils overlying groundwater aquifers are relatively dry (i.e., moist but not saturated), they act as an efficient sink for methane. In fact, methanotrophic microorganisms in near-surface soils (e.g., forests) are so efficient that they are able to biodegrade the very low concentrations of methane that diffuse from atmospheric air into the soil gas. These terrestrial soils act as a consumer, rather than as a producer, of atmospheric methane *[Castro et al., 1995]*. Methanotrophic microorganisms in soils oxidize the methane to CO_2, which is then released to the atmosphere as the major biogenic gas associated with subsurface degradation processes.

Besides methane oxidation, the contribution of groundwater-produced methane to the atmosphere is limited by the concentration of degradable organic carbon. Naturally-derived fulvic acids are ubiquitous DOC (dissolved organic carbon) constituents of groundwater; however, they are generally quite refractory and limited in their role as methanogenesis precursors *[Aravena and Wassenaar, 1993]*. Both aceto-trophic (i.e., acetate fermenting) and

CO_2-reducing (i.e., hydrogen oxidizing) methanogens operate under highly reduced conditions. In most ground-water systems, the concentration of degradable organic substrates is insufficient to lower redox conditions into this methane-producing range. As a consequence, more oxidative processes such as iron and sulfate reduction serve as the predominant biodegradation pathways for natural organic matter in aquifers.

Preliminary results from a current research project suggest that there may be exceptions to the dogma regarding atmospheric contributions of methane by unconfined groundwater aquifers. These exceptions are related to both post-industrial human practices and to a unique set of hydrogeologic conditions. The normally limited supply of de-gradable organic carbon to groundwater has been augmented by the post-industrial practice of storing and transporting liquid petroleum products in the subsurface. This practice has resulted in the local introduction of organic carbon at concentrations that are orders-of-magnitude higher than the natural background. These petroleum products not only serve as an excellent substrate for biodegradation, they also create a substantial oxidative demand that rapidly shifts redox conditions into a range that favors methanogenesis in lieu of (or in addition to) the more oxidative biodegradation pathways.

When the methane-producing ground-water is overlain by fractured bedrock, rather than by unconsolidated porous media, the opportunity for methano-trophic organisms to oxidize the methane may be diminished. Upward movement of methane through discrete fractures limits the volume of soil into which CH_4 diffuses and reduces the surface area available for methano-trophic activity. Methanotrophs require inorganic nitrogen and other nutrients *[de Visscher et al., 1999]*, which are often limiting in the coarse-grained soils created by surface weathering of consolidated rock.

Preliminary results indicate that petroleum-contaminated groundwater in fractured bedrock may create another situation where post-industrial practices contribute to the atmospheric loading of CH_4. The spatial distribution of methane in thin surface soils overlying bedrock suggests that methane flow through fractures or fracture networks does indeed occur. Moreover, a comparison CH_4 and CO_2 flux rates from ground-water with those from the ground surface indicates that while most of the aquifer-produced methane is oxidized before reaching the atmosphere, the oxidation efficiency is at least a factor of 50 less in these fractured rock settings than in nearby unconsolidated soils. Because the methane uptake capacity of these thin surface soils has not yet been measured, it is unknown whether the reduced oxidation efficiency is related to soil properties, methanotroph activity, gas-phase migration dynamics, or other unidentified factors.

Atmospheric flux rates associated with the petroleum-contaminated aquifer were on the order of several milligrams of carbon (as CH_4) per square meter per day (mgC/m^2-day), which is sub-stantially less than that reported for major sources. For example, methane flux rates from landfills may exceed 10^6 mgC/m^2-day *[de Visscher et al., 1999]*, while those from wetlands and rice

paddies peak at several hundred mgC/m^2-day *[Kagotani et al., 1996]*. Nonetheless, the preliminary data suggest these methane production rates equal or exceed consumption rates that have been reported in the literature for various soils *[Kagotani et al., 1996; Castro et al., 1995]*. As previously noted, atmospheric methane consumption refers to process whereby the CH$_4$ flux is actually into (rather than out of) soils, where methane is converted to CO$_2$ and microbial biomass.

Although atmospheric methane contributions from contaminated aquifers overlain by fractured rock are certainly minimal on a worldwide basis, they may constitute an important localized source and they definitely have the potential of shifting soils from a sink to a source of atmospheric methane. This shift is of particular importance where buildings are constructed over contaminated groundwater, permitting methane to diffuse vertically and accumulate within structures. This potential problem is exacerbated by site grading activities that tend to disturb the bacterial community (including methanotrophs) and temporarily inhibit methane oxidation in shallow soils. Finally, the atmospheric contribution of groundwater-generated methane may represent yet another mechanism by which greenhouse gases are produced from liquid petroleum products.

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