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The hydrogeochemistry of methane: Evidence from English groundwaters

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Abstract

The presence of methane (CH_4) in groundwater is usually only noticed when it rises to high concentrations; to date rather little is known about its production or natural 'baseline' conditions. Evidence from a range of non-polluted groundwater environments in England, including water supply aquifers, aquicludes and thermal waters, reveals that CH_4 is almost always detectable, even in aerobic conditions. Measurements of potable waters from Cretaceous, Jurassic and Triassic carbonate and sandstone aquifers reveal CH_4 concentrations of up to 500 μg/l, but a mean value of <10 μg/l. However, aquiclude and thermal waters from the Carboniferous and Triassic typically contain in excess of 1500 μg/l. Such high concentrations have so far only been found at redox (Eh) potentials below 0 mV, but in general CH_4 concentration and Eh value are poorly correlated. This suggests a lack of thermodynamic equilibrium, which is confirmed by comparing pe values calculated from the redox couple C(4)/C(−4) with those derived from Eh. Genesis of CH_4 appears to occur on two timescales: a rapid if low rate of production from labile carbon in anaerobic microsites in the soil, and a much longer, millennium scale of production from more refractory carbon. Methane is rarely measured in groundwater; there is no single ionic determinand which acts universally as a proxy, but a combination of high HCO_3 and low SO_4 concentrations, or the reverse, is an indication that high amounts of CH_4 may be present.

Keywords: Methane; Aquifers; Redox; Carbon isotopes; Chalk; Limestone; Sandstone

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1. Introduction

There are three reasons to study the occurrence of methane (CH_4) in groundwaters: (i) as part of the contribution to the atmospheric budget ('emissions'), (ii) as a potential explosive hazard ('safety'), and (iii) more fundamentally its production characteristics. For the UK, emissions and safety have been addressed by Gooddy and Darling (2005). The present paper complements that approach by considering the third factor via a detailed study of hydrogeochemistry of a range of groundwater types.

The presence of CH_4 in groundwater is usually only noticed when it rises to problem concentrations. These have on occasion caused explosive incidents in Europe and North America (e.g. Altnöder and Hutter, 1981; Buswell and Larson, 1937; Kelly et al., 1985). In some of these cases it is clear that CH_4 has leaked into the groundwater from adjacent strata, whereas in others the origin is less evident. In the UK rather little appears to be known about the occurrence of CH_4 in groundwater beyond a few high-profile incidents (Hooker and

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Bannon, 1993; HSE, 2000). The present paper is not concerned with such incidents but instead focuses on 'baseline' conditions by looking at regional distributions of dissolved CH_4 and the differences between aquifer types. A knowledge of typical background CH_4 concentrations will inter alia provide a more secure context for the interpretation of future methane survey or incident data, particularly for NW Europe where similar aquifer types are exploited.

2. Background

2.1. Occurrence of methane

Apart from some rather specific instances, such as the supposed 'abiogenic' CH_4 in ophiolite complexes or crystalline shield rocks (Neal and Stanger, 1983; Sherwood et al., 1988), most CH_4 finding its way into groundwater has been produced from organic matter, either via thermal ('thermogenic') or bacterial ('biogenic') mediation (Schoell, 1988). Thermogenic CH_4 is associated with many petroleum reservoirs or natural gas fields and also with their storage and distribution systems (Barker and Fritz, 1981; Kelly et al., 1985). Biogenic CH_4 has been documented in anaerobic groundwater environments, including peat bogs, lignite deposits, and glacial, lacustrine and eolian sediment (Barker and Fritz, 1981; Coleman et al., 1988; Grossman et al., 1989).

The origin of CH_4 in groundwater systems can be deduced using several lines of evidence. Simple hydrochemical methods in the field or laboratory can often be used to determine origins (Games and Hayes, 1976; Jakobsen and Postma, 1999). Where these are more cryptic, study of the gas phase itself may be necessary. For example, the presence of C_{2+} hydrocarbons in significant proportion indicates a thermogenic origin for the gas, while microbial CH_4 rarely contains detectable hydrocarbons higher than ethane, and typically has very high C_1/C_2 ratios (Barker and Fritz, 1981). Carbon stable isotope ratios can be diagnostic of 'light' biogenic or 'heavy' thermogenic or abiogenic origins (Schoell, 1988).

Traditionally CH_4 has been predicted to occur in groundwaters only when conditions are sufficiently reducing (e.g. Edmunds et al., 1984), otherwise oxidation should occur (Smith et al., 1991). In effect this implies a necessity for confined aquifer conditions where dissolved oxygen (DO) concentrations have been reduced to significantly less than the normal detection limit of 0.1 mg/l. In practice, the present study shows that groundwater CH_4 is almost ubiquitously present above detection limit whether the aquifer is confined or not.

This wide distribution of CH_4 in English aquifers suggests an origin predominantly via bacterial activity rather than from thermogenic ('natural gas') or abiogenic ('deep methane') quasi-point sources, for which there is generally little evidence (though instances of gas seepage in locations not covered in this study are recorded by Selley, 1992). Bacterial (or biogenic) CH_4 can be produced via two routes: decarboxylation (fermentation) of acetate, or reduction of CO_2 (Whiticar et al., 1986). The first of these produces both CH_4 and CO_2, the second CH_4 only. The difference between these processes has implications for $\delta^{13}C$ distributions (e.g. Clark and Fritz, 1997), but most baseline CH_4 concentrations are too low (i) to allow the determination of $\delta^{13}C_{CH4}$ and (ii) to have a significant effect on DIC (dissolved inorganic carbon) in concentration or isotopic terms.

In order to produce CH_4, methanogenic bacteria require an absence of oxygen. Particularly where aquifers are unconfined, there is likely to be O_2 available in both the saturated and unsaturated zones. However, in both zones it is possible for anaerobic 'hot spots' to develop around organic matter (Murphy et al., 1992), when the uptake of O_2 exceeds the rate of its diffusivity (Vinten et al., 1996). This might permit production of CH_4 at a low rate.

Both acetate fermentation and CO_2 reduction processes may proceed simultaneously (Conrad, 1999) but neither is a very thermodynamically favourable reaction (Chapelle, 1993). Generally, acetate fermentation is the primary pathway for methane formation in lake sediments (Kuivila et al., 1989), whereas CO_2 reduction tends to dominate in marine sediments (Hoehler et al., 1994). The reason for this is that sulphate is abundant in seawater and its reduction in marine sediments is an important precursor for methanogenesis and is responsible for most acetate metabolism (Whiticar, 1999). Reduction of CO_2 can only occur where conditions are sufficiently reducing to produce H_2, a situation typical of environments such as landfills or peat bogs (Lansdown et al., 1992). For most groundwaters, therefore, acetate fermentation appears to be a more likely route to CH_4 production (e.g. Chapelle, 1993), although CO_2 reduction has been identified as the dominant process in certain cases (e.g. Barker and Fritz, 1981; Aravena et al., 1995).

Data are compared from six groundwater environments: the Chalk (Upper Cretaceous), the Lower Greensand (Lower Cretaceous), the Lincolnshire Limestone (Middle Jurassic), the Sherwood Sandstone (Triassic),