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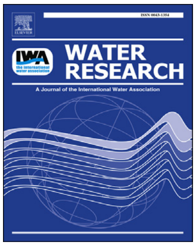

Evaluating degradation of hexachlorcyclohexane (HCH) isomers within a contaminated aquifer using compound-specific stable carbon isotope analysis (CSIA)

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ABSTRACT

The applicability of compound-specific stable carbon isotope analysis (CSIA) for assessing biodegradation of hexachlorocyclohexane (HCH) isomers was investigated in a contaminated aquifer at a former pesticide processing facility. A CSIA method was developed and tested for efficacy in determining carbon isotope ratios of HCH isomers in groundwater samples using gas chromatography – isotope ratio mass spectrometry (GC-IRMS). The carbon isotope ratios of HCHs measured for samples taken from the field site confirmed contaminant source zones at former processing facilities, a storage depot and a waste dump site. The ^{13}C-enrichment in HCHs provided evidence for biodegradation of HCHs especially downstream of the contaminant source zones. CSIA from monitoring campaigns in 2008, 2009 and 2010 revealed temporal trends in HCH biodegradation. Thus, the impact and progress of natural attenuation processes could be evaluated within the investigated aquifer. Calculations based on the Rayleigh-equation approach yielded levels of HCH biodegradation ranging from 30 to 86 %. Moreover, time- and distance-dependent *in situ* first-order biodegradation rate constants were estimated with maximal values of 3×10^{-3} d^{-1} and 10×10^{-3} m^{-1} for α-HCH, 11×10^{-3} d^{-1} and 37×10^{-3} m^{-1} for β-HCH, and 6×10^{-3} d^{-1} and 19×10^{-3} m^{-1} for δ-HCH, respectively. This study highlights the applicability of CSIA for the assessment of HCH biodegradation within contaminated aquifers.

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1. Introduction

Persistent organic pollutants (POPs) are a major contaminant group of subsurface compartments and pose substantial environmental and health risks (Minh et al., 2006; Weber et al., 2011). Hexachlorocyclohexane (HCH) isomers are globally dispersed POPs as a result of the production and application of HCH containing pesticides. HCHs cause substantial environmental impacts and are widespread in soil and groundwater (Bhatt et al., 2009; Vijgen et al., 2011). Due to their combination of toxicity and environmental persistence, the commercial production and use of HCHs has been regulated by the Stockholm Convention on POPs since 2004 and the production of the three main HCH isomers (α, β & γ-HCH) has been banned since 2009 (Vijgen et al., 2011). This measure may limit future risk from HCH contamination. However, significant impact still exists due to the extensive use of HCHs in the past, as well as the ongoing production and application of Lindane (γ-HCH) in several countries. Stockpiles from previous manufacturing and leachates from dump sites into groundwater lead to serious point source contaminations of HCHs which require management strategies (Bhatt et al., 2009; Vijgen et al., 2011). An appropriate strategy might be *Monitored Natural Attenuation* (MNA) consisting of regular evaluation of the extent and sustainability of intrinsic processes leading to the reduction of the risk and amount of a contamination (US-EPA, 1999). Since biodegradation can cause a sustainable and efficient decrease in pollutant mass, it is an important natural attenuation process and needs to be taken into account for MNA strategies (Bombach et al., 2010; Illman and Alvarez, 2009; Wiedemeier et al., 1999).

Biodegradation is a sustainable removal process of HCHs in the subsurface (Bhatt et al., 2009) and a cost efficient alternative to physico-chemical remediation of HCH contaminated groundwater and soils (Alvarez et al., 2012; Langenhoff et al., 2013; Phillips et al., 2006). The molecular structure of the HCH isomers plays a key role in biodegradation as it has been shown that α and γ isomers are degraded faster than β and δ isomers (Lal et al., 2010; Mehboob et al., 2013). However, concentration-based assessment of *in situ* pollutant biodegradation within contaminated aquifers is limited, because the concentration of contaminants can also be significantly decreased by physical processes like volatilization, sorption, dilution and dispersion. Thus, the decline of pollutant concentrations can only provide indirect indication for *in situ* pollutant biodegradation. In order to directly prove pollutant biodegradation, advanced tools are recommended (Bombach et al., 2010; Illman and Alvarez, 2009).

One of the most promising tools for monitoring *in situ* biodegradation of organic contaminants in aquifers is compound-specific stable carbon isotope analysis (CSIA) (Meckenstock et al., 2004). Molecules with light carbon isotopes (^{12}C) in the reactive position require less energy for bond cleavage and, thus, tend to be degraded faster than molecules containing a heavy carbon isotope (^{13}C), resulting in an ^{13}C-enrichment in the remaining stock of the pollutant. This process is called stable isotope fractionation and can be detected via changes in carbon isotope ratios (^{13}C/^{12}C, most commonly given as δ^{13}C) of a pollutant toward more positive δ^{13}C-values. Therefore, CSIA allows for the assessment of pollutant biodegradation based on the degree of carbon isotope fractionation observed at a contaminated field site.

In laboratory studies, significant changes in carbon isotope ratios have been observed for HCH biodegradation under both oxic and anoxic conditions. Anaerobic degradation exhibited higher carbon isotope fractionation of HCHs than aerobic degradation (Badea et al., 2011, 2009; Bashir et al., 2013). However, the applicability of CSIA has not previously been demonstrated for the evaluation of *in situ* biodegradation at a HCH-contaminated field site.

In this study, CSIA was applied for assessing biodegradation of HCHs in a contaminated aquifer. Besides hydrogeochemical parameters and pollutant concentrations, carbon isotope ratios of HCHs were measured for three monitoring campaigns taking place in 2008, 2009 and 2010, in order to determine the progress and sustainability of HCH biodegradation. To our best knowledge, this is the first study which addresses the use of CSIA for assessing the fate of HCHs within a groundwater system.

2. Materials and methods

2.1. *Field site*

2.1.1. *Site history*

The field site is located in the area of a former pesticide formulating plant that included both a formulation site and a packaging facility. The pesticide formulation began in 1935 and continued for more than five decades. The pesticide products prepared at the site were mainly HCH-based but also included other pesticides, e.g. dichlorodiphenyltrichloroethane (DDT). As known from historical information, HCH was not produced on-site, but technical HCH was purchased from suppliers and γ-HCH was purified for use in pesticide formulation. HCH contamination of soil and groundwater were mainly caused by losses of HCH-containing raw materials and products during purification, pesticide formulation and storage as well as irrigation and dumping of production-related wastes.

2.1.2. *Hydrogeology*

The highest pollutant concentrations were found within the upper quaternary aquifer, which consists of 12–15 m thick (glacio-) fluvial sand and gravel deposits. This aquifer is largely separated from the underlying tertiary aquifer by a 30 m thick clay- and coal-bed layer. The lower aquifer exhibits almost no contamination. The mean effective groundwater flow velocity of the upper aquifer was estimated at 0.3 m/d. The matrix of the upper aquifer displayed a low organic carbon content of only 0.014 %, thus minor retardation of HCHs is expected (Lotse et al., 1968).

In the early decades of the 20th century, drainage measures were initiated to facilitate nearby mining activity, which led to a lowering of the groundwater table and a reversal of groundwater flow direction in the area of the field site. Groundwater resurgence and realignment to the previous groundwater flow direction have occurred since the termination of these measures in the early 1990s. During the last