



Multi-element compound specific stable isotope analysis of chlorinated aliphatic contaminants derived from chlorinated pitches

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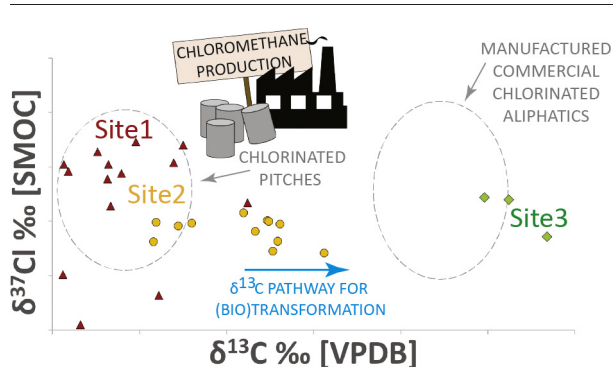
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HIGHLIGHTS

- $\delta^{13}\text{C}$ of chloroethenes from chlorinated pitches was strongly depleted at two sites.
- $\delta^{37}\text{Cl}$ and $\delta^2\text{H}$ of chloroethenes from pitches were similar to commercial compounds.
- Multi-element CSIA allowed detecting transformations following protection measures.
- Data from CSIA allowed a conviction for water poisoning and environmental disaster.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 2 March 2018

Received in revised form 22 May 2018

Accepted 23 May 2018

Available online xxxx

Editor: Yolanda Picó

Keywords:

Chlorinated aliphatics

Source apportionment

CSIA

Chlorinated pitches

Bussi sul Tirino

Ferrara

ABSTRACT

Tetrachloroethene and trichloroethene are typical by-products of the industrial production of chloromethanes. These by-products are known as “chlorinated pitches” and were often dumped in un-contained waste disposal sites causing groundwater contaminations. Previous research showed that a strongly depleted stable carbon isotope signature characterizes chlorinated compounds associated with chlorinated pitches whereas manufactured commercial compounds have more enriched carbon isotope ratios. The findings were restricted to a single case study and one element (i.e. carbon). This paper presents a multi-element Compound-Specific Stable Isotope Analysis (CSIA, including carbon, chlorine and hydrogen) of chlorinated aliphatic contaminants originated from chlorinated pitches at two sites with different hydrogeology and different producers of chloromethanes. The results show strongly depleted carbon signatures at both sites whereas the chlorine and the hydrogen signatures are comparable to those presented in the literature for manufactured commercial compounds. Multi-element CSIA allowed the identification of sources and site-specific processes affecting chloroethene transformation in groundwater as a result of emergency remediation measures. CSIA turned out to be an effective forensic tool to address the liability for the contamination, leading to a conviction for the crimes of unintentional aggravated public water supply poisoning and environmental disaster.

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1. Introduction

Contamination of groundwater by CAHs (Chlorinated Aliphatic Hydrocarbons) is widespread in many countries (Moran et al., 2007; Rivett et al., 1990; Scheidleder et al., 1999). Chlorinated ethenes such as tetrachloroethene (PCE) and trichloroethene (TCE) are often ubiquitous in the aquifers of urban and periurban areas where mixing and overlapping of different point-source plumes create a distribution pattern more similar to that of diffuse sources than to a point contamination (Alberti et al., 2017; Balderacchi et al., 2014; Graber et al., 2008; Yu et al., 2015; Zogorski et al., 2006). Consequently, the source apportionment becomes a challenging and essential task to address the liability for the contamination and the remediation costs according to the “polluter pays principle” (see Directive 2004/35/EC on Environmental Liability).

Compound Specific Isotope Analysis (CSIA) is an effective tool to apportion the source of groundwater contamination (Hunkeler, 2016; Morrison and Murphy, 2013; Schmidt et al., 2004). The isotopic signature of contaminants may reflect the production process of a compound, in terms of identification of the producer or of the production stock, or the origin of raw materials utilized in the process (Beneteau et al., 1999; Ertl et al., 1998; Hunkeler et al., 2005; Shouakar-Stash et al., 2003). Concerning CAHs, up to the 1970s their production as commercial compounds was based upon chlorination of acetylene (C_2H_2) obtained by lime (CaO), coal (C) and water as raw materials (Doherty, 2000a; Doherty, 2000b; Doherty, 2012). The $\delta^{13}C$ composition of organic carbon in coal is typically in the range of -23 to -29% (Bechtel et al., 2008; Elswick et al., 2007; Gleason and Kyser, 1984; Hohnes and Brownfield, 1992; Jeffery et al., 1955; Rimmer et al., 2006; Singh et al., 2012). More recent production methods used ethylene as a feedstock for 1,2-dichloroethane (12DCA) with further 12DCA chlorination. Alternatively, CAHs were produced via propane chlorinolysis (Doherty, 2000a). The $\delta^{13}C$ of ethylene and propane is reported to be $>-36\%$ (e.g. Berner and Faber, 1996; Goldstein and Shaw, 2003; Hinrichs et al., 2006). A $\delta^{13}C$ range of -23 to -37% characterizes PCE and TCE spilled into groundwater as manufactured commercial compounds (Hunkeler et al., 2005; Hunkeler et al., 2011; Morrison and Murphy, 2013; Sherwood Lollar et al., 2000; Shouakar-Stash et al., 2003; van Warmerdam et al., 1995; Wilson, 2010).

PCE and TCE are also the main components of the so-called “heavy ends” or “chlorinated pitches” that are by-products of the thermal chlorination and subsequent distillation process in the industrial production of chloromethanes. Such production was widespread in many petrochemical plants during the second half of the last century, and its by-products were often disposed improperly in un-contained dumping sites. The raw materials employed in the synthesis of chloromethanes were gaseous chlorine (Cl_2) and methane (CH_4). While natural materials generally have a $\delta^{13}C > -35\%$, biogenic methane can be as depleted as -90% . (Fuex, 1977). Thus, when biogenic methane is used as raw material, a very typical depleted isotopic fingerprint is found in the CAHs derived either as products or by-products (Rossberg et al., 2006). About 80% of the Italian natural methane is biogenic, 10% is thermogenic and another 10% has a mixed origin. The isotopically light biogenic methane was mostly used in the chloromethane production. The $\delta^{13}C$ signature of Italian biogenic methane and mixed biogenic-thermogenic methane is reported to range from -53 to -76% (Mattavelli and Novelli, 1988).

CSIA of $\delta^{13}C$ was effectively applied to identify the origin of CAHs contamination in Ferrara (northern Italy) (Nijenhuis et al., 2013). A significant depletion of $\delta^{13}C$ was observed for groundwater contaminations originated from leaching of chlorinated pitches where biogenic methane was the feed stock for chlorination ($-87\% < \delta^{13}C < -64\%$ for PCE and TCE). These values were clearly separated from the ones detected at sites contaminated by spilling of CAHs with the same chemical structure but heavier isotope composition ($-31\% < \delta^{13}C < -21\%$). Thus, CAHs produced from light methane can be separated from those

produced from carbon derived from oil or coal which are typically isotopically heavier.

However, CSIA was restricted to a single site and to a unique element (i.e. carbon). This paper aims to investigate the potential of multi-element CSIA ($\delta^{13}C$, $\delta^{37}Cl$, δ^2H) of CAHs for apportioning groundwater contamination caused by dumping of chlorinated pitches from different chloromethane producers in various hydrogeologic settings. The paper also aims to assess whether isotope fractionation due to contaminant transformation (e.g. degradation) may affect the fingerprinting of chlorinated pitches for source identification. To address these aims, three sampling surveys have been performed between 2012 and 2017 for multi-element CSIA of CAHs at two selected sites. In one of the two sites, the source apportionment of CAH contamination is also discussed in the context of a forensics investigation.

2. Materials and methods

2.1. Sampling sites

Carbon, chlorine and hydrogen stable isotope ratios of CAHs were analyzed at two sites where chlorinated pitches were dumped in the past decades: the Ferrara site (“F site”, Emilia-Romagna region, Northern Italy) that was formerly investigated for $\delta^{13}C$ (Nijenhuis et al., 2013), and the Bussi sul Tirino site (“B site”, Abruzzo region, Central Italy). At both sites, the chlorinated pitches were by-products from a chloromethane production taking place in nearby petrochemical plants in the second half of the last century. At the F site the contamination affects shallow sandy aquifers in the low alluvial plain of the Po river whereas at the B site contaminants occur within a complex system of travertine and macroclastic deposits filling the narrow and deep valley of the upper Pescara river. The hydrogeological setting of the two sites is described in the Supplementary Material (SM from now on).

The industrial activities that caused groundwater contamination at the F site are described by Nijenhuis et al. (2013). At the B site, an un-contained dump used for disposal of industrial wastes (“T dump” in Fig. 1) was discovered in 2007. A capping was placed in 2012 on top of the T dump along with a sheet pile wall 22 m deep as an emergency protection measure. About 2 km down-gradient from the T dump there is a well field (“P wells” in Fig. 1) that provided 700 to 2000 m^3/h of water for about 700,000 inhabitants of the city of Pescara and surroundings between 1980 and 2007. Based on monitoring campaigns performed by the regional environmental protection agency (ARTA), PCE, TCE, chloroform (CF), and carbon tetrachloride (CT) were systematically detected from 1992 to 2007 in the P wells at concentrations of 1 to 10 $\mu g/L$ for single analytes. Such concentrations are already around the maximum admissible concentration thresholds according to the Italian legislation (Legislative Decree 31/2001). A forensic hearing started in 2014 at the Court of Assizes of l’Aquila to address the liability for the contamination in the area of the P wells.

2.2. Groundwater sampling

In the F site, groundwater was sampled at two sub-sites in 2016. Five samples were collected at the “F_C sub-site” where chlorinated pitches were disposed in un-contained dumps between the late 1950s and the early 1970s according to a historical investigation. One sample was taken at the “F_M sub-site” that was contaminated by PCE and TCE from a former metal degreasing activity operating between the 1960s and the 1980s. Both sub-sites were previously studied for carbon isotope composition (Nijenhuis et al., 2013). The F_M sub-site was sampled again in 2016 to perform a simultaneous comparison between the isotopic signatures of manufactured commercial chlorinated compounds and those originated from chlorinated pitches at the F site. These samples are referred to as the “F16 survey”. Details about the sampling points are in Table S1 of the SM.

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