



Dual carbon - chlorine isotope fractionation during dichloroelimination of 1,1,2-trichloroethane by an enrichment culture containing *Dehalogenimonas* sp

Mònica Rosell^a, Jordi Palau^{a,b,*}, Siti Hatijah Mortan^{c,1}, Gloria Caminal^d, Albert Soler^a, Orfan Shouakar-Stash^{e,f}, Ernest Marco-Urrea^c

^a Grup MAiMA, Mineralogia Aplicada, Geoquímica i Geomicrobiologia, Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Ciències de la Terra, Universitat de Barcelona (UB), Martí Franquès s/n, 08028 Barcelona, Spain

^b Institute of Environmental Assessment and Water Research (IDAEA), CSIC, Hydrogeology Group (UPC—CSIC), Jordi Girona 18-26, 08034 Barcelona, Spain

^c Departament d'Enginyeria Química, Biològica i Ambiental, Universitat Autònoma de Barcelona (UAB), 08193, Bellaterra, Barcelona, Spain

^d Institut de Química Avançada de Catalunya (IQAC), CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain

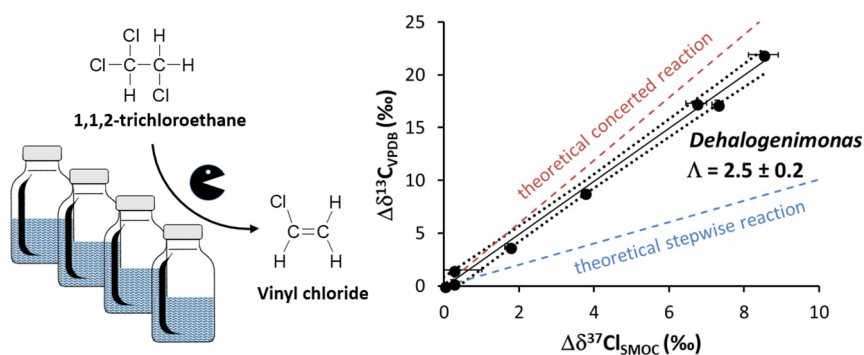
^e Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

^f Isotope Tracer Technologies Inc., Waterloo, Ontario N2V 1Z5, Canada

HIGHLIGHTS

- *Dehalogenimonas* transforms 1,1,2-trichloroethane (1,1,2-TCA) to vinyl chloride.
- Dual C-Cl isotope analysis applied for the first time for 1,1,2-TCA degradation.
- Significant C and Cl isotope fractionation during 1,1,2-TCA dichloroelimination
- Calculated Λ can allow distinguishing 1,1,2-TCA degradation pathways in the field.

GRAPHICAL ABSTRACT



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ABSTRACT

Chlorinated ethanes are frequent groundwater contaminants but compound specific isotope analysis (CSIA) has been scarcely applied to investigate their degradation pathways. In this study, dual carbon and chlorine isotope fractionation was used to investigate for the first time the anoxic biodegradation of 1,1,2-trichloroethane (1,1,2-TCA) using a *Dehalogenimonas*-containing culture. The isotopic fractionation values obtained for the biodegradation of 1,1,2-TCA were $\epsilon_c = -6.9 \pm 0.4\%$ and $\epsilon_{Cl} = -2.7 \pm 0.3\%$. The detection of vinyl chloride (VC) as unique byproduct and a closed carbon isotopic mass balance corroborated that dichloroelimination was the degradation pathway used by this strain. Combining the values of $\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$ resulted in a dual element C-Cl isotope slope of $\Lambda = 2.5 \pm 0.2\%$. Investigation of the apparent kinetic isotope effects (AKIEs) expected for cleavage of a C-Cl bond showed an important masking of the intrinsic isotope fractionation. Theoretical calculation of Λ suggested that dichloroelimination of 1,1,2-TCA was taking place via simultaneous cleavage of two C-Cl bonds (concerted

* Corresponding author at: Grup MAiMA, Mineralogia Aplicada, Geoquímica i Geomicrobiologia, Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Ciències de la Terra, Universitat de Barcelona (UB), Martí Franquès s/n, 08028 Barcelona, Spain.

E-mail address: jordi.palau@ub.edu (J. Palau).

¹ Current address: Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, Gambang, 26300 Kuantan, Pahang, Malaysia.

1. Introduction

1,1,2-Trichloroethane (1,1,2-TCA) has been widely used as a solvent and chemical intermediate in the industry (Pankow and Cherry, 1996). Improper storage and accidental spills have contributed to 1,1,2-TCA being a frequent detected contaminant in groundwater at industrial facilities (ATSDR, 1989). In the United States, it is ranked 166 out of 275 substances on the Priority List of Hazardous Substances based on a combination of its frequency, toxicity, and potential for human exposure (ATSDR, 2015).

Quantification of the distribution and fate of chlorinated contaminants and degradation products in the subsurface is a complex task since biological, chemical, and physical processes may affect them (Němeček et al., 2017). Biological transformation of 1,1,2-TCA is influenced by the intrinsic heterogeneity of natural environments that allows for different redox conditions to occur either spatially or temporally separated. Under anoxic conditions, reductive dechlorination is expected to be the prevailing mechanism to transform 1,1,2-TCA by two different biodegradation pathways: hydrogenolysis and dichloroelimination. In the case of dichloroelimination, two vicinal C–Cl bonds of 1,1,2-TCA are cleaved to produce vinyl chloride (VC), whereas during hydrogenolysis 1,1,2-TCA is sequentially transformed by single C–Cl bond cleavage to 1,2-dichloroethane (1,2-DCE) and monochloroethane (Moe et al., 2016; Zhao et al., 2015) (Fig. 1). The key organisms catalyzing hydrogenolysis and dichloroelimination are organohalide-respiring bacteria (OHRB), which can use 1,1,2-TCA as respiratory electron acceptor (Leys et al., 2013). To date,

dichloroelimination of 1,1,2-TCA has been described for OHRB belonging to the genus *Dehalobacter* and *Dehalogenimonas* (Grostern and Edwards, 2006; Mortan et al., 2017; Yan et al., 2009), but hydrogenolysis only for *Desulfitobacterium* (Zhao et al., 2015). Under oxic conditions, no bacteria are currently known to use 1,1,2-TCA as growth substrate, but cometabolism of 1,1,2-TCA can occur during aerobic oxidation of methane, propane, butane, n-pentane, n-hexane or ammonia (Frasconi et al., 2006, 2008, 2013; Vannelli et al., 1990). The only byproducts identified for aerobic cometabolism of 1,1,2-TCA include chloroacetic acid (which was sequentially oxidized to glyoxylic acid) and minor amounts of VC in microcosms containing a *Pseudomonas* sp. (Castro and Belser, 1990). Abiotic transformation of 1,1,2-TCA can produce a wide array of byproducts, including VC (Patterson et al., 2016), ethane (Song and Carraway, 2005) or 1,1-dichloroethene (1,1-DCE) (Pagana et al., 1998) (Fig. 1).

Knowledge on degradation pathways occurring in an aquifer contaminated with 1,1,2-TCA is a key aspect to design suitable bioremediation strategies. However, this is a challenge when the site contains multiple chlorinated aliphatic hydrocarbons because the same daughter products of 1,1,2-TCA dechlorination can be formed from other precursors (i.e., VC is produced from anaerobic reductive dechlorination of DCE isomers or 1,2-DCE) (Hunkeler et al., 2002). It is important to note that VC, produced during biotic or abiotic reductive dichloroelimination of 1,1,2-TCA, is even much more toxic than 1,1,2-TCA.

Compound-specific isotope analysis (CSIA) has emerged in recent years as a technique with great potential to elucidate specific reaction pathways even if no products are detected (Elsner, 2010). The magnitude of carbon and chlorine kinetic isotope effects (KIEs) during contaminant degradation relies on the observation that lighter stable isotopes (i.e., ^{12}C , ^{35}Cl) react at faster rates than the heavier ones (i.e., ^{13}C , ^{37}Cl). For a given compound and reaction, single element isotope fractionation values (ϵ) are determined in laboratory degradation experiments according to the Rayleigh equation. However, ϵ values associated to biodegradation cannot be accurately measured in the field because other processes such as sorption or mixing through dispersion also affect contaminant concentration.

Two-dimensional CSIA brings the potential to overcome the limitation of single element isotope fractionation values to identify contaminant degradation pathways in the field. Combined changes in isotope ratios of two elements (i.e., $\Delta\delta^{13}\text{C}$ and $\Delta\delta^{37}\text{Cl}$) for a given reactant generally correlate in a dual element isotope plot obtaining a slope ($\Lambda = \Delta\delta^{13}\text{C}/\Delta\delta^{37}\text{Cl}$) that reflects the isotope effects of both elements. Hence, Λ values may act as direct indicator for different initial reaction mechanisms. To interpret dual element CSIA data sets obtained from contaminated field sites, it is necessary to know experimental carbon and chlorine isotope enrichment factors and Λ values derived from microbial strains catalyzing known transformation reactions (Cretnik et al., 2013; Kuntze et al., 2016). However, to our knowledge, chlorine isotope fractionation (ϵ_{Cl}) and Λ values are not available for 1,1,2-TCA. Hunkeler et al. (2002) showed that dichloroelimination of 1,1,2-TCA to VC in anaerobic microcosms inoculated with contaminated groundwater was accompanied of a relatively weak carbon isotopic fractionation of 1,1,2-TCA ($\epsilon_{\text{C}} = -2.0 \pm 0.2\%$). Recently, in a laboratory flow-through column experiment consisting of both biodegradable organic carbon and zero valent iron, ϵ_{C} changed from $-14.6 \pm 0.7\%$ to $-0.72 \pm 0.12\%$, being this last value assigned to anaerobic biodegradation (Patterson et al., 2016).

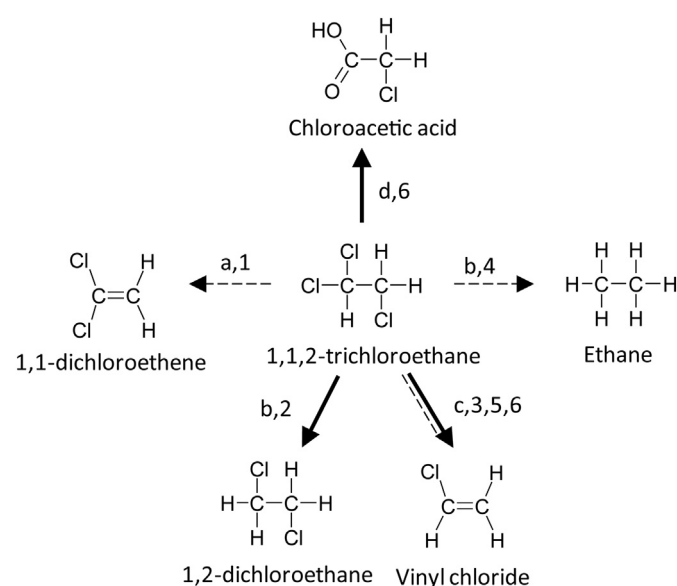


Fig. 1. Degradation pathways of 1,1,2-TCA: (a) dehydrochlorination, (b) hydrogenolysis, (c) dichloroelimination, (d) hydrolysis. Numbers indicate the dechlorinating agent: (1) base mediated abiotic reaction in aqueous solution (Pagana et al., 1998); (2) *Desulfitobacterium* sp. strain PR (Zhao et al., 2015); (3) *Dehalobacter* and *Dehalogenimonas* spp. (Grostern and Edwards, 2006; Mortan et al., 2017; Yan et al., 2009); (4) nanosized zero-valent iron (Song and Carraway, 2005); (5) zero valent iron and zinc (Patterson et al., 2016); (6) *Pseudomonas* sp. (Castro and Belser, 1990). Bold arrow: biotic reaction; dashed arrow: abiotic reaction.

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