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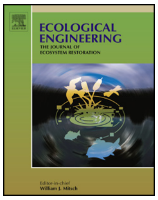

Biogeochemical modelling of *in situ* biodegradation and stable isotope fractionation of intermediate chloroethenes in a horizontal subsurface flow wetland

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ABSTRACT

The use of wetlands as a bioremediation treatment technology for halogenated hydrocarbons has recently gained interest. However, the impact of biogeochemical dynamics over a wetland's life-span on contaminant removal remains poorly understood. Based on the results of a constructed wetland experiment, we established a reactive transport model (RTM) that includes the transition from oxidation to reductive dehalogenation of *cis*-1,2-dichloroethene (cDCE) and corresponding carbon isotope signatures to quantify removal pathways in wetland environments. cDCE was removed during the entire life-span of the wetland despite significant changes in its biogeochemistry. Model results showed that during the oxic phase, 88% of cDCE throughput was removed, with oxidative cDCE mineralization accounting for 53.3 mg m^{-2} d^{-1} (45%) and carbon isotope enrichment factors ranging from $\varepsilon_{\text{DCE-Oxid}} = -1$ to -4.0‰. During the anoxic phase, the wetland removed 85% of cDCE mainly by volatilization and reductive dehalogenation ($\varepsilon_{\text{DCE-Dehal}} = -32$ to -36 ‰), with the latter degrading 21.3 mg m^{-2} d^{-1} of cDCE (28%) and producing 13.7 mg m^{-2} d^{-1} of vinyl chloride (VC). cDCE oxidation ($\varepsilon_{\text{DCE-Oxid}} = -9.4$ to -11.5 ‰) accounted for only 9.1 mg m^{-2} d^{-1} (12%). 4.4 mg m^{-2} d^{-1} of the VC produced in the wetland was biodegraded via oxidation (32%), while 2.8 mg m^{-2} d^{-1} (20%) was converted into non-toxic ethene via dehalogenation. Plant uptake of cDCE accounted for up to 23% of the mass removal during the oxic phase and 16% during the anoxic phase (6% for VC). Altogether, the RTM enables a mechanistic representation and quantitative prediction of the fate of intermediate chloroethenes in redox-dynamic environments such as wetlands.

1. Introduction

Intermediate halogenated hydrocarbons such as toxic dichloroethene (DCE) and carcinogenic vinyl chloride (VC) generally result from reductive dehalogenation of tetrachlorethene (PCE) and trichlorethene (TCE) and often accumulate in anoxic aquifers. Wetland systems are redox-dynamic environments that can intercept flow of chloroethenes-polluted water from shallow aquifers during groundwater discharge. Biogeochemical processes mainly control pollutant degradation in natural or treatment wetlands (Borch et al., 2010; Imfeld et al., 2009) including the degradation of intermediate chloroethenes (Braeckevelt et al., 2011; Imfeld et al., 2010, 2008; Kassenga et al., 2004; Tawney et al., 2008). However, how biogeochemical processes in redox-dynamic environments regulate destructive and non-destructive removal of intermediate chloroethenes remains an unsolved issue, thereby encouraging novel approaches to address this.

The degradation of chloroethenes in wetlands has been investigated under aerobic (Tawney et al., 2008) and reducing conditions (Kassenga et al., 2004, 2003; Lorah and Olsen, 1999; Lorah and Voytek, 2004) but more rarely across the entire wetland life-span (Amon et al., 2007; Imfeld et al., 2010, 2008). Under oxic conditions, DCE biodegradation occurs metabolically or cometabolically (Bradley and Chapelle, 2000; Coleman et al., 2002a). DCE can be anaerobically oxidized under Mn(IV)-, Fe(III), or SO_4^{2-} -reducing conditions (Bradley and Chapelle, 1998a; Bradley and Landmeyer, 1998), while reductive dehalogenation of DCE and eventual transformation to ethene occurs under strictly anaerobic conditions

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(Maymó-Gatell et al., 1997). Compound-specific isotope analysis (CSIA) was used previously to assess DCE biodegradation and shifts in degradation pathways in a wetland according to changes in biogeochemical conditions (Imfeld et al., 2008). Although DCE degradation in aquifers has been studied extensively, due to the lack of applicable conceptual and predictive approaches, little is known about the respective role and dynamics of competing removal mechanisms in wetlands.

Reactive transport models (RTMs) have been used to evaluate pollutant behaviour and biogeochemical conditions in different environments (Blum et al., 2009; Centler et al., 2010; Prommer et al., 2008; Thullner et al., 2007; Wynn and Liehr, 2001). RTMs have been used in the context of wetland technology to evaluate the microbial dynamics (Murphy and Ginn, 2000), hydraulic (Brovelli et al., 2011; Gérard et al., 2004; Knowles et al., 2011) or root uptake processes (Langergraber, 2005; Nowack et al., 2006), and to predict the impact of environmental conditions or operational parameters on wetland functioning (De Biase et al., 2012; Ojeda et al., 2008). Recently, CSIA data have been included in RTMs to identify the dominant degradation pathways, differentiate between destructive and non-destructive processes (*e.g.*, diffusion and volatilization) and estimate the extent of biodegradation (Blum et al., 2009; Pooley et al., 2009; Van Breukelen, 2007; Van Breukelen et al., 2005). In turn, RTMs underlined the potential and limits of isotope-based interpretation in the field (Centler et al., 2013; Eckert et al., 2012; Olivier and Patrick, 2010; Thullner et al., 2012; Van Breukelen and Prommer, 2008). Multicomponent RTMs can assist in the prediction of pollutant degradation in wetlands (De Biase et al., 2013; Langergraber, 2007) while accounting for non-linear and multiple species interactions and stable isotope fractionation. RTMs thus can support the mechanistic interpretation of reactive transport of intermediate halogenated hydrocarbons in redox-dynamic environments.

The aim of this study was to provide a quantitative and mechanistic understanding of the transport and biodegradation of intermediate halogenated hydrocarbons in wetland systems, using *cis*-DCE (cDCE) as a model compound. The specific objectives of this study were to (i) determine whether redox gradients are relevant features regulating biodegradation and isotope fractionation processes across space, (ii) evaluate the relative contribution of degradative versus non-destructive processes including plant uptake and volatilization, and (iii) determine how removal processes are influenced by temporal changes of hydrochemical conditions. A multicomponent RTM was established using hydrochemical and cDCE carbon isotope composition data acquired previously in a horizontal subsurface flow lab-scale wetland (Imfeld et al., 2008). The RTM accounts for biogeochemical reactions, including *in situ* biodegradation of cDCE and the associated shifts in its carbon isotope composition, as well as non-destructive processes of cDCE removal (*i.e.* plant-uptake and volatilization). The RTM allowed for the quantification of individual removal process and cDCE biodegradation pathways, thus providing crucial information to assist in the design and operation of wetlands treating intermediate halogenated hydrocarbons.

2. Materials and methods

2.1. Wetland experiment

A schematic representation of the constructed horizontal subsurface flow wetland is shown in Fig. 1. The wetland was built within a stainless steel tank (2.01 × 0.6 × 0.05 m) filled with quartz sand to a depth of 0.53 m, included a pond section near the outflow and was planted with *Juncus effusus*. The wetland had an average saturation depth of 0.48 m and was maintained at an average temperature of 11 ± 2 °C throughout the experiment. 90% of the pore space was water saturated, with a 0.05 m unsaturated zone in the top region of the sand compartment. Groundwater was continuously pumped at a flow rate of 1.73 L d^{-1} resulting in a hydraulic loading rate of 17.2 L m^{-2} d^{-1}.

Hydrogeochemical and cDCE carbon stable isotope data indicated that the wetland's life-span included a transition from initially oxic to anoxic conditions during the wetland experiment (Imfeld et al., 2008). This biogeochemical transition is separated into two time periods (days 0–53 for the oxic phase and days 337–430 for the anoxic phase) and used as reference periods in the model framework. Average hydrochemical species concentrations used for model calibration were obtained from sampling ports located at three elevations (0.36, 0.24, and 0.12 m; labelled 1–3, respectively) and four distances from the inlet (0.06, 0.49, 0.94 and 1.39 m; labelled A–D, respectively). Due to the low hydrochemical variability observed within the upper two sections during the oxic phase, the data was pooled into upper and lower elevations. Simulations for this period where therefore calibrated against the upper and lower elevations (1 and 3, respectively). Groundwater inflow characteristics are presented in Table 1 for the oxic and the anoxic phases. Additional details including wetland operation, sampling and analytical methods and hydrochemical characteristics of water supply are provided in Imfeld et al. (2008).

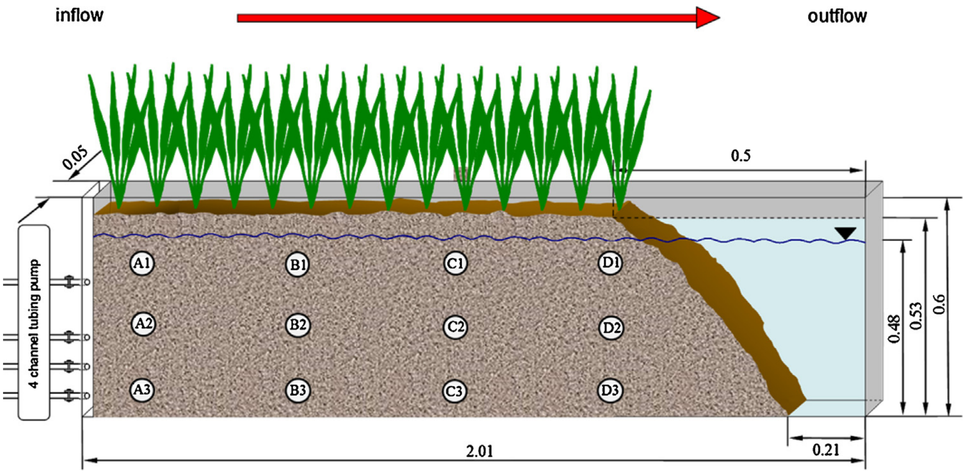

Fig. 1. Wetland set-up and location of sampling ports, all distances in m (modified after Imfeld et al., 2008).