Science of the Total Environment 554–555 (2016) 203–210

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Chlorination and dechlorination rates in a forest soil — A combined modelling and experimental approach

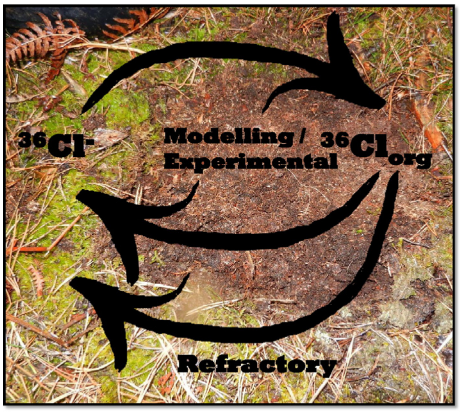
Malin Montelius [a],*, Teresia Svensson [a], Beatriz Lourino-Cabana [b], Yves Thiry [c], David Bastviken [a]

[a] *Department of Thematic Studies — Environmental Change, Linköping University, 581 83 Linköping, Sweden*
[b] *EDF, Laboratoire National d'Hydraulique et Environnement, 78401 Chatou, France*
[c] *Andra, Research and Development Division, Parc de la Croix Blanche, 1/7 rue Jean Monnet, 92298 Châtenay-Malabry Cedex, France*

HIGHLIGHTS

- Chlorination and dechlorination rates in soil were revealed by a radiotracer method.
- Chlorination was hampered by nitrogen addition.
- Both Cl^- and many Cl_{org} compounds are highly reactive in soils.
- Some formed Cl_{org} seem to be refractory.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 November 2015
Received in revised form 29 February 2016
Accepted 29 February 2016
Available online xxxx

Editor: Adrian Covaci

Keywords:
Chlorine cycling
Chloride
Organic chlorine
Radioactive chlorine-36
Modelling

ABSTRACT

Much of the total pool of chlorine (Cl) in soil consists of naturally produced organic chlorine (Cl_{org}). The chlorination of bulk organic matter at substantial rates has been experimentally confirmed in various soil types. The subsequent fates of Cl_{org} are important for ecosystem Cl cycling and residence times. As most previous research into dechlorination in soils has examined either single substances or specific groups of compounds, we lack information about overall bulk dechlorination rates. Here we assessed bulk organic matter chlorination and dechlorination rates in coniferous forest soil based on a radiotracer experiment conducted under various environmental conditions (additional water, labile organic matter, and ammonium nitrate). Experiment results were used to develop a model to estimate specific chlorination (i.e., fraction of Cl^- transformed to Cl_{org} per time unit) and specific dechlorination (i.e., fraction of Cl_{org} transformed to Cl^- per time unit) rates. The results indicate that chlorination and dechlorination occurred simultaneously under all tested environmental conditions. Specific chlorination rates ranged from 0.0005 to 0.01 d^{-1} and were hampered by nitrogen fertilization but were otherwise similar among the treatments. Specific dechlorination rates were 0.01–0.03 d^{-1} and were similar among all treatments. This study finds that soil Cl_{org} levels result from a dynamic equilibrium between the chlorination and rapid dechlorination of some Cl_{org} compounds, while another Cl_{org} pool is dechlorinated more slowly. Altogether, this study demonstrates a highly active Cl cycling in soils.

---

* Corresponding author.
E-mail address: malin.montelius@liu.se (M. Montelius).

http://dx.doi.org/10.1016/j.scitotenv.2016.02.208
0048-9697/

1. Introduction

Chlorinated organic compounds (Cl_{org}) are typically of interest because of their substantial industrial and economic importance, and because of the release of organochlorine pollutants (Miglioranza et al., 2004). In addition to anthropogenic production, over 2200 naturally formed Cl_{org} have been identified (e.g., Gribble, 2009; Harper, 1985). In soils, naturally formed Cl_{org} are mainly produced biotically by microorganisms such as fungi and bacteria (Bastviken et al., 2009; Winterton, 2000; Öberg, 2002), but can also be formed abiotically (Schöler and Keppler, 2003). Recent results suggest that different tree species and associated microorganisms in the rhizosphere strongly influence both the Cl_{org} and overall Cl levels in soils (Montelius et al., 2015).

In boreal and temperate soils, 48% to almost 100% of the total Cl is found as Cl_{org} in the upper soil layers (Johansson et al., 2003a, 2003b; Matucha et al., 2010; Redon et al., 2011; Svensson et al., 2007). Several studies of bulk chlorination have quantified chlorination rates in different types of soils (e.g., Bastviken et al., 2007, 2009; Gustavsson et al., 2012; Lee et al., 2001; Ortiz-Bermúdez et al., 2007; Redon et al., 2011). These studies demonstrate that chloride (Cl^-) is transformed to Cl_{org} at substantial rates; for example, 10–17% of lignin fragments were chlorinated within 130 days (Ortiz-Bermúdez et al., 2007) and 3–10% of added Cl^- can be converted to Cl_{org} within 50 days (Gustavsson et al., 2012). These previous experimental quantifications of chlorination rates have focused on the gross chlorination of bulk organic matter. In contrast, field studies of total Cl cycling have assessed the net formation of Cl_{org} without distinguishing between chlorination and dechlorination (Redon et al., 2011; Rodstedth et al., 2003).

The natural transformation of Cl^- to Cl_{org} means that soil can store Cl_{org}, substantially affecting soil Cl residence times. Redon et al. (2011) estimated the Cl retention time to be five-fold higher when taking Cl_{org} into account. Data on the chlorination and dechlorination rates of organic matter are needed in order to understand the biogeochemical cycling and dynamics of Cl and to calculate the residence times of, for example, Cl_{org} pollutants and the radioactive ^{36}Cl present in nuclear waste. Information about Cl residence times can therefore be important for human and environmental risk assessment modelling (Bytwerk et al., 2011).

Cl_{org} residence times have been estimated based on theoretical models assuming that Cl_{org} has the same turnover rates as does general organic matter (Montelius et al., 2015; Redon et al., 2011; van den Hoof and Thiry, 2012; Öberg and Sandén, 2005). This may not be the case, however. The release of Cl from the organic matter pool (here referred to as dechlorination) does not necessarily depend on the complete mineralization of the organic matter to which the Cl is bound, as Cl could also be released without complete degradation of the organic compounds. The natural Cl_{org} pool is complex and includes various compounds. Previous studies of organochlorine degradation have typically focused on specific chlorinated compounds or compound classes (Abramowicz, 1990; Bunge et al., 2003; Lorenz et al., 2000; Pant and Pant, 2010). In addition, work on specific microbial dehalogenation processes (e.g., Jugder et al., 2015; Maymo-Gatell et al., 2001) has demonstrated that some specific Cl_{org} are resistant to degradation while others may be more easily transformed by selective halogen removal or overall organic matter decomposition (Sollins et al., 1996). Many bacterial and fungal genera can dehalogenate Cl_{org} of various types under either oxic or anoxic conditions (Field and Sierra-Alvarez, 2004). Under oxic and anoxic conditions, the microbial community can use Cl_{org} as an organic electron donor and carbon source or degrade it by co-metabolism while growing on other substrates. Under anoxic conditions, dehalogenation can also occur with Cl_{org} as the electron acceptor (i.e., halorespiration) (McCarty, 1997). Combinations of redox conditions can be favourable for dechlorination, and some highly chlorinated compounds require mixed microbial communities and exposure to both anoxic and oxic conditions to be fully degraded (Fritsche and Hofrichter, 2000). In such cases, the highly chlorinated compounds are partly dehalogenated under anoxic conditions to less-chlorinated compounds that are more readily mineralized under oxic conditions. Some dechlorination may also occur via abiotic processes including hydrolysis, mineral surface reactions, photolysis, and oxidation by molecular oxygen (Bailey et al., 2002).

For a better understanding of overall ecosystem Cl cycling, information about specific compounds is not sufficient; instead, we need data on bulk Cl_{org} dechlorination. A limited number of pioneering studies discussing the balance between chlorination and dechlorination in soils have indicated that nitrogen fertilization either hampers chlorination or enhances dechlorination (Johansson et al., 2001; Öberg et al., 1996), but without being able to separate chlorination from dechlorination. Other similar studies could not detect any clear effects of nitrogen addition (Bastviken et al., 2006) nor clarify the effects of other key variables, such as water content and organic matter quality. We found no previous reports of the direct measurements of bulk Cl_{org} dechlorination needed to resolve these inconsistencies and reveal the extent to which dechlorination occurs in soils under different conditions.

The present study uses radiotracer experiments combined with modelling to examine the simultaneous chlorination and dechlorination of organic matter in boreal forest soil and to estimate chlorination and dechlorination rates. We hypothesized that (1) dechlorination would occur at measurable rates similar in magnitude to chlorination rates and (2) that a steady-state situation with largely similar chlorination and dechlorination rates would develop over time under stable conditions. The experiments were designed to elucidate the potential effects of environmental factors (water, labile organic matter, and ammonium nitrate) under controlled laboratory conditions.

2. Materials and methods

2.1. Soil sampling and soil characteristics

Soil was collected at Stubbetorp (latitude 58° 43′95″N; longitude 16° 20′29″E) in southeast Sweden in late October 2013. The sampled area had formerly been covered by coniferous forest dominated by pine (*Pinus sylvestris*) (81%) and Norwegian spruce (*Picea abies*) (13%), but was cut in 2010, leaving only seed trees. This area is representative of boreal coniferous forests used for forestry. The bedrock in the area is poor in Cl^-, the mean annual precipitation is 600 mm, and the mean annual temperature is approximately 6 °C. Soil samples were collected from five randomly selected locations within a circle 15 m in diameter. Given previous findings of active chlorination in the humus layer (e.g., Bastviken et al., 2007, 2009), samples from this layer (5–15 cm below the soil surface) were used in the experiments. The samples were pooled and mixed to form a composite sample. The soil was transported in polyethylene plastic bags to the laboratory and was then refrigerated at 4 °C until used in experiments.

A subsample of the soil was collected before the experiment and used to determine original soil water content, soil organic matter, pH, total organic carbon (TOC) in soil water extracts, extractable Cl^-, and total organic halogens (TOX) as follows. Soil water content was calculated from the soil mass before and after drying at 105 °C for 24 h. Soil organic matter content was determined by loss on ignition (LOI) at 550 °C for 2 h, assuming the carbon content to equal 50% of LOI. The pH was measured in extracts of water according to ISO 10390:1994. TOC in soil extracts was determined using a Shimadzu (Japan) TOC-V_{CSH} TOC analyser and was extracted from approximately 0.9 g of dry soil to a total water volume of 80 mL. The Cl^- present in the samples was extracted using the same procedure as described below for $^{36}Cl^-$, except that the last two extractions were conducted using 0.01 M KNO_3 instead of KCl. The extracts were frozen and, after thawing, analysed for Cl^- concentrations using ion chromatography with chemical suppression (MIC-2 modular anion system; Metrohm) according to ISO 10304-1:1992. The residual soil was dried and milled, and 0.02 g