Halogen (F, Cl, Br, I) contents in silt and clay fractions of a Cambisol from a temperate forest

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ABSTRACT

In spite of considerable efforts to understand the role of halogens (F, Cl, Br, I) in soil, concentration data for different soil size fractions is still sparse and information on the sorption behavior of halogens in natural soils is limited. We determined total halogen concentrations in different soil horizons and particle size fractions (i.e., coarse silt with 20–63 µm, medium and fine silt with 2–20 µm, coarse clay with 0.2 to <2 µm and medium clay with 0.02–0.2 µm) of a Cambisol from a temperate forest ecosystem in SW Germany. Furthermore, we estimated the minimum proportions of sorbed halogens onto clay minerals and pedogenic oxides for different soil horizons and different particle size fractions.

Vertical depth profiles of halogens in the individual soil particle size fractions matched with the bulk soil vertical patterns. The lack of vertical differences of total halogens concentrations (F_{tot}, Br_{tot}, and I_{tot}) in the mineral soil during soil development may be due to steady state or equilibrium conditions between weathering, sorption processes, and surface input. In contrast, the vertical depth pattern of Cl_{tot} tended to decrease, suggesting the process of Cl accumulation in the topsoil and nutrient uplift. While F was likely mainly incorporated into the crystal lattice of clay minerals and gibbsite occupying OH-sites, significant amounts of the halogens with larger ionic radii (Cl, Br, and I) were sorbed. The largest amounts (around 90% Cl and 70% Br and I, respectively) were sorbed on the smallest particle size fraction investigated (medium clay fraction; 0.02–0.2 µm), although this fraction only contributed about 1 wt% to the bulk soil. This is probably related to the highest sorption capacity of small particles due to their large surface area.

Our study provides new data on sorption behavior of the various halogens in soils of forest ecosystems, which is different between F and the heavier halogens (Cl, Br, I) and further depends on soil particle sizes. The understanding of the chemical behavior of halogens in soils has implications for the retention processes of pollutants in landfills or radioactive waste disposal.

Keywords: Sorption processes, particle size fractions, Cambisol, fluorine, chlorine, bromine, iodine

INTRODUCTION

The halogens, fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) are important elements in natural ecosystems and their understanding is necessary for a variety of organic and inorganic reactions in soils, the critical zone and in the Earth’s crust in general (e.g., Fuge 1988; Bastviken et al. 2007; Redon et al. 2011; Öberg and Bastviken 2012; Kendrick and Burnard 2013). While Cl is an essential micronutrient for plants and microorganisms (Raven 2017), F, Br, and I are not essential micronutrients but appear to be involved in a large variety of organic processes (e.g., Yuita 1983; Fuge 1988; Marschner 1995; Kabata-Pendias 2011) and act as important ligands in inorganic processes such as metal transport (Lecumberri-Sanchez and Bodnar 2018). In large concentrations, halogens can have harmful effects on living organisms (Chubar et al. 2005). Processes within soils (such as halogenation; e.g., Asplund and Grimvall 1991; Montelius et al. 2015, 2016) and external halogen input (such as atmospheric deposition, wash-off, and canopy leaching; e.g., Lovett et al. 2005; Roulier et al. 2019) strongly influence the halogen distribution in soils. The Cl distribution, for example, is strongly governed by chlorination processes in the organic layer, which results in an accumulation of Cl_{org} (tot = organic + inorganic fractions) in the organic layer and decreasing Cl_{tot} concentrations with increasing soil depth (e.g., Bastviken et al. 2007; Montelius et al. 2016; Epp et al. 2020). In contrast, F_{tot}, Br_{tot}, and I_{tot} concentrations increase with increasing soil depth (Epp et al. 2020), which may be linked to sorption on, for example, positively charged surfaces of pedogenic oxides [iron (Fe), manganese (Mn), and aluminum (Al) oxides and (oxy) hydroxides] that form during pedogenesis (Gerzabek et al. 1999; Loganathan et al. 2007; Cortizas et al. 2016; Roulier et al. 2019). Further explanations for these depth profiles could be weathering and subsequent leaching (Davison and Weinstein 2006; Liu et al. 2014 and references therein; Fuge 2019) or the combination of the level of, for example, bromination linked to the age of soil organic matter (SOM) and stabilization of brominated organic substances by complexation with Al (Cortizas et al. 2016).

Modification of host rock material and primary mineral weathering and formation of secondary minerals such as clay...