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- < 2 µm and medium clay with 0.02-0.2 µm) of a Cambisol from a temperate forest ecosystem in SW Germany. Further, 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
($F_{\text{tot}}$, $Br_{\text{tot}}$ and $I_{\text{tot}}$) 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 $Cl_{\text{tot}}$ 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 retention processes of pollutants in landfills or radioactive waste disposal.

Key words: 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.e., Fuge 1988; Bastviken
et al. 2007; Redon et al. 2011; Öberg and Bastviken 2012; Kendrick and Burnard 2013). While
Cl is an essential micro-nutrient for plants and micro-organisms (Raven 2017), F, Br and I are no essential micro-nutrients 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 like 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; Montelius et al. 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 result in an accumulation of \( \text{Cl}_{\text{tot}} \) (where \( \text{tot} = \text{organic} + \text{inorganic} \) fractions) in the organic layer and decreasing \( \text{Cl}_{\text{tot}} \) concentrations with increasing soil depth (e.g., Bastviken et al. 2007; Montelius et al. 2016; Epp et al. 2020). In contrast, \( F_{\text{tot}} \), \( Br_{\text{tot}} \) and \( I_{\text{tot}} \) 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 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 minerals are governed by progressive soil formation (Chadwick and Chorover 2001; Cornelis et al. 2014). In general, soils consist of highly variable particle size mixtures with gaseous and liquid interstitial phases. Numerous reactions such as sorption and desorption processes take place at interfaces of water and charged surfaces of the solid soil.
phase, for instance clay minerals or pedogenic oxides (Scheffer et al. 1998; Schoonheydt and Johnston 2006). These sorption processes are strongly dependent on the size and type of the particle surfaces, where the specific surface size increases with decreasing particle size. With respect to silicate phases, allophane (Al$_2$O$_3$*(SiO$_2$)$_{1.7}$*(H$_2$O)$_{2.8}$) and imogolite (Al$_2$SiO$_3$(OH)$_4$) have the largest specific surfaces ranging between 700 and 1100 m$^2$ g$^{-1}$ (Parfitt 1989; Scheffer et al. 1998 and references therein). With specific surfaces between 600 and 800 mg$^2$ g$^{-1}$ smectite and vermiculite have the largest specific surfaces among clay minerals. In comparison, specific surface areas of pedogenic oxides, like goethite and hematite range between 50 and 150 m$^2$ g$^{-1}$, whereas ferrihydrite has by far the largest surface of 300 to 400 m$^2$ g$^{-1}$ (Parfitt 1989; Scheffer et al. 1998 and references therein).

Due to their large specific surface area, clay minerals and pedogenic oxides are particularly effective sorbents for a large variety of ions. While clay minerals are generally negatively charged in the pH range of most soils, pedogenic oxides are rather positively charged and, thus, can sorb anions (Scheffer et al. 1998) such as inorganic F$^-$, Cl$^-$, Br$^-$ or I$^-$. Sorption of halogens on pedogenic oxides or clay minerals increases with decreasing pH (Weerasooriya and Wickramarathna 1999; Goldberg and Kabengi 2010). Decreasing sorption behavior is linked to increasing solution ionic strength of the background electrolyte and no adsorption was reported at pH 8.8, the point of zero net proton charge (Weerasooriya and Wickramarathna 1999). With regard to sorption of ions, two scenarios are distinguished: (1) inner-sphere adsorption, where ligand exchange takes place, hence the ion and the ligands which form complexes are in direct contact, and (2) outer-sphere adsorption, where hydrated ions are bound to mineral surfaces by electrostatic interactions, i.e., where water molecules are interconnected between ions and the ligands (e.g., Sposito 1989; Scheffer et al. 1998; Strawn and Sparks 1999). Fluoride was described to form inner-sphere complexes with pedogenic oxides, while Cl$^-$, Br$^-$ and I$^-$ have been found to show relatively weak adsorption behavior on clay minerals and oxides and are

The objective of this study was to assess the total (sum of organic + inorganic) halogen concentrations (F, Cl, Br, I) of three soil horizons in four particle size fractions (i.e., 20-63 µm (coarse silt), 2-20 µm (fine and medium silt), 0.2 - < 2 µm (coarse clay) and 0.02 – 0.2 µm (medium clay) in the mineral soil of a Cambisol. We further estimated minimum proportions of sorbed halogens onto clay minerals and pedogenic oxides and investigated differences in the sorption behavior of F and Cl, Br and I. Furthermore, we paid attention to potential vertical depth patterns of total halogen concentrations. The distinction between organic and inorganic halogens was not addressed in the present study.

Material and Methods

Study area

We investigated a Cambisol developed on gneissic host rock located in a spruce forest (Picea abies (L.) H. Karst). Typically, this soil type consists of an organic layer on top of the mineral soil, a mineral topsoil and mineral subsoil (Fig. 1). The investigated soil samples derive from the Kammentobel valley, close to the Feldberg peak in the Schwarzwald, SW Germany (Tab. 1). The annual temperature in 2018 ranged between 23 and -20 °C and total precipitation was ~1500 mm (Deutscher-Wetterdienst 2019; WetterKontor 2019). The samples of this study represent a carefully selected subset of soil samples that were previously analyzed by Epp et al. (2020) regarding their bulk halogen (F, Cl, Br and I) composition and pedogenic oxide content (see chapter 2.3). The vegetation comprises spruce trees (Picea abies (L.) H. Karst) and blueberry (Vaccinium myrtillus L.). The investigated soil can be classified as Cambisol according to IUSS-Working-Group-WRB (2015) and developed on strongly weathered gneisses (migmatites) from the Schwarzwald low mountain range. The investigated soil profile...
comprises a depth of 57 cm and soil horizon Bw2C in the subsoil can be found until a depth of
~ 70 cm, then the transition to the host rock is reached. In total, triplicate samples from each soil
horizon i.e., mineral topsoil (Ah) and subsoil (Bw1, Bw2C) were selected. Further details on
the study site are given in Epp et al. (2020). The vertical halogen distribution in the four
investigated particle sizes will be presented as a preliminary data set and is included in this
study as there have not been many studies on this topic so far.

Sample preparation

The soil material used in this study was first sieved (< 2 mm) and dried at 40 °C for five days
in order to minimize loss of halogens to the gaseous phase. For further investigation, respective
samples from each location were combined to form composite samples. The dry and sieved soil
samples (< 2 mm) were then mixed with Millipore water (18.2 MΩ*cm). Subsequently the soil
water mixture was passed through 500, 250, 125, 63 and 20 µm stainless steel sieves to capture
the remaining solid material after each sieve size for further size-specific particle separation.

The fraction < 20 µm was transferred into a 1 L Atterberg cylinder with a drop height of 25 cm
and suspended with Millipore water. This procedure was applied to separate the clay fractions
< 2 µm from the remaining medium and fine silt fraction (2-20µm) according to Stokes’ law
(Stokes 1901) as described by Atterberg (1912). Note that the clay particle size fractions do,
from a mineralogical point of view, not exclusively consist of clay minerals, but also contain to
a certain extent pedogenic oxides. The sediment was shaken in the cylinder and left to stand for
22 hours. During this period heavier silt and sand sized particles (> 2 µm) sedimented, whereas
clay-sized particles (< 2 µm) remained in suspension and could be separated from the
remainder. Subsequently, the cylinder was refilled with Millipore water and the procedure was
repeated until the supernatant liquid was no longer muddy. Depending on the soil horizon, this
procedure took up to 10 runs for the mineral top- and subsoil.
The obtained clay fractions < 2 µm were then separated by vacuum filtration (Welch Ilmvac\textsuperscript{TM}) using 0.8 µm cellulose nitrate membrane filters with a diameter of 10 cm (neoLab\textsuperscript{®}). In order to separate the coarse clay (0.2- < 2 µm) from the medium clay (0.02-0.2 µm) fraction, all samples were cooled-centrifuged with a ROTANTA 460RS, using a 5624 rotor. The separation was conducted according to Tributh and Lagaly (1986) and the following frame conditions were applied: 100 ml plastic centrifuge tubes with a diameter of 4 cm, \( r_0 = 10.3 \text{ cm} \), \( r = 12.3 \text{ cm} \) and the sediment was mixed with 80 ml Millipore water. As a first step, the fine clay fraction (< 0.02 µm) was separated by 4400 rotations per minute (RPM min\textsuperscript{-1}) for \( t = 6 \text{ h 22 min.} \)

Subsequently, the first 2 cm were sampled by pipetting and the tubes were refilled with Millipore water to 80 ml. In total, three runs were implemented, but it turned out that the fine clay fraction was too fine to get reliably completely separated or used for further investigations.

Since the fine clay fraction was partly removed and not further considered, it is only referred to the medium clay fraction as the finest fraction. In order to separate the medium clay fraction from the coarse clay fraction, the samples were centrifuged at 2000 RPM min\textsuperscript{-1} for \( t = 21 \text{ min.} \)

In total 57 runs were required to separate the fine and medium from the coarse clay fraction.

In order to minimize potential contamination with halogens we did not use H\textsubscript{2}O\textsubscript{2} to eliminate organic particles or any dispersing agents (such as HCl) as pre-treatment in any of the separation steps. Therefore, the determined halogen concentrations of the samples represent the sum of organic and inorganic halogen components. By using Millipore water during sieving and grain size separation steps, water-soluble (and loosely bound/exchangeable) halogens were removed prior the analyses. We know from previous analysis that in the bulk soil, water-extractable halogen proportions ranged from 0.4 % (F) to 9 % (Cl) (Epp et al. (2020). Note that total halogen concentrations (\( F_{\text{tot}} \), \( Cl_{\text{tot}} \), \( Br_{\text{tot}} \), \( I_{\text{tot}} \); i.e., organic + inorganic halogens) of all three soil horizons (Ah, Bw1, Bw2C) based on combustion ion chromatography (CIC, see halogen
analyses below) measurements represent both halogens incorporated in the crystal lattice and halogens sorbed to particle surfaces.

Possible organic contamination during sample treatment can be excluded, since total organic carbon ($C_{org}$) content of soil fractions was 40% lower than total $C_{org}$ of bulk soil. The different particle size fractions contained various $C_{org}$ amounts. The bulk $C_{org}$ concentration in soil horizon Bw1 (after taking the relative amount compared to bulk soil into consideration) contained in the coarse silt fraction 6 g kg$^{-1}$, in the medium and fine silt fraction 10 g kg$^{-1}$, in the coarse clay fraction 1 g kg$^{-1}$ and in the medium clay fraction < 1 g kg$^{-1}$.

Desorption experiments

To remove strongly sorbed halogens on soil particles, the already grain size-separated samples were mixed with a solution of 350 mg K$_2$HPO$_4$ (≥ 99%, Roth) in 10 mL Millipore water for which the pH was adjusted to 3-4 by adding 140 µL HNO$_3$ (65%, suprapure, Merck). It is generally known that phosphate is highly exchangeable with other anions (Manning and Goldberg 1996). Kaolinite and illite generally have a specific surface area of 10 - 100 m$^2$ g$^{-1}$, whereas clay minerals and pedogenic oxides in extreme cases reach values up to 1000 m$^2$ g$^{-1}$ (Parfitt 1989; Santamarina et al. 2002 and references therein). These values are most likely only representative of the smaller grain size fractions and thus represent maximum specific surface areas. To assure excess of phosphate, we assumed a total specific surface area of 1000 m$^2$ g$^{-1}$ and used an initial phosphate content of 2.5 µmol m$^{-2}$ (Torrent et al. 1990). Each analyzed sample varied with respect to total mass used and the total surface area of our samples reached up to 150 m$^2$. For this maximum surface 0.4 mmol would have sufficed, thus we have used a 2 mmol phosphate to provide more than adequate surface coverage. The samples were left in the solution for three days and were occasionally shaken. The silt fractions were then separated from the K$_2$HPO$_4$ solution by vacuum filtration, briefly washed with Millipore water and subsequently dried at room temperature. The clay fractions were centrifuged and supernatant
solutions pipetted. The same procedure was repeated with Millipore water as a wash step and solid samples were dried at room temperature for subsequent analysis by CIC.

Halogen analyses

After size fractionation, all samples were manually mortared and homogenized before analysis of total halogen concentrations by combustion ion chromatography (CIC). The same applies to subsamples that have been additionally treated with K₂HPO₄ to remove the surface-sorbed halogens and to solely assess the residual fraction of mostly structurally bound halogens. For the CIC analyses, an autosampler for solid samples (MMS 5000; Analytik Jena) connected to a combustion oven and to a 930 Compact IC Flex chromatograph (Metrohm, Germany) with chemical suppression and a peristaltic pump for regeneration (100 mmol L⁻¹ H₂SO₄) was used. In brief, inorganic and organic halogens in a sample are transformed into inorganic forms and are transferred into the gaseous phase through combustion. The halogens are trapped from the carrier gas by an adsorption solution that is transferred to an IC column. Separation of analytes was achieved with a Metrosep A Supp 5 – 250/4.0 column (Metrohm) using an eluent consisting of 8 mmol L⁻¹ Na₂CO₃ (suprapure, Merck ®). The limits of detection were: 0.8 mg kg⁻¹ for F, 0.2 mg kg⁻¹ for Cl and 0.02 mg kg⁻¹ for Br and I (calculated according to DIN 32645). Based on the analysis of standard solutions (single element solutions of F, Cl, Br and I; Roth; 1000 mg L⁻¹) and various reference materials (SO₃, GSN), the long-term reproducibility (1σ) was within a 20 % margin for F and 10 % for Cl, Br and I. A detailed description of the analytical method can be found in Epp et al. (2019).

Liquid samples of the residual K₂HPO₄ extraction solution were analyzed for F_{inorg} and Cl_{inorg} using an autosampler for liquid samples (858 Professional Sample Processor, Metrohm). The extraction solutions were filtered in the ion chromatograph, which contains an internal filter of 0.2 µm pore size. Limits of detection were for F 0.2 mg L⁻¹ and for Cl 0.5 mg L⁻¹ (calculated
according to DIN 32645), while Br$_{\text{inorg}}$ and I$_{\text{inorg}}$ concentrations were below the detection limit as the samples have been diluted by a factor of 1000 to avoid column overload by phosphate.

Complementary analyses

We used dried (40 °C) and sieved (<2 mm) bulk sample material for the analyses of pedogenic oxides. The analyses of poorly crystalline pedogenic oxides (Fe$_{\text{ox}}$ and Al$_{\text{ox}}$) and the sum of poorly crystalline and crystalline pedogenic oxides (Fe$_{\text{d}}$ and Al$_{\text{d}}$) have already been reported in Epp et al. (2020). Hence, further methodical aspects can be found in this previous study. Coarse clay and medium clay fractions of soil horizons Ah, Bw1 and Bw2C were analyzed by means of X-ray diffraction (XRD). The XRD analyses were conducted on texture samples on a glass slide with preferred orientation using a Bruker D8 Advance at the University of Tübingen. Total carbon (C$_{\text{tot}}$) concentrations were analyzed from homogenized samples with an Elemental Analyzer (Vario EL III, Elementar Analysensystem GmbH). Due to very minor amounts of CaCO$_3$ (< 1 %) in the acidic mineral soil (pH < 4.5), C$_{\text{tot}}$ is considered to be adequate to total organic C (C$_{\text{org}}$).

Data analysis

IBM® SPSS® Statistics Version 25 was used for all statistical evaluation. Spearman rank correlations were conducted to detect possible correlations between halogen concentrations and various soil parameters. Generally, for $p < 0.05$, differences and correlations were considered as statistically significant. The Shapiro-Wilk test was applied to test for normal distribution and the Levene test was assessed for checking the homogeneity of variances. If homogeneity of variance was not given, the Welch test was used and the Games-Howell as post-hoc test.

Halogen concentrations of F$_{\text{sorb}}$, Cl$_{\text{sorb}}$, Br$_{\text{sorb}}$ and I$_{\text{sorb}}$ between different particle sizes were compared using the one-way ANOVA to determine possible relations of halogen concentrations and grain size.
Results

Soil properties

On average, 40 wt% of bulk soil consisted of coarse silt (20-63 µm; 15 wt%) and fine to medium silt (2-20 µm; 25 wt%) particles. The clay fractions represented by far the smallest weight portion of the investigated bulk soil, with 3 wt% of coarse clay (0.2-<2 µm) and <1 wt% of medium clay (0.02-0.2 µm) particles, only. Based on XRD analyses, coarse and medium clay samples were composed of vermiculite, illite, kaolinite and gibbsite, i.e., did not contain any swellable clay minerals. The organic carbon concentration in the different particle size fractions ranged between 2.5 and 10 wt. % (Tab. 2) and was on average about 15 % lower after phosphate treatment (Fig. 2a). In the following, we present first total halogen concentrations ($X_{tot}$) in the samples, followed by a summary of the results of the desorption experiments.

Total halogen concentrations

Total F concentrations of all four particle size fractions overlapped across the vertical depth profile, the concentrations ranging between 500 and 1200 mg kg$^{-1}$. Within the mineral soil, $F_{tot}$ concentrations were relatively constant (Fig. 3) and overall, $F_{tot}$ concentrations were negatively correlated with the particle size ($r = -0.536, p = 0.002$).

Total Cl concentrations in the vertical profile tended to show a slight decrease in all four particle sizes with increasing soil depth (Fig. 3). In the coarse silt, medium and fine silt and in the coarse clay fractions $Cl_{tot}$ concentrations ranged between 100 and 180 mg kg$^{-1}$, but very high $Cl_{tot}$ concentrations occurred in the medium clay fraction with up to 2500 mg kg$^{-1}$ Cl (Fig. 3). In addition, $Cl_{tot}$ concentrations were negatively correlated with particle size ($r = -0.405, p = 0.021$).
Vertical Br$_{\text{tot}}$ concentration profiles showed a tendency to increase with depth in all four particle sizes (Fig. 3) and with decreasing particle size Br$_{\text{tot}}$ concentrations increase ($r = -0.863$, $p < 0.001$). This is indicated by vertical profiles that tend to be shifted to higher concentrations with decreasing particle size instead of overall overlapping profiles. Similar to what was observed with Cl$_{\text{tot}}$, Br$_{\text{tot}}$ concentrations were highest in the medium clay fraction (140 to 220 mg kg$^{-1}$), somewhat higher than in the coarse silt, medium and fine silt fraction and in the coarse clay fraction (20 and 80 mg kg$^{-1}$).

Similarly, I$_{\text{tot}}$ concentrations tended to increase with depth in all four particle sizes (Fig. 3) and were negatively correlated with particle size ($r = -0.820$, $p < 0.001$). The concentrations increased with decreasing particle size, since the vertical profiles did hardly overlap but instead tended to shift to higher concentrations with decreasing particle size. Total I concentrations ranged in the coarse silt, the medium and fine silt fraction and in the coarse clay fraction from 6 to 26 mg kg$^{-1}$ and in the medium clay fraction from 25 to 60 mg kg$^{-1}$.

In almost all samples, F$_{\text{tot}}$ concentrations were by far higher than Cl$_{\text{tot}}$, Br$_{\text{tot}}$ and I$_{\text{tot}}$ and only for the smallest grain size fraction (medium clay), Cl$_{\text{tot}}$ was similar to F$_{\text{tot}}$. (Tab. 2). Molar halogen ratios were similar in the coarse silt fraction (F/Cl = 8, F/Br = 70, F/I = 390), in the medium and fine silt fraction (F/Cl = 10, F/Br = 50, F/I = 200), and in the coarse clay fraction (F/Cl = 10, F/Br = 45, F/I = 250), while in the medium clay fraction, F/Cl = 1, F/Br = 15 and F/I = 100. Concentration differences among Cl, Br and I were not large, as the molar ratio of Cl/Br was on average 8 (and 50 for Cl/I), almost six times lower compared to the molar F ratios.

Sorption behavior

The difference between X$_{\text{tot}}$ and remaining halogens in the solid phase after phosphate treatment was interpreted as strongly sorbed halogens (X$_{\text{sorb}}$). The remaining halogens in the samples largely represent halogens that are incorporated into crystal lattices (X$_{\text{inc}}$) and potentially unknown amounts of soil-bound organo-halogens. These cannot be quantified by our method,
as phosphate treatment may not be sufficient to desorb such organically bound halogens. Thus, the calculated amounts of sorbed halogens represent minimum values. Halogens in supernatant phosphate solutions represent the dissolved inorganic concentrations ($X_{\text{inorg}}$). Notable differences between F and Cl, Br and I with regard to sorbed proportions are as follows:

**Fluorine**

In almost all size fractions, F was mostly structurally bound (i.e., incorporated into crystal lattices) and only small amounts of the total F (generally <10 %) where sorbed (Tab. 2, Fig. 4) that did not differ significantly between the particle sizes ($\rho > 0.05$). Only in the 20-63µm fraction of soil horizon Bw1 around 50 % of F were sorbed (Tab. 2, Fig. 4). Dissolved $F_{\text{inorg}}$ concentrations in the supernatant phosphate solution were generally decreasing with soil depth (Fig. A1).

**Chlorine**

In the coarse, medium and fine silt fractions, $Cl_{\text{inc}}$ concentrations tended to decrease with depth from 150 to 90 mg kg$^{-1}$ (Tab. 2), with on average 20 % $Cl_{\text{sorb}}$ (Fig. 4). In the coarse clay fraction $Cl_{\text{inc}}$ tended to decrease slightly with depth (130 to 110 mg kg$^{-1}$; Tab. 2), with 25-30 % $Cl_{\text{sorb}}$ in soil horizons Ah and Bw2C, but only 5 % $Cl_{\text{sorb}}$ in Bw1 (Fig. 4). In contrast, in the medium clay fraction, most Cl (>80 %) is sorbed (Tab. 2). Dissolved $Cl_{\text{inorg}}$ in the supernatant phosphate solutions varied between 0.4 and 4.5 mg L$^{-1}$ irrespective of soil depth (Fig. A1).

**Bromine**

In the coarse silt fraction, $Br_{\text{inc}}$ concentrations tended to decrease with depth from 40 to 25 mg kg$^{-1}$ and on average, only 10% of $Br_{\text{tot}}$ were sorbed (Tab. 2, Fig. 4). In the medium and fine silt fraction $Br_{\text{tot}}$ concentrations tended to increase with depth from 40 to 70 mg kg$^{-1}$. In soil horizon Ah only 3 % sorbed, whereas in the mineral subsoil 30 % was sorbed (Tab. 2, Fig. 4).
coarse clay fraction, on average 20 % Br was sorbed and the highest portion of Br (60-70\%) was sorbed in the medium clay fractions, similar to what was observed for Cl (Tab. 2, Fig. 4).

Iodine

In the coarse silt fraction I\textsubscript{inc} concentrations tended to decrease with depth from 7 to 2 mg kg\(^{-1}\) (Tab. 2). Only about of 5 % of I\textsubscript{tot} was sorbed in the Ah horizon, whereas it was between 60 and 70 % in soil horizons Bw1 and Bw2C (Fig. 4). In the medium and fine silt fractions I\textsubscript{inc} concentrations varied between 5 and 9 mg kg\(^{-1}\) with on average 60 % of I\textsubscript{sorb}. Similar observations were made in the coarse clay and medium clay fractions (8 - 13 mg kg\(^{-1}\) and 12 – 18 mg kg\(^{-1}\) I\textsubscript{inc}, respectively) with 50 -70 % of I\textsubscript{sorb}.

Discussion

Total halogen concentrations in different soil size fractions

The patterns for F\textsubscript{tot}, Cl\textsubscript{tot}, Br\textsubscript{tot} and I\textsubscript{tot} in soil size fractions < 63 µm (this study), were very similar to those of bulk soil sample profiles described in Epp et al. (2020), which included particle sizes up to 2 mm (Fig. 3). Bulk soil data was always in the lower concentration range compared to halogen concentrations analyzed in the present study (Fig. 3). This is explained by negligible amounts of clay minerals (Hosking et al. 1957) or pedogenic oxides in soil size fractions > 63 µm, resulting in lower total halogen concentrations.

F\textsubscript{tot} profiles of all investigated soil size fractions did not show any vertical patterns with depth (Fig. 3). All vertical F\textsubscript{tot} profiles strongly overlapped, thus no concentration differences emerged between the individual soil fractions (Fig. 3).

High F concentrations in soil are due to weathering of F-rich minerals in the host rock (Totsche et al. 2000; Zhang et al. 2010 and references therein). The host rock of the study site contains
F-bearing minerals such as biotite, and F released by weathering can subsequently be incorporated into secondary clay minerals or adsorbed onto pedogenic oxides. Commonly, the intensity of weathering in a vertical soil profile decreases with increasing depth (Linser and Scharrer 1966) and thus, it is expected that F, pedogenic oxide or clay mineral concentrations should show distinctive depth patterns. However, concentrations of pedogenic oxides and clay minerals did not vary within the top- and subsoil (Fig. 2 c & d) and point to a constant intensity of weathering in the depth profile. Very low Fe_{ox}/Fe_d ratios between 0.06 and 0.1 of the soil column (Epp et al. 2020) indicated that scarcely any iron from silicate weathering is supplied. Formerly present biotite from the host rock may already be entirely dissolved. Hence, no vertical concentration differences of F_{tot} within the mineral soil may be attributed to steady state or equilibrium conditions between F-release by weathering, subsequent surface adsorption or incorporation into the crystal lattice of clay minerals and gibbsite and surface input and subsequent accumulation in upper soil horizons. Besides, the lack of differences between the soil horizons during soil development could have been caused by a low solubility and slow reaction kinetics of clay minerals (Meyer and Howard 1983).

Within the top- and subsoil, Cl_{tot} was also relatively constant. Since the organic particles were not explicitly removed during sample preparation, it is very likely that the investigated samples still contained organic compounds which either incorporated or adsorbed halogens. The tendency for vertical depth patterns of Cl point to an accumulation of Cl in the Ah horizon and probably nutrient uplift in the subsoil, hence, the same processes as in the bulk soil (see details in Epp et al. 2020). Chlorination in the organic layer is the underlying fixation process which results in an accumulation of Cl in the organic layer and in the Ah horizon (Hjelm et al. 1995 and references therein; Öberg and Grön 1998; Redon et al. 2011). The lack of depth variations may indicate steady state or equilibrium conditions between surface input, sorption processes
and nutrient uplift. Also large reservoirs of Cl in soil (e.g., Redon et al. 2011) could have led to
the lack of differences in the horizons during soil development.

With regard to sorption processes, higher adsorption to soil particles in subsoil horizons (deeper
than 50 cm) was described by Li et al. (1995) for the case of Br and was attributed to exchange
reactions between Br and negatively charged organic compounds. The same study reported
adsorption of Br to be rather negligible in the topsoil (upper 50 cm). These results are in contrast
to our findings, since sorption of Br in the topsoil was not negligible, and we found on average
a minimum amount of 11 % of Br\textsubscript{tot} to be sorbed to pedogenic oxides or organic compounds.

Such contrasting findings can be explained by different soil types and concomitant soil
properties. In the study of Li et al. (1995) a Spodosol was investigated which is typically
characterized by a low pH, moist and acidic conditions which results in redistribution of organic
matter and Fe- and Al oxides from mineral topsoil into the mineral subsoil (Yli-Halla et al.
2006; Chesworth et al. 2008). In contrast, our investigated Cambisol showed organic soil
horizons (Oi and Oe) on top and in the different particle size fractions a C\textsubscript{org} concentration of
up to 10 % in the mineral top- and subsoil (Ah, Bw1 and Bw2C) clearly indicating the presence
and the potential importance of organic compounds. The discrepancy with our data can be
explained by different soil properties. The Bw1 soil horizon in our investigated Cambisol
contains pedogenic oxides where Br\textsubscript{inorg} sorption is significant, also in depths > 50 cm.

Although the medium clay fraction only contributes 1 wt% to bulk soil, F\textsubscript{tot} concentrations in
this fraction were the same as in the other investigated fractions. In addition, around 50 wt% of
Br\textsubscript{tot} and I\textsubscript{tot} and even 70 wt% of Cl\textsubscript{tot} were found in the medium clay fraction. Similar or even
much higher concentrations in samples that contribute only marginally to the total sample
weight further indicate the importance of halogen incorporation and sorption processes in soils.

In sum, our results showed that the lack of halogen variations with depth may be due to
equilibrium conditions between weathering, sorption processes and surface input. Besides, large halogen pools may inhibit vertical concentration differences during soil development.

Differences in sorption behavior between F and the heavier halogens (Cl, Br, I)

Fluorine has a much smaller radius compared to Cl, Br and I (Latscha et al. 2011). Also, changes in ionic strength have a very minor effect on the adsorption of F to kaolinite but strongly affects Cl, Br and I adsorption, which has been interpreted to resemble inner-sphere complexation for F but outer-sphere complexation for Cl, Br and I (Weerasooriya and Wickramarathna 1999). Thus, we assume that compared to Cl, Br and I, F is less prone to be sorbed to surfaces but is rather incorporated into the crystal lattice of, for example, clay minerals (e.g., kaolinite, illite) and gibbsite, occupying OH-sites (Romo 1054; Kau et al. 1998; Weerasooriya et al. 1998; Bower and Hatcher 1967). The substitution of OH$^-$ by F$^-$ in clay minerals is strongly pH-dependent (Romo and Roy 1957; Fuge 1988; Du et al. 2011) and is enhanced in acidic solutions (Chubar et al. 2005). The soil pH of 3-4 for the present location (Epp et al. 2020; Fig. 2b) offers therefore perfect conditions for an extensive OH$^-$ exchange by F$^-$. In contrast, anion substitution is not likely to be a valid mechanism for Cl$^-$, Br$^-$ and I$^-$. Rather adsorption to mineral surfaces via outer-sphere complexation is expected for Cl, Br$^-$ and I (Weerasooriya and Wickramarathna 1999). In the pH range of common soils (including those of the investigated sample location, see above), pedogenic oxides mostly have positively charged surfaces (Scheffer et al. 1998 and references therein) and thus serve as sorbing agents for halogens. This was confirmed, for example, by positive correlations between total Br and total I concentrations and pedogenic oxides as already described in Epp et al. (2020). Our results suggest that most F (on average 93 %) was incorporated into crystal lattices of minerals – likely of clay minerals, whereas on average and over all soil horizons, a least 32 % of Cl, 25 % of Br and 55 % of I were sorbed onto pedogenic oxides. On the other hand, this also means that significant amounts of Cl, Br and I have not been desorbed by phosphate
treatment (see subsection Sorption behavior of the Results section). This suggests that either significant incorporation into the crystal lattice of clay minerals or pedogenic oxides happened, or more likely, that soil-bound organo-halogens play a major role for the heavier halogens. To investigate this further, alternative extractions (e.g., NaOH or TMAH) and surface-specific analytical methods need to be applied.

Implications

The obtained data along with our previously published study allowed us to portray the sorption behavior of F, Cl, Br and I in a vertical soil profile from a temperate forest in four different soil size fractions. We found remarkable differences in the sorption behavior between F and the other halogens (Cl, Br and I): For fluorine, total concentrations are relatively similar for all particle sizes and the share of $F_{sorb}$ is mostly low to negligible and largely independent from particle size. In contrast, $Cl_{tot}$, $Br_{tot}$ and $I_{tot}$ concentrations increased with decreasing particle size and were by far highest in the smallest soil fraction (0.02-0.2 µm) and further, about 90% of $Cl_{tot}$ and about 70% of $Br_{tot}$ and $I_{tot}$ are sorbed in the mineral subsoil (Fig. 4). In general, sorption should increase with decreasing grain size (Sposito 1984; Scheffer et al. 1998), since the specific surface size of particles is strongly dependent on the particle size (Sposito 1984). Thus, our results for Cl, Br and I are in line with the generally expected halogen sorption behavior.

Steady state or equilibrium conditions between weathering, sorption processes and surface input probably caused lacking distinctive vertical concentration differences of $F_{tot}$, $Cl_{tot}$, $Br_{tot}$ and $I_{tot}$ in the mineral soil during soil development. Other biogeochemical processes might be negligible compared to the large halogen stocks in the soil which may inhibit visible concentration differences. The fact that the medium clay fraction only accounted for 1 wt.% of...
the bulk soil while it contained most of Cl, Br and I emphasized the importance of halogen sorption to clay minerals and/or pedogenic oxides.

Further understanding of sorption behavior on clay minerals may have implications for retention of organic and inorganic pollutants. Landfill sludges can contain for example Cl-bearing organic and inorganic pollutants. Material used in such landfills contain large amounts of clay minerals which enhance the sorption of organic compounds. Furthermore, the radionuclides $^{36}$Cl and $^{129}$I have a long half-life and their disposal and its effects are of current importance. Thus, understanding the sorption behavior of halogens on for instance clay minerals is crucial for retention processes of pollutants in landfills or potentially for radioactive waste disposal. In conclusion, our results revealed the importance of sorption processes for Cl, Br and I and incorporation processes for F which control the vertical halogen distribution in a Cambisol of a temperate forest.

Acknowledgements

We are grateful to Frieder Lauxmann for his help with the XRD analyses. Further thank goes to Lukas Schmid for his support with the centrifugation during the elaborate preparation process. Annelie Papsdorf and Sabine Flaiz is thanked for the CN analyses. Furthermore, we are very grateful to Christian Mikutta, Stefan Dultz and Peter Kühn for very constructive discussions and to two anonymous reviewers for their insightful comments on an earlier version of this manuscript. This study was funded by the German Research Foundation (DFG) [grant numbers Ma2135/20-1, Oe516/8-1].

References


incorporation in pyromorphite-group minerals. American Mineralogist 104:1673-1688.


**Figures**

**Figure 1.** (a) Simplified overview of all soil sample locations from the Feldberg, southwest Germany, including depiction of the typical forest at the investigated site. C = with canopy, OC = without canopy, (b) Schematic vertical soil profile of the investigated Cambisol and the corresponding soil horizons.

**Figure 2.** (a) Amount of C\textsubscript{org} in % of different particle sizes and soil depth, (b) pH data for each soil depth, pH = CaCl\textsubscript{2}, (c) amount of coarse, medium and fine clay fractions in % (in relation to bulk soil composition) for each soil depth, (d) content of pedogenic oxides in mg kg\textsuperscript{-1} for each soil depth. Al\textsubscript{ox}, Fe\textsubscript{ox} = poorly crystalline Al and Fe oxides, Al\textsubscript{d} and Fe\textsubscript{d} = sum of poorly crystalline and crystalline Al and Fe oxides. (b) – (d) data from Epp et al. (2020).

**Figure 3.** (a)-(d) Vertical depth patterns of total halogen concentrations (incorporated and adsorbed + inorganic and organic; mg kg\textsuperscript{-1}) in four different soil size fractions. Dark blue = bulk soil data from Epp et al. (2020), n = 18, light blue = halogen concentration in soil size fraction 20-63 µm, n = 6; pink = halogen concentration in soil size fraction 2-20 µm, n = 6; grey = halogen concentration in soil size fraction 0.2-<2 µm, n = 6 and green = halogen concentration in soil size fraction 0.02-0.2 µm, n = 6. For the horizon thicknesses on the y axis average values were taken over all profiles for each soil horizon. The error bars show the standard deviation.
Figure 4. (a)-(d) four different soil size fractions coarse silt (20-63 µm), fine to medium silt (2-20 µm), coarse clay (0.2-<2 µm) and medium clay (0.02-2 µm) versus adsorbed (%) halogen amount in mineral topsoil (Ah) and subsoil (Bw1 and Bw2C). Grey bars illustrate the entire range of halogens in percentage. Black dot marks mean values over all horizons in each particle size.

Appendix

Figure A1. (a) and (b) Dissolved inorganic F and Cl concentrations in the supernatant phosphate solution in each soil size fraction and each soil horizon after the desorption treatment of the soil samples in mg L⁻¹. Residual solution of all soil size fractions of each soil horizon were analyzed by ion chromatography.

Figure A2. (a)-(d) Adsorbed halogen concentrations of all soil size fractions versus Alox, Feox (poorly crystalline Al and Fe oxides) and vs Al_d and Fe_d (sum of poorly crystalline and crystalline Al and Fe oxides).
Tab. 1 Coordinates of sample positions.

<table>
<thead>
<tr>
<th>ID</th>
<th>Name</th>
<th>Lage (Gauss-Krüger, Potsdam, R + H)</th>
<th>WGS84</th>
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<tr>
<td>C1</td>
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<td>N 47.875794 E 7.995611</td>
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<tr>
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Tab. 2 Halogen concentrations in mineral topsoil and subsoil of different soil size fractions. Horizons were classified according to IUSS Working Group-WRB (2015). Total = halogen concentration adsorbed + incorporated (= inorganic + organic), inc. = halogen concentration incorporated, ads. = halogen concentration adsorbed, "-" = no further sample material available.

<table>
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<tr>
<th>Horizon (each n = 1)</th>
<th>Size fraction (wt.%)</th>
<th>Br</th>
<th></th>
<th></th>
<th></th>
<th>Cl</th>
<th></th>
<th></th>
<th></th>
<th>F</th>
<th></th>
<th></th>
<th>I</th>
<th></th>
<th></th>
<th>C_{org} (wt.%)</th>
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<td>76</td>
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<td>84</td>
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<td>76</td>
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<td>653</td>
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</table>
Figure 2

(a) % C<sub>org</sub> vs. depth (cm)

(b) pH vs. depth (cm)

(c) % clay fraction vs. depth (cm)

(d) pedogenic oxides (mg kg<sup>-1</sup>) vs. depth (cm)
Figure 3

(a) Sorbed Cl vs. soil size fraction (µm) for Ah, Bw1, and Bw2C.

(b) Sorbed F vs. soil size fraction (µm) for Ah, Bw1, and Bw2C.

(c) Sorbed Br vs. soil size fraction (µm) for Ah, Bw1, and Bw2C.

(d) Sorbed I vs. soil size fraction (µm) for Ah, Bw1, and Bw2C.
Figure 4

(a) $\text{Cl}_\text{tot} \text{ (mg kg}^{-1}\text{)}$

(b) $\text{Br}_\text{tot} \text{ (mg kg}^{-1}\text{)}$

(c) $\text{F}_\text{tot} \text{ (mg kg}^{-1}\text{)}$

(d) $\text{I}_\text{tot} \text{ (mg kg}^{-1}\text{)}$

Legend:
- bulk soil (Epp et al. 2020)
- 20-63 µm
- 2-20 µm
- 0.2-<2 µm
- 0.02-0.2 µm