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RESEARCH ARTICLE

Chlorine in plants and soils of a tropical lower montane forest in Ecuador: Development during two decades

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Abstract
Aims Cl is a micronutrient mainly supplied via deposition of marine aerosols. We assessed the development of Cl concentrations and stocks in plants and soils of a tropical montane forest far from a downwind ocean during two decades (1998–2019).
Methods We measured Cl concentrations in solid samples with a new combustion-based method.
Results The Cl concentrations in leaves of 17 tree species ranged 0.04–1.6 g kg^{-1}. Three tree species showed Cl concentrations below the minimum requirement of 0.2 g kg^{-1}. Twigs had the largest Cl concentration of all plant compartments (2.1 ± SD1.5 g kg^{-1}) and leaves the smallest. The Cl concentrations decreased from litterfall (0.52 ± 0.14) to the soil organic layer (0.12 ± 0.06), within the organic layer from top to bottom and further in the mineral soil (0.02–0.03) reflecting leaching losses and the retention of Cl in soil organic matter. The parent rocks (metamorphic sand to clay stone interlayering) contained 0.44 ± 0.20 g kg^{-1} Cl. The vegetation stored more Cl (28 ± 17 g m^{-2}) than the organic layer (2.9 ± 3.1) and mineral soil (fine earth 0–1 m, 22 ± 8.6) together. One meter of rock contained up to 168 g m^{-2} Cl. Wood production took up 0.36 ± 0.24 g m^{-2} yr^{-1} Cl. Litterfall cycled 0.55 ± 0.17 g m^{-2} yr^{-1} Cl representing 86 ± 72% of the standing Cl stock in leaves (0.64 ± 0.50 g m^{-2}). The leaching potential of Cl^- from leaves was likely < 10% of the reported Cl^- bulk deposition of 1.2 g m^{-2} yr^{-1}. There were no significant temporal

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trends of Cl concentrations in leaves, litterfall, organic layer, and mineral soil.

Keywords Bark · Leaching potential · Leaf · Litterfall · Organic layer · Rock · Root · Soil · Twig · Uptake

Introduction

Chlorine is an essential micronutrient for plants (Broyer et al. 1954; Marschner 2012), but Cl concentrations of plants and soil have less frequently been reported than those of other nutrients (Montelius et al. 2015; Svensson et al. 2021; 2023). One reason for the scarcity of solid phase Cl concentrations might be the lack of a routine method to measure them (Neidhardt et al. 2022; Svensson et al. 2023). The available plasma-based ionization methods combined with absorption spectrometry require extensive sample pretreatment (usually digestions with strong acids) and have high detection limits. Colorimetric and electrochemical methods, in contrast, show a good sensitivity and selectivity, but their use is mostly restricted to aqueous solutions (Rössner and Schwedt 1983; Mello et al. 2013). More recently, combustion-based methods coupled to ion chromatography (Neidhardt et al. 2022) or colorimetry (Svensson et al. 2023) to determine total Cl concentrations in solid phases have been reported. However, a routine method with a similar efficiency as the modern elemental analysis systems for C and N is still lacking.

Chlorine regulates the activities of several enzymes e.g., as a cofactor for the oxygen evolution in photosynthesis. Chlorine stabilizes the electric potential of the cell membrane and regulates its pH gradient and electrical excitability. Moreover, Cl^- balances the electric charge of cationic nutrients. Chlorine also increases the water-use efficiency of plants, but excess uptake might reduce the N-use efficiency (Marschner, 2012; Wege et al. 2017; Colmenero-Flores et al. 2019). For most plants, the minimum requirements range from 0.2 to 0.4 g kg^{-1} (dry weight) while Cl concentrations in plant tissue usually vary between 2.0 and 20 g kg^{-1} (Marschner 2012; Wege et al. 2017; Colmenero-Flores et al. 2019). Plants can even contain more Cl than required because Cl provides additional benefits for plants such as disease resistance and tolerance (Xu et al. 1999; Van den Hoof and Thiry 2012). Different to the early view that Cl^- deposited from the atmosphere to forested ecosystems is little retained in the catchment and hardly taken up by the vegetation (Eriksson 1955; Schlesinger 1997), recent work has shown that vegetation uptake substantially influences the Cl cycling (Montelius et al. 2015; Svensson et al. 2023). Moreover, Cl^- can be incorporated in soil organic matter as organo-Cl compounds (Öberg and Sandén 2005; Bastviken et al. 2009; Montelius et al. 2016). The natural chlorination of organic matter plays an important role in temperate and boreal soils which frequently contain more organically bound Cl than Cl^- (Johansson et al. 2003; Gustavsson et al. 2012; Redon et al. 2013). One consequence of the incorporation of Cl into organic matter would be an increase in the residence time of Cl in the soil organic layer on top of the mineral soil (Vogt et al. 1986). Otherwise, Cl^- would be quickly leached, because of its weak retention in soils with dominating negative surface charge (Borggaard 1984; Wang et al. 1987). Tree species, plant communities, and soil moisture contents influence Cl concentrations in soils and plants resulting in a pronounced small-scale heterogeneity of Cl concentrations (Montelius et al. 2015; Svensson et al. 2023). Up to now, most information about Cl concentrations in soils and plants of forest ecosystems originates from temperate and boreal sites (Montelius et al. 2015; Svensson et al. 2021; 2023). In the only study of a subtropical forest, we are aware of, Asbury and McDowell ((McDowell, et al., 1994)) estimated the annual Cl accretion into wood at 0.01–0.03 g m^{-2} yr^{-1} based on Cl concentration data in subtropical and tropical tree wood published by Rodin and Bazilevich (1967).

Because Cl is an essential plant nutrient and plants can even take up more Cl than they need, there might be Cl^- leaching from the canopy by rainfall. If there was substantial leaching of Cl^- from canopy leaves, canopy interaction models used to estimate dry deposition which rely on the assumption that Cl^- is an inert tracer would be biased (Ulrich 1983; Staelens et al. 2008). The use of canopy interaction models is necessary because more direct methods are laborious, expensive, and frequently fail to mimic the scavenging structure of the forest canopy (Ulrich 1983; Zhang et al. 2012; Mariraj Mohan 2016). Earlier work had shown that temperate deciduous forests indeed show leaching in the phase of leaf senescence and abscission in autumn with estimates ranging from 6% up to 50% of the annual throughfall flux of Cl^- (Ulrich 1983; Thimonier et al., 2008; Staelens et al. 2008). In evergreen coniferous or subtropical forests, there was substantially less Cl^- leaching, while up to now no evergreen tropical forest was studied (Staelens et al. 2008). It seems likely that in such forests Cl^- leaching from leaves occurs less, also because Cl^- belongs to the least easily leached ions from intact leaves of which < 1% of the total Cl concentration in leaves can be leached (Tukey 1970). One approach to estimate plant-internal retranslocation and leaching is the comparison of Ca-normalized Cl concentrations in leaves and leaf litterfall (Vitousek and Sanford 1986; Scott et al.1992). Because Ca is a phloem-immobile nutrient in plants while Cl is comparatively phloem-mobile (Marschner 2012), plant-internal retranslocation and leaching result in a decrease of the Cl/Ca concentration ratios from fresh leaves to leaf litterfall (Vitousek and Sanford 1986; Scott et al. 1992).

The lower montane forest in the south of Ecuador on the rim of the Amazon basin is dominated by the easterly trade winds during most of the year. The distance to the Atlantic Ocean in downwind direction is > 2500 km so that the dominating winds carry little sea salt (Makowski Giannoni et al. 2016). Only between September and February, when the intertropical convergence zone moves to the south, northerly and westerly winds carrying sea salt from the equatorial Atlantic and the Caribbean in the north, and the Pacific in the west reach this forest (Makowski Giannoni, et al., 2016). In line with this, Wilcke et al. (2001) reported a bulk deposition of 1.2 g m^{-2} yr^{-1}, which is lower than in forests closer to the Sea such as in Panama (3.5 g m^{-2} yr^{-1}, Cavelier et al. 1997), Jamaica (3.5 g m^{-2} yr^{-1}, Hafkenscheid 2000), or Puerto Rico (12.6 g m^{-2} yr^{-1}, McDowell 1998). Assuming that the deposited Cl^- is the major source of plant-available Cl, it is likely that the tropical montane forest in south Ecuador is comparatively Cl-poor. If this was true, the ecosystem might accumulate the deposited Cl^-, which should result in increasing Cl concentrations in plants and soils at the decadal scale.

We aimed to (1) establish and evaluate a novel, combustion-based electrochemical quantification method to determine Cl concentrations in plants and soils, (2) determine the Cl concentrations and stocks in soils and plants of a humid tropical montane forest, (3) evaluate if the Cl stocks in standing leaves and annual Cl fluxes with litterfall together with Cl/Ca concentration ratios in leaves and litterfall can be used to assess the leaching potential of Cl^- from leaves, and (4) assess if Cl concentrations and stocks changed in the past two decades. We hypothesized that (1) the new method with a simpler analytic procedure than previous methods reaches a comparable accuracy and precision as other available methods, (2) the study ecosystem shows a low bioavailability of Cl^- and thus Cl concentrations in plants at the lower end of sufficient nutrition, (3) the leaching potential of Cl from leaves is low compared to the reported Cl bulk deposition of 1.2 g m^{-2} yr^{-1} (Wilcke et al. 2001), and (4) the study ecosystem accumulated Cl from 1998 to 2018 reflected by increasing Cl concentrations in plants, litterfall, and soil with time. To test our hypotheses, we quantified total Cl concentrations and stocks in plant compartments (leaves, bark, twigs, roots), litterfall, organic layer, mineral soil and rock samples collected in several years between 1998 and 2018.

Materials and methods

Study site

The study site is located in the Ecuadorian province of Zamora-Chinchipe (latitude 3°58'S and longitude 79°4' W). The core of the study site has been described in previous work as Microcatchment (MC) 2 (e.g., Wilcke et al. 2001, 2013, 2017), which is 9.1 ha large, reaches from 1850 to 2200 m above sea level and shows 30°–50° steep slopes. Soil and plant samples were collected from the catchment and its near surroundings. Mean annual precipitation (April 1998-March 2019) was 2300 ± 230 mm and mean annual temperature approximately 15 °C.The soils are mainly Folic Dystric Cambisols (IUSS Working Group WRB 2022) developed from metamorphic rock (phyllite, meta-siltstone, meta-sandstone). They show a dominance of negative surface charge, because of the presence of three-layer clay minerals (Schrumpf et al. 2001). The soils are acidic with a low base saturation and high organic matter concentrations (Table S1). Hydromorphic properties occur frequently. The species-rich vegetation is an evergreen lower montane forest with a canopy height of

20–30 m (Homeier et al. 2008). The most common tree families are Lauraceae, Rubiaceae, Melastomataceae, and Euphorbiaceae and the most abundant tree species is *Graffenrieda emarginata* (Ruiz & Pav.) Triana (Melastomataceae). In the understory, megaphyllous shrubs (e.g., Piperaceae) and herbs (Cyclanthaceae, Heliconiaceae, Zingiberaceae) are prevalent (Homeier et al. 2008).

Sampling and sample processing

From November 2005 to February 2006, young fully-developed sun-exposed leaves from 26 individuals of 14 abundant tree species of the study site were sampled (Table S2). Common species were sampled in triplicate. In addition, we sampled sun-exposed leaves of 41 individuals of seven species from 2008 to 2018, eight bark and nine twig samples from three individuals of each of three species in 2011, and 20 fine-root segments from eight species in 2016 (Pierick et al. 2021).

Litterfall was collected along three 20 m-long transects located at approximately 1900, 1950 and 2000 m above sea level, each covering approximately 10 m in elevation. Litterfall samples were collected weekly with three 0.25 m^2 traps per transect. The monthly bulked samples of June and December from 1999 to 2019 were analyzed for Cl concentrations.

From 2002 to 2018, we sampled 22 organic layers (2 in 2002, 3 in each of 2004, 2006 and 2018 and 11 in 2016) in the study area and separated them into Oi, Oe, and Oa horizons. At one location, we lost the Oe and Oa horizons and at another one, we could not separate the Oe and Oa horizons. From 1998 to 2018, we sampled 42 A horizons, 34 B horizons and 26 C horizons from the wall of each of 42 hand-dug soil pits in a representative way. In 1998, 20 pits were dug, in 2002 two pits, in each of 2004, 2006, and 2018 three pits, and in 2016 eleven pits. Moreover, in 1998 we collected five unweathered rock samples from the surface of recent landslides, including a phyllite, a meta-sandstone, a meta-siltstone, a light laminite (i.e., an interlayering of phyllite to meta-sandstone with a high sandstone content), and a dark laminite (i.e., an interlayering of phyllite to meta-sandstone with a high phyllite content).

After drying all samples to a constant mass at 40 °C in a drying oven, leaf, litterfall, and organic horizon samples were shredded with a knife mill (Grindomix GM 200, Retsch, Haan, Germany) and ground to a fine powder with a planetary ball mill (PM 200, Retsch). Samples of the mineral soil were sieved to < 2 mm and also ground with the planetary ball mill. Rock samples were ground in an agate grinding set using a vibratory disk mill (Siebtechnik GmbH, Mülheim an der Ruhr, Germany).

Measurements

The total Cl concentrations of all solid samples (leaves, litterfall, soil, rock) were determined with an elemental analyzer Rapid CS cube (Elementar Analysensysteme, Langenselbold, Germany) in a modification for Cl detection. Samples packed in tin capsules were combusted at 1150 °C to convert the Cl in solid samples to gaseous HCl. Synthetic air was used as carrier gas. The gaseous fractions were passed through a drying column containing Sicacide (Merck, Darmstadt, Germany), a sulfuric acid drying agent on inert carrier material, to remove water and minimize condensation and loss of HCl. Subsequently, HCl was detected by an electrochemical cell in which the HCl reacted with elemental Ag releasing electrons which produced an electrical current proportional to the Cl concentration in the sample. The device was equipped with a "200 ppm" solid-state electrochemical detector with a measuring range of 0.5 to 50 µg of Cl. To meet this concentration range, the mass of the samples was adjusted depending on the sample-specific Cl concentration. As a consequence, we used 20–30 mg of sample for plant materials and litterfall, 50–70 mg for organic horizons and up to 100 mg for mineral soil horizons and rocks. To convert all Cl in the sample to HCl, a high H:Cl ratio was necessary. Therefore, 3–5 mg polyethylene powder (Elementar Analysensysteme, Langenselbold, Germany) was added to 10–100 mg of plant, litter, or soil sample as an H source.

We used a NH_4Cl solution for calibration. For this purpose, 1.51 g NH_4Cl was dissolved in 1 L ultrapure water (> 18 MΩ cm) to produce a stock solution of 1000 mg L^{-1} Cl^-, which was further diluted to the different target concentrations. The diluted solutions were dried for two hours at 80 °C before analysis. To assess the accuracy of our measurements, we included a certified reference material (NIST CRM 1515 "Apple Leaves"), conducted recovery tests of added Cl^- (as dissolved NH_4Cl) for each matrix type and remeasured 20 mineral soil samples of a Chilean climatic transect that had previously been measured for total Cl concentrations by combustion coupled to subsequent ion chromatography (C-IC) by Neidhardt et al. (2022). Repeated measurements of each sample type (plant, litterfall, all soil horizons, and rocks) were used to determine the measurement precision. To eliminate matrix effects, we used standard addition calibrations by adding known masses of NH_4Cl in dissolved form to each sample matrix except for the samples of 2016. The Cl concentrations in each matrix were determined with the mean of 3–14 individual standard calibrations, examples of which are shown in Figs. S1 and S2. We used the mean calibration line of all repeated standard calibrations for each matrix to quantify Cl concentrations in the respective matrix (leaves, bark, twigs, roots, Oi, Oe, Oa, A and B horizons, and rocks). For the 2016 samples, we eliminated the matrix effect for each matrix by calculating a day factor for each measurement run. We spiked two samples of the same matrix we were analyzing (e.g., litterfall or leaves) with a known amount of NH_4Cl measured before and after a run of samples. The mean recovery of the two spikes served as day factor. Because the Cl detection method is cross-sensitive to CO_2 and NO_x and to gasses forming during incomplete combustion (e.g., CO, CH_4) with the former occurring in samples with Cl concentrations < 100 mg kg^{-1} and the latter at sample masses > 50 mg according to the manufacturer's information, CO_2 and NO_x may cause a negative peak at the beginning of the integration. Our new Combustion – Electrochemical Cell (C-EC) method allows for the measurement of 30–50 samples per work day.

Total Ca concentrations in leaves and litterfall were determined after pressure digestion with concentrated HNO_3 in a microwave oven (MARSXpress, CEM, Matthews, NC, USA) and subsequent concentration measurement with an Inductively-coupled Plasma Optical Emission Spectrometer (ICP-OES, Agilent 5100 VDV, Waldbronn, Germany).

Calculations and statistical analysis

To determine the Cl stocks in aboveground and belowground biomass, we used biomass data from the same study site (Leuschner et al. 2013; Homeier and Leuschner 2021) and multiplied the biomass measures from the literature with our Cl concentration measurements in the various plant compartments. The Cl stock of the understory trees and shrubs and standing or lying coarse woody debris were ignored since understory biomass in mature tropical moist forests typically only accounts for $< 3\%$ of above-ground biomass (Moser et al. 2011) and the coarse woody debris contained $< 1.8\%$ of the total nutrient stock (but Cl was not included) in the dead organic matter (including the organic layer) at our study site (Wilcke et al. 2005). The Cl stock of the soil was calculated for each horizon as the product of Cl concentration, horizon thickness, bulk density and for mineral soil horizons additionally the fraction of fine earth. The soil bulk densities were measured by collecting an undisturbed soil column with a stainless-steel ring of a volume of 100 cm^3, oven-drying and weighing. If bulk density was not available, we assumed the mean values determined by Wilcke et al. (2002) for the organic horizons (i.e., 0.08, 0.11, and 0.20 g cm^{-3} for Oi, Oe, and Oa, respectively) and 1.0, 1.3, and 1.3 g cm^{-3} for A, B, and C horizons, respectively. For phyllite, we used a density of 2.7 g cm^{-3} and for the other rock types of 2.3 g cm^{-3}. To determine the fraction of the fine earth, we estimated the stone content volumetrically for each horizon at the soil pit in the field. If such estimates were not available with assumed a stone content of 10%, 30%, and 70% for A, B and C horizons, respectively.

We tested the monthly time series of the litterfall for significant temporal trends with the Seasonal Mann–Kendall test (Hirsch et al. 1982) using the function SeasonalMannKendall() from the package Kendall (McLeod 2011) in the statistical software R (R Core Team 2017).

Results

Evaluation of the measurement method

All standard addition calibrations were linear and the coefficients of determination near 1.00 (Figs. S1-S2 as examples). All calibration lines intersected the X axis in the negative area so that a positive Y axis intercept resulted as is expected if there is a matrix effect.

The repeated measurement of NIST SRM 1515, "Apple Leaves" resulted in a Cl concentration of $536 \pm$ SD 42 mg kg^{-1} ($n = 15$) after the elimination of the matrix effect, which deviated by 8% from the certified value of 582 ± 7.5 mg kg^{-1} while the mean ± SD of our measurement overlapped with the certified value + SD. The mean recovery of the NH_4Cl standards spiked to samples of all matrices was 102 ± 15% ($n = 175$). The regression of our measurements on the previous measurements of Neidhardt et al. (2022) for 20 samples along a climatic transect in Chile, which was forced through the origin, resulted in a slope close to unity and a nearly perfect coefficient of determination of 1.00 (Fig. 1).

The coefficient of variation (CV = SD/mean × 100 [%]) of the measurements of NIST SRM 1515 was 7.8%. The mean CV of 43 double and 2 triple measurements of all matrices was 12 ± 16%. The mean precision of the measurement of plant, litterfall, and rock samples was higher (CV 5.4 ± 5.8%, n = 21) than that of the soil horizons (18 ± 19%, n = 24).

Chlorine concentrations

There were no significant temporal trends of the Cl concentrations in any sample type, for which several samples between 1998 and 2018 were collected (leaves, litterfall, soil; Figs. S3-S5). Therefore, we combined all samples of the same type, no matter when they were collected and calculated arithmetic means. The mean Cl concentrations in the solid phases decreased in the order, twigs > bark > roots > leaves > litterfall > Oi ≈ Oe > Oa > rocks > A > B ≈ C horizons (Fig. 2).

The Cl concentrations in the leaves showed considerable species-specific variation (Fig. 3). The leaves of *P. oleifolius*, *A. lojaensis* and *H. americanus* showed the largest Cl concentrations and those of *P. opaca*, *Miconia* sp. and *A. verticillata* the smallest. Nine tree species had leaf Cl concentrations above and five near the range of the minimum requirement of 0.2–0.4 g kg^{-1}. The species *A. verticillata*, *Miconia* sp., and *P. opaca* had mean Cl concentration in the leaves below this range.

Chlorine stocks

The total biomass of the vegetation (above- and belowground) stored a similar amount of Cl as the organic layer and the fine earth of the soil to a depth of up to 1 m together (Table 1). The shallower the considered soil depth was, the larger was the contributon of the vegetation to the total Cl stock. When only the main root zone was considered (i.e., the organic layer and the fine earth of the mineral soil to a depth

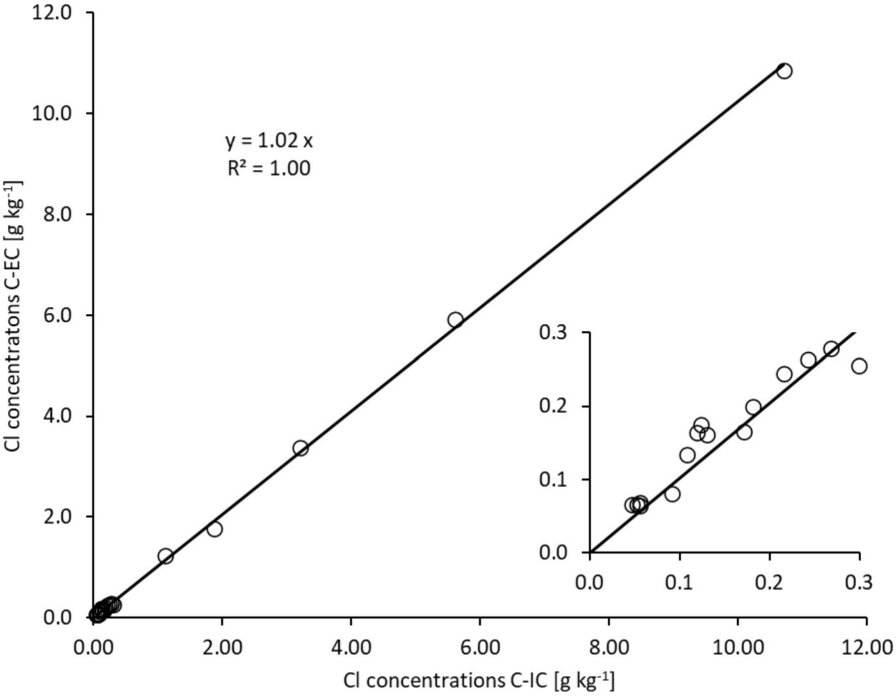

Fig. 1 Relationship between the Cl concentrations in 20 mineral soil samples from four soil profiles (5 depth intervals: 0–1, 1–5, 5–10, 20–30, 40–50 cm) along a climatic gradient in Chile measured with Combustion-Ion Chromatography (C-IC; Neidhardt et al. 2022) vs. our new Combustion – Electrochemical Cell (C-EC) approach. The inlet figure shows a magnification of the lower concentration range

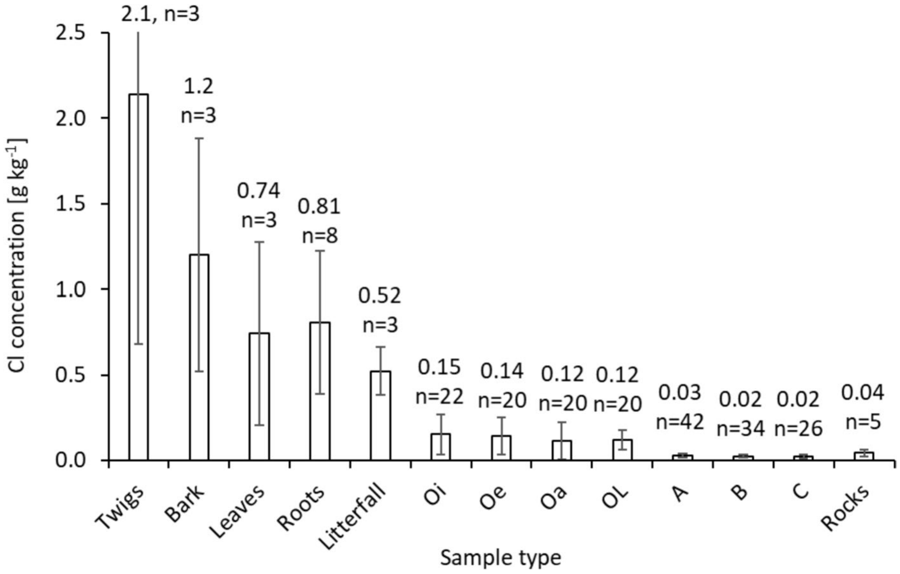

Fig. 2 Mean Cl concentrations of the studied sample types and standard deviations; n is the number of independent samples. Oi, Oe and Oa are differently decomposed organic soil horizons, A, B, C are mineral soil horizons, OL is organic layer (including the Oi, Oe, and Oa horizons)

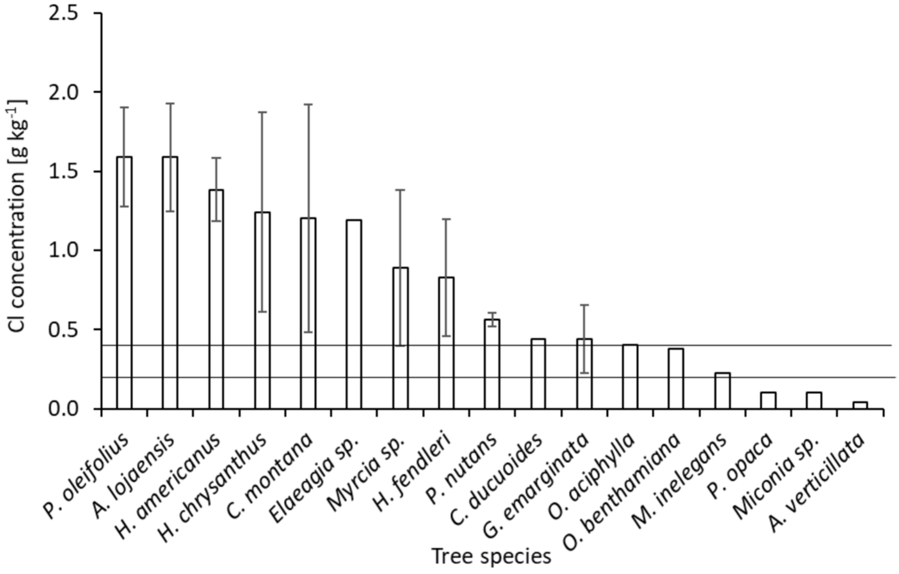

Fig. 3 Mean Cl concentrations and standard deviations ($n = 1$–13 tree individuals) in the leaves of the 17 studied tree species ordered according to the Cl concentrations. The horizontal lines indicate the range of the minimum requirement of Cl (Marschner 2012; Wege et al. 2017; Colmenero-Flores et al. 2019). See Table S2 for full species names

of 0.3 m), the total biomass stored 3.3 times as much Cl as the soil. The roots stored 7.6% of the total Cl stock in the biomass of the trees. The mean Cl stock in 1 m of the rocks was 102 ± 43.6 g m^{-2}, the Cl-richest rock, the light laminite, stored 168 g m^{-2} Cl and the Cl-poorest, the phyllite, 56.6 g m^{-2} Cl.

Plant-bound Cl fluxes

Mean annual litterfall from 1999 to 2019 (i.e., n = 21 years) varied from 1015 ± 165 to 1116 ± 208 g m^{-2} yr^{-1} among the three measurement transects. The Cl fluxes with fine litterfall varied from 0.40 ± 0.17 to 0.73 ± 0.22 g m^{-2} yr^{-1} and averaged 0.55 ± 0.17 g m^{-2} yr^{-1} (Fig. S3). The mean Cl fluxes with fine litterfall accounted for 86 ± 72% of the standing Cl stock in the leaves (Table 1). The large error is attributable to the wide variation of Cl concentrations in the leaves of the studied tree species. Leaf litterfall, which was measured at the lower end of our study area at four sites in three different studies in parallel to our litterfall measurements, contributed

Table 1 Chlorine stocks in plant compartments, aboveground (AGB) and belowground biomass (BGB), the organic horizons Oi, Oe, and Oa, the total organic layer (including all three O horizons), and the fine earth (excluding stones) of the mineral soil to a depth of 0.3, 0.5, and 1 m, respectively

			Contribution to the total ecosystem stock to		
Compartment	Cl stock [g m^{-2}]	Standard deviation [g m^{-2}]	0.3 m soil depth [%]	0.5 m soil depth [%]	1 m soil depth [%]
Leaves	0.64	0.50	1.8	1.6	1.2
Stem wood	25	17	69	60	47
Total AGB	26	17	71	62	48
Coarse roots	1.6	1.2	4.4	3.9	3.0
Fine roots	0.50	0.38	1.4	1.2	0.95
Total BGB	2.1	1.3	5.8	5.1	4.0
Total biomass	28	17	77	67	52
Oi	0.30	0.36	0.82	0.71	0.56
Oe	1.3	2.1	3.8	3.3	2.6
Oa	1.4	2.1	3.7	3.2	2.5
Organic layer	3.0	3.1	8.0	7.0	5.5
0–0.3	5.5	4.0	15		
0–0.5	11	5.8		26	
0–1 m	22	8.6			42

We used biomass data of Leuschner et al. (2013) and Homeier and Leuschner (2021) from 18 plots in our study area (except for the root data, which are from a single location at the lower end of our study area). We assumed that our Cl concentration measurement of twigs/barks is representative for wood and that of roots for both, coarse and fine roots. Furthermore, the percent contribution of the compartments to the total Cl stocks in the whole ecosystem down to the three different mineral soil depths is shown. Where necessary, the error was propagated according to the Gaussian law.

on average 69 ± 27% to total fine litterfall (Röderstein et al. 2005; Moser et al. 2007; Werner and Homeier 2015). Based on the leaf lifespan of 23 ± 8.9 months reported by Moser et al. (2007) for the lower end of our study area, the annual Cl flux contributed by leaf litterfall assuming no plant-internal retranslocation and leaching prior to abscission would be a maximum of 0.33 ± 0.28 g m^{-2} yr^{-1}. The mean Cl/Ca concentration ratios in fresh leaves of 13 tree species, for which these data were available, were 0.15 ± 0.12. If the three tree species with Cl concentrations near or below the range of sufficient nutrition were omitted, this ratio increased to 0.19 ± 0.11. The litterfall had a mean Cl/Ca ratio of 0.05 ± 0.01 (n = 3). This resulted in Ca-normalized Cl concentration ratios between fresh leaves and litterfall of 3.2 ± 2.7 and 4.1 ± 2.5 considering all 13 tree species and only the 10 species clearly above the range of the minimum Cl requirement, respectively. We also calculated the Ca-normalized Cl concentration ratios between senescent and fresh leaves using data of Butenschoen et al. (2014), who determined Ca concentrations in senescent leaves of six tree species collected from fresh litterfall. In this calculation, we additionally assumed that the Cl concentration of the fine litterfall represented that of the senescent leaves. As results, ratios of 1.0 ± 0.74 and 1.4 ± 1.3 emerged for all six tree species and after elimination of one species with particularly high Ca concentrations, respectively.

Mean wood production of 18 plots (trees with a diameter at breast height > 10 cm) in the study area was 215 ± 135 g m^{-2} yr^{-1} (Homeier and Leuschner 2021). If it was assumed that this wood had the same Cl concentration as the mean of twigs and bark (Fig. 2), i.e., 1.7 ± 0.40 g kg^{-1}, a Cl accretion in wood of 0.36 ± 0.24 g m^{-2} yr^{-1} would result and thus a total net plant uptake of 0.91 ± 0.30 g m^{-2} yr^{-1} as sum of Cl accretion in wood and Cl flux with fine litterfall. The latter accounts for 76% of the bulk deposition of 1.2 g m^{-2} yr^{-1} Cl^{-} reported by Wilcke et al. (2001) for the study area. Sixty % of the estimated total plant uptake was cycled with fine litterfall.

The residence time in the organic layer calculated as quotient of the Cl stock in the organic layer and the annual Cl flux with litterfall was 5.2 ± 3.2 yr (Vogt et al. 1986). This number lacks the root litter input into the organic layer, which was estimated at 393 ± 77 g m^{-2} yr^{-1} for the lower end of our study area (Röderstein et al. 2005). Considering the root litter input would reduce the residence time of Cl in the organic layer to 3.3 ± 3.7 yr.

Discussion

Method evaluation

Our Cl measurements revealed that all studied samples showed a matrix effect that needed to be corrected. The matrix effect was pronounced but similar within the same sample types (particularly organic vs. mineral samples). We successfully eliminated the matrix effect by standard addition, either as full calibration (Figs. S1-S2) or by adding a single standard (only for samples from 2016). The accuracy of our measurements was confirmed by (i) a recovery of the certified Cl concentration in NIST CRM1515 (apple leaves) within the error margins of the certificate. Moreover, (ii) the spiked NH_4Cl standards with a known Cl mass were consistently recovered at values near 100% of the expected Cl concentrations. Finally, (iii) the comparison of our measurements using the new C-EC method with those of the Combustion-Ion Chromatography (C-IC) method of Neidhardt et al. (2022) resulted in an almost perfect match (Fig. 1).

The finding that the precision for the Cl concentration measurements in plant materials, litterfall, and rocks was $< 10\%$ was also satisfying. However, the Cl concentration measurement in organic and mineral soil samples, which had consistently the lowest Cl concentrations, could only be measured with a precision of $< 20\%$. We cannot rule out that this lower precision is related with a higher heterogeneity of the soil than the other sample types, which would have required a better homogenization.

Overall, our first hypothesis that our new Cl measurement method (C-EC), which was as simple as elemental analysis methods for C and N, performed similarly well as other available and more complicated measurement methods was fully supported.

Chlorine bioavailability

The mean Cl concentration of 0.74 g kg^{-1} in the leaves was below the range of 2–20 g kg^{-1} reported by Marschner (2012) for plants in general and at the lower end of the range of 0.18–14 g kg^{-1} reported by Svensson et al. (2021) for 32 temperate forests mainly from eastern USA and central to northern Europe (Fig. 2). The fact that we found larger Cl concentrations than the minimum requirement of 0.2–0.4 g kg^{-1} (Marschner 2012; Wege et al. 2017; Colmenero-Flores et al. 2019) in the leaves of 14 of the studied 17 tree species nevertheless indicated a sufficient Cl supply for most plants at our study site (Fig. 2). However, the tree species *A. verticillata*, *Miconia* sp., and *P. opaca* potentially suffered from Cl insufficiency and five more species showed Cl concentrations just in the range of the minimum requirement. Moreover, some individuals of *Elaeagia* sp., *O. aciphylla*, and M. *inelegans* showed insufficient Cl supply < 0.2 g kg^{-1} Cl in leaves, possibly depending on the soil moisture conditions and the local composition of the vegetation as had been shown for boreal ecosystems by Svensson et al. (2023).

The Cl concentrations in twigs and bark were considerably higher than reported by Svensson et al. (2021) for temperate forests (twigs: 0.03–0.13, bark: 0.03–0.3 g kg^{-1}, Fig. 2) but still in an intermediate position of the reported range of Cl concentrations in leaves. The comparatively high Cl concentrations in twigs and bark resulted in 10 times higher Cl accretion rates in wood than reported for a subtropical forest in Puerto Rico by McDowell and Asbury (1994). Apparently, the studied tropical trees accumulated more Cl in the wood and bark than the temperate trees in Svensson et al. (2021). Interestingly, the bark had the double Cl concentrations of the wood although it is exposed to leaching by stemflow. We can only speculate that this may be attributable to bark-dwelling organisms that accumulate Cl.

The Cl concentrations in litterfall at our study site were at the upper end or above the range of 0.05–0.53 g kg^{-1} (median 0.15 g kg^{-1}) in the study of Redon et al. (2011) on 51 French forests with different tree compositions including coniferous and deciduous trees (Fig. 2). One reason for the higher Cl concentration of litterfall might be the contribution of woody plant parts with higher Cl concentrations than reported for temperate forests (Svensson et al. 2021).

However, we did not measure Cl concentrations in some constituents of the litterfall such as flowers, fruits, seeds, or epiphytes.

The Cl concentrations of the organic layers at our study sites were at the lower end of the range of Cl concentrations reported by Redon et al. (2011) for French forests of 0.05–1.0 (mean: 0.25) and 0.05–0.44 g kg^{-1} in the compilation of Svensson et al. (2021) excluding the results of Redon et al (2011), which are also reported in Svensson et al. (2021). The same was true for the Cl concentrations in the mineral soil for which 0.03–0.21 (mean: 0.06) and 0.02–0.1 g kg^{-1} were reported in Redon et al. (2011) and Svensson et al. (2021), respectively (Fig. 2). The decreasing Cl concentration with increasing soil depth at our study site suggests that Cl deposition from the atmosphere was more important than rock weathering although the rocks had a higher Cl concentration than the mineral soil and thus provided some bioavailable Cl by weathering (Fig. 2). However, Wilcke et al. (2017) reported that the weathering release of Ca, Mg, K, and Na was at least one order of magnitude lower than the aboveground fluxes of these elements with throughfall, stemflow, and litterfall and it seems reasonable to assume the same for Cl. A contribution of nutrient uplift by the plants as suggested by Epp et al. (2020) seems unlikely, because Jobbágy and Jackson (2001) reported that only limiting nutrients are uplifted to an extent that results in their accumulation in the topsoil. Our study forest was, however, shown to be N and P co-limited (Wullaert et al. 2010; Homeier et al. 2012). Moreover, the fact that the decrease in Cl concentrations with increasing soil depth paralleled a decrease in soil organic matter concentrations in the same direction (Wilcke et al. 2002) suggested that chlorination of organic material might have contributed to our finding, because even in mineral soils up to 80% of total Cl can be organically bound (Svensson et al. 2021). This assumption is also supported by the long residence times of Cl in the soil organic layer of > 3 yr although Cl$^-$ should be quickly leached.

Overall, the comparison with the literature about Cl concentrations in solid phases of terrestrial ecosystems gives a mixed result. The Cl concentrations in the leaves and soils suggested that the study ecosystem was Cl-poor, while this was not true for the bark, twigs and litterfall. Almost two thirds of the studied plant species apparently took up more Cl than physiologically required. This was only partly in line with the expectation for an ecosystem located far from the Sea. We conclude that our second hypothesis of a generally low Cl bioavailability is only partly supported, possibly because of considerable sea salt deposition during the time when the innertropical convergence zone had migrated far to the south (Makowski Giannoni et al. 2016).

Potential chloride leaching from the canopy

Using the share of senescent leaves in fine litterfall of 69% to estimate the contribution of leaf fall to the Cl flux with litterfall of 0.55 g m^2 yr^{-1} yields 0.38 g m^2 yr^{-1}, which is close to the 0.33 g m^2 yr^{-1} of the expected leaf litterfall based on the leaf lifespan of 23 months (Moser et al. 2007). The difference between these two estimates is 0.05 g m^2 yr^{-1}, which would be available for plant-internal retranslocation or leaching. However, this is a rough estimate, because 31% of the fine litterfall consists of other plant debris than leaves including twigs, bark, seeds, fruit, epiphytes etc., the mass contribution and Cl fluxes of which are unknown. The comparison of the Ca-normalized Cl concentration ratio of fresh leaves to litterfall of 3.2 to 4.2 if the Ca concentration of the fine litterfall is used suggests a potential plant-internal retranslocation plus leaching of 69–76% of the Cl in the leaf fall, i.e., 0.23–0.25 g m^2 yr^{-1}. Again, this number is a rough estimate because of the unknown role of the other litterfall components. If we used the Ca concentrations of senescent leaves reported by Butenschoen et al. (2007), the retranslocation plus leaching potential would decrease to 26% of the Cl in the leaf fall, i.e., 0.09 g m^2 yr^{-1} or even zero if the one species with particularly high Ca concentrations in senescent leaves was omitted. Unfortunately, we do not avail Cl concentrations of the senescent leaves so that this estimate again is influenced by the unknown role of the other fine litterfall components and their Cl/Ca ratios. The mean of these five rough estimates would be 0.12 ± 0.11 g m^2 yr^{-1} representing 13% of total plant uptake (fine litterfall plus wood accretion) and 10% of bulk deposition. The highest value would account for 21–27% of plant uptake and bulk deposition, which are available for plant-internal retranslocation and leaching. Because of the comparatively good phloem mobility of Cl$^-$ (Marschner 2012), it can be assumed that part of these estimates is plant-internally redistributed so that leaching is likely even lower. We conclude that our third hypothesis assuming a low leaching potential of Cl^- from the canopy is supported.

Temporal development of Cl concentrations and stocks

Because we did not observe a temporal trend in the annual Cl fluxes with litterfall from 1998 to 2019 (Fig. S3), we assume that there was no accumulation of Cl in the vegetation during this period. This assumption is corroborated by the finding that there was also no trend in the Cl concentrations of the leaves, which we sampled on three to four dates between 2008 and 2018. Similarly, the absence of a temporal trend in the Cl concentrations in the organic layer (Fig. S4) and A horizons (Fig. S5A) and the stocks of the uppermost 0.3 m of the mineral soil (Fig. S5B) did not point at an accumulation of Cl in organic layer and the main root zone of the mineral soil. However, the soil in the study region is heterogeneous and the partly low number of samples collected in individual years might not have been representative for the whole study area. As a consequence, we have to reject our fourth hypothesis that the study ecosystem accumulated Cl during the observation period. This either implies that outputs via the streamflow compensated inputs resulting in steady-state conditions with respect to Cl concentrations and stocks or that Cl was accumulated in the deep subsoil, which we did not analyze.

Conclusions

Our results demonstrate that the measurement of Cl in solid samples by a combination of combustion with a solid-state electrochemical detector is a viable option with a high accuracy and satisfying precision supporting our first hypothesis that the new Combustion-Electrochemical Cell (C-EC) method reaches a similar accuracy and precision as other available methods.

The fact that only a few tree species showed low Cl concentrations in their leaves near to the range of insufficient nutrition while twigs and barks showed high Cl concentrations and litterfall fluxes were also high compared with the literature does not support our second hypothesis that the study ecosystem was generally Cl-poor. Obviously, the seasonal sea salt input from nearer oceans to the north and west delivered enough Cl^- for plant nutrition.

Our rough estimates of potential Cl^- leaching from leaves indicated on average at most a small contribution of leaching to plant uptake and bulk deposition of likely < 10% if plant-internal retranslocation before leaf abscission was considered, supporting our third hypothesis that the leaching potential of Cl^- from leaves is low relative to bulk deposition.

We did not observe temporal trends of Cl fluxes with litterfall and stocks in the leaves, soil organic layer, mineral A horizon, and uppermost 0.3 m of the mineral soil so that we have to reject our fourth hypothesis that the study ecosystem accumulates deposited Cl^-.

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Author contribution The study conception and design were developed by Jürgen Homeier, Kerstin Pierick, Carlos Valarezo, Andre Velescu, and Wolfgang Wilcke. Material preparation, data collection and analysis were performed by Pablo Alvarez, Timo Gerbert, Jürgen Homeier, Kerstin Pierick, Tobias Steinert, Moritz Stenger, Andre Velescu, and Wolfgang Wilcke. The first draft of the manuscript was written by Tobias Steinert and Wolfgang Wilcke and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability The data will be uploaded to the data warehouse of the Research Unit “Environmental changes in biodiversity hotspot ecosystems of south Ecuador: Response and feedback effects (RESPECT, DFG FOR2730)” hosted by the University of Marburg, Germany and will become public after an embargo time. The data are immediately available from the corresponding author on reasonable request.

Declarations

Competing interests The authors have no relevant financial or non-financial interests to disclose.

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