Organochlorine turnover in forest ecosystems: The missing link in the terrestrial chlorine cycle

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[1] Research in the last 20 years has shown that chlorine undergoes transformations between inorganic and organic forms as part of a complex biogeochemical cycle in terrestrial systems. Natural organochlorine production appears to be associated with the decomposition of plant material on the soil surface, though the chlorine cycle budget implies that a proportion of natural organochlorine enters soil through plant litter and atmospheric deposition as well. Organochlorine compounds may form through biotic and abiotic pathways, but the rates and magnitude of production in the field remain undefined. We have performed a time-dependent trace of chlorine concentration through forest ecosystems, revealing distinct fractions of naturally produced organochlorine in plant biomass. Aliphatic organochlorine constitutes an intrinsic component of healthy leaves that persists through senescence and humification of the plant material, making a substantial contribution to the pool of soil organochlorine. Plant leaves also contain soluble aromatic organochlorine compounds that leach from leaf litter during early decay stages. As decay progresses, high concentrations of insoluble aromatic organochlorine accrue in the humus, through *de novo* production as well as adsorption. The rates of aromatic organochlorine production and degradation vary seasonally and conversely. This study presents the first unambiguous evidence that there exist multiple pools of chlorinated organic matter in the soil environment and that leaf litter deposition makes a significant and refractory contribution to the soil organochlorine pool, providing key insights into the biogeochemical chlorine cycle.

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1. Introduction

[2] Inorganic chloride (Cl_{inorg}) delivered to soil through atmospheric deposition can undergo plant uptake, leaching, and reactions to form organochlorine (Cl_{org}). Natural chlorination may occur through biotic [*Bastviken et al.*, 2009; *Niedan et al.*, 2000; *Reina et al.*, 2004] and abiotic [*Fahimi et al.*, 2003; *Holmstrand et al.*, 2006; *Keppler et al.*, 2000; *Schoeler and Keppler*, 2002] processes under environmental conditions. Accumulated evidence indicates that Cl_{inorg} converts to Cl_{org} during the decay and humification of plant material on the soil surface [*Asplund and Grimvall*, 1991; *Asplund et al.*, 1989; *Flodin et al.*, 1997; *Hjelm et al.*, 1995; *Müller and Schmitz*, 1985; *Myneni*, 2002b; *Öberg*, 2002]. The terrestrial chlorine (Cl) budget also suggests that throughfall (wet deposition after interaction of rainwater with tree leaves) may contribute as much Cl_{org} to forest soil as in situ chlorination [*Öberg et al.*, 1997]. Similar budget estimates imply that small fractions of natural Cl_{org} enter soil through atmospheric and plant litter deposition as well [*Öberg and Grøn*, 1998].

[3] In addition to being produced in soil systems, Cl_{org} can be naturally broken down to Cl_{inorg}, through biotic [*Holliger et al.*, 1998; *Neilson*, 1990] and abiotic [*Lee and Batchelor*, 2004] processes. Bacteria belonging to the *Dehalococcoides* genus, for example, reductively dechlorinate an array of anthropogenic Cl_{org} pollutants [*Adrian et al.*, 2000; *Fennell et al.*, 2004; *Maymo-Gatell et al.*, 1997]. Although their capabilities have been exploited in bioremediation efforts [*Häggblom and Bossert*, 2003], the activity of dehalogenating microorganisms with respect to natural Cl_{org} remains uncertain. Thus, a comprehensive description of the biogeochemical Cl cycle is important for understanding the fate of anthropogenic Cl_{org} pollutants in the environment.

[4] The dominant mechanisms and rates of soil Cl_{org} production and degradation are poorly understood, in part because natural organic matter (NOM) degradation is a

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complex process, mediated by various microorganisms and subject to photodegradation, leaching, and physical weathering. Another complicating factor is the chemical heterogeneity of NOM, which consists of variably sized molecules with multiple functionalities, including phenolic, carboxyl, hydroxyl, and amino groups. To contend with the complexity of NOM, most bulk natural Cl_{org} quantification performed to date has relied on degradative techniques, in particular the adsorbable organohalogen (AOX) sum parameter, which entails reaction of digested, acidified samples with activated carbon prior to combustion, followed by detection of inorganic halides [*Biester et al.*, 2004; *Hjelm et al.*, 1999; *Jokela et al.*, 1992; *Öberg and Sandén*, 2005; *Öberg et al.*, 1997, 2005; *Putschew et al.*, 2003]. As a result, the molecular identities of the various natural Cl_{org} fractions contributing to soil Cl_{org} remain largely unspecified.

[5] Recent synchrotron-based X-ray studies have probed Cl speciation in heterogeneous NOM samples without extraction [*Leri et al.*, 2007, 2006; *Myneni*, 2002b; *Reina et al.*, 2004]. Cl 1*s* X-ray absorption near-edge structure (XANES) spectra reflect contributions from all forms of Cl present in a sample, allowing Cl to be probed directly in complex chemical mixtures such as NOM [*Myneni*, 2002a]. Unlike the AOX sum parameter technique, XANES spectroscopy requires physical sample preparation only, shrinking the risk of unintentional chlorination during chemical digestion and acidification. Spectral features in the XANES energy region reveal the bonding state of Cl, while the fluorescence intensity of the spectra is proportional to total Cl concentration. Cl 1*s* XANES spectroscopy therefore ensures a complete portrait of Cl speciation, with simultaneous measurement of total Cl concentration [*Leri et al.*, 2006].

[6] Using this technique, we monitored Cl cycling in oak- and pine-dominated forest soils (Pine Barrens, NJ, USA) over a 3 year period. By quantifying different chemical fractions of natural Cl_{org}, we show that soil contains multiple types of chlorinated organic matter, with molecularly distinct inputs from throughfall, litterfall, and plant matter decomposition. Our measurements also reveal seasonal variations in microbial production and degradation of Cl_{org}, which could have important ramifications for our understanding of Cl_{inorg} availability to plants in forest ecosystems.

2. Materials and Methods

2.1. Sample Collection and Preparation

2.1.1. Tree Leaf and Litter Layer Sampling

[7] Tree leaves and litter were collected from the Brendan Byrne State Forest in the Pine Barrens, NJ, USA. The soil in this forest is sandy and acidic (pH 3.5–5.5) and tends to be well drained. The vegetation is dominated by oak, maple, and pine trees of various species. Leaf litter on the forest floor occurs in two to three distinct layers, depending on the season, which are distinguishable by visual inspection. Each litter layer corresponds to one season's litter deposition. Thus, the topmost layer represents material from the most recent litterfall (which is thus the least decayed), the middle layer the previous year's deposition, and the bottommost layer that of 2 years prior (the most degraded leaf litter). After more than 3 years of decay on the forest floor, the litter exists in a highly humified state, decomposed to the extent that individual leaf species are no longer discernible. At each sampling, leaf litter was collected from sections of the forest floor where the litter layers were undisturbed. Samples were stored in Ziploc® bags at 4°C until analysis. Decay times for leaf litter samples collected from the forest floor are estimated based on an abscission date of 1 October.

2.1.2. Leaf Litter Decay Studies in the Field Experimental Station

[8] Senescent leaves were manually detached from *Quercus alba* (white oak) trees in the Brendan Byrne State Forest prior to natural abscission. White oak leaves were selected as substrates for a single-species study because of their relative recalcitrance to degradation—leaves of this species remain easily identifiable after 2 years of degradation on the forest floor. The detached leaves were air-dried for one week, weighed, and placed into experimental trays suspended five feet above the soil surface, in a forest clearing. Experimental trays consisted of polypropylene plastic and contained a layer of coarse, rigid polypropylene mesh on which the plant material rested. Fine polypropylene mesh fitted over the trays and secured with nylon string prevented loss of experimental substrates and entry of extraneous solids. All materials for the field station apparatus were acid-washed and triple-rinsed with deionized water prior to use. Mass loss and Cl quantification were performed on a monthly basis using two mass balance trays. See auxiliary material for images of the field station apparatus.[1]

[9] Leachate resulting from the interaction of rainwater with the decaying leaves was routed from the trays into carboys for collection and analysis of dissolved organic matter. In the laboratory, collected leachate was vacuum-filtered through 5.0 μm polycarbonate disks to remove particulates. Dissolved organics were extracted from filtered leachates using Empore C_{18} disk cartridges (3M Bioanalytical) in a 90/10 methanol/water mixture. This organic extract was dried onto individual Teflon sample holders under a stream of N_2 for X-ray spectroscopic analysis.

2.1.3. Solubility Studies

[10] Detached white oak leaves at various growth and decay stages were subjected to aqueous leaching in the laboratory to remove soluble forms of Cl. Approximately 20 g of intact leaves were soaked in ~3 L deionized water in large polyethylene basins with gentle shaking. Leaves were removed from the basins at intervals and air-dried prior to pulverization for quantitative Cl analysis.

2.1.4. Soil Extractions

[11] Soil cores (30 cm) collected from the Brendan Byrne State Forest in NJ displayed dark organic-rich layers above sandy, mineral-rich horizons. Samples from the organic-rich section were analyzed in situ by Cl 1*s* XANES spectroscopy. Sections from 5 to 26 cm down the soil profile were extracted in NaOH to minimize background scattering in the X-ray measurements. Six grams of soil were extracted in three mL of N_2-sparged 0.1 M NaOH for 6 h under

[1] Auxiliary materials are available in the HTML. doi:10.1029/2010gb003882.

anaerobic conditions. Extracts were dried on Teflon sample holders under a stream of He gas prior to Cl 1*s* XANES analysis.

2.2. Cl 1*s* XANES Spectroscopy

[12] Synchrotron-based X-ray absorption near-edge structure (XANES) spectroscopy was used to determine Cl concentration and speciation in leaf, litter, and soil samples. The absolute fluorescence intensity of Cl 1*s* XANES spectra is directly proportional to Cl concentration. A series of NaCl standards in a matrix of uniform bulk density gives calibration curves with strong linear relationships, permitting quantification of absolute Cl concentrations in homogenized, pelletized natural samples [*Leri et al.*, 2006]. Cl 1*s* XANES peak positions, widths, and relative areas vary according to the bonding state of Cl and can be used as an indicator of Cl speciation [*Reina et al.*, 2004]. In environmental sample spectra, the relative proportions of Cl bonded to aliphatic carbon, Cl bonded to aromatic carbon, and Cl_{inorg} are determined with <10% error by least squares fitting normalized sample spectra with spectra of representative model compounds [*Leri et al.*, 2006; *Myneni*, 2002b]. While Cl 1*s* XANES spectra reveal the immediate bonding environment around Cl in natural samples, they furnish little information on the overall size and structure of the chlorinated molecules. Indirect evidence, such as the relative solubility of the various Cl_{org} fractions, provides additional insight regarding the structure of the Cl_{org} molecules identified.

[13] Cl 1*s* XANES spectra were acquired at beamline X19A at the National Synchrotron Light Source at Brookhaven National Laboratory (Upton, NY). The beamline has a fixed-exit double-crystal Si (111) monochromator. The beam is collimated and focused with Rh-coated mirrors and steered through a 10 μm Be window. Upstream of the sample chamber, the beam passes through an ion chamber, I_0, where the intensity of the incident beam is monitored to allow normalization of X-ray fluorescence yield from the sample. The I_0 and the sample chambers were purged with He to maximize photon flux at the Cl K absorption edge. To screen out high-order harmonics, the monochromator was detuned to reduce incident photon flux by 50%.

[14] Samples were mounted on Kapton tape and exposed directly to the incoming X-ray beam at a 45° angle. The beam spot size on the sample was 2×1 mm^2. Sample fluorescence was measured over an energy range of 2800–2880 eV using a Canberra PIPS detector. For Cl concentration measurements, spectra were collected with a 0.25 eV step size near the absorption edge and 0.5–2.0 eV step sizes above and below the edge. For Cl speciation measurements, higher-resolution spectra were collected using a 0.08 eV step size close to the edge and 0.1–0.5 eV step sizes above and below the edge. Labview XDAC software associated with beamline X19A was used to collect Cl 1*s* XANES spectra. The energy of the spectrometer was calibrated to the absorption maximum in the Cl 1*s* XANES spectrum of the chlorophenol red standard at 2821.24 eV. Cl 1*s* XANES data were processed using SIXPack version 0.43 [*Newville*, 2001; *Webb*, 2005], WinXAS version 2.0 [*Ressler*, 1998], and MS Excel, according to previously described analyses [*Leri et al.*, 2006]. See auxiliary material for Cl 1*s* XANES spectra of Cl-containing model compounds and natural samples.

3. Results and Discussion

3.1. Cl Fluxes in White Oak and Mixed Leaf Litter

[15] In healthy tree leaves and needles (of *Quercus*, *Acer*, and *Pinus* genera), total Cl concentrations vary by growth stage, rainfall, coastal proximity, and other environmental parameters, with the majority of Cl present in the form of Cl_{inorg}. For example, in the early autumn, senescent leaves of *Q. alba* (white oak) in the New Jersey Pine Barrens exhibit a total Cl concentration of about 500 mg·kg^{-1}, with Cl_{inorg} accounting for ~335 mg·kg^{-1}. The remaining Cl is covalently bonded to aromatic and aliphatic carbon, in approximately equal proportions. Within three months after white oak leaves fall to the ground and begin to decay, the majority of Cl_{inorg} and aromatic Cl_{org} leaches from the leaves (Figure 1b). By contrast, aliphatic Cl_{org} concentrations remain steady throughout the first year of decay, after which they exhibit a small increase.

[16] After the first year on the forest floor, the aromatic Cl_{org} concentration in decaying white oak leaves increases (Figure 1b). Decayed white oak leaves collected from the middle mulch layer (estimated weathering time >1.5 years) display a combination of aliphatic and aromatic Cl_{org} that persists in the leaf tissue after more than a week of immersion leaching in deionized water (see auxiliary material). The insolubility of the aromatic Cl_{org} in highly weathered leaves makes this fraction distinct from the soluble aromatic Cl_{org} that leaches rapidly from leaves at the onset of weathering. The insoluble aromatic Cl_{org} may constitute part of the macromolecular humic substances that are produced through NOM degradation and have been shown to contain Cl_{org} [*Myneni*, 2002b]. However, some contribution to the insoluble aromatic Cl_{org} pool may come from adsorption of the soluble aromatic Cl_{org} fraction.

[17] The observed trends in Cl concentrations with decay time are not limited to leaves of a single tree species. Homogenized plant detritus from the floor of the oak- and pine-dominated forest shows a similar loss of soluble aromatic Cl_{org} and Cl_{inorg} in the initial months of decay and displays a refractory aliphatic Cl_{org} component (Figure 1c). The observed fluctuations in Cl_{org} concentrations must be partly attributable to the intrinsic chemical heterogeneity of the natural samples. However, particularly in the case of mixed plant litter, it becomes apparent that the systematic changes in aromatic Cl_{org} concentration at later decay stages reflect seasonal variations in biogeochemical processes. Aromatic Cl_{org} concentrations increase in the spring and summer months (March through October), at rates that rise from 12 to 30 mg·kg^{-1}·mo^{-1} over 3 successive years on the forest floor, and decrease at −9 to −20 mg·kg^{-1}·mo^{-1} from October through March (Figure 2).

[18] On the surfaces of decaying leaves, high aromatic Cl_{org} concentrations have been found to coincide spatially with fungal colonies [*Leri et al.*, 2007]. Specific chlorinated metabolites, many of which contain aromatic Cl_{org} functionalities, have been isolated from certain soil fungi and

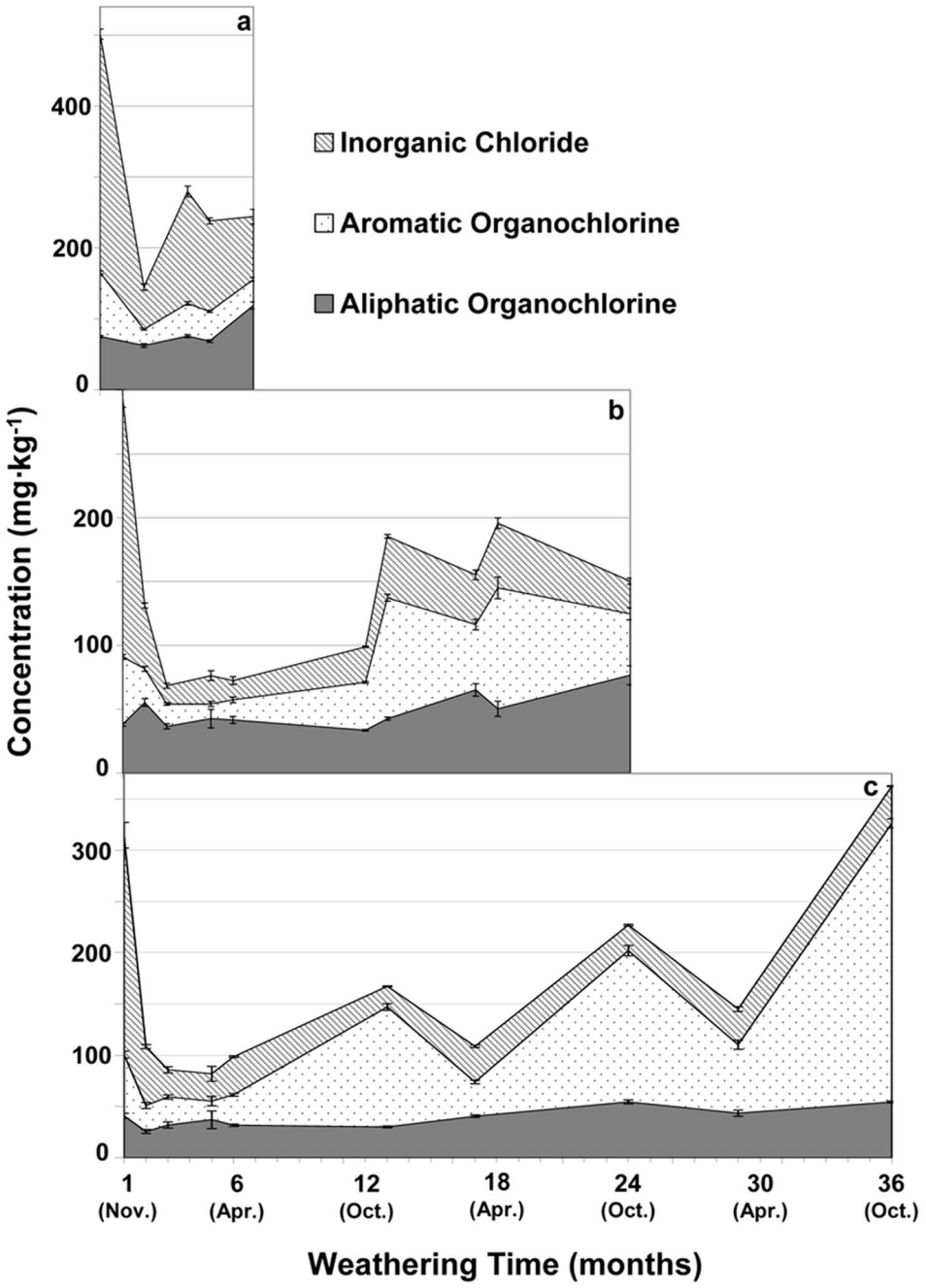

Figure 1. Cl species concentrations in plant material as a function of decay time. (a) White oak litter in the aboveground field station (the timescale starts at zero, when the leaves were placed in the apparatus). (b) White oak litter on the forest floor. (c) Mixed oak- and pine-dominated litter on the forest floor. Litter samples from the Brendan Byrne State Forest, New Jersey.

lichen specimens [*Gribble*, 2003; *Turner and Aldridge*, 1983; *Swarts et al.*, 1998; *Yosioka et al.*, 1968], and such molecules may be incorporated into NOM through adsorption and/or humification processes. However, chloroperoxidase (CPO)-like activity has been detected in forest soils [*Asplund et al.*, 1993; *Latumus et al.*, 1995], and the organic substrates of CPO-mediated reactions could be nonspecific. The CPO enzyme may release hypochlorous acid (HOCl) or an equivalent "Cl^{+}" intermediate extracellularly [*Blasiak and Drennan*, 2009; *Libby et al.*, 1992]. Enzymatically produced reactive "Cl^{+}" species could target phenolic-rich portions of NOM, macromolecular and otherwise, in electrophilic chlorination reactions. Such a mechanism could provide an effective pathway for oxidative breakdown of the

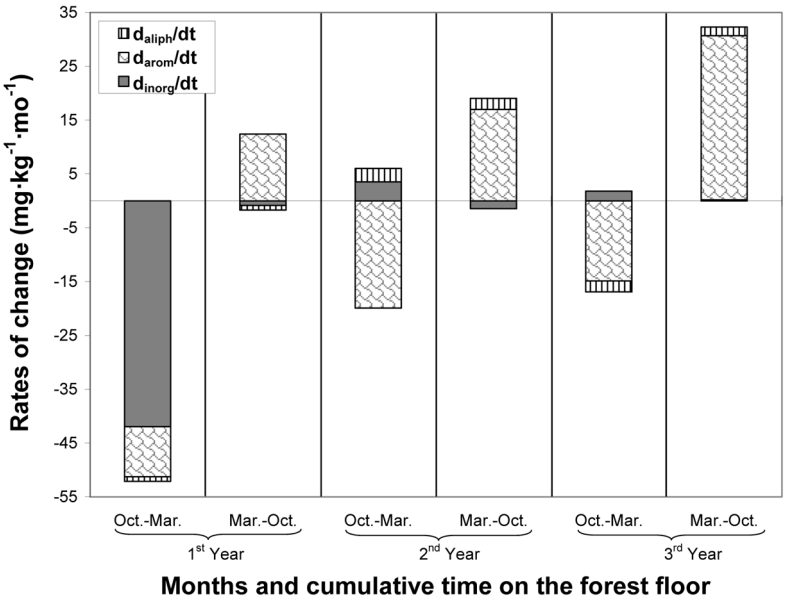

Figure 2. Seasonal rates of change in aliphatic/aromatic Cl_{org} and Cl_{inorg} in mixed oak- and pine-dominated plant litter over 3 years on the Brendan Byrne State Forest floor.

more recalcitrant portions of NOM, such as lignin, with stable Cl_{org} forming as a by-product. For example, ascomycetes fungi display CPO activity and produce chlorinated lignols in the process of breaking down plant material [*Ortiz-Bermúdez et al.*, 2007]. Isolated CPO chlorinates aromatic moieties in fulvic acid, a component of NOM [*Niedan et al.*, 2000], and induces conversion of Cl_{inorg} to Cl_{org} in healthy plant material [*Reina et al.*, 2004].

[19] Increased microbial activity could be responsible for the rise in aromatic Cl_{org} production during the warmer months (Figure 2). The cumulative increase in aromatic Cl_{org} concentrations in white oak and mixed leaf litter over several years of decay (Figures 1b and 1c) is likely attributable to progressive microbial colonization. The degree of microbial colonization was not controlled in our analyses, as each sampling expedition targeted separate locations on the forest floor to avoid procuring litter from previously disturbed areas.

[20] The seasonal decrease in aromatic Cl_{org} concentrations in decaying leaf litter (Figure 1c) implies that dechlorination outpaces chlorination in the autumn and winter (Figure 2). Several varieties of Cl_{org}-respiring soil microorganisms have been identified, including psychrotolerant bacteria that dechlorinate polychlorinated biphenyls at low temperatures [*Lambo and Thakor*, 2006]. Despite the intrinsic heterogeneities of the natural samples and the seasonal interchange of chlorination and dechlorination, leaf litter exhibits a cumulative increase in aromatic Cl_{org} with decay time (Figure 1c).

3.2. Cl fluxes in Soil Profiles

[21] The humified organic material that becomes the soil organic (*O*-) horizon contains high levels of aliphatic and aromatic Cl_{org}. Correspondingly, most Cl present at the top of the soil column is bonded to carbon (Figure 3). With soil depth, Cl speciation shifts from predominantly organic to inorganic. This shift may result from reduced transport of Cl_{org} down the soil profile due to low solubility and/or mineralization of chlorinated organic matter with release of Cl_{inorg}. Biodegradative dechlorination can occur through oxidative [*Hammel and Tardone*, 1988; *Hirai et al.*, 2004] and reductive [*Adrian et al.*, 2000; *Fennell et al.*, 2004; *Holliger et al.*, 1998; *Maymo-Gatell et al.*, 1997] mechanisms, the latter of which could occur in anaerobic microenvironments in these relatively aerated soils. Reducing conditions could promote abiotic dechlorination reactions as well [*Lee and Batchelor*, 2004].

3.3. Field Weathering Experiments and Relative Solubility of Cl Fractions

[22] To assess the role of soil microorganisms in Cl_{org} dynamics, senescent white oak leaves harvested prior to natural abscission were allowed to decay in trays suspended five feet above the soil surface. No antimicrobial agents were added to the field station substrates, in order to preserve natural Cl speciation as much as possible. Although not strictly abiotic, the setup minimized contact of the decaying leaves with the soil microbial milieu and also allowed for sampling of leachate from the interaction of rainwater with the decaying leaves.

[23] Unfortunately, the timescale for the field station experiment fell under 1 year (the point at which aromatic Cl_{org} begins to increase in litter on the forest floor), owing to ecological damage to the apparatus. However, the trends for Cl_{inorg} and aliphatic/aromatic Cl_{org} during the initial months of weathering aboveground (Figure 1a) mirror those on the soil surface (Figure 1b). Leachate collected during the first month of weathering contains dissolved aromatic Cl_{org} (see

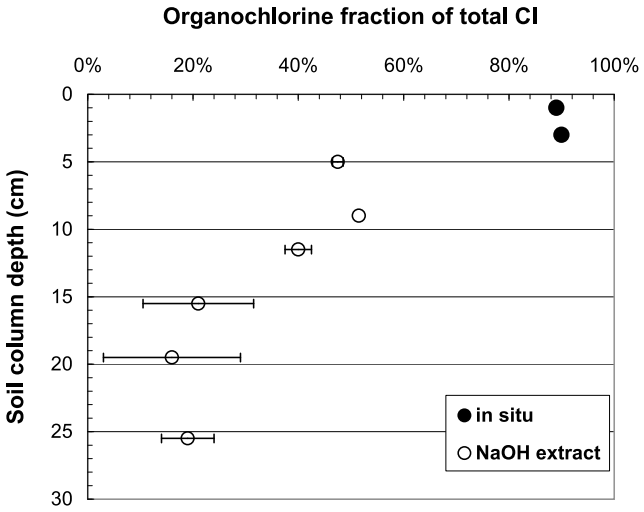

Figure 3. Cl speciation as a function of soil depth. Soil cores from the Brendan Byrne State Forest, New Jersey. Base extractions were performed on mineral-rich soil sections from below the organic (*O*-) horizon to minimize background scattering in the X-ray measurements.

auxiliary material), presumably the fraction that leaches from leaf litter in the early decay stages (section 3.1). Soluble aromatic Cl_{org} was detectable only in leachates from the first few months of degradation, suggesting that these compounds originate in the senescent leaves. The soluble aromatic Cl_{org} compounds may represent chlorinated counterparts of the polyphenolic molecules known to leach from plant litter during initial decay stages [*Kuiters and Sarink*, 1986]. These aromatic Cl_{org} molecules may be phytochemical or else products of microbial and/or photochemical chlorination processes on the leaf surfaces. By contrast, the insoluble aromatic Cl_{org} that appears at high concentrations in decaying plant litter from the forest floor (section 3.1) is linked to the actions of litter-degrading microorganisms in the soil [*Leri et al.*, 2007].

[24] The presence of aliphatic Cl_{org} in leaves weathering in the aboveground field station (Figure 1a) supports the claim that these compounds are associated with the plant material itself. In healthy white oak leaves detached from trees at early growth stages, aliphatic Cl_{org} was detected at ~25 $mg \cdot kg^{-1}$ after aqueous leaching (see auxiliary material), which implies that these compounds may be of phytochemical origin. X-ray measurements indicate that the aliphatic Cl_{org} is a superficial component that becomes diluted upon homogenization of the leaf material (see auxiliary material). These compounds may constitute part of the cuticle, the long-chain hydrocarbon waxes that protect leaf surfaces. The absolute mass of aliphatic Cl_{org} in white oak leaves remains relatively constant throughout the aboveground decay experiments, suggesting that the observed increase in aliphatic Cl_{org} concentration (Figures 1a and 1b) is attributable to comparative enrichment rather than *de novo*

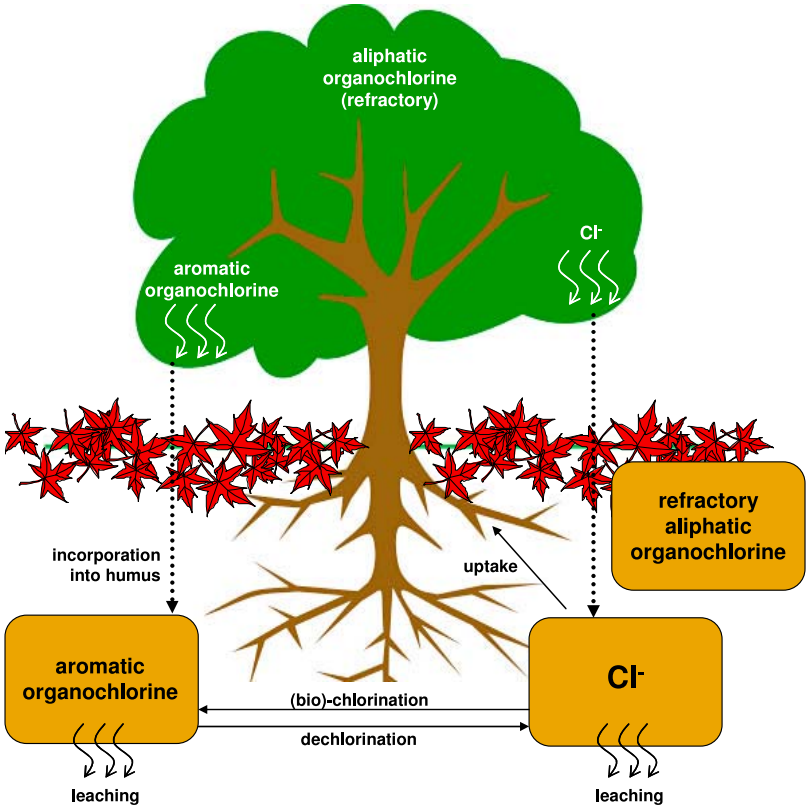

Figure 4. Schematic of biogeochemical Cl cycling in the forest ecosystem.

production. Thus, the aliphatic Cl_{org} detected in new growth leaves persists through maturation, senescence, abscission, and ultimate humification, contributing ~1/6 of the total Cl_{org} in the soil organic horizon (Figure 1c). This value exceeds prior estimates of litterfall contribution to Cl_{org} in topsoil [*Öberg et al.*, 2005] by more than 30-fold. Underestimation may have resulted from the inherent limitations [*Müller*, 2003] of the AOX sum parameter technique employed in many previous measurements.

4. Summary and Implications for the Cl Cycle in Forest Ecosystems

[25] This study provides the first concrete, quantitative evidence that there are multiple chemical fractions of natural Cl_{org} in soil systems, shedding new light on the terrestrial Cl cycle (Figure 4). Plant litter contributes refractory aliphatic Cl_{org} and soluble aromatic Cl_{org} to the soil Cl_{org} pool. The aliphatic Cl_{org} fraction, which may be of phytochemical origin, makes a substantial contribution to the soil Cl_{org} pool and persists through advanced stages of NOM decay. The soluble aromatic Cl_{org} molecules may adsorb onto soil humus, leach in groundwater, or undergo natural dechlorination reactions. Aromatic Cl_{org} is also produced *de novo* in decaying plant litter by soil microorganisms, with peak production during warmer months. This insoluble aromatic Cl_{org} may appear as a consequence of plant matter degradation processes that rely on oxidized Cl species, with phenolic plant macromolecules, such as lignin, as organic substrates in electrophilic chlorination reactions.

[26] The concentration of aromatic Cl_{org} in decaying plant litter varies seasonally but exhibits a cumulative increase with decay time. This leads to the enrichment of Cl in surface soil in the form of chlorinated organic matter. The soil column displays a change in Cl speciation from organic to inorganic with depth, which may be attributable to biodegradation and/or abiotic transformations. For example, natural Cl_{org} could function as an electron acceptor for reductively dechlorinating organisms under anaerobic conditions down the soil column. A better understanding of the formation and degradation of natural Cl_{org} will ultimately influence the assessment of anthropogenic Cl_{org} pollution dynamics in terrestrial ecosystems.

[27] Chlorinated organic matter produced naturally at high concentrations and degraded below the *O*-horizon may help sustain forest ecosystems by supplementing Cl_{inorg} in soil. As a plant micronutrient, Cl_{inorg} is required for the water-splitting reaction of photosynthesis [*Kawakami et al.*, 2009; *Popelková and Yocum*, 2007], for charge balance in the opening and closing of stomata [*MacRobbie*, 1982; *Raschke and Fellows*, 1971], and possibly for plant developmental processes [*Colmenero-Flores et al.*, 2007]. However, since Cl_{inorg} does not show strong binding affinity for soil components [*White and Broadley*, 2001], it is subject to extensive leaching [*Kauffman et al.*, 2003], which may limit its availability to plants in regions with high rainfall, well drained soil, and/or low-Cl_{inorg} deposition. The fixation of Cl in soil as Cl_{org} and its ultimate breakdown to Cl_{inorg} may enhance its availability to inland plants, ensuring operation of the oxygen-evolving photosystem II and other key physiological processes. The fluxes of plant-derived and microbially produced Cl_{org} fractions described here provide a preliminary basis for understanding the retention and stabilization of Cl in forest soil.

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