



Formation of Chlorinated Hydrocarbons in Weathering Plant Material

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When we think of chlorine, we often relate it to the salt used in food preparation, chloride in the oceans, chlorine gas from swimming pools, and gaseous chlorofluorocarbons that have close links to the depletion of stratospheric ozone. We rarely think of thousands of chlorinated hydrocarbons that exist in the natural systems, several of which are highly toxic to humans (1). The C-Cl bond, common to all organo-Cl compounds, is strong and gives high stability to organo-Cl compounds. For this reason, several organo-Cl compounds have been synthesized and used extensively for years in agricultural and industrial applications. For the same reason, these molecules tend to stay in the environment for a longer time, and threaten to contaminate aquatic and soil systems (2). There are also reported occurrences of bioaccumulation of anthropogenic chlorinated compounds in areas remote from human settlements (3,4), and such widespread distribution of organo-Cl compounds is believed to be due to the high stability of man-made organohalogens and their long-range transport in the environment. The behavior and the ultimate fate of organo-Cl compounds in the environment are not well understood, and need a critical evaluation using the *in-situ* molecular techniques.

Interestingly, several living organisms make a variety of organo-Cl compounds using different enzymes and inorganic-Cl (5). Researchers have also shown that some chlorinated compounds, previously considered to be from anthropogenic sources, are also produced by microbial processes in soil systems (6). Experimental work suggests that the dominant products of biohalogenation reactions are volatile small chain chlorinated alkanes with trace quantities of less-volatile chlorinated organics. However, direct evidence for the persistent and less-volatile organochlorine compounds is unavailable. Solid phase speciation of organo-halogens, especially for the organic molecules that are associated with humic substances and mineral oxides in soils and sediments, has been a major problem because few spectroscopic and chemical techniques provide information on the structural molecular chemistry of halogens. Using *in-situ* synchrotron-based X-ray spectroscopy methods, we showed that organo-Cl compounds are the dominant forms of Cl in weathering plant material. Our results also suggest that they are formed at rapid rates in the natural systems (7). Improved understanding of the biogeochemistry of these compounds is useful for the evaluation of Cl-cycle and its influence on other elemental cycles in the environment, and the toxicity of both natural and man-made organo-Cl compounds.

The X-ray absorption (specifically, the near-edge X-ray absorption fine structure, NEXAFS) spectra of organo-Cl compounds are significantly different from those of inorganic forms, and the chemical forms of Cl in complex organic matrices can be identified directly without chemical or mechanical pretreatment of samples. For instance, Cl in -I (inorganic chloride, Cl⁻) and +VII (perchlorate, ClO₄⁻) oxidation states exhibit absorption-edges at 2820.7 eV and 2830.2 eV, respectively, with those of intermediate oxidation states in between these two energies (Fig. 1a).

In contrast to these inorganic Cl species, Cl connected to C atoms in organic compounds exhibits intense low-energy features corresponding to the $1s \rightarrow \pi^*$ and σ^* electronic transitions of the C-Cl bonds well below the Cl-main absorption edge (absorption maximum ~ 2821 eV) (Fig. 1b). Further, Cl atoms connected to aromatic and cyclic C exhibited these features ~0.5 eV higher than that of aliphatic mono-chlorinated compounds, and the spectral resolution at these energies is sufficient enough to distinguish these broad classes of compounds.

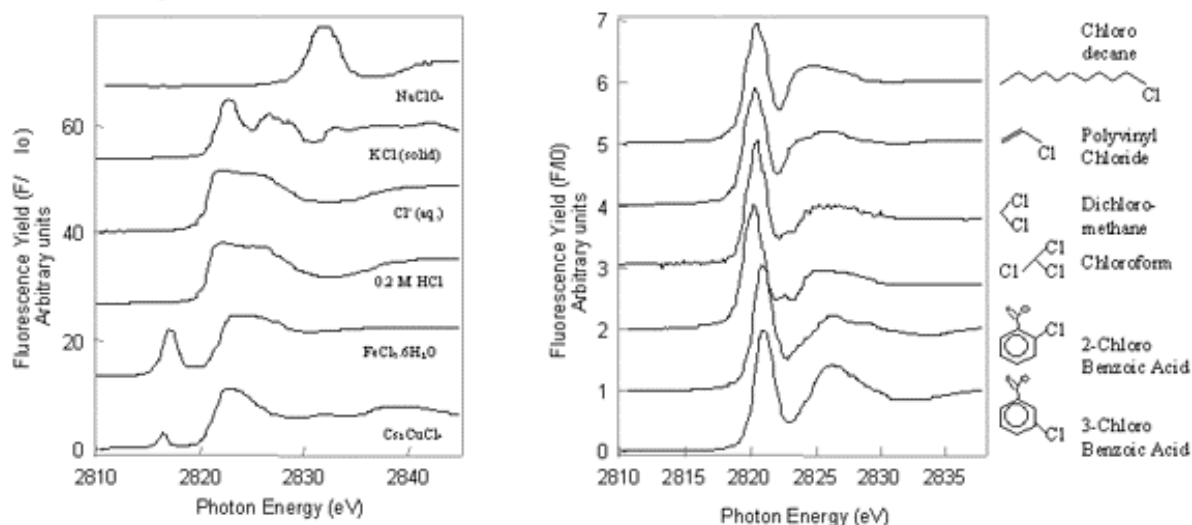


Fig. 1 Cl K-edge X-ray absorption spectra of different inorganic (a) and organic compounds (b). The coordination environment of organo-Cl is shown next to their respective spectra. All of the spectra are calibrated against absorption maximum in KCl (2822.8 eV).

When compared to these structural models, naturally occurring organic molecules isolated from river water, soil, and peat (often called humic substances) exhibit an intense absorption edge at $\sim 2821 (\pm 0.1)$ eV (not shown). Their spectral-fit with those of inorganic chloride, and aliphatic and aromatic organo-Cl compounds indicate that these isolated humics primarily contain chlorinated phenols (primarily mono-, and di-chloro compounds), with $< 30\%$ aliphatic organo-Cl. Inorganic Cl^- is also found to be one of the abundant Cl-species in some of the isolated molecules. Humic and fulvic acids share a common set of organo-Cl compounds (i.e. common edge structures), but the relative concentration of

organo vs. inorganic chlorine varies in the different fractions. In contrast to the isolated humics in soil samples, the fresh-plant materials of different plant species exhibit spectral features corresponding to the inorganic- Cl^- only (Fig. 2). The senile plant leaves either attached to the plant or collected on soil surfaces also showed spectral features of inorganic Cl^- and aromatic Cl. However, the highly humidified plant leaves of all the examined plant species showed intense spectral features at $2821.1 (\pm 0.1)$ eV, which corresponds to the aromatic organo-Cl.

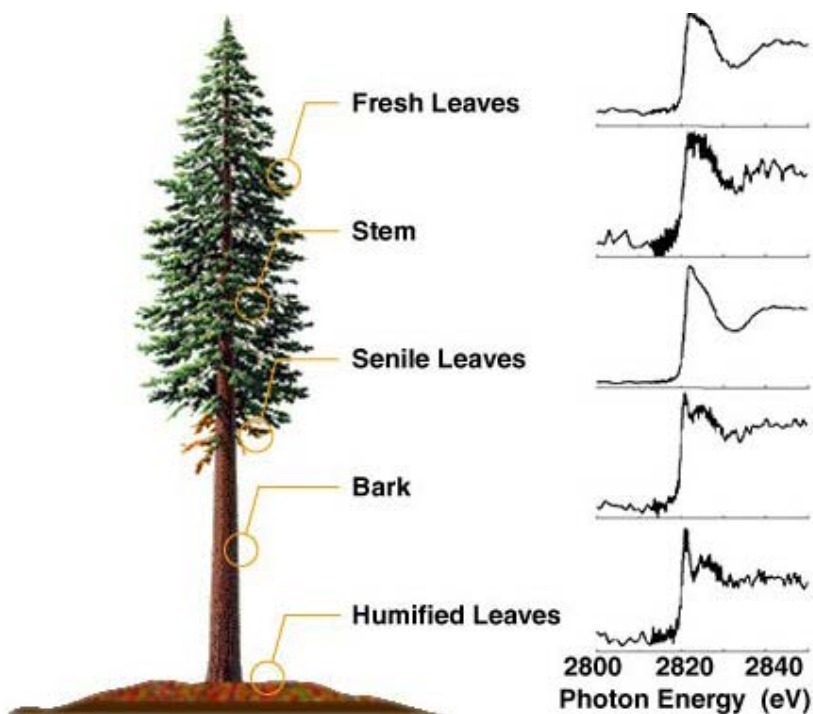


Fig. 2 Cl K-edge X-ray absorption spectra of fresh and weathered leaves of *Sequoia sempervirens*.

The results presented here directly document the occurrence of the stable naturally produced, organo-Cl compounds in the terrestrial ecosystems. We are continuing these studies to understand the coordination chemistry and molecular sizes of these compounds in natural systems, enzymatic processes involved in their formation, and the role of these compounds in biogeochemical cycling of other elements in soil and aquatic systems.

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This work has been referenced in the following articles:

- W. H. Casey, "Geochemistry: The Fate of Chlorine in Soils", *Science* **295**, 985 (February 8, 2002)

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