

Risk assessment and the cycle of natural

Rapid and extensive natural chlorination & dechlorination of soil organic matter

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During recent decades, the extent to which soil organic matter can be chlorinated by natural processes has been debated. The amounts of organically bound chlorine (Cl_{org}) in soils are often as large as or greater than the quantities of inorganic chlorine (chloride; Cl_{in}). Such high levels of Cl_{org} even in very remote areas imply that its presence cannot be explained by anthropogenic emissions alone. Here, the authors present evidence from ^{36}Cl tracer experiments that natural transformation of chlorine between Cl_{in} and Cl_{org} in soils can be rapid and extensive, with specific rates up to 10% of the standing stock transformed per day, and that chlorination relies primarily on microbial or enzymatic processes.

To investigate potential chlorination rates, coniferous forest soil from the organic horizon with $^{36}\text{Cl}_{\text{in}}$ was amended, and over time the amounts of ^{36}Cl subsequently present as chloride (Cl_{in}) and non-extractable organic chlorine were monitored (Cl_{org} ; using water and 0.1M potassium nitrate as extractants). Three different experiments were performed.

In the first, transformation of Cl over 133 days under oxic conditions was studied. This experiment showed a rapid initial increase in $^{36}\text{Cl}_{\text{org}}$ and after eight days, 23% of the added $^{36}\text{Cl}_{\text{in}}$ had been transformed into $^{36}\text{Cl}_{\text{org}}$. The proportion of ^{36}Cl as $^{36}\text{Cl}_{\text{org}}$ remained at this level until day 20. After that, the fraction of $^{36}\text{Cl}_{\text{org}}$ started to decrease and reached a plateau at 8% by day 133. The decline in $^{36}\text{Cl}_{\text{org}}$ after day 20 can only be explained by substantial transformation of Cl_{org} to Cl_{in} . The long term abundance of Cl_{org} is controlled by several different processes including chlorination and dechlorination.

In the third experiment, the chlorination potential under oxic and anoxic conditions was studied. Results indicated much higher net rates of formation of $^{36}\text{Cl}_{\text{org}}$ under oxic conditions than in the absence of oxygen. This indicates that the natural formation



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Current research interests include chlorine biogeochemistry, natural chlorination and dechlorination of organic matter, carbon biogeochemistry, and trace gas biogeochemistry including methane dynamics.

of $^{36}\text{Cl}_{\text{org}}$ is regulated by biotic processes requiring oxygen, or that dechlorination processes are substantially greater under anoxic conditions resulting in lower net chlorination rates.

All experiments showed substantial transformation of $^{36}\text{Cl}_{\text{in}}$ to $^{36}\text{Cl}_{\text{org}}$ within days under oxic conditions. The first experiment also indicates rapid dechlorination of organochlorines in soil. To estimate rates, the possibility of simultaneously occurring chlorination and dechlorination has to be considered. The best estimates of initial specific chlorination and dechlorination rates were in similar ranges, but dechlorination rates were always greater than chlorination rates. Combined with the frequent observation that Cl_{org} exceeds Cl_{in} in organic soils, this suggests that some of the Cl_{org} formed is resistant to dechlorination and accumulates in spite of high specific dechlorination rates. Results indicate that a maximum of 10% of the $^{36}\text{Cl}_{\text{org}}$ formed during the experiment could have been refractory and that the remainder (>90%) was subjected to dechlorination.

The specific rates estimated in the present study represent potential rates since our experimental conditions were dissimilar to field conditions. Hence, our estimated specific rates should be considered with caution. However, even if specific chlorination rates under field conditions are 10-fold lower than the estimates in the present study, the whole Cl_{in} pool is turned over by transformation to Cl_{org} at least twice a year. Therefore, even a conservative interpretation of our results supports the conclusion that soil chlorine transformations are rapid and extensive.

The biodegradability of organochlorine compounds

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Key to the natural chlorine cycle is the biodegradation of organochlorine compounds, converting chlorine back to chloride. Microorganisms have developed diverse strategies for degrading organochlorine compounds, from reductive dehalogenation to hydrolytic and oxygenolytic chloride release. Biodegradation should be considered as a redox reaction in which an electron donor is oxidised at the expense of an electron acceptor.

Lower chlorinated compounds serve as an electron donor and carbon source by being oxidised if an adequate electron acceptor is present. Higher chlorinated compounds can serve as electron acceptors by being reductively de-halogenated in the presence of electron-donating compounds in the halorespiration process. Chlorinated solvents can also be cometabolically biotransformed by accidental reactions with enzymes and cofactors involved in the de-gradation of other substrates. Examples of cometabolism include oxidation of chlorinated solvents by monooxygenases and reduction of chlorinated solvents by commonly-occurring reduced cofactors in anaerobes (vitamin B12).

Some natural organochlorines have a large turnover in the biosphere, e.g. chloromethane, chloroform and methylated derivatives of chlorophenol. Chloromethane is a good carbon and energy source for aerobic bacteria (*Hyphomicrobium* and *Methylobacterium*) which mineralise the compound completely to CO_2 and Cl^- . The doubling times of



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aerobic chloromethane-utilising bacteria range from 5.7 to 7.7h. The anaerobe, *Acetobacterium dehalogenans* is known to ferment chloromethane to acetate and Cl^- in the presence of CO_2 . Aerobic and anaerobic bacteria use methyltransferases as the first step in chloromethane degradation.

The only known biodegradation of chloroform is co-metabolic. Under aerobic conditions, chloroform is co-oxidised by methane or ammonia oxidising bacteria using monooxygenases. Phosgene is a transient intermediate of the co-oxidation reaction resulting in the formation of CO_2 . Chloroform is also reductively dehalogenated via the intermediates dichloromethane and chloromethane in anaerobic environments.

Numerous bacteria use chlorophenols as a carbon and energy source under aerobic conditions. The most studied strains utilising pentachlorophenol belong to the genera *Mycobacterium* and *Sphingomonas*. Extensive evidence shows that chlorophenols are mineralised by these bacteria. The doubling times of aerobic chlorophenol utilising bacteria range from 2.3 to 19.8h.

Two main strategies are used for the aerobic degradation of chlorophenols. Lower chlorinated phenols are initially attacked by mono-oxygenases yielding chlorocatechols as the first intermediates. Polychlorinated phenols are converted to chlorohydroquinones as the initial intermediates. Under anaerobic conditions, chlorophenols serve as electron acceptors for halo-respiring bacteria. The doubling times of these bacteria range from 3.5 to 87h. Once dechlorinated, the phenolic carbon skeletons are converted to CH_4 and CO_2 by other anaerobic microorganisms in the environment.

Naturally-occurring chlorinated dioxins may not be as important in mass terms as chloromethanes and chlorophenols. The biodegradation of dioxins is well-established. Lower chlorinated dioxins can be degraded by aerobic bacteria and higher chlorinated dioxins are reductively dechlorinated in anaerobic sediments. Halo-respiring bacteria can dechlorinate higher chlorinated dioxins.

Organochlorines with large anthropogenic inputs can also be biodegraded. Anthropogenic chlorinated persistent organic pollutants (e.g. polychlorinated benzenes and polychlorinated biphenyls) are slowly reductively dechlorinated in anaerobic sediments. Once partially dehalogenated, they become susceptible to further biodegradation by aerobic bacteria.

Literature suggests that organochlorine compounds are subject to biodegradation in the environment as part of the natural chlorine cycle. It is no longer

valid to assume that such compounds will persist indefinitely in the environment.

The biogeochemical cycle of chlorine

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In the early 1990s, it was revealed that large amounts of naturally produced Cl_{org} are present in soil. Later studies showed that chlorine participates in a complex biogeochemical cycle in which the terrestrial environment appears to be a key component. Recent studies suggest that a large portion of the Cl_{in} that is deposited in terrestrial environments is transformed to Cl_{org} in soil or vegetation. The majority appears to become chlorinated organic matter. The process is not understood, but there is strong evidence that the transformation is driven by biotic processes, although abiotic processes have also been shown to exist.

In temperate regions, the chlorinated organic matter is subsequently transported to deeper soil layers with the soil water. It precipitates and is eventually mineralised, leading to the release of Cl_{in} following the movement of soil water to surface water. The general understanding since the 1950s has been that Cl_{in} in surface water mirrors the chemical composition of precipitation.

In contrast, recent research suggests that Cl_{in} in surface water to a large extent originates from decomposing organic matter, which may be years, decades or thousands of years old. The inputs and outputs of Cl_{in} in most catchments are in balance. This situation - with large-scale storage in soil, complex biogeochemical transformation processes and yet balanced input and output - may appear confusing. However, similar patterns have historically been documented for elements such as carbon, nitrogen and sulphur.

Although the fact that chlorine participates in a complex biogeochemical cycle is well accepted within the specialist scientific community, it is not widely known among researchers.

The field remains practically a virgin area and several issues remain unclear. For example, it is known that chlorinated volatiles (VOCs) are formed naturally, and it appears that both biotic and abiotic sources are involved. However, the magnitude of scale, the underlying processes and the relationship between VOCs and the formation of chlorinated organic matter remain unclear.

It is also unclear how the natural transformation and transportation processes are influenced by environmental variables. For example, it is not known whether various practices such as fertiliser or road salt applications or land-use changes enhance or diminish the natural formation of chlorinated compounds with an ecotoxicological impact.

To develop appropriate policies for the management of anthropogenic chlorinated compounds, a better understanding of the natural cycle is undoubtedly needed.

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