

G. Öberg

The natural chlorine cycle – fitting the scattered pieces

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Abstract Chlorine is one of the most abundant elements on the surface of the earth. Until recently, it was widely believed that all chlorinated organic compounds were xenobiotic, that chlorine does not participate in biological processes and that it is present in the environment only as chloride. However, over the years, research has revealed that chlorine takes part in a complex biogeochemical cycle, that it is one of the major elements of soil organic matter and that the amount of naturally formed organic chlorine present in the environment can be counted in tons per km². Interestingly enough, some of the pieces of the chlorine puzzle have actually been known for decades, but the information has been scattered among a number of different disciplines with little or no exchange of information. The lack of communication appears to be due to the fact that the points of departure in the various fields have not corresponded; a number of paradoxes are actually revealed when the known pieces of the chlorine puzzle are fit together. It appears as if a number of generally agreed statements or tacit understandings have guided perceptions, and that these have obstructed the understanding of the chlorine-cycle as a whole. The present review enlightens four paradoxes that spring up when some persistent tacit understandings are viewed in the light of recent work as well as earlier findings in other areas. The paradoxes illuminated in this paper are that it is generally agreed that: (1) chlorinated organic compounds are xenobiotic *even though* more than 1,000 naturally produced chlorinated compounds have been identified; (2) only a few, rather specialised, organisms are able to convert chloride to organic chlorine *even though* it appears as if the ability among organisms to transform chloride to organic chlorine is more the rule than the exception; (3) all chlorinated organic compounds are persistent and toxic *even though* the vast majority of naturally produced organic chlorine

is neither persistent nor toxic; (4) chlorine is mainly found in its ionic form in the environment *even though* organic chlorine is as abundant or even more abundant than chloride in soil. Furthermore, the contours of the terrestrial chlorine cycle are outlined and put in a concrete form by constructing a rough chlorine budget over a small forested catchment. Finally, possible ecological roles of the turnover of chlorine are discussed.

Introduction

Chlorine is one of the most abundant elements on the surface of the earth. Until recently, it was widely believed that all chlorinated organic compounds were xenobiotic, that chlorine does not participate in biological processes and that it is present in the environment only as chloride (Cl⁻). However, evidence from many years of research has revealed that chlorine plays an active role in a complex biogeochemical cycle. For example, a vast array of organisms are able to convert chloride to organic chlorine, there are thousands of chlorinated compounds that are produced naturally, and organically bound chlorine is as abundant as the ion – at least in soil. Interestingly enough, some of the pieces of the chlorine puzzle have actually been known for decades, but the information has been scattered among a number of different disciplines with little or no exchange of information. The lack of communication appears to be due to the fact that the points of departure in the various fields have not corresponded and a number of paradoxes are actually revealed when the known pieces of the chlorine puzzle are fit together. It seems that a number of generally agreed statements, or tacit understandings, have guided perceptions in this field, and that these have obstructed the understanding of the chlorine cycle as a whole. A great deal of information of relevance for the understanding of the biogeochemical cycle of chlorine has been produced in areas with no connection to each other. For example, whereas the structure and composition of unknown compounds are the focus of environmental analytical chemis-

G. Öberg (✉)
Department Thematic Studies, Campus Norrköping, Linköpings
Universitet, 60174 Norrköping, Sweden
e-mail: gunilla.Oberg@tema.liu.se
URL: <http://www.tema.liu.se/people/gunob/>

try, the elemental composition per se is outside the scope of pharmacology since in this case it is the biological effect of the substance that is the major interest. Each discipline has formed its own theoretical framework in line with its own specific questions. In the process, a number of generally agreed statements have been formed that are unproblematic when viewed in relation to the point of departure of each discipline. However, such tacit understandings appear as paradoxes when viewed in the light of findings from other areas and obstruct our understanding of the chlorine cycle as a whole.

It is now more than 10 years since the discussion on the natural chlorine cycle was initiated (Asplund et al. 1989). The "First International conference on Naturally Produced Organohalogens" was held in 1993 (Grimvall and de Leer 1995); the second was held in 2001 in Heidelberg (<http://www.natural-organohalogens.com>) and numerous reviews have been written on the subject (e.g. Neidleman and Geigert 1986; Naumann 1994; Gribble 1996; Öberg 1998). Still, it appears as if the old "truths" continue to dictate the perceptions. As paradoxical as it may appear, this is a well-known phenomenon, described variously as paradigms (Kuhn 1962), figures of thought (Asplund 1985) or discourses (Hajer 1995) that govern our understanding of the surrounding world. To shift from one paradigm to another or to change a discourse [I use the word discourse here in the sense that a tacit agenda guides what we do and what we do not discuss, which type of knowledge we judge as interesting, true and of value, as well as what we find dull, false and worthless] is troublesome and takes time.

The aim of this paper is to enlighten four paradoxes that spring up when these generally agreed statements are viewed in the light of recent research or earlier findings from other areas. The aim is to illuminate the discourse, promote the consciousness of its mere existence and illustrate the need for cross-disciplinary communication. Furthermore, the contours of the terrestrial chlorine cycle are outlined and put in a concrete form by constructing a rough chlorine budget over a small forested catchment. This budget is constructed in order to more clearly elucidate which parts of the cycle are fairly well known and which components are more or less unknown, thereby making it easier to pinpoint which processes are central when analysing the relationship between the turnover of organic chlorine and its possible interference with the flux of chloride through soil. Finally, possible ecological roles of chlorine turnover are discussed.

The four paradoxes to be discussed are that it is generally agreed that:

1. Chlorinated organic compounds are xenobiotic *even though* more than 1,000 naturally produced chlorinated compounds have been identified.
2. Only a few, rather specialised, organisms are able to convert chloride to organic chlorine *even though* it appears as if the ability among organisms to transform chloride to organic chlorine is more the rule than the exception.

3. All chlorinated organic compounds are persistent and toxic *even though* the vast majority of naturally produced organic chlorine is neither persistent nor toxic.
4. Chlorine is mainly found in its ionic form in the environment *even though* organic chlorine is as abundant or even more abundant than chloride in soil.

The first paradox: It is generally believed that chlorinated organic compounds are xenobiotic

The statement that chlorinated organic compounds in general are xenobiotic has been widely embraced among scientists as well as the public (e.g. Kühn et al. 1977; New Encyclopaedia Britannica 1981; Keller 1989). How this aberrant statement became widely accepted can be traced to the environmental debate and the fact that a large number of man-made substances, later shown to be environmentally hazardous, are chlorinated. The debate on the release and dispersal of man-made compounds has, as a consequence, to a large extent focussed on chlorinated compounds. Somehow, although not explicitly stated, the concept that "many man-made environmentally hazardous substances are chlorinated" has been transformed into the concept that "all chlorinated organic compounds are man-made". The latter statement has become widely accepted and thus presented as fact. It would be an interesting challenge to make an analysis of texts from the disciplines involved in order to describe this process more fully. However, this is outside the scope of this paper and for reasons given below, I confine myself here to conclude that communication between the field of environmental chemistry and a number of other disciplines has obviously been rather poor.

... even though at least 1,500 naturally produced compounds are chlorinated

There are publications treating naturally produced chlorinated organic compounds written as early as the late nineteenth century (Paterno and Oglialoro 1877; Drechsel 1896). However, it was not until some decades later that the elemental composition of the compounds identified was determined (Asahina and Shibata 1954). The number of naturally produced chlorinated compounds identified has increased steadily throughout the twentieth century, and is thoroughly described in the numerous comprehensive surveys that have been produced since the 1950s (e.g. Asahina and Shibata 1954; Bracken 1954; Fowden 1968; Siuda and de Bernardis 1973; Fenical 1981; Engvild 1986; Gribble 1992). The number of naturally produced chlorinated compounds reported today is around 1,500 (Gribble 1996), covering for example alkenes, terpenes, steroids, fatty acids and glycopeptides (Table 1). In other words, the information on naturally produced organochlorine compounds is quite extensive in a historical sense as well as with regard to the number and structures of identified compounds. Sev-

Table 1 Chemical structure and trivial names of 21 of the more than 1,500 naturally produced chlorinated compounds. The compounds are chosen to exemplify the abundance in variation in the chemical structure of chlorinated compounds that are produced by specific organisms

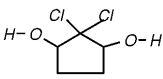
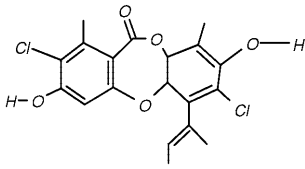
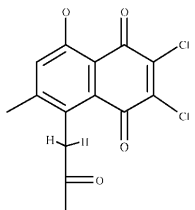
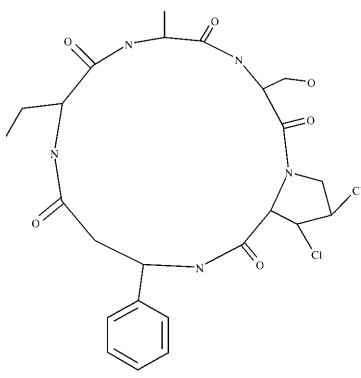
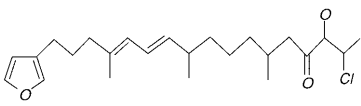
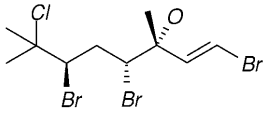
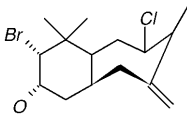
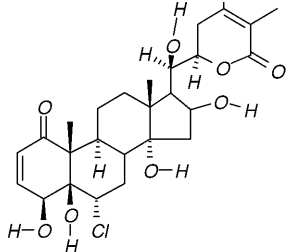
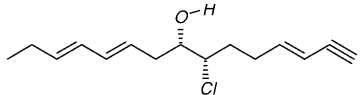
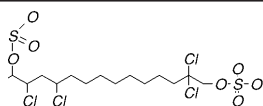
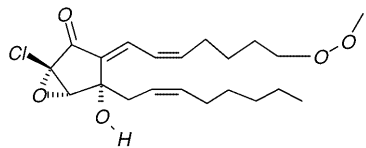
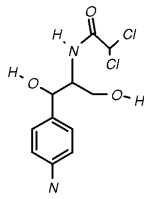
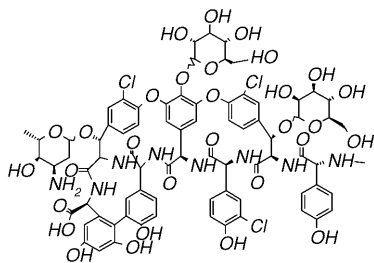
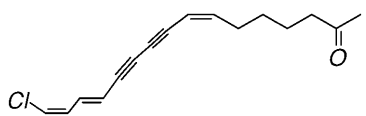
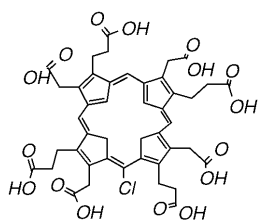
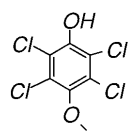
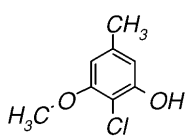
Structure	Trivial name	Reference
	Caldariomycin	Clutterbuck et al. 1937
	Nornidulin	Bracken 1954
	Mollisin	Miller 1961
	Islanditoxin	Miller 1961
	Konakhin	N'Diaye et al. 1991
	(Chlorinated monoterpene)	Faulkner 1977
	Elatol	Sims et al. 1974
	Physalolactone	Ray et al. 1978
	Prerogioloxepane	Guella et al. 1992

Table 1 (continued)

Structure	Trivial name	Reference
	(A chlorosulfolipid)	Haines 1973
	(An epoxy prostanoid/ a prostaglandin)	Iguchi et al. 1987
	Chloroamphenicol (chloromycetin)	Gottlieb et al. 1948
	Chloropolysporin C	Takatsu et al. 1987
	(A chloroacetylene)	Walker and Faulkner 1981
	(A chlorinated porphyrin)	Lin et al. 1993
	Drosophilin	Anchel 1952
	(Volatile phenolic compound)	Gavin et al. 1978
CH ₃ Cl	Chloromethane (methylchloride)	Harper 1985
CH ₂ Cl ₂	Dichloromethane	Blackman et al. 1992
CHCl ₃	Chloroform	Pyysalo 1976
CCl ₄	Carbontetrachloride	McConnell and Fenical 1977

eral decades of research strongly indicate that enzymes with high substrate specificity and regioselectivity are involved in the formation of specific compounds (Speed et al. 1987; Facey et al. 1996; van Pee 1996, 2001; Hoffmann et al. 1998).

The second paradox: It is generally believed that only a few, rather specialised, organisms are able to convert chloride to organic chlorine

Another widespread apprehension is that the ability to produce chlorinated organics is something out of the ordinary. This apprehension can be deduced from the first paradox. The line of reasoning is logical, since the thesis that “all chlorinated organic compounds are xenobiotic” actually implies that such compounds cannot be formed by organisms. This is simply the meaning of the word xenobiotic. Consequently, it is just as common to claim that organisms that produce chlorinated compounds are non-existent, extremely rare, or at least highly specialised, as it is to claim that chlorinated organics are xenobiotic. This line of reasoning is often found interwoven in discussions on chlorinated compounds and it is clearly not an overstatement to claim that it is generally believed that organisms that are able to produce such compounds are rare and specialised. However, this apprehension leads to a second paradox when viewed in light of the fact that thousands and thousands of organisms are actually known to produce chlorinated organics.

... even though a myriad of organisms are known to produce chloroorganics

The voluminous literature on naturally produced chlorinated organic compounds is evidence that organisms able to convert chloride to organic chlorine are at least as many and as various as the compounds they form (e.g. Miller 1961; Fowden 1968; Turner 1971; Siuda and de Bernardis 1973; Fenical 1975; Minale 1976; Thomson 1978; Duursma and Dawson 1981; Turner and Aldridge 1983; Engvild 1986; Gribble 1992). The literature is most impressive on marine algae and terrestrial fungi, bacteria and lichens (Table 2). However, there are also reports on freshwater organisms, a variety of plants and insects and a few examples of higher animals and mammals (Gribble 1996).

Below, I give a short, and certainly not comprehensive, review of the various points of departure that, according to my readings, dominate studies dealing with organisms able to produce chlorinated compounds.

How should this organism be systematised?

Microorganisms and angiosperms are often hard to pinpoint taxonomically. Hence, these types of organisms are by tradition systematised by combining morphological

features with other types of information. Chemotaxonomy, i.e. identification of species through the use of the organism's chemical constituents, has been widely used since at least the latter half of the nineteenth century. Hence, a considerable part of the scientific papers on chlorinated compounds represents taxonomical works. Examples of such works are: “Beiträge zur Chemie einiger Seethiere” (A reflection on the chemistry of a sea animal; Drechsel 1896); “A lichen substance containing chlorine” (Nolan 1934); “Nidulin and ustin: two chlorine containing metabolic products of *Aspergillus nidulans*” (Dean et al. 1953) and “Chemical and chemotaxonomical studies of ferns, XXXVII Chemical constituents of Costa Rican Ferns (2)” (Tanaka et al. 1981). The development of new biotechnological techniques has rendered organic chemistry superfluous as a taxonomical tool. Hence, the taxonomic disciplines nowadays rarely provide information on organisms able to produce chlorinated organic compounds.

Why and how does this organism affect other organisms?

There are a number of fields where the focus is to pinpoint the chemical structure of the compound that underlies the biological activity induced by a certain organism. Now and then the identified compounds contain chlorine. As in the taxonomical context, the elemental composition per se is here of no interest. Broadly speaking, three areas can be identified: pharmacology, agriculture and ecotoxicology.

Chlorinated compounds with various types of biological activities are reported at least as early as during the 1930s (e.g. Clutterbuck et al. 1937; Oxford et al. 1939; Raistrick and Smith 1939) and the number has steadily increased since then. Examples of titles within the pharmacological area of research are: “Some properties of an antibiotic obtained from a species of *Streptomyces*” (Gottlieb et al. 1948); “Ansamitocin, a group of novel maytansinoid antibiotics with antitumor properties from *Nocardia*.” (Higashide et al. 1977) and “Halocyanines: novel antimicrobial tetrapeptide-like substances isolated from the memocytes of the solitary Ascidian *Halocynthia roretzi*” (Azumi et al. 1990). Even though a vast number of naturally produced biologically active chlorinated compounds have been identified, and the number constantly increases, few have actually been commercialised. By way of example, to my knowledge, only 4 of the around 80 chlorinated pharmaceuticals in use in Sweden today are of natural origin (LINFO 2000; Table 3). Obviously, it is a long way from basic research to commercial use.

Biologically active chlorinated compounds have also attracted interest because of their potential use in the control of pests. The following titles exemplify such studies: “A polyhalogenated insecticidal monoterpene from the red alga *Plocamium telfairiae*” (Watanabe et al. 1989); “Insecticide and acaricide activities of polyhalogenated monoterpenes from Chilean *Plocamium car-*

Table 2 Examples of organisms that are able to convert chloride to organic chlorine

Type of organism	Organism		Reference
	Scientific name	Common name	
Bacteria	<i>Pseudomonas aeruginosa</i> <i>Chromobacterium sp.</i> <i>Bacillus subtilis</i>		Takeda 1958 Andersen et al. 1974 Rapp et al. 1988
Blue-green bacteria	<i>Fischerella muscicola</i> <i>Hapalosiphon fontinalis</i> <i>Westiellopsis prolifica</i> <i>Schizothrix calcicola</i>		Park et al. 1992 Moore et al. 1984 Smitka et al. 1992 Mynderse and Moore 1978
Actinomycetes	<i>Streptomyces carzinostaticus</i> <i>Actinosporangium vitaminophilum</i> <i>Actinomadura melliaura</i> <i>Saccarothrix aerocologines</i>		Nozoe et al. 1992 Ezaki et al. 1983 Matson et al. 1989 Lam et al. 1989
Fungi	<i>Caldariomyces fumago</i> <i>Aspergillus terreus</i> <i>Penicillium patulum</i> <i>Pithomyces chartarum</i>		Clutterbuck et al. 1940 Kiryama et al. 1977 McMaster et al. 1960 Hodges et al. 1963
Basidiomycetes	<i>Phellinus pomaceus</i> <i>Agaricus bisporus</i> <i>Mollisia ventosa</i> <i>Periconia macrospinosa</i> <i>Amanita solitaria</i>	Cultivated mushroom	White 1982 Turner et al. 1975 Nakanishi et al. 1989 Giles and Turner 1969 Chilton and Tsou 1972
Ascomycetes	<i>Lachnum papyraceum</i> <i>Ascochyta viciae</i>		Stadler et al. 1993 Nawata 1969
Unicellular eucaryotes	<i>Dictyostelium discoideum</i>	Amoeba	Morris et al. 1987
Algae			
Brown	<i>Macrocystis pyrifera</i> <i>Fucus vesiculosus</i> <i>Ascophyllum nodosum</i>		Manley and Dastoor 1987 Gschwend et al. 1985 Gschwend et al. 1985
Red	<i>Asparagopsis taxiformis</i> <i>Bonnemaisonia asparagoides</i> <i>Gigartina stellata</i> <i>Meristiella gelidium</i>		McConnell and Fenical 1977 McConnell and Fenical 1980 Gschwend et al. 1985 Collen et al. 1994
Green	<i>Enteromorpha linza</i> <i>Ulva lacta</i>	Sea lettuce	Gschwend et al. 1985 Gschwend et al. 1985
Lichen	<i>Evernia prunasti</i> <i>Parmelia perlata</i> <i>Lecidea carpatica</i> <i>Ramalina ceruchis</i>		St. Pfau 1934 Asahina and Shibata 1954 Huneck and Santesson 1969 Culbertson 1969
Mosses	<i>Bazzania trilobata</i>	Liverwort	Martini et al. 1998
Phytoplankton	<i>Nitzschia stellata</i> <i>Porosira glacialis</i> <i>Porosira pseudodenticulata</i>		Sturges et al. 1993 Tokarczyk and Moore 1994 Sturges et al. 1993
Higher plants	<i>Piper hookeri</i> <i>Solanum tuberosum</i> <i>Pisum sativum</i> <i>Centaurae solstitialis</i> <i>Valeriana officinalis</i>	Wild pepper Potato Green peas Yellow star thistle	Singh et al. 1971 Varnes 1982 Marumo et al. 1968 Cassady et al. 1979 Popov et al. 1973
Insects	<i>Rhipicephalus sanguineus</i> (and other ticks) <i>Schistocerca gregaria</i> <i>Blatella germanica</i>	Brown dog tick Locust German cockroach	Chow et al. 1975 Andersen 1972 Sakuma and Fukami 1993
Marine Invertebrates	<i>Basella rubra</i> <i>Ptychodera flava laysanica</i> <i>Biflustra perfragilis</i> <i>Batzella sp.</i> <i>Trididemnum solidum</i>	Malabar nightshade Marine acorn worm Bryozoa Sponge Marine tunicate	Kameoka et al. 1991 Higa and Scheuer 1977 Blackman et al. 1992 Sakemi et al. 1989 Sings et al. 2000

Table 3 Naturally produced chlorinated compounds presently used as pharmaceuticals or pesticides in Sweden

Trivial name	Organism	Field of application	Source
Griseofulvinum (Griseofulvin)	<i>Penicillium griseofulvum</i> <i>P. janczewski</i>	Internally against dermal mycosis	LINFO 2000
Chloroamphenicolum (kloramfemikol; chloromycetin)	<i>Streptomyces venezuelae</i>	Droplets against eye infection	LINFO 2000
Teicoplaninum (Teikoplanin)	<i>Actinoplanes teichomyceticus</i>	Used to prevent bacterial infections after implantation of non-human material	LINFO 2000
Vancomycinum (Vankomycin)	<i>Streptomyces orientalis</i>	Used in connection with complicated bacterial infections	LINFO 2000
2,4-Dichlorophenol	<i>Penicillium sp.</i>	Herbicide	Ando et al. 1970
Hexachloroacetone	<i>Asparagopsis taxiformis</i>	Fungicide	Moore 1977
Strobilurin B	<i>Strobilurus tenacellus</i> and <i>Mycena spp.</i>	Fungicide	Schramm et al. 1978

tilagineum” (San-Martin et al. 1991) and “Lachnumon and lachnumol A, new metabolites with nematicidal and antimicrobial activities from the Ascomycete *Lachnum papyraceum*” (Stadler et al. 1993). As in the case of pharmaceuticals, rather few naturally produced compounds are currently in commercial use as pesticides (Table 3).

In the pharmacological and agricultural contexts, the biologically active compounds are of interest because they can be used to control unwanted organisms such as pathogens or pests. In addition, biologically active compounds, naturally produced or not, are of interest because they may cause indirect or direct harm, as for example when livestock unintentionally eats poisonous plants or when detrimental microorganisms proliferate as the result of bad preservation. An example of a thoroughly investigated plant that is widespread, common in pastures, and has caused severe harm due to its toxicity is “tansy ragwort” (*Senecio jacobaea*; Barger and Blackie 1937; Bredenkamp et al. 1985). This plant, along with other species of the *Senecio* family, contains a variety of rather nasty alkaloids such as jaconine, chlorodeoxyscleratine, doronine and merenskinine N-oxide. Other examples of works reporting chlorinated toxins over the years are: “Islanditoxin, a toxic metabolite produced by *Penicillium islandicum*” (Marumo et al. 1955); “Chronic toxicity and carcinogenicity in mice of the purified mycotoxins, luteoshyrin and cyclochlorotine” (Uraguchi et al. 1972) and “Panterinine, a cytotoxic aromatic alkaloid, and 7-deazainosine from the Ascidian *Aplidium pantherinum*” (Kim et al. 1993).

What causes this peculiar feature?

Another line of research that has rendered information on chlorinated compounds is investigation of the root of peculiarities such as strange or outstanding odour, taste or colour. For example, the extensive literature on chlorinated compounds produced by sea hares (*Aplysia sp.*)

emanates from the purple substance that these animals excrete into the water when disturbed (Faulkner 1977). Other examples are as revealed by their titles: “The colouring matters of *Penicillium nalgiovensis* Laxa.” (Raistrick and Ziffer 1951); “Odor of dried shell powder of Antarctic krill and liquid seasoning of the hydrolysate” (Kobuta et al. 1980) and “Volatile flavour components of Malabar-Nightshade (*Basella rubra* L.)” (Kameoka et al. 1991).

What are the chemical characteristics of the compounds this organism produces?

Finally, a vast number of studies with the aim of finding and characterising new compounds have resulted in the identification of chlorinated compounds. This type of publication has increased more than the areas mentioned above. It is commonly argued that Nature holds innumerable unknown compounds, which might be of future use to humans. This appears to be a driving force in the search for new natural products. I end this part of the paper with some titles to exemplify this field: “Die Inhaltsstoffe von *Lecidea carpatica* (Koerb.) Szat. und die Struktur des Thuringions, eines neuen Xantons” (the content of *Lecidea carpatica* and the structure of the Thuringions, a new Xanton; Huneck and Santesson 1969); “New chlorine-containing sesquiterpene lactones from *Chrysanthemum parthenium*” (Wagner et al. 1988) and “Identification and synthesis of novel chlorinated *p*-anisylpropanoid metabolites from Bjerkandera species” (Wijnberg 1998).

Is the ability to transform chloride to organic chlorine more the rule than the exception?

Organisms that have caught human interest through, for example, traditional medicine, production of perfumes or control of pests, have been more intensively investigated

than other organisms. This is also true for organisms that have been identified with the aid of chemotaxonomy or by investigations in other fields referred to above. It is therefore not surprising that these types of organisms are well represented among those that are able to produce chlorinated compounds. Few studies have been conducted with the aim of surveying the ability among taxonomic groups of organisms as a whole. It is therefore difficult to conclude whether the types of organisms that are well represented are depicted because they have been more thoroughly investigated than others or because the ability to produce chlorinated compounds is more common among them.

Most studies that deal with biotic formation of organic chlorine focus on the ability to produce specific compounds (e.g. Harper et al. 1988; de Jong 1993; Abrahamsson et al. 1995; Gan et al. 1998). Another, less frequent, approach is to test if certain organisms contain enzymes that are able to convert chloride to organic chlorine (e.g. Morrison and Schonbaum 1976; Hunter et al. 1987; van Pee 1996). A third way to approach the issue is to focus on the conversion of chloride to organic chlorine by certain organisms without regard to the chemical characteristics of the compound formed or the enzymes that catalyse the process. Only a small number of studies have used this approach, but these studies indicate that the ability to transform chloride to organic chlorine is much more common than suggested by studies on specific compounds or enzymes. In 1940, Clutterbuck and co-workers followed the chlorine metabolism of 139 fungi and found that 132 of these species were able to convert more than 1% of the chloride in the medium to organic chlorine (Clutterbuck et al. 1940). It has also been found that the majority of white-rot strains tested are able to convert chloride to organic chlorine (Verhagen et al. 1996; Öberg et al. 1997). The conclusion that the ability to transform chloride to organic chlorine is rather common is strengthened by recent reports that myeloperoxidase, a haem protein secreted by phagocytosis, catalyses the formation of HOCl or ClO⁻ (Hazen et al. 1996). Such enzymes are present in most mammals including humans, which suggests that formation of organic chlorine takes place within humans (Neidleman and Geigert 1986). It is well known that reactive chlorine species in the presence of organic structures yields organic chlorine. This suggests that reactive oxidants generated during phagocytosis actually induce the conversion of inorganic chloride to organic chlorine.

All in all, although incomplete, this scattered information makes it tempting to suggest that the ability to convert inorganic chloride to organic chlorine is more the rule than the exception among organisms. In some cases this ability gives rise to the formation of very specific compounds; in other cases the chlorination is rather unspecific.

Production, formation or conversion?

The terminology used in the different fields that in one way or another deal with chloride metabolism is rather

confusing, which justifies a comment on the issue. Organisms that produce specific intracellular enzymes that catalyse the formation of a specific chlorinated compound can without doubt be said to produce the compound in question. However, organically bound chlorine is also produced by extra-cellular enzymes that catalyse the formation of reactive chlorine (e.g. HOCl) which in turn oxidises and chlorinates almost any organic compound present. In a way, one may say that organisms that produce such enzymes are also able to produce organic chlorine, but the word "produce" is rather misleading and risks lulling the reader to presume that a more direct process is at hand than actually is. Hence, under such circumstances, it might be clearer to speak of "formation" or even "indirect formation" of organic chlorine. Another problem is that both the words "production" and "formation" imply formation of specific compounds which complicates the discussion when the focus is the turnover of chlorine per se. This is especially true if the process is combined with the word "metabolite", which is often the case, not only when referring to intracellular processes but also in relation to extracellular processes. Since "metabolite" originally refers to compounds that are produced during cell-metabolism, the word tacitly gives the reader the impression of a rather specific metabolic process rendering specific compounds.

In summation, some chlorinated compounds are biotically produced within cells, but others are formed outside the microorganisms via the action of exo-enzymes. A large number of specific compounds are indeed produced, but it is also clear that a rather unspecific large-scale formation of chlorinated organic matter takes place. Perhaps, in this context, is it clearest to speak of organisms that are able to induce the conversion of chloride to organic chlorine. Such a formulation will include processes driven by intracellular as well as extracellular enzymes, direct as well as indirect processes and it directs the focus from specific compounds to chlorine metabolism and the biogeochemistry of chlorine as a whole.

The third paradox: It is generally believed that all chlorinated organic compounds are persistent and toxic

The development of new chemical techniques formally exploded during the 1950s, which made it possible to synthetically produce a vast variety of compounds with quite diverse properties. Some of the new substances were found to be excellent as isolators (e.g. polychlorinated biphenyls), others were used as plastics (e.g. polyvinyl chloride) or softeners (e.g. phthalates). During this period, the ability to synthesise aromatic substances was developed, and it was discovered that such compounds often became more stable when chlorinated. The majority of the new compounds had one feature in common, which was also one of the keys to their success: they were not reactive and they resisted biodegradation. However, a decade later, this very feature was the reason

these compounds came under scrutiny as environmental problems started to pile up. Another group of compounds that was developed during this period and introduced on a large-scale basis was various types of pesticides. In this field, it was found that addition of chlorine at certain locations often rendered a higher biological activity. The most renowned compound is perhaps dichlorodiphenyltrichloroethane (DDT), which earned its inventor the Nobel prize and saved the lives of millions of people due to its efficiency when used against the malaria-carrying mosquito. DDT appeared fully degradable, but it was later found that its degradation products caused severe environmental problems.

In summary, the majority of organic compounds that have been the focus of the environmental debate either because they or their degradation products are persistent, toxic, or both, are chlorinated. It is not hard to understand that this has led to the conclusion that all chlorinated organic compounds are persistent and/or toxic. However, this is a fallacy.

... even though the vast majority are neither persistent nor toxic

Even though quite a few naturally produced chlorinated substances show a high biological activity, as for example those used as pharmaceuticals and pesticides (Table 3), and some are rather toxic, the vast majority of these compounds are neither persistent nor toxic. A large number of the 1,500 chlorinated compounds that are known to be naturally produced are easily degraded by various organisms and the vast majority is not biologically active and consequently not toxic. As outlined in the following section, it has been found that chlorine is one of the major elements of soil organic matter. Like other natural constituents of organic matter, organic matter-bound chlorine is mineralised during the degradation of the organic matter (Öberg 1998; Öberg and Grøn 1998). Hence, organic matter-bound chlorine is easily and continuously degraded in soil and most likely also in other compartments of the environment. In summation, it is clear that some, but by no means all, processes that generate conversion of chloride to organically bound chlorine yield persistent or toxic compounds.

Nevertheless, during the 1970s, and until the 1990s, the notion that chlorinated compounds per se are environmentally hazardous was repeated over and over again, either clearly stated or hidden between the lines. The most extreme case of this line of argumentation is the "chlorine-ban" when Greenpeace proposed an action in the late 1980s that proclaimed a ban towards all chemicals that contained chlorine. Even though most texts nowadays are more balanced and more often focus on the type of compound in combination with the concentration at which it is found, the apprehension that all chlorinated compounds are environmentally hazardous still appears to be rather common among scientists as well as among the public.

The fourth paradox: It is generally believed that chlorine is mainly found in its ionic form in the environment

It is generally agreed that the ionic form of chlorine, i.e. chloride (Cl^-), is not retained in soil and that it follows the movement of water whatever direction it takes. It is also generally agreed that soil acts neither as a sink nor as a source of chloride. In this context, it must be stressed that the seasonal variability of the biomass must be taken into account, as plants as well as other organisms contain chloride. The major source of chloride is the sea. Through the action of sea spray, chloride is widely transported and deposited as wet and dry deposition over land and water. The deposition of chloride varies from far below 1 kg ha^{-1} in inland Russia and China to around 100 kg ha^{-1} on the Norwegian west coast. In humid climates, chloride from the sea is deposited on the ground via the air and eventually, by the movement of water through the ground, transported to lakes and rivers and back to the sea again. In soils in more arid climates, where evapo-transpiration exceeds wet deposition, chloride is occasionally transported upwards as this is the direction of the water movement. Eventually, such a movement will cause salinisation of the soil.

The general apprehension is that there are no processes, except temporary uptake by plants, that interfere with the transport of chloride in soil. The only source sometimes discussed is weathering of the bedrock, but even this is most often dismissed, as the chloride content of the bedrock in general is extremely low. The role of organically bound chlorine in the cycling of chloride is never discussed or even considered.

The principle that soil works neither as a sink nor as a source of chloride is widely applied in biogeochemical modelling and chloride in this context is referred to as a conservative element with respect to water.

... even though organically bound chlorine is as abundant as chloride in soil

During the 1970s, a method was developed to monitor the formation of chlorinated organic compounds during disinfection of drinking water (Kühn et al. 1977). The method was developed as a response to findings indicating that chlorination of drinking water induced the formation of carcinogenic substances. The disinfection process yielded a great number of chlorinated compounds, and it was unclear which compounds caused the harm. However, studies indicated that the higher the total concentration of chlorinated compounds, the higher the carcinogenic nature of the water. The idea of the method developed was to detect the sum of all chlorinated organic compounds, irrespective of their structure. However, the authors also market their method as suitable for monitoring on a more general basis. The line of argument was that the sum of chlorinated organic compounds is a suit-

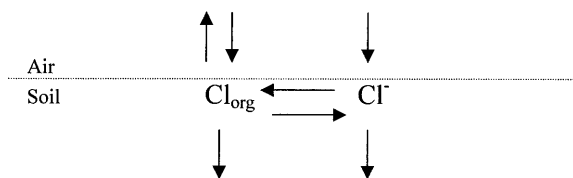


Fig. 1 A conceptual model of the chlorine cycle in soil. *Vertical arrows* Deposition of chloride and organic chlorine; loss of chloride and organic chlorine by leaching. *Upper horizontal arrow* transformation of chloride to organic chlorine, *lower horizontal arrow* mineralisation of organic chlorine to chloride (after Öberg 1998)

able indicator of anthropogenic activity since such compounds are xenobiotic, a statement that obviously can be traced back to the first paradox. During the 1980s, the method became widely used as a general tool for monitoring anthropogenic substances. In Germany, for example, four classes of industrial influence were defined based on the concentration of organic chlorine where a concentration of $5 \mu\text{g l}^{-1}$ was set as the limit between a negligible and a moderate influence (Hoffman 1986).

In the late 1980s, a study was conducted on the influence of a paper mill on the surrounding surface water (Wigilius et al. 1988). During this study, it was noted that, according to the German norm, the concentrations in the water upstream of the mill would have to be classified as significantly, or even substantially, influenced by human activities. In addition, it was observed that all surface waters so far investigated contained organic chlorine (Asplund et al. 1989). The concentrations in general were rather low, but the calculations revealed that the amounts transported by the river water was considerable when compared to the annual discharges from, for example, the pulp and paper industry. It was also noted that the concentrations seemed to be related to the amount of organic matter. This led our research group to investigate the occurrence and origin of organically bound chlorine in soil (Asplund and Grimvall 1991; Hjelm 1996; Johansson 1996, 2000). By combining environmental chemistry, microbiology and soil science, we discovered a piece in a puzzle that we did not know existed: the biogeochemical cycle of chlorine (Fig. 1).

Since then, it has been revealed that organic chlorine is ubiquitous in soil. The organically bound chlorine in soil originates from rain, throughfall, litterfall and an intrinsic production in soil (Öberg and Grøn 1998). The reason why litter contains organic chlorine is as yet unknown. As it is not uncommon for plants to form such compounds (Engvild 1986), it is tempting to suggest that the chlorine content in litter is due to the plants themselves, or perhaps microorganisms on the leaves that transform chloride to organic chlorine. There is strong evidence that various forms of biotic processes drive the formation of organic chlorine in soil (de Jong 1993; Öberg et al. 1996, 1997; de Jong and Field 1997). The numerous soil organisms reported to have this ability, as cited above, further strengthen this conclusion. A recent

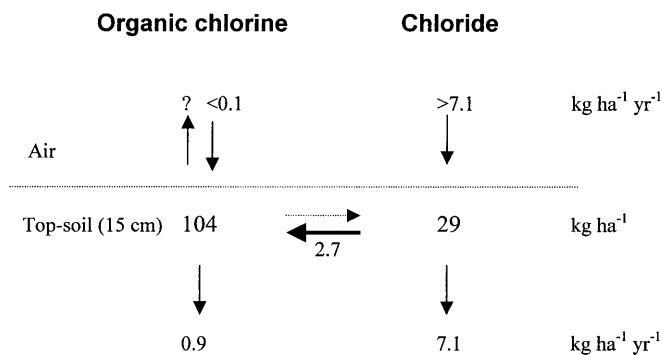


Fig. 2 A roughly estimated chlorine budget of the Stubbetorp catchment, South East Sweden ($59^{\circ}44'N$; $16^{\circ}21'E$). *Vertical arrows* Deposition of chloride and organic chlorine (wet+dry); loss of chloride and organic chlorine by leaching. *Upper horizontal arrow* Transformation of chloride to organic chlorine, *lower horizontal arrow* mineralisation of organic chlorine to chloride. The run-off and the wet-deposition of chloride are based on long-term field data and are thus the most reliable components of the budget. Provided that the remaining fluxes are negligible, the dry-deposition is assumed to equal the run-off minus the wet-deposition, rendering a total deposition of $7.1 \text{ kg Cl}^{-} \text{ ha}^{-1} \text{ year}^{-1}$. However, the size of the other components strongly indicates that the soil acts as a chloride sink, at least during the period 1986–1990. This suggests that the dry-deposition was actually larger than previously estimated

report suggests that abiotic processes may also be of importance in the chlorine cycle (Keppler et al. 2000).

A rough chlorine budget of a small catchment

In order to put the chlorine cycle in a more concrete form, the components of the chlorine cycle of a small forested catchment is constructed here. This has not previously been done. The budget is constructed in order to elucidate more clearly which parts of the cycle are fairly well known and which components are more or less unknown. This will, for example, make it easier to pinpoint which processes are central when analysing the relationship between the turnover of organic chlorine and its possible interference with the flux of chloride through soil.

A small catchment in southern Sweden (Stubbetorp; $59^{\circ}44'N$; $16^{\circ}21'E$) was chosen since the hydrochemistry of the area has been carefully monitored (1986–1990; Maxe 1995) and the chloride as well as the organic chlorine content has been determined in top-soil samples. In addition, loss by leachate has been measured in lysimeters placed in climate chambers. The components that have not been specifically studied in the catchment are constructed by extrapolation from other studies.

Storage in soil

In July 2000, ten soil cores (15 cm depth, diameter 0.80 dm^2) were collected in the catchment. The amount

of chloride and organic chlorine was determined. The storage was estimated at 29 kg Cl⁻ ha⁻¹ and 104 kg Cl_{org} ha⁻¹, respectively (Fig. 2; M. Rodhstedt, C. Ståhlberg, P. Sandén and G. Öberg, unpublished data). The detected concentrations of both variables are well in line with previous studies conducted in other coniferous forest soils in Scandinavia (Öberg and Grøn 1998; Johansson 2000; Johansson et al. 2001).

Input and output of chloride by deposition and leaching

The stream-water chemistry in the area has been regularly monitored, usually by weekly sampling but more intensely during high flow periods. The run-off is continuously measured in a weir. The loss of chloride by run-off was estimated at 7.1 kg Cl⁻ ha⁻¹ year⁻¹ during 1986–1990 (Maxe 1995). Wet-deposition data was achieved by combining rainwater chemistry data from the network of the Meteorological Department at the University of Stockholm with the amount of precipitation as measured by the Swedish Meteorological and Hydrological Institute (Maxe 1995). The wet-deposition of chloride in the catchment was estimated at 4.0 kg Cl⁻ ha⁻¹ year⁻¹ (Maxe 1995). The other component of the deposition, i.e. the dry-deposition, is complicated to monitor and is therefore generally calculated as the output (run-off) minus the input by wet-deposition. This means that estimates of dry-deposition are solid as long as the transformation of organic chlorine to chloride and vice versa is minor. Assuming that this was the case, Maxe (1995) estimated the dry-deposition 1986–1990 at 3.1 kg Cl⁻ ha⁻¹ year⁻¹.

Input and output of organic chlorine by deposition and leachate

The concentration of organic chlorine in wet-deposition has been studied by several authors and, in general, it is less than 10 µg Cl_{org} l⁻¹ (Laniewski et al. 1995). According to Maxe (1995), the annual wet-deposition in the area is 696 mm, which gives an annual wet-deposition of 70 g Cl_{org} ha⁻¹. The dry-deposition is not known, but if we assume that it is in the same order of magnitude as the wet-deposition, the total deposition of organic chlorine is unlikely to be larger than 100 g Cl_{org} ha⁻¹.

The loss of organic chlorine by leaching is poorly understood and has not been studied in the Stubbetorp catchment. However, an ongoing laboratory study using soil cores collected in the catchment and incubated under controlled conditions in climate chambers and irrigated with artificial rain, gave a concentration of organic chlorine in the soil leachate of around 400 µg Cl_{org} l⁻¹ (M. Rodhstedt, C. Ståhlberg, P. Sandén and G. Öberg, unpublished data). Assuming that this is representative of the area as a whole, the amount of organic chlorine transported each year from upper soil layers as soil leachate can be roughly estimated to about 0.9 kg Cl_{org} ha⁻¹.

Mineralisation of organic chlorine (release of chloride) and formation of organic chlorine (consumption of chloride)

To our knowledge, no studies have been conducted anywhere to follow net-changes in the organohalogen content in soil in a field-study. We have analysed data from a lysimeter study and groundwater data, both from the catchment, in order to test if the soil acted as a sink or a source of chloride (P. Sandén and G. Öberg, unpublished data). Both studies indicate that a substantial amount of chloride was withdrawn from the water as it moved from the surficial to deeper levels. The lysimeter data yielded an estimate corresponding to 2.7 kg Cl⁻ ha⁻¹ year⁻¹. The sampling regime of the groundwater data did not permit quantitative estimates of withdrawal. Chlorination of organic matter is a plausible cause of the observed withdrawal of chloride from the surficial soil layers. The study indicates that the soil in the Stubbetorp catchment acted as a sink of chloride during the period 1988–1989, which in turn suggests that a net formation of organic chlorine was taking place.

Output through volatilisation

Research on the formation of halogenated volatiles from terrestrial sources has shown that common white-rot fungi are able to methylate chloride (Harper 1985, 1995; Harper et al. 1988; McNally et al. 1990; Watling and Harper 1998; Khalil et al. 1999). It has also been found that higher plants are able to produce rather high amounts of chloromethane (Harper 1995; Gan et al. 1998). In addition, there is evidence that the concentration of methyl chloride and chloroform is higher in soil than in the ambient air, which indicates that such compounds are formed there (Laternus et al. 1995; Hoekstra et al. 1998; Haselmann et al. 2000). Finally, a recent study suggest that an abiotic formation of chloromethane involving redox reactions with organic matter, iron and chloride takes place in soil (Keppler et al. 2000). However, even though the first report on the issue was published already in 1985 (Harper 1985), information is still very scattered. As pointed out by several authors, it is still not possible to reliably quantify the relative contribution from terrestrial sources to the atmospheric burden of chlorinated volatiles (e.g. Khalil et al. 1999). The major reason for this is the lack of sound field data, with quantification so far mainly based on extrapolations from laboratory studies of single species (e.g. Watling and Harper 1998). The exception is a recent study focussing on the emission of methyl-chloride and bromide from coastal salt marches indicating fluxes of 2–12 kg ha⁻¹ year⁻¹ (Rhow et al. 2000). The figures are still far too uncertain to even guess how large the emissions of chlorinated volatiles might be from Swedish soils.

Summary

The rough estimates of the chlorine budget of the Stubbetorp catchment are summarised in Fig. 2. The construction of this budget strongly indicates that the storage of organic chlorine is of such magnitude that even small changes in this storage are likely to influence the transport of chloride through soil. From a budget-perspective, the estimates clearly show that the deposition of organic chlorine from wet- and dry-deposition is negligible compared to the other fluxes. Furthermore, the estimates suggest that considerable amounts of organic chlorine are lost with the soil leachate. The numerous reports on the formation of chlorinated volatiles from terrestrial environments suggest that the formation of chlorinated volatiles might act as a chloride sink, although the data does not permit even a rough estimate of its size. Even though the figures are most uncertain, the calculations strongly indicate that the loss by leaching and perhaps also volatilisation makes the soil act as a sink of chloride that cannot be considered negligible in relation to the transport of chloride through soil. As calculation of the dry-deposition is based on the assumption that the soil acts neither as a sink nor as a source of chloride, this suggests that the estimates of dry-deposition of chloride are an underestimate. All in all, our present state of knowledge permits us to conclude that the turnover of organic chlorine is liable to have a considerable influence on the geochemical cycling of chloride in soil.

Ecological role of the chlorine cycle

It is nowadays clear and beyond question that chlorine does participate in a complex biogeochemical cycle and that an immense number of organisms are able to convert chloride to organic chlorine, and vice versa – but why?

Most information on biotic utilisation of chlorine is – as outlined above – coupled to specific compounds, most profoundly compounds with striking characteristics such as toxicity, colour, and odour. The role of specific chlorinated substances produced by organisms is rather variable as already touched upon. Toxic compounds, as well as those that have a strong taste, colour or odour, seem to serve as antifeedants or other forms of protection. This appears to be especially common among marine invertebrates such as sea hares, nudibranches and other molluscs, as well as sponges and ascidians. Chlorinated tyrosine-containing proteins are suggested to strengthen the cuticle and improve adhesion between protein sheets in invertebrates (Hunt and Breuer 1971; Welinder 1972). A few chlorinated compounds have been identified as pheromones in ticks (e.g. Berger 1972; Chow et al. 1975; Khalil et al. 1981) and cockroaches (Sakuma and Fukami 1993). Some compounds have a biosynthetic role, for example the chloromethane that regenerates veratryl alcohol during degradation of lignin by some white-rot fungi (Harper et al. 1990), and chlorinated anisyl alcohols have been suggested to act as methyl donors

during lignin degradation (de Jong 1993). However, biologically active compounds are by definition active in low concentrations and consequently rarely produced in large quantities. From an evolutionary and ecological point of view, it is therefore not likely that the widespread and abundant occurrence of chlorine in organic matter can be attributed to the formation of such compounds.

The ability to produce enzymes able to catalyse the formation of reactive chlorine such as HOCl appears to be a general trait in all types of organisms from microbes to humans (e.g. Neidelman and Geigert 1986; Eiserich et al. 1996). Such compounds appear to be involved in intracellular defence mechanisms. However, it is not likely that large quantities of reactive chlorine are produced within cells as such compounds not only pose a threat towards intruders but also towards the organism itself.

In addition to intra-cellular enzymes, *exo*-enzymes able to catalyse the formation of organic chlorine are present in soil (Hunter et al. 1987; Asplund et al. 1991, 1993). The presence of hydrogen peroxide is necessary for the reaction to take place, and it has therefore been suggested that the enzymes present in soil act in a manner similar to chloroperoxidases (Hewson and Hager 1979). In the presence of hydrogen peroxide and chloride, such enzymes catalyse the formation of reactive chlorine, most likely HOCl, which in turn oxidises almost any organic substrate. We have suggested that reactive chlorine, through the induction of oxidation processes, enables biodegradation of organic matter and at the same time forms organic chlorine as a by-product (Öberg et al. 1997; Johansson et al. 2000). In line with this, the ability to produce such enzymes would give an organism an evolutionary advantage, especially if it were also able to degrade the chlorinated organic matter. The extent of this process is hard to monitor, but it cannot be excluded that such a process could yield rather large amounts of organic chlorine, provided that it is widely used by microorganisms that are involved in the degradation of organic matter. To summarise, it can be concluded that a number of various processes lead to the formation of organic chlorine and that the ecological roles of these appear to be variable as the processes. We can also conclude that there is little or no information available on the relative contribution of, for example, biotic vs abiotic, intracellular vs extracellular, specific vs non-specific chlorination processes.

If little is known of the extent and role of the processes underlying chlorination processes, even less is known of the extent and role of dechlorination of naturally formed organically bound chlorine. Most studies on dechlorination deal with dechlorination of specific pollutants, which allows conclusions only concerning naturally produced substances that resemble these. Reductive dechlorination by anaerobic bacteria has been shown to be coupled to energy conservation, which is termed “dehalorespiration” (Holliger et al. 1998). The role of the aerobic dehalogenation processes that take place in soil remains to be elucidated.

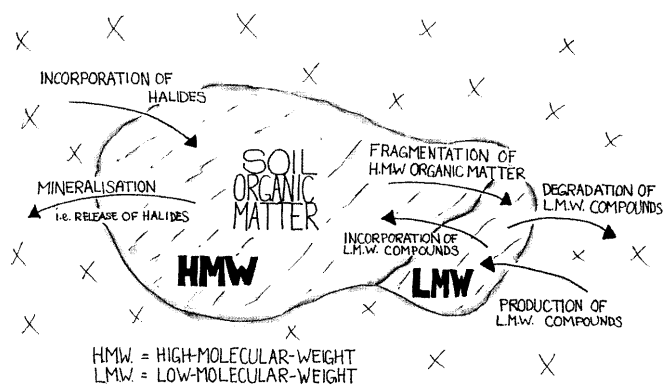


Fig. 3 Processes affecting the amount and structure of chlorinated organic matter in soil (after Hjelm 1996)

Chlorine is as common as phosphorous in organic matter and consequently, together with this element, the sixth most common element in organic matter. The other major elements i.e. carbon, oxygen, hydrogen, nitrogen, sulphur and phosphorous, participate in the basic processes of life. The most abundant elements are, for example, more widely used as electron acceptors than the rare ones. The widespread occurrence of chlorine in organic matter makes it tempting to suggest that chlorine is more actively involved in basic processes than hitherto understood.

Final comment

My intention with this paper has been to fit some of the scattered pieces of the chlorine cycle puzzle together. Most of the pieces are still missing, but it is evident that chlorine participates in an extensive biogeochemical cycle (Fig. 3).

We know that a very large number of organisms are able to convert chloride to organic chlorine, but we do not know if the ability to convert chloride to organic chlorine is actually more the rule than the exception among organisms. We know that biotic, and perhaps also abiotic, processes drive formation and degradation of organic chlorine in soil, thereby releasing and consuming chloride (Fig. 1), but we do not know how, and to what extent, these processes interact with the geochemical cycling of chloride. We know that organic chlorine is lost from soil through volatilisation and leaching and that the amount of organic chlorine in soil is of the same order of magnitude as the amount of inorganic chlorine, at least in Scandinavian soils. We also know that a multitude of other processes influence the structure and chemical character of the chlorinated organic matter in soil (Fig. 2). However, we do not know the extent of these processes, how they are influenced by environmental variables, or their ecological roles. Furthermore, it appears as if the biogeochemical cycling of chlorine is related to the turnover of organic matter, but it is rather unclear how this relationship operates.

The point of departure of this paper has been some tacit understandings that have obstructed endeavours to get a glimpse of the whole picture. The scientific strive to understand the features and processes of the world around us inevitably leads to simplifications and the scientist must always rely on previous findings. In this process, things become generally agreed and placed in "black boxes" as Latour puts it (Latour 1987). Everything cannot be questioned at each and every moment. Some things must be taken for granted. Consequently, scientists within a field must adopt more or less tacit agreements of which questions are considered interesting and which are not, and which black boxes ought to be opened and which shall remain closed. Science has become more and more specialised and the tacit agreements differ strongly in different fields. A tacit agreement may not pose a problem in one specific context but when placed in another, it may be highly troublesome or even paradoxical. This is unfortunate, but nevertheless inevitable. However, active scientists rarely conduct discussions on the discourses that guide our perceptions. Far too often, there is a marked ignorance of how much the choice of perspective guides the interpretation. Consequently, the awareness that the perception of a phenomenon within one's field might not correspond with the perception within another scientific field is rather low. Hence, even though the tacit understandings will inevitably continue to differ among disciplines, science is likely to become more useful if these issues are actively discussed within, as well as between, various disciplines.

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