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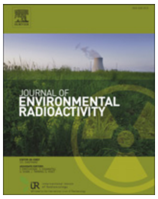

Modelling of the natural chlorine cycling in a coniferous stand: implications for chlorine-36 behaviour in a contaminated forest environment

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ABSTRACT

Considered as one of the most available radionuclide in soil–plant system, ^{36}Cl is of potential concern for long-term management of radioactive wastes, due to its high mobility and its long half-life. To evaluate the risk of dispersion and accumulation of ^{36}Cl in the biosphere as a consequence of a potential contamination, there is a need for an appropriate understanding of the chlorine cycling dynamics in the ecosystems. To date, a small number of studies have investigated the chlorine transfer in the ecosystem including the transformation of chloride to organic chlorine but, to our knowledge, none have modelled this cycle. In this study, a model involving inorganic as well as organic pools in soils has been developed and parameterised to describe the biogeochemical fate of chlorine in a pine forest. The model has been evaluated for stable chlorine by performing a range of sensitivity analyses and by comparing the simulated to the observed values. Finally a range of contamination scenarios, which differ in terms of external supply, exposure time and source, has been simulated to estimate the possible accumulation of ^{36}Cl within the different compartments of the coniferous stand. The sensitivity study supports the relevancy of the model and its compartments, and has highlighted the chlorine transfers affecting the most the residence time of chlorine in the stand. Compared to observations, the model simulates realistic values for the chlorine content within the different forest compartments. For both atmospheric and underground contamination scenarios most of the chlorine can be found in its organic form in the soil. However, in case of an underground source, about two times less chlorine accumulates in the system and proportionally more chlorine leaves the system through drainage than through volatilisation.

1. Introduction

Chlorine is a wide-spread element in natural environments. It is considered as one of the more mobile elements in soil and is also an essential micronutrient for higher plants (White and Broadley, 2001). Chlorine occurs in nature as two stable isotopes; chlorine-35 and chlorine-37 with ^{35}Cl being the most prevalent. Of the seven radioactive chlorine isotopes, only one, chlorine-36, has a half-life longer than 1 h. ^{36}Cl decays with a half-life of 300,000 years by emitting a beta-particle and electron capture; most of the decays (98%) are by beta-particle emission. ^{36}Cl is generated naturally by spallation in the atmosphere of argon-36 by cosmic ray protons, by interactions between cosmic radiation and Cl, Ca and K in near-surface rocks and soils, and by neutron activation of ^{35}Cl in soil and rock (White and Broadley, 2001). ^{36}Cl is also produced anthropogenically during nuclear tests and nuclear industrial processes; i.e. ^{36}Cl is produced by neutron activation of ^{35}Cl present in materials used in nuclear reactors. As a consequence, waste fuel and certain construction materials originating from dismantling nuclear installation might contain ^{36}Cl. Its mobility combined with its long half-life thus makes ^{36}Cl a radionuclide of potential concern for long-term management of radioactive wastes. High mobility in the soil column and a ready availability in soil solution (Ashworth and Shaw, 2006) allow ^{36}Cl to potentially contaminate the biosphere easily. Considered as one of the most available radionuclide for plants (Colle et al., 2002), ^{36}Cl was shown to have the same behaviour as stable Cl in soil and plants (Kashparov et al., 2007). Consequently, radio-chlorine is likely to be recycled in the biosphere and impact the food chain over a very long time.

Because chloride (Cl^-), its wide-spread anionic form, has few affinities for the soil solid phase, chlorine is often considered as a conservative tracer of soil–water movements with no implication in biological processes. While this view is valid in deep geological layers, it is questioned when considering surface soils due to the

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thousands of chlorinated organic compounds that are produced naturally in the biosphere (Winterton, 2000). The natural chlorination of soil organic matter (SOM) through biotic processes (Bastviken et al., 2009) seems largely responsible of the formation of organochlorine which was found to accumulate in large amount in certain organic soils e.g. coniferous forest (Redon et al., 2011). In many cases, the organic chlorine pool is often greater than the inorganic pool. In fact, the natural cycle of chlorine in soils is complex involving simultaneous formation and degradation of chlorinated organic compounds but attempts to rationalise sources and fluxes of organic and inorganic chlorines in soils are still scarce (Clarke et al., 2009). To evaluate the risk of dispersion and accumulation of ^{36}Cl in the biosphere due to a potential atmospheric or underground contamination, there is a need for an appropriate understanding and modelling of the chlorine cycling dynamics in a range of representative ecosystems.

The objective of this study is to develop a model describing the biogeochemical fate of chlorine in a coniferous forest based on measurements of stable chlorine performed in a pine forest around Mol (Belgium). During the measurements particular attention has been paid to the partitioning of the organic and inorganic chlorine into the different compartments of the ecosystem to better evaluate the contribution of the organic chlorine formation to the accumulation of chlorine within the ecosystem. Since ^{36}Cl has the same behaviour as stable chlorine in soils and plants, this model was then used as a questioning tool to estimate, under a range of contamination scenarios, the possible redistribution of ^{36}Cl between the different forest compartments.

2. Materials

2.1. Study area and measurements

The experimental Scots pine (*Pinus sylvestris* L.) stand is located at Mol in the Belgian Campine region. The local area has a rural and forested character with a high proportion of humid soils and wet zones. The topography is flat and the altitude is 15 m. The 60 year old stand is part of a 189 ha forest dominated by Scots pine, with some patches of oak trees. In 2004, the stand density was 359 trees ha^{-1}. The mean height, circumference (at 1.3 m) and stand basal area of the Scots pine were respectively 22 m, 0.91 m and 24.4 m^2. In addition to grasses and mosses, the understorey vegetation mainly consists of *Sorbus aucuparia*, *Prunus serotina*, *Rubus* sp and *Athyrium felix femina*. The soil is a podzol and is classified as a distric Cambisol. The water table depth is very shallow. It fluctuates between 1.2 m and 0.5 m during spring and shows very strong intra-seasonal variations. A detailed description of the site can be found in Vincke and Thiry (2008).

During 2005 and 2006, a large number of soil and vegetation samples have been collected at this site. These samples were used to determine vegetation biomass and soil mass, as well as the levels of organic and inorganic chlorine in different compartments of the ecosystem. The chlorine content has been determined using the Neutron Activation Analysis technique. The procedures to differentiate the organic and inorganic chlorine content within the soil and vegetation samples have been adapted from Öberg et al. (2005). During the sampling campaign, the following items have been collected: water (precipitation and through-fall), tree (needles of one year and older, twigs, branches, wood, bark, roots), understorey (grasses, mosses, shrubs, ferns, fungi, berries) litter-fall (needles, bark, branches), and organic and mineral soil layers. The sampling procedures have been described in detail by Van Hees and Vandenhove (2009). In addition to a chlorine budget, the biological cycling dynamics in the pine stand was quantitatively described in terms of annual fluxes based on annual biomass production and respective average chlorine concentrations in the various tree compartments (Thiry, 2010). The calculations used to assess the element cycling were described in Goor and Thiry (2004).

2.2. Speciation and distribution of chlorine in soil and vegetation

In the pine stand, which is characterised by an atmospheric deposition of 12.6 kg ha^{-1} yr^{-1} of stable chlorine, a quantitative description of the chlorine budget and cycle resulted in the following conclusions (Thiry, 2010):

- The accumulation of chlorine in the soil at the pine stand is linked to the formation of organic chlorine. The transformation of inorganic to organic chlorine takes place once the decomposition of the humus has started in the O_f layer. Under our conditions, the rate of organic matter chlorination is estimated around 0.62 kg Cl ha^{-1} yr^{-1}. 80% of the transformed inorganic chlorine originates from wet depositions. In the whole soil profile the concentration of organic chlorine is 3–4 times larger than the concentration of inorganic chlorine.
- Within the different tree compartments, the foliage has the largest chlorine concentration (590 μg Cl g^{-1} d.m.), accounting for roughly 35% of the total chlorine present in the tree. More than 90% of the chlorine in the leaves and the bark is in its inorganic form. This highlights the high chlorine mobility in the tree. The higher concentration of chlorine in the leaves compared to the soil (27–279 μg g^{-1}) can be explained by the selective uptake of chlorine by the vegetation. On average, 20% of the chlorine present in the whole tree is in its organic form.
- The annual uptake of chlorine through root absorption is ninefold larger than the chlorine demand by the tree, which is the total quantity of element mobilised by the current production of biomass (Goor and Thiry, 2004). This uptake takes place at a rate equivalent to the atmospheric deposition. The excess of chlorine is removed from the tree and returned to the soil through internal transfers at leaf level and subsequently through-fall. Under our conditions, litter-fall plays a minor role in Cl return to the soil.
- The chlorine content within the tree biomass represents only 0.9% of the total chlorine content present in the whole pine stand. The chlorine content in the understorey and in the root system cannot be neglected since they represent respectively 1.2% and 0.5% of the total chlorine within the ecosystem at the stand. Most of the chlorine can be found in the forest floor (5.7%) and in the mineral soil layer (91.7%).
- Assuming that the system is in equilibrium, the residence time of chlorine was estimated based on a mass balance. In the tree the residence time is very short; i.e. 0.4 years. The residence time is longer in the forest floor and in the soil, respectively 3 and 47 years. The residence time of chlorine in the soil seems to be mainly regulated by the dynamics of the chlorination of organic matter and the biodegradation of organo-chlorinated compounds. The residence time of chlorine in the whole system is 48 years.

3. Methods

3.1. Model development

In this study, the cycling of chlorine in the coniferous stand is represented by a seven-compartment model consisting of a mineral soil subdivided into an organic (C_1) and inorganic (C_2) chlorine pool, a forest floor component subdivided as well into organic (C_4) and inorganic (C_3) chlorine pool, a root component (C_5), an aboveground tree component (wood and leaves, C_6) and a leaf surface