



## Research paper

# Monthly record of the Cl and $^{36}\text{Cl}$ fallout rates in a deciduous forest ecosystem in NE France in 2012 and 2013



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## ABSTRACT

This study aims at determining the chlorine and chlorine-36 fallout rates in an experimental beech forest site located in NE France (48°31'55" N, 5°16'8" E). A monthly record of Cl and  $^{36}\text{Cl}$  concentrations in rainfall samples collected above the canopy was performed during two years, from March 2012 to February 2014. The results show that the Cl concentrations mainly originate from sea-spray while the  $^{36}\text{Cl}$  concentrations originate from the stratosphere and therefore present a seasonal dependency. Abrupt and important inputs of  $^{36}\text{Cl}$  from the stratosphere indeed yield sharp increases of the recorded concentrations during the spring-summer. We also show that a too short sampling period might bias the determined  $^{36}\text{Cl}$  fallout rate. To smooth the seasonal and sporadic bursts of  $^{36}\text{Cl}$ , a minimum of 6 months sampling period is required. A mean  $^{36}\text{Cl}$  fallout rate of  $(77 \pm 21)$  atoms  $\text{m}^{-2} \text{s}^{-1}$  can be deduced from our study, which is 45% higher than the modelled value. This discrepancy suggests more studies aiming at measuring the  $^{36}\text{Cl}$  fallout rate worldwide are necessary.

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## 1. Introduction

Mainly naturally produced in the stratosphere through the spallation of  $^{40}\text{Ar}$  by energetic primary and secondary cosmic-ray particles, the cosmogenic nuclide  $^{36}\text{Cl}$  has also been introduced into the environment due to the atmospheric nuclear weapon tests in the Pacific during the 1950's (Bentley et al., 1982; Elmore et al., 1982; Phillips et al., 1990). The Accelerator Mass Spectrometry (AMS) technique is the only technique whose sensitivity makes possible the unambiguous identification and measure of the long-lived  $^{36}\text{Cl}$  (Gosse and Phillips, 2001). Since its development during the 1980's,  $^{36}\text{Cl}$  was mainly used as a tracer for hydrological studies because of its long half-life ( $T_{1/2} = 3.01 \times 10^5$  a) and the established conservative behaviour of chlorine. However, all these studies rely on the knowledge of the input signal of  $^{36}\text{Cl}$  in the studied area which most of the time is assumed because of a lack of data. An accurate determination of the  $^{36}\text{Cl}$  fallout rate requires measuring the  $^{36}\text{Cl}$  concentrations in modern precipitations (Davis

et al., 1998).

Several studies have been dedicated to the spatial distribution of  $^{36}\text{Cl}$  in rainwaters at the scale of a country (Herut et al., 1992), and of a continent (USA: Bentley et al., 1986 and Europe: Johnston and McDermott, 2008) and even at the global scale (Scheffel et al., 1999). Only a few studies focused on  $^{36}\text{Cl}$  fallout rate monthly variations (USA: Hainsworth et al., 1994; Knies et al., 1994; Japan: Tosaki et al., 2012; and Spain: Santos et al., 2004). These studies highlighted 1- a latitudinal dependence of the  $^{36}\text{Cl}$  fallout rate, essentially linked to the stratosphere–troposphere mixing zone which is maximal at mid latitudes (between 30° and 60°) (Lal and Peters, 1967; Keywood et al., 1998) and 2- a seasonal variation of the  $^{36}\text{Cl}$  fallout rate due to an annual variation in the tropopause height. However the sources and the major factors influencing the  $^{36}\text{Cl}$  fallout rate are still under debate. How does site location and meteorological conditions affect the fallout rate? Why the available data do not fit with the values predicted by models? How does the sampling period influence the calculated  $^{36}\text{Cl}$  fallout rate? Moreover, the study of the  $^{36}\text{Cl}$  fallout rate is tied to the study of Cl. What are the sources of the Cl fallout rate and which parameters influence it? Does the Cl fallout rate also exhibit a seasonal variability?

To answer these questions, the  $^{36}\text{Cl}$  and Cl concentrations were

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accurately measured in rainwater samples collected every month during two years in an experimental site located in NE France. The data presented in this work allow first to discuss the different sources of Cl and  $^{36}\text{Cl}$  in this region and then to calculate accurate fallout rates that can be compared to previously published measured and modelled values.

## 2. Material and methods

### 2.1. Sampling site

The forest site is in the experimental forest site of Montiers installed and monitored by Andra-Ope and by INRA-BEF teams and is located at Montiers-sur-Saulx (48°31'55" N, 5°16'8" E), North-East of France, within an experimental beech forest site located in a rural area far away from urban pollution. The site of Montiers was installed purposely in the frame of the long term monitoring and testing system named Ope (Observatoire Pérenne de l'Environnement) belonging to the French experimental and environmental research network and managed by Andra (French National Radioactive Waste Management Agency). The climate of the area is humid temperate, with an annual precipitation value of 1100 mm and mean annual temperature of 12.6 °C ([www.andra.fr/ope](http://www.andra.fr/ope)).

The rainwater samples were collected every four weeks during a period of 2 years (from March 2012 to February 2014) from a 45 m high tower with four passive collectors located at the top of the tower. Those collectors consist of a 0.22 m<sup>2</sup> cylindrical funnel with a raised edge connected to a high density polyethylene collecting container of 20 L (Lequy et al., 2013). There is a nylon sieve of 0.2 mm between the funnel and the container to avoid insects and coarse debris. Every four weeks, an average aliquot is collected from the several containers and transferred into a 2 L HDPE bottle for Cl and  $^{36}\text{Cl}$  analyses. A 20 mL aliquot is created for major elements analysis.

### 2.2. Chemical preparation and measurement

The major elements concentrations were determined at the BEF laboratory of INRA (National institute of Agronomic research) (Nancy, France) after filtration at 0.45 μm [ $\text{SO}_4^{2-}$ ] was measured using a Dionex ICS-2100 ion chromatography (IC) system, while [ $\text{Na}^+$ ], [ $\text{Mg}^{2+}$ ] and [ $\text{Ca}^{2+}$ ] were measured using an inductively-coupled plasma atomic emission spectrometry (ICP-AES). The associated uncertainties are estimated between 5% and 20% depending on both the measured element and its concentration range (<http://helium.crgp.cnrs-nancy.fr/SARM/pages/solutions.html>).

The 2 L samples were divided into two homogenous 1 L replicated samples, weighed, acidified with  $\text{HNO}_3$  and stored at 4 °C until Cl and  $^{36}\text{Cl}$  analysis were undertaken at the CEREGE laboratory. If some debris (algae or small insects) were visible in the samples, they were centrifuged several times to separate the solid debris from the liquid sample.

Chlorine and chlorine-36 concentrations were simultaneously determined by Isotope Dilution-Accelerator Mass Spectrometry (ID-AMS) from the measurements of  $^{36}\text{Cl}/^{35}\text{Cl}$  and  $^{35}\text{Cl}/^{37}\text{Cl}$  ratios at the AMS national facility ASTER (Accélérateur pour les Sciences de la Terre, Environnement, Risques) located at CEREGE. Samples were processed in batches comprising 10–15 samples. To minimize contaminations, all the vials were previously washed with ultra-pure water and ultra-pure reagents were used. The spike added to the solution is a  $\text{Na}^{35}\text{Cl}$  enriched spike from ChemLab ( $^{35}\text{Cl} = 99.89\%$ ). The main objective of the chemical preparation is to separate chlorine while minimizing the isobaric interferences of  $^{36}\text{S}$  on  $^{36}\text{Cl}$ , which can disrupt the AMS measurements. Chloride

was extracted as AgCl by the addition of  $\text{AgNO}_3$  under acidic condition. AgCl was then redissolved with  $\text{NH}_3$  and a saturated solution of  $\text{Ba}(\text{NO}_3)_2$  was added to precipitate sulphur as  $\text{BaSO}_4$ . This precipitate was removed from the solution by centrifugation and filtration at 0.45 μm, minimizing the quantity of S in the target sample. The AgCl is then reprecipitated under acidic condition and washed three times with ultra-pure water. It is finally dried at 80 °C during at least two nights and pressed in a 6.6 mm diameter Nitarget holder for chlorine and chlorine-36 concentration measurements by Isotope Dilution-Accelerator Mass Spectrometry (ID-AMS).

Spiked blanks processed with each 10–15 samples batch have a mean  $^{36}\text{Cl}/^{35}\text{Cl}$  ratio of  $(4 \pm 1) \times 10^{-15}$  at  $\text{at}^{-1}$ . The applicability of ID-AMS technique for water samples with low chloride concentrations (between 0.1 and 10 mg L<sup>-1</sup>) was specifically investigated by Bouchez et al. (2015). The determination of both chlorine and chlorine-36 concentrations and the calculation of their associated uncertainties are exhaustively presented in Bouchez et al. (2015) in which it is demonstrated that the reproducibility on the measured  $^{35}\text{Cl}/^{37}\text{Cl}$  and  $^{36}\text{Cl}/^{35}\text{Cl}$  is respectively 3% and 5%, yielding uncertainties on Cl and  $^{36}\text{Cl}$  concentrations of  $\pm 5\%$  and  $\pm 7\%$  respectively. In this study, the uncertainties associated to [ $^{36}\text{Cl}$ ] range from 7 to 18%, high uncertainties being related to low counting statistics of the measured  $^{36}\text{Cl}/^{35}\text{Cl}$ . Half of the samples were measured twice and values of [Cl],  $^{36}\text{Cl}/\text{Cl}$  and [ $^{36}\text{Cl}$ ] of each replicated sample are given in Table A3.

## 3. Results

### 3.1. Major element

Major element concentrations of rainwater samples collected monthly from 2012 to 2014 are shown in Table 1 and presented in Fig. 1. Over the investigated time period, [ $\text{Cl}^-$ ] ranges from 0.3 to 1.9 mg L<sup>-1</sup>, [ $\text{Na}^+$ ] from 0.22 to 1.21 mg L<sup>-1</sup>, [ $\text{Mg}^{2+}$ ] from 0.04 to 0.21 mg L<sup>-1</sup>, [ $\text{Ca}^{2+}$ ] from 0.2 to 3.8 mg L<sup>-1</sup> and [ $\text{SO}_4^{2-}$ ] ranges from 0.4 to 2.7 mg L<sup>-1</sup>.

The four elements Cl, Na, Ca and Mg exhibit high variations of their concentrations along the year with abrupt increases. An abrupt increase of the concentrations is simultaneously observed between August and September 2012 for Cl, Na, Ca and Mg. An increase in the Cl and Na concentrations is also observed in March 2012, between December 2012 and February 2013, and between November 2013 and February 2014. Although only 56% of the measured magnesium concentrations are above the detection limit with associated uncertainties higher than 20%, its temporal variability appears similar to that of Na and Cl, with an additional slight increase between July and August 2013. Regarding Ca, its concentration generally lies between 0.16 mg L<sup>-1</sup> and 0.85 mg L<sup>-1</sup>. In addition to the abrupt increase also seen in the record of the other elements, the Ca concentrations slightly increase in April 2012 and, as for Mg, between July and August 2013.

Sulfate has a behaviour different from the four other chemical elements previously discussed, with no apparent abrupt increase but sporadic small increases in March and April 2012, June 2012, July\* 2013, and December 2013.

In summary, Na, Cl and Mg exhibit similar trends, their concentrations increasing in August 2012 and in fall-winter, whereas there is no obvious relationship between any of those three elements and Ca and  $\text{SO}_4$ . Moreover, the most prominent peak in August 2012 is observed in all records but  $\text{SO}_4$ , suggesting that this peak does not have an anthropogenic origin.

When Na concentrations are plotted against Cl concentrations (Fig. 2), a linear correlation is observed. Moreover most  $\text{Na}^+/\text{Cl}^-$  ratios, including those associated with abrupt increases in Cl

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