



Sources and behavior of perchlorate ions (ClO_4^-) in chalk aquifer of Champagne-Ardenne, France: preliminary results

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Abstract. Perchlorate (ClO_4^-) is an environmental contaminant of growing concern due to its potential human health effects and widespread occurrence in surface water and groundwater. Analyses carried out in France have highlighted the presence of ClO_4^- in drinking water of Champagne-Ardenne (NW of France), with two potential sources suspected: a military source related to the First World War and an agricultural source related to the past use of Chilean nitrates. To determine the sources of ClO_4^- in groundwater, major and trace elements, ^2H and ^{18}O , ClO_3^- and ClO_4^- ions and a list of 39 explosives were analyzed from 35 surface water and groundwater sampling points in the east of the city of Reims. ClO_4^- ions were found in almost all sampling points (32 out of 35) with a max value of $33 \mu\text{g L}^{-1}$. ClO_4^- concentrations were highest in groundwater ranging from 0.7 to $33 \mu\text{g L}^{-1}$ (average value of about $6.2 \mu\text{g L}^{-1}$) against from < 0.5 to $10.2 \mu\text{g L}^{-1}$ in surface water (average value of about $2.7 \mu\text{g L}^{-1}$). Most of the water samples showing high ClO_4^- levels ($> 4 \mu\text{g L}^{-1}$) were collected near a military camp, where huge quantities of ammunitions have been used, stored and destroyed during and after the First World War.

1 Introduction

Perchlorate (ClO_4^-) is an inorganic anion and a powerful oxidizer with high solubility and mobility in water. Relatively stable under ambient conditions, perchlorate may persist for many years, possibly decades, under typical surface water and groundwater conditions (Sturchio et al., 2014). Perchlorate salts are widely used as oxidizer in solid rockets fuel and as component of fireworks, pyrotechnics, flares and explosives (Urbansky, 1998). In addition, natural sources such as sodium nitrate deposits in Chile (Urbansky et al., 2001) and formation in the atmosphere have also been reported (Dasgupta et al., 2005). Perchlorate is an environmental contaminant of concern in water because of its potential ability to inhibit iodide uptake and to impact neurodevelopment, especially for foetuses and infants (Leung et al., 2010). Since

1997, perchlorate has been listed as a contaminant in drinking water monitoring programs in the USA (USEPA, 1998). The current health advisory level for ClO_4^- is set at $15 \mu\text{g L}^{-1}$ based on the reference dose recommended by the US EPA. However, in many countries, drinking water standard for ClO_4^- is yet to be defined. Many studies have underlined perchlorate contamination in water from numerous countries such as the USA, Canada (Backus et al., 2005), China (Wu et al., 2010), Japan (Kosaka et al., 2007) and India (Kannan et al., 2009).

In France, the interest of research on ClO_4^- has increased since 2011 because of the discovery of ClO_4^- contamination in several drinking water resources in South-Western France, in the Paris Basin and in North-Eastern France (Lopez et al., 2015). In the Champagne-Ardenne region (NE of France), the measurement campaigns carried out by the

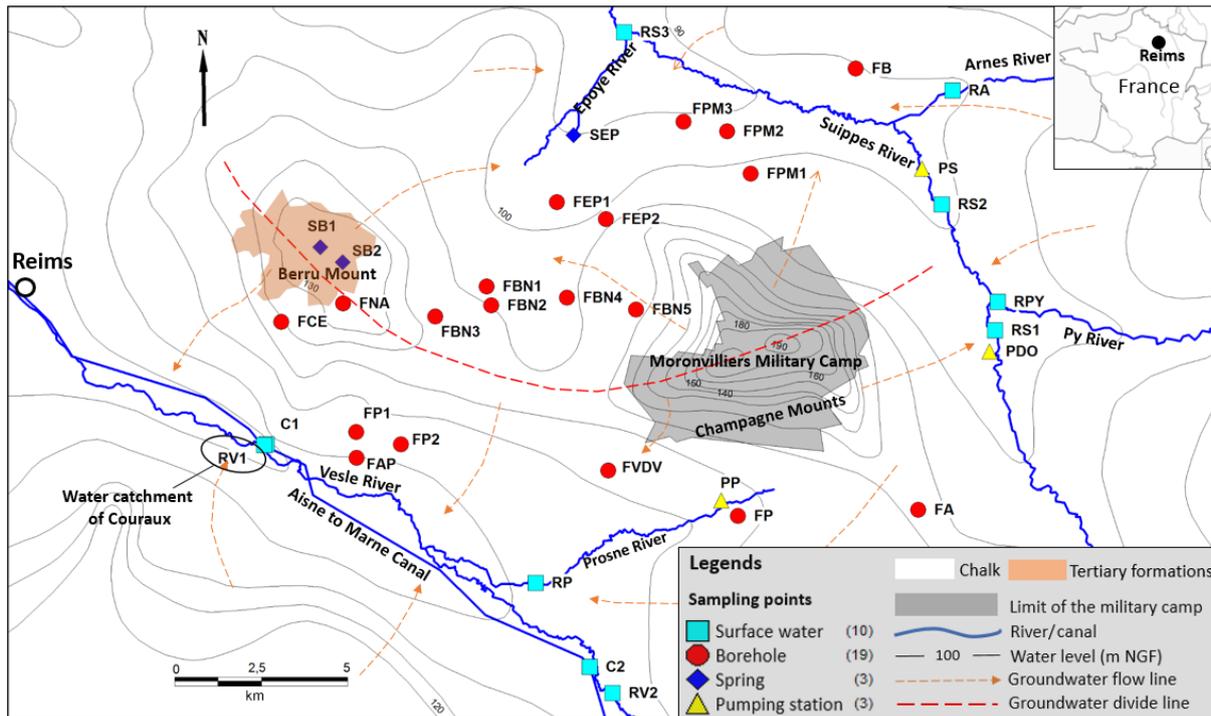


Figure 1. Location of the study area, main rivers and sampling points (water level data from Rouxel-David et al., 2002).

Regional Health Agency (ARS) in 2014 have showed high levels of ClO_4^- ions ($> 15 \mu\text{gL}^{-1}$) in raw water resources intended for human consumption. Two potential sources of ClO_4^- in groundwater are suspected: military and agricultural. Indeed, the Champagne-Ardenne region was highly marked by the events of the First World War that may have emitted large quantities of perchlorates and other explosives in the environment, and France has imported, between 1875 and 1920, large quantities of natural nitrates as fertilizers from Chile, which are particularly rich in ClO_4^- ions. The study site in an intensive agricultural area, thereby it is concerned with the use of these Chilean nitrates.

The objectives of this study are (1) to identify the sources of ClO_4^- and other explosives in groundwater and to establish links between their occurrence and the type of human activities (military and/or agricultural), (2) to understand the transfer mechanisms of ClO_4^- in the Champagne chalk aquifer, with studies on flow and mineralization processes in the aquifer. A study area has been selected in the Champagne-Ardenne region for a continuous monitoring of water chemistry to observe a temporal and spatial evolution of the concentrations of the molecules concerned. In this paper, we will focus on the results of the 2 screening measurement campaigns carried out in 2017, with the purpose to obtain a water chemical map of the study area and to proceed a further monthly monitoring over the next 2 years.

2 Materials and methods

2.1 Study area

2.1.1 Location

The study area is located in the east of Reims (NE of France; Fig. 1) and covers approximately 600 km^2 between the Suipe River (as the northern and western boundary) and the Vesle River (as the southern boundary), where some water catchments intended for drinking water supply are significantly impacted by the presence of ClO_4^- ions.

It corresponds to an agricultural zone (traditional crops of wheat and beet, for which Chilean nitrates were largely used to increase the production until the 1920s) located on the former battlefield of the First World War (military camp of Moronvilliers and the surrounding trench areas). In addition to some forests covered at the Berru Mount and the Champagne Mounts, the whole zone is used as agricultural lands.

2.1.2 Hydrogeological context

The aquifer of the study area is the unconfined Champagne chalk aquifer, which is a crucial water resource of the region. In some areas, the chalk is partially covered with Tertiary (the Berru Mount; Fig. 1) or Quaternary formations (the valleys of the Vesle River, the Suipe River and their tributaries).

The total porosity of the Chalk is about 40 %, with only 1 to 5 % related to the effective porosity (Rouxel-David et al., 2002; Vachier et al., 1987). The Champagne Mounts con-

stitute the major reliefs where the transmissivity ranges from 10^{-6} to $10^{-5} \text{ m}^2 \text{ s}^{-1}$. In the valleys, these values are much higher, ranging from 10^{-2} to $0.3 \text{ m}^2 \text{ s}^{-1}$. The Darcy velocity of the water flow in the saturated zone varies between 0.16 m yr^{-1} at the reliefs and 315 m yr^{-1} in valleys (Rouxel-David et al., 2002).

The study area is divided into two parts by the groundwater divide line across the summit of Berru Mount and the Champagne Mounts, which delimits the Vesle River watershed in the south and the Suippe River watershed in the north. According to water levels (Rouxel-David et al., 2002), the chalk aquifer of the study area is generally drained by rivers except the water catchment of Couraux (Fig. 1) which supplies the drinking water for the Reims area. Due to the drawdown of groundwater level caused by pumping, the catchment is partially fed by river water, especially during low water period. The precipitation constitutes the only recharge of the Champagne chalk aquifer, mainly between September and April.

2.2 Sampling

Two chemical screening campaigns have been carried out in June and September 2017. In June, 25 groundwater (22 boreholes and 3 springs) were collected. All the selected sampling points are situated on areas both agricultural and concerned by military activities. Ten points of surface waters, distributed in the Aisne to Marne Canal, Vesle River, Suippes River and their tributaries (Table 1 and Fig. 1) were also sampled to take into account the groundwater/surface water exchanges in the diffusion of the molecules. In September, a total of 25 water samples were collected (Table 1). The points with non-detectable or very low ClO_4^- levels were not sampled and a new one has been added in the Suippes River. The physicochemical parameters (pH, conductivity, temperature, alkalinity, dissolved oxygen and redox potential) were measured at the sampling points.

2.3 Instrumental analysis

The quantification of ClO_4^- was performed using a two-dimension ion chromatography on an ion chromatography (DIONEX ICS 2000) at BRGM (Orléans, France), with a detection limit of $0.5 \mu\text{g L}^{-1}$. Quantitative analysis of cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) and anions (NO_3^- , SO_4^{2-} , Cl^- , F^-) was done by ICP Optical Emission Spectrometry (ICAP 6300, THERMO) and Ion Chromatography system (DIONEX ICS 2000) respectively at GEGENAA (Reims, France). The analysis of 39 explosives (e.g. TNT, trinitrophenol, trinitronaphthalene) was performed by the company Envilytix GmbH (Wiesbaden, Germany).

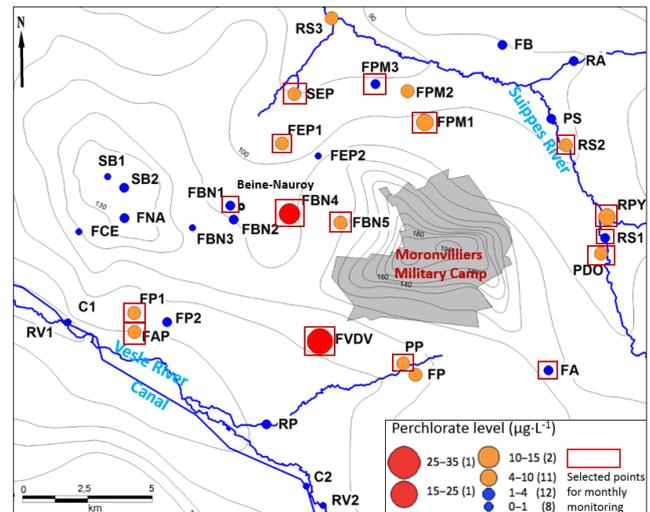


Figure 2. Perchlorate levels in waters in June 2017 and selected sampling points for the monthly monitoring.

3 Results and discussion

3.1 Major ions

Calcium and bicarbonate are the predominant ions in water, which is consistent for groundwater in Chalk aquifer. However, spatially heterogeneities are present not only on Ca^{2+} and HCO_3^- but also on Na^+ , Cl^- , SO_4^{2-} and NO_3^- contents. This may be due to human activities and/or mineralization conditions of the aquifer, assumptions to be confirmed.

3.2 Perchlorate and explosives

The two screening campaigns show almost similar results for ClO_4^- concentrations (Table 1). Perchlorate ions were found in almost all the samples, and the mean ClO_4^- concentrations in groundwater and surface water samples were 6.2 and $2.7 \mu\text{g L}^{-1}$, respectively. 15 among the 35 water points (43%) present ClO_4^- levels higher than $4 \mu\text{g L}^{-1}$ (concentration beyond which infants should not consume water according to French health authorities advices) and 1 sampling point exhibits ClO_4^- concentrations higher than $15 \mu\text{g L}^{-1}$ (US EPA reference dose). Twenty sampling points (57%) show ClO_4^- levels lower than $4 \mu\text{g L}^{-1}$.

Most of the sampling points showing ClO_4^- concentrations above $4 \mu\text{g L}^{-1}$ are found around the military camp of Moronvilliers, where large quantities of ammunition were used, stored and destroyed during and after the Great War. The maximum ClO_4^- level is $33 \mu\text{g L}^{-1}$ (FVDV, south of military camp of Moronvilliers; Fig. 2). According to historical data, this sampling point is located at a former military airfield used during the Great War. In addition, the military camp of Moronvilliers is located upstream of this point, representing a potential source of ClO_4^- . Samples from FBN4, FVDV and

Table 1. Information on sampling locations and perchlorate concentrations. The values in bold are the maximum concentrations of perchlorate in June and September. The symbol “X” represents the points selected for monthly monitoring.

Point ID	Sample type	Latitude (° N)	Longitude (° E)	Altitude (m NGF)	Depth (m)	ClO ₄ ⁻ _June (µg L ⁻¹)	ClO ₄ ⁻ _Sept (µg L ⁻¹)	Selected for monthly monitoring
FCE	Exploited borehole	49.24205	4.12656	175	85	0.5	N.S.	
FNA	Exploited borehole	49.24662	4.15105	165	47	1.3	N.S.	
FBN3	Borehole	49.24280	4.18759	124.9	56	0.9	N.S.	
FBN1	Borehole	49.25048	4.20809	134	47.6	3.9	< 0.5	X
FBN2	Borehole	49.24554	4.20989	122	32	2.9	< 0.5	
FPM1	Exploited borehole	49.27875	4.31364	107	24	10.5	9.6	X
FBN4	Borehole	49.24725	4.23997	111	28	17.5	17	X
FBN5	Borehole	49.24383	4.26732	140	46.75	7.8	2.7	X
FEP1	Borehole	49.27210	4.23658	107	25	9.2	10.2	X
FEP2	Borehole	49.26752	4.25589	107	23	0.7	3.1	
FPM3	Borehole	49.29255	4.28730	103	21	2.6	2.4	X
FPM2	Borehole	49.28989	4.30454	121	34.3	5.5	5.8	
FP1	Borehole	49.21308	4.15558	95	18.9	6	3.8	X
FAP	Borehole	49.20634	4.15561	89.5	15	5.5	2.8	X
FP2	Borehole	49.20966	4.17316	97	20.75	1.3	1.8	
PP	Exploited borehole	49.19371	4.29981	110	80	6.6	6.3	X
FVDV	Borehole	49.20202	4.25525	107	21.65	33	37.7	X
FP	Borehole	49.18969	4.30624	116	23.6	4.8	6.6	
FB	Borehole	49.30563	4.35599	108	22.5	2.2	N.S.	
PS	Exploited borehole	49.27923	4.38166	98.5	16	2.7	3.3	
PDO	Exploited borehole	49.23141	4.40722	111	25	9	8.7	X
FA	Borehole	49.19046	4.37777	123	33.9	2	2.4	X
SB2	Spring	49.25732	4.15116	216		2.1	N.S.	
SB1	Spring	49.26133	4.14238	225		< 0.5	N.S.	
SEP	Spring	49.28945	4.24359	92		4.7	1.8	X
RV1	River	49.21076	4.11505	84		0.8	N.S.	
C1	Canal	49.20874	4.12446	85		< 0.5	N.S.	
RP	River	49.17311	4.22585	93		3.6	N.S.	
RV2	River	49.14414	4.25526	99		0.6	N.S.	
C2	Canal	49.15137	4.24642	96		< 0.5	N.S.	
RS1	River	49.23697	4.40956	107		1.8	4.3	X
RPY	River	49.24423	4.41038	110		10.2	12.3	X
RS2	River	49.27000	4.38921	110		4.5	6.7	X
RA	River	49.30098	4.40443	105		1.1	< 0.5	
RS3	River	49.31591	4.26468	110		4.2	4.6	
RS4	River	49.31420	4.27165	92		N.S.	5	

N.S.: Non sampled points.

FP show also chlorate (ClO₃⁻) levels slightly higher than the other samples.

The sampling points showing ClO₄⁻ levels lower than 4 µg L⁻¹ are mainly located on the Berru Mount, in the Vesle River and the Aisne to Marne Canal. ClO₄⁻ concentrations in the canal are less than 0.5 µg L⁻¹. Since water in the canal is not (or little) related to the chalk aquifer, it verified the fact that ClO₄⁻ in river waters come from the exchanges with groundwater. ClO₄⁻ concentrations in rivers are partly diluted by upstream water and drainage of low-level parts of the aquifer so that generally lower levels of ClO₄⁻ than those in groundwater are measured.

However, some surface waters show significantly higher levels in ClO₄⁻ (> 10 µg L⁻¹), such as the RPY (the Py River) and RS2 (downstream of the Py in the Suipe River; Fig. 2 and Table 1). ClO₄⁻ sources exist thus in the Py catchment area. As the point RS1 (upstream of the Py, in the Suippes river) has a low level of ClO₄⁻ (< 4 µg L⁻¹), the high level on RS2 is most likely from the contribution of the Py river. Indeed, the Py River is originated from downstream of the military camp of Suippes, potentially representing a source of ClO₄⁻.

Note that explosives have not been detected in surface and groundwater samples, which may be due to their low persistence in soil and water.

Sixteen sampling points were selected based on the results of the 2 sampling campaigns for a monthly monitoring over the next 2 years (Fig. 2). Sampling points showing high ClO_4^- concentrations were selected. Although the ClO_4^- levels on FBN1 and FA were low, these two sampling points will also be collected to ensure a consistent distribution of sampling points in the west and the southeast of the study area.

4 Conclusion and perspective

The preliminary results of the 2 sampling campaigns allowed us to obtain the chemical facies of groundwater, the levels and distribution of perchlorate ions in the study area. Most of sampling points showing high levels of ClO_4^- are located around the military camp of Moronvilliers, representing a potential source of perchlorate. That must be confirmed with further studies.

Over the next 2 years, measurements will be performed on 16 sampling points in the study area to determine the contents of major and trace elements, ClO_3^- and ClO_4^- ions in waters and stable isotopes of water molecule (^2H and ^{18}O). In parallel, the measurement of the isotopic signature of oxygen and chlorine in ClO_4^- will make it possible to precise the sources of perchlorates (agriculture and/or military). A better understanding of the chalk aquifer properties and flow mechanisms will be reached by the measurement of the residence time of groundwater and the monthly monitoring of the chemical composition of waters. Finally, this multi-tracer approach will allow us to predict the spatial and temporal evolution of ClO_4^- concentrations, and thus offer innovative information to make appropriate recommendations in terms of water management.

Data availability. The data supporting the findings of this study came from the site study results and are available within the article.

Competing interests. The authors declare that they have no conflict of interest.

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