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FELLOWSHIP FINAL REPORT

Groundwater contamination in France: A legacy of World War I

Neil C. Sturchio[1,3], Daniel Hube[2], Patrick Ollivier[2]

[1]University of Delaware, 255 Academy Street, Newark, DE 19716, USA
[2]Bureau de Recherches Géologiques et Minières, 3 Avenue Claude Guillemin, BP 36009, 45060 Orléans Cedex 2, France
3 LE STUDIUM Institute for Advanced Studies, 45000 Orléans, France

REPORT INFO

Fellow: **Prof. Neil C. Sturchio**
From University of Delaware, USA
Host laboratory in region Centre-Val de Loire: BRGM Orleans
Host scientist: **Dr. Patrick Ollivier**
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ABSTRACT

The present study was conducted to elucidate the connections of modern groundwater pollution to specific munitions materials used and destroyed during and after World War I (WWI). Large quantities of unexploded munitions are still present in the tunnels and soils of former battlefields. We performed analyses of the isotopic compositions of nitroaromatics, nitrate, and perchlorate in samples of munition and contaminated groundwater collected at three sites along the WWI battlefront in northern France. The isotopic data from these samples indicates a direct connection between the groundwater contamination and the WWI munitions. Potential adverse effects on public health from munitions compounds in groundwater indicate an urgent need for further evaluation of the continuing presence of legacy WWI munitions and their contribution to chronic groundwater pollution in the region.

1- Introduction

The battlefields of World War I (WWI) in France preserve a major legacy of environmental contamination from the extensive use of munitions (Hube, 2017). The chemical contents of WWI munitions included nitro-aromatic compounds, nitrate and nitrite high explosives, chlorate, and perchlorate (ClO_4). The widespread occurrence of ClO_4 in groundwater of northern France, especially in the region affected by military activities during WWI, was first revealed by a nationwide survey of groundwater quality conducted by ANSES (French Agency for Food, Environmental, and Occupational Health and Safety) in 2011. A map showing the distribution of ClO_4 concentrations in untreated drinking water supplies of France is shown in Figure 1 (ANSES, 2013). Perchlorate is a persistent contaminant that is soluble in water and highly mobile. It presents a substantial health risk to the human population because of its effect on thyroid hormone production and the development of the nervous system. This study applied measurements of the isotopic composition of ClO_4 to better understand the source of this compound in the drinking water supplies of northern France. Likely sources include residues of WWI French munitions that contain ClO_4 synthesized electrochemically at a factory in Chedd, France (Hube, 2017), and imported Chilean Nitrate that contains natural ClO_4 and was widely used as an agricultural fertilizer in northern France (from about 1880-1950). These types of ClO_4 have distinct isotopic compositions (Sturchio et al., 2011).

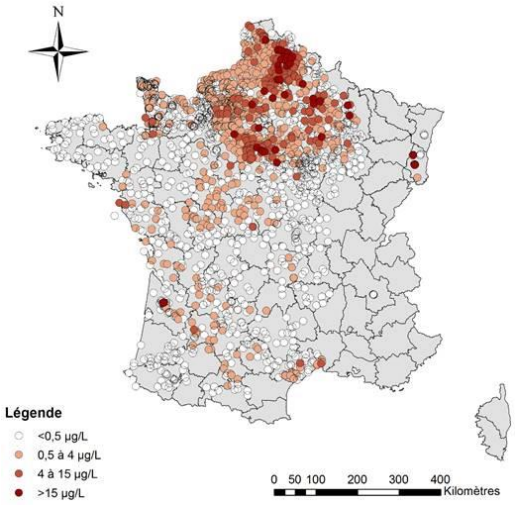

Fig. 1. ClO_4 in French water (ANSES, 2013).

Three areas along the WWI battlefront were selected for detailed study based on maps of ClO_4 concentrations in drinking water, historical archives, and the presence of warfare tunnels and munitions destruction sites. The selected areas each had multiple study locations: Amiens area (British/German tunnels, battlefields, and munitions destruction site); Reims and Argonne area (French/German tunnels and battlefields) and Vosges area (French/German tunnels and battlefields). Samples of unexploded ordnance (UXO; including artillery shells, hand grenades, explosive charges, and bullets) were collected for isotopic analysis of ClO_4. Large-volume samples of groundwater and surface water were also collected for this purpose.

2- Experimental details

Perchlorate was extracted from large-volume groundwater samples for isotopic analysis using a perchlorate-selective bifunctional ion-exchange resin according to methods described by Hatzinger et al. (2011) and perchlorate isotopic composition was determined by methods described by Böhlke et al. (2017). Perchlorate from unexploded ordnance was obtained by dissolution of explosive material in water followed by separation of perchlorate by methods scaled down from those used for groundwater perchlorate isotopic analysis. The amount of perchlorate required for replicate isotopic analysis by these methods is about 1 milligram. The extracted perchlorate was purified and precipitated as a $CsClO_4$ salt. The salt was sealed in an evacuated borosilicate tube and decomposed at ~630 ^oC to produce CsCl salt and gaseous O_2. The O_2 gas was then transferred to the dual-inlet of an isotope-ratio mass spectrometer for isotopic analysis of oxygen. The CsCl salt was converted to CH_3Cl gas by reaction with CH_3I at 300 ^oC, then purified gas chromatigraphically in a helium carrier gas and transferred to the mass spectrometer for isotopic analysis of chlorine. Isotopic data for perchlorate were normalized to the values of USGS-37 and USGS-38 $KClO_4$ isotope reference materials (Böhlke et al., 2017) which were prepared and analyzed along with the samples.

3- Results and discussion

Our sampling of groundwater and munitions in selected locations revealed extensive pollution of groundwater by nitroaromatic compounds and their degradation products, perchlorate, nitrate (NO_3), and nitrite. The specific nitroaromatics found at highest concentrations in groundwater include those present in the munitions. Isotopic data for carbon and nitrogen in nitroaromatics extracted from munitions shows that the chemical degradation products of TNT (i.e., 2,4-DNT and 2,6-DNT) are enriched in ^{15}N.

Isotopic data for perchlorate show that most ClO_4 in sampled groundwater is from a synthetic source, consistent with its derivation from WWI munitions. However, isotopic evidence for ClO_4 derived from Chilean Nitrate was found at two sites in agricultural areas where this material was apparently used as fertilizer.

Nitrate was a common component of WWI explosives. Sources included Chilean Nitrate that was used for the production of nitroaromatics as well as the ammonium nitrate component of explosives. Isotopic data for NO_3 indicate that most NO_3 sampled in groundwater shows a typical soil NO_3 isotope composition, In contrast, nitrate from recovered UXO shows ^{17}O enrichment indicating a Chilean nitrate source. The nitrate in UXO samples also appears to have undergone substantial denitrification.

4- Conclusion

Widespread environmental impact of WW1-related pollutants is evident in elevated concentrations of nitroaromatics and perchlorate that can be related to WW1 munitions use during warfare, some of which remain stored in tunnels and dispersed at post-war munitions destruction sites. The magnitude of the pollution legacy of World War 1 has yet to be fully realized after more than 100 years. Much additional research is needed to fully assess the magnitude and extent of this legacy,

and to develop an effective strategy to mitigate its environmental impact.

5- Perspectives of future collaborations with the host laboratory

Further collaborations are in progress with the host laboratory at BRGM, and additional work is planned to extend this investigation to additional areas with new measurements. Potential adverse effects on public health from munitions compounds in groundwater indicate an urgent need for further evaluation of the continuing presence of legacy WWI munitions and their contribution to chronic groundwater pollution in the region.

6- Articles published in the framework of the fellowship

The results of this project will be documented in an article that is in preparation for publication, titled *"Environmental Time Bomb: Tracing the Explosive Legacy of World War I in Northern France"*, by Daniel Hubé and others.

7- Acknowledgements

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8- References

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