

# Tracking perchlorate contamination sources in France: an historical approach

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## TRACKING PERCHLORATE CONTAMINATION SOURCES IN FRANCE: AN HISTORICAL APPROACH

Perchlorate ( $\text{ClO}_4^-$ ) is a stable energetic oxyanion of chlorine forming high water-soluble salts. Chronic exposure to perchlorate disturbs thyroidic functions. During 2011- 2015,  $\text{ClO}_4^-$  has been detected in drinking water with concentrations above french recommended levels, in the northeast of France, along frontlines of World War I (WWI), and outside, in agricultural environment. For time, there are no scientific large scale researchs focusing on the real perchlorate sources in France and their relationships with the observed contamination. Moreover, the extent, the time and space fates of the contamination of groundwater have not been studied yet.

This desktop study aims to highlight the origins and possible  $\text{ClO}_4^-$  sources in the specific historical frame of France. Detailed archivist researchs have been conducted in France, in London and in the USA. Furthermore, high explosives (HE) loading shells of Great War, discovered near Verdun have been sampled by the BRGM and analyzed for perchlorate, chlorate ( $\text{ClO}_3^-$ ), nitrate, ammonium and NitroAromatic Compounds (NAC).

Two origins of perchlorate have been identified: natural  $\text{ClO}_4^-$  as impurity of Chilean nitrates and (electro)synthetic perchlorate. Chilean nitrates had been massively imported in France before the WWII as fertilizers for intensive agriculture of beet and wheat and to supply the industry in nitrogen to produce nitric acid, synthetic fertilizers and NAC.  $\text{ClO}_4^-$  has thus polluted "*conversion salpeter*" ( $\text{KNO}_3$ ), entering the composition of traditional black powder, ammonium nitrate and TNT of artillery shells, increasing dangerously the sensitivity to detonation when firing the projectiles. The presence of  $\text{ClO}_4^-$  impurities had been measured by the BRGM in sampled NAC HE as well in black powder by German chemists at the end of the XIX<sup>th</sup> century. Premature blastings of shells during firing due to  $\text{ClO}_4^-$  impurities were described by the gunners since 1880. During Trench War (1915-1917), enormous needs of HE for trench artillery and grenades motivated the development and large scale production of 4 types of synthetic (per)chlorated HE compositions, based on mixes of  $\text{ClO}_3^-$  or  $\text{ClO}_4^-$  energetic oxidizer with paraffinic fuels colored by methylene blue. 130 900 tons of (per)chlorate HE have been produced in France during WWI in France. The paraffin coating the salts may drastically hindered the dissolution rates of the explosives. The perchlorate could be introduced in the soil by old soil fertilizing, sparsed low-order detonation of projectiles, corrosion of the thin steel bodies of unexploded ordnances, or by massive ammunition surpluses breaking-down operations during the interwar period.

Further researches are needed to define the kinetic dissolution of  $\text{ClO}_4^-$  in HE, to develop analytical and isotopic tools to fingerprint the origin of perchlorate. Specific methodologies are required too to define the sources, agricultural and/or military, of perchlorate in the specific case of France. Projects aiming these objectives are currently starting in the Vosges Mountain, in the region of Verdun, and in the Champagne area.