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Human health risks related to the consumption of foodstuffs of plant and animal origin produced on a site polluted by chemical munitions of the First World War

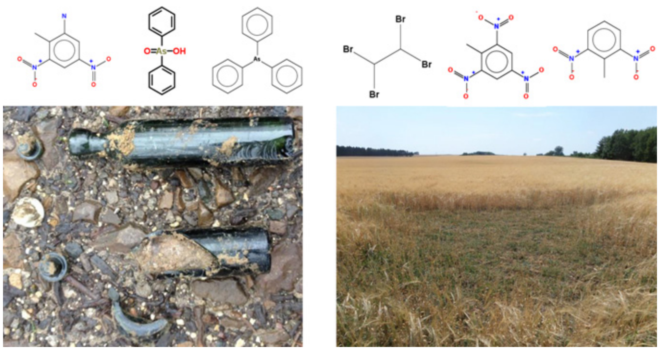
Sébastien Gorecki [a], Fabrice Nesslany [b], Daniel Hubé [c], Jean-Ulrich Mullot [d], Paule Vasseur [e], Eric Marchioni [f], Valérie Camel [g], Laurent Noël [h], Bruno Le Bizec [i], Thierry Guérin [a], Cyril Feidt [j], Xavier Archer [k], Aurélie Mahe [a], Gilles Rivière [a,*]

[a] *French Agency for Food, Environmental and Occupational Health & Safety, 14 rue Pierre & Marie Curie, F-94700 Maisons-Alfort, France*
[b] *Laboratoire de Toxicologie Génétique, Institut Pasteur de Lille, Lille, France*
[c] *BRGM, French Geological Survey, 6 avenue Claude Guillemin, 45000, Orléans, France*
[d] *Navy Expert Lab of Toulon, BCRM Toulon, BN/LASEM, 83800 Toulon, Cedex 9, France*
[e] *CNRS UMR 7360, University of Lorraine, Metz, France*
[f] *Université de Strasbourg, CNRS, UMR 7178, F67037 Strasbourg, France*
[g] *UMR Ingénierie Procédés Aliments, AgroParisTech, Inra, Université Paris-Saclay, 91300 Massy, France*
[h] *The French Directorate General for Food, Ministry of Agriculture, Agro-16 Food and Forestry, Paris, France*
[i] *ONIRIS - LABERCA, Atlanpole – La Chantrerie, BP 40706, Nantes F-44307, France*
[j] *Université de Lorraine, INRA, 2 avenue de la forêt de Haye, TSA 40602, 54518 Vandoeuvre Cedex, France*
[k] *Central Laboratory of Police Prefecture (LCPP), 39 bis rue de Dantzig, 75015, Paris, France*

HIGHLIGHTS

- Persistent contamination of WW I explosives and chemical munitions transfer to agricultural production.
- Different methodologies for health risk assessment have been proposed for poorly studies contaminants.
- Despite uncertainties, conclusions for consumption of foods were drawn.

GRAPHICAL ABSTRACT



Abbreviations: 2-ADNT, 2-amino-4,6-dinitroluene; 4-ADNT, 4-amino-2,6-dinitrotoluene; Anses, French Agency for food, environmental and occupational health & safety; BMDL, Benchmark dose lower bound; BRGM, French Bureau of Geological and Mining Research; DNB, Dinitrobenzene; DPAA, Diphenylarsinic acid; 2,4-DNT, 2,4-dinitrotoluene; 2,6-DNT, 2,6-dinitrotoluene; HGBV, Health-based guidance value; HRA, Health Risk Assessment; HQ, Hazard Quotient; IARC, International Agency for Research on Cancer; IECR, Individual excess cancer risk; ICP-MS, Inductively coupled plasma mass spectrometry; INCA2, Second French consumption study; LB, Lower bound; LOAEL, Lowest observed adverse effect level; LoD, Limit of detection; LoQ, Limit of quantification; MOE, Margin of exposure; NOAEL, No observed adverse effect level; OECD, Organization for Economic Co-operation and Development; OEHHA, Office of Environmental Health Hazard Assessment; POD, toxicological point of departure; TBE, Tetrabromoethane; TDS2, Second French total diet study; TEs, Trace Elements; TNT, 2,4,6-trinitrotoluene; TPA, Triphenylarsine; TRV, Toxicological reference value; TTC, Threshold of Toxicity Concern; UB, Upper bound; US EPA, United States Environmental Protection Agency; QSAR, Quantitative Structure-Activity Relationship; WHO, World Health Organization; WWI, First World War.

* Corresponding author.

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ABSTRACT

Shells fired during World War I exhibited different explosive compounds and some of these weapons also contained a wide variety of chemical warfare agents. At the end of the war, for safety purposes, the large quantity of weapons remaining on the former front needed to be dismantled and destroyed. A large amount of the remaining shells was destroyed in specific sites which led to the contamination of the surroundings in Belgium and France.
In the 1920s, 1.5 million chemical shells and 30,000 explosive shells were destroyed in a place close to the city of Verdun, in the East of France. In this paper, the risk for human health related to the consumption of foodstuffs produced on this site was assessed. To this end, food products of plant and animal origin were sampled in 2015–2016 and contaminant analyses were conducted. Human exposure was assessed using a specifically built methodology. The contaminants considered in this study were trace elements (TEs - primarily Zn, As, Pb and Cd), nitroaromatic explosives (trinitrotoluene, 2,4-dinitrotoluene, 2,6-dinitrotoluene, 2-amino-4,6-dinitroluene and 4-amino-2,6-dinitrotoluene), phenylarsenic compounds including diphenylarsinic acid and triphenylarsine, perchlorate, tetrabromoethane and vinyl bromide. Depending on the compound, different approaches were used to assess the risk for both adults and children.
Exposure to these contaminants through the consumption of foodstuffs produced locally on the considered site was unlikely to be a health concern. However, as for inorganic arsenic, given the presence of highly contaminated zones, it was suggested that cereals should not be grown on certain plots.

1. Introduction

During the First World War (WWI), it is estimated that over 1 billion shells and projectiles were fired in Europe by the belligerents on the battlefield. The projectiles contained different high explosives and some of them were loaded with a wide variety of chemicals (toxic warfare agents, incendiary agents). As far as explosives are concerned, >400,000 tons of nitroaromatic compounds were manufactured by Germany, the most important being 2,4,6-trinitrotoluene (TNT), along with dinitrobenzene (DNB) and dinitrotoluene (DNT) isomers (Bausinger et al., 2007). Different chemical warfare agents were also massively produced and used on a large-scale on the battlefield for their lethal or incapacitating properties. Among the most commonly used chemicals in ammunitions were arsenical compounds (emetic agents), sulfur mustard (also called yperite, a blister agent), phosgene (a choking agent) and hydrogen cyanide (a blood agent) (Pitschmann, 2014). Additionally, about 11,000 tons of arsenical warfare agents were produced in Germany and France during WWI. Due to their vomiting properties, diphenylchloroarsine ("Clark 1"), diphenyloarsinous cyanide ("Clark 2"), phenylarsine dichloride ("Pfiffikus") and dichloroethylarsine ("Dick") were some of the most commonly used arsenicals, only used by the German armies for the loading of "Blue Cross" or "Green Cross 2,3" shells which appeared late in Great War (Bausinger and Preuss, 2005). Half of the poison-gas shells fired on the battlefield by Germans during the last year of WWI were Blue Cross shells. The French did not use organo-arsenical compounds to load chemical shells. However, arsenic trichloride ($AsCl_3$, "Marsite" for the French) just like tin tetrachloride ($SnCl_4$) ("Opacite" for the French) were mixed with suffocating agent as smoke-producing compounds in French chemical projectiles of the Great War (Belot, 1997 – unpublished).

At the end of the war, the large quantity of fired and unfired munitions remaining on the former front and in numerous ammunition dump sites in the former backlines needed to be broken down. Hundreds of thousand tons of these weapons were dumped in the Northern European seas after WWI, in shallow waters (Missiaen et al., 2010). Recent research shows that >1.7 billion tons of ammunitions remained at the Armistice in dumps as surpluses and coming from salvaging conducted by the allies (Hubé, 2016). In 1920, 1.1 million tons had to be broken down for safety purposes and to recover scrap, metals, and some chemical constituting the shells. A large amount of these remaining shells was destroyed in specific sites what led to the contamination of the surroundings in Belgium and in France (Bausinger et al., 2007; Bausinger and Preuss, 2005). Bausinger and Preuss (2005) showed that the soil nearby a former ammunition destruction facility in Belgium was polluted by arsenic, copper, lead, nitroaromatic explosive compounds and their derivatives (nitrobenzenes, nitrotoluenes), as well as triphenylarsine (a pyrolysis by-product of organoarsenical agents).

These studies enabled to shed a light on the impact of ammunition destruction activities on soil contamination in Europe. In 2015, the French Bureau of Geological and Mining Research (BRGM) undertook an environmental assessment of a well-known former site used for the destruction of WWI chemical shells, called "La place à gaz" (BRGM, 2015) and previously studied by Bausinger and Preuss (2005). This site is a small zone located in the North East of France, close to the city of Verdun, in the Spincourt forest. "La place à gaz" was operated during 1926–1928 and over 200,000 German arsenical containing weapons were burnt there. However, historical research recently conducted by the BRGM revealed that this zone was part of a much larger-scale site, called the "Muzeray-Spincourt-Vaudoncourt" complex (also referred to as the "Clere & Schwander Meuse" complex). This site was operated from 1919 to 1925 by the historic French ministry of war ammunitions. One and a half million chemical shells and 300,000 explosive shells have been gathered there by the armies for destruction, making it the largest chemical ammunitions breaking down facility known on the former western front.

The "Clere & Schwander Meuse" site now covers >100 ha of farmlands and grasslands. The agricultural productions implanted in this zone are cereals for human consumption (soft winter wheat, winter and spring barley) and maize silage for the feeding of the dairy cow herds of two local farms. The analysis undertaken by the BRGM in the "Clere & Schwander Meuse" area revealed the presence in agricultural soils of nitrates, zinc, arsenic, organo-arsenical agents, tetrabromoethane (a solvent used for the manufacturing of arsenic warfare agents) and locally high levels of nitroaromatic compounds (BRGM, 2015).

Consequently, the French Agency for food, environmental and occupational health & safety (Anses) was asked to determine whether the consumption of plant and animal products originating from this area was safe for consumers. In this paper a specific methodology to assess the health risks related to the consumption of foodstuffs produced on areas with a battlefield history is proposed, and the results obtained in the particular case of the "Clere & Schwander Meuse" site are presented. To this end, food products of plant and animal origin were sampled in 2015–2016 and concentrations of organic and inorganic chemical contaminants were measured using developed specific analytical methods. Human exposure was assessed based on local individual consumption or/and national diet study. Risk was assessed for adults and children