Environmental contamination with persistent cyclic mustard gas impurities and transformation products

Katarzyna Chmielińska, Daniel Hubé, Tobias Bausinger, Markus Simon, Gilles Rivière, Patrik Fauser and Hans Sanderson

ABSTRACT
The battlefield of Verdun has seen some of the heaviest shelling in the history of mankind. This site as well as clean-up facilities in Germany may constitute contamination hot-spots and point-sources with leaking to groundwater. This study collected existing toxicological and ecotoxicological data on mustard gas degradation products, together with physical – chemical properties of listed compounds. It also provides quantities of these products measured in the groundwater of France, Germany and the pore water of the Baltic Sea. We indicate a deficiency of information on the toxicity of 1-oxa-4,5-dithiepane and 1,2,5-trithiepane. In the groundwater of the German city of Munster 1-oxa-4,5-dithiepane was measured up to 250 µg/L, thus exceeding safe levels. Ecotoxicological studies classify this compound as toxic to aquatic organisms. 1,2,5-trithiepane is not a persistent compound. It was measured, however, in the groundwater at 1 µg/L level. This suggests that it could be formed from an active source of mustard gas. Considering the lack of toxicological data and the uncertainty about the amount of munition deposits, we suggest that research into the toxicity and exposure of 1-oxa-4,5-dithiepane and 1,2,5-trithiepane is needed for sites of concern.

1. Introduction
2018 was the centennial celebration of the end of the Great War, World War I (WW1). This was a great celebration, but it also reminded the world community of the atrocities that occurred during the war. It is however also an occasion to revisit questions about potential environmental pollutants released during the hostilities and from old munitions (Bausinger, Bonnaire, & Preuss, 2007, Gorecki et al., 2017, Van Meirvenne, Meklit, Verstraete, De Boever, & Tack, 2008). There are no definitive records of the amount of munitions deployed during the conflict, but it is estimated that between 1914 and 1918 approximately 1 billion artillery shells were fired equating to roughly 15 million tons of warfare materials (explosives, metals, and chemical warfare agents) (Bausinger et al., 2007). Many of these pollutants can persist in soil for decades and can contaminate soil leachate as well as groundwater resources (Gorecki et al., 2017).

Historical sources provide information on the use of mustard gas on the battlefields of northern France, on the border with Belgium (Guicherd & Matriot, 1921). In addition, the location of the warfare agents’ tests and production site in western Germany has been documented (Martens, 1990). After the war, the destruction of chemical weapons became an issue. Due to a lack of knowledge, this was often done as ‘leaving to be reclaimed by nature’. The materials were left in the forest after the battle of Verdun. To this day, due to the danger of unexploded ordnance, there is a fenced zone with limited access. The ecosystem is characterised by strong human interference. Part of the stockpiled chemical weapons has been deposited in the Baltic Sea also after the Second World War. Impurities and transformation products of the mustard gas were detected and measured in the close vicinity of the Danish island Bornholm (Söderström et al., 2018).

This research is intended to draw attention to data gaps in terms of the exposures and toxicities of one of the most widely used chemical warfare agents – mustard gas (HD). The aim of this paper is thus to summarise the measured exposure data from areas with known use or disposal of HD. This paper will highlight the HD cyclic
degradation product occurrence and environmental toxicity at the three sites of elevated concern.

2. Experimental

2.1. Sites

2.1.1. Verdun, France

Some of the most intensive fighting took place near Verdun in France in the trench warfare in 1916 (Battle of Verdun) where more than 700,000 humans lost their lives. Further fights occurred near Verdun during the years 1917 (Second battle of Verdun) and 1918 (Meuse-Argonne American offensive). An area covering around 65 square miles (170 square km) on the Verdun ridge has since 1919 been declared a Zone Rouge (‘Red Zone’) (Figure 1), which is completely devastated and of restricted access due to the presence of numerous unexploded ordnances (UXOs). The private grounds have been taken over (according to the circular of the 10th of June 1921) and forested by the State at the beginning of the twenties. The costs of recovering the ground surpassed the market value of this land back in 1914 – mainly owing to the presence of UXOs, warfare remnants and topographical disturbances.

According to the Encyclopaedia Britannica, it is estimated that over 10 million munition shells remained in the soil around Verdun, and ammunition disposal units continue to remove around 40 tons of unexploded munitions from the area each year. Some types of chemical shells can only be distinguished by qualified experts in the laboratory conditions. However, in some cases, the chemical munitions can remain indistinguishable from explosive shells until they are imaged – for example, with an X-ray. Certain fillings retain their toxicity over the decades, and they are prone to leak when discovered and handled (Encyclopedia Britannica inc., 2019).

The research of Bausinger (Bausinger et al., 2007) and Hubé (Hubé, 2016, Hubé, 2017) further documents that ‘the war does not end the day of the last shot’ (Lohs, 1991). Between 2.5 and 3 million tons of old munitions of the Great War were disposed and destroyed during the interwar period causing local, but severe, topsoil contaminations. Bausinger reviewed the exposure to mainly arsenic-based chemical warfare agents in the battlefields near Ypres and Verdun (Bausinger et al., 2007, Bausinger, Dehner, & Preuß, 2004). Specifically, in the areas where arsenical chemical munitions were open – burned in specifically designed burning trenches during the interwar period and found severe local topsoil contamination by arsenic and heavy metals.

However, different types of poisonous toxic compounds were used in WW1. One of the most used forms was the blister agent – Sulphur mustard (in short known as HD or Yperite), first used in Nieuport, Belgium in 1917. It was widely applied in the trench warfare. This

![Figure 1. Zone Rouge near Verdun in France (Guicherd & Matriot, 1921).](image)
yellow to dark brown liquid with slight garlic or horseradish type odour is also called ‘Lost’ (by the Germans), Ypérite (by the French) and ‘Hun-Stoff’ (by the British). It is estimated that 10,149 tons of HD were used during WW1, mainly by the Germans (3/4 of the total) (Haber, 1988). With passing time, the risk of HD leaking from shells is decreasing because of its degradation. However, it causes an overpressure of the headspace of the shell with risks of cracking of the shell and gas release to the surroundings.

Hubé described industrial-scale old chemical ammunition operations during the interwar period near Verdun. He related these activities with the occurrence of severe contamination with arsenical compounds, metals (Zn, Pb, Sn), chlorinated and brominated dioxins and furans, nitroaromatics compounds, together with residues from chemical warfare agents (Hubé, 2017). After WW1 remediation near Verdun was commenced, as shown in Figure 2. More than 1,500,000 German, French and British chemical shells have been destroyed by a private company near Verdun between 1919 and 1925. Yperite shells were defused and emptied, the Yperite was seeped in 2.5 m deep pits or collected to be burned in furnaces. Hydrochloric acid and sulphur dioxide of the smoke produced caused damages on the surrounding crops. At last, the emptied shells were burned to remove the Yperite drips. The steel was finally sold as scrap.

Recently, there are also reports of findings of tertiary degradation products in groundwater samples (Hubé et al. 2018 unpublished data), and in a standing water pool near Verdun (Figure 3).

2.1.2. Munster, Germany
In the area of Munster, a town in Lower Saxony, Germany, during WW1 the German Army operated a chemical warfare test site and a filling facility for chemical munitions. After the war, in October 1919 an uncontrolled explosion took place. The explosive force destroyed some storage infrastructure, including buildings and railway tank wagons filled with chemical warfare agents, resulting in the chemicals being released into the environment. During World War II the testing and filling of chemical munitions and the small-scale production of chemical warfare agents were resumed at the same location. Among the chemicals filled into munitions was HD. In 1948, the British military performed controlled explosions as a decommissioning effort. It was not until 1956, when the German Army entered the area that the Munster Training Area underwent a comprehensive clean-up (Martens, 1990). Due to the size and complexity of the site, decontamination operations were difficult and mustard gas degradation products may still be detected in environmental samples. Today, the territory serves as a military training area. In 2015 an article in the local newspaper reported traces of mustard gas degradation products in drinking water wells (Böhme Zeitung, 2019). A continuous monitoring of drinking...
water for these compounds has been carried out and reported in the online database of the local municipality authorities (Bispingen, 2019).

2.1.3. Baltic Sea, Denmark

After World War II (WWII), 65,000 tons of chemical weapons were dumped in the Baltic Sea near the Danish island Bornholm. Tertiary degradation products of HD have been detected in chemical warfare agent dumpsites in the Baltic Sea (Söderstrøm et al., 2018, Beldowski et al., 2016). Figure 5 illustrates the primary dumpsite where some 7027 tons of HD along with other chemical warfare agents were dumped in 1947 after WWII, primarily in the circle but also in the secondary dump site (the box) (Sanderson & Fauser, 2015). Especially the cyclic HD compounds have been detected in dumpsites in the Baltic Sea (Söderstrøm et al., 2018), and hence these are the focus of this paper.

2.2. Compounds

HD is the parent compound. It is a blistering agent that can alkylate DNA and cause cancer. It was widely used in WWI (>10,000 tons) (Haber, 1988) and mass-produced by Germany after WW1 (25,000 tons). Physical–chemical properties of HD and its degradation products are listed in Table 1. Henry’s Law constant for HD indicates that volatilisation is a possible degradation pathway.

The data collected in Table 1 include values modelled in the EPI Web software. Please note that the water solubility might be overestimated for the six–membered heterocycles (CAS # 505-29-3 and 15,980-15-1), which are expected to have a lower solubility in water and would, therefore, need further assessments.

Hydrolysis is an important degradation process of mustard gas. It follows a first-order kinetics rate equation, with a half-life of minutes (Ashmore & Nathanail, 1999). Henry’s Law constant for HD indicates that HD deposited on the surface of the soil will evaporate within 30–50 h, depending on weather conditions (Munro et al., 1999). Thiodiglycol, the primary hydrolysis degradation product of mustard gas, can rapidly oxidise further and is far less toxic than HD. Another group of mustard-related compounds frequently detected in environmental samples are cyclic thioethers which can be considered as 1) byproducts are formed during the mustard synthesis; 2) degradation products are formed during decontamination processes; and 3) environmental degradation products of HD are formed. According to Jung et al., mustard gas toxicity can be attributed also to undergoing specific pathway of degradation, which lead to the formation of the toxic sulphonium ions. These are formed when HD hydrolysis proceeds in the limited water conditions (Jung, Kah, Lim, & Lee, 2017). The most environmentally relevant and important cyclic compounds, six- and seven-membered ring systems, are given in Table 1. Figure 6 presents a couple of pathways of some of the detected metabolites in the environment (Söderstrøm et al., 2018). These are the metabolites of HD that are more persistent and more frequently found than other HD metabolites and are hence the focus of this paper.

2.3. Environmental toxicity tests and chemical analysis

Ecotoxicological tests with the green algae Raphidocelis subcapitata and the water flea Daphnia magna, were conducted according to the guidelines OECD 201 and

| Name              | #CAS          | Structure          | Log Kow | Log Koc | Henry’s Law constant atm-m/mol at 25°C | Water solubility mg/L at 25°C |
|-------------------|---------------|--------------------|---------|---------|----------------------------------------|-----------------------------|
| mustard gas       | 505-60-2      | ![Structure](image) | 2.14    | 2.12    | 2.45x10⁻⁵                              | 605.3                       |
| thiodiglycol      | 111-48-8      | ![Structure](image) | -0.63   | -0.25   | 1.14x10⁻¹⁰                            | water miscible              |
| 1,4 – dithiane    | 505-29-3      | ![Structure](image) | 0.77    | 0.67    | 4.2x10⁻⁵                               | 22,040                      |
| 1,4 – oxathiane   | 15,980-15-1   | ![Structure](image) | 0.53    | 1.13    | 2.56x10⁻⁷                              | 39,800                      |
| 1-oxa-4,5- dithiepane | 3886-40-6   | ![Structure](image) | 1.49    | 1.55    | 8.31x10⁻⁸                              | 4667                        |
| 1,2,5- trithiepane | 6576-93-8    | ![Structure](image) | 2.34    | 2.03    | 7.58x10⁻⁶                              | 746.2                       |
211, respectively, in accordance with Good Laboratory Practice (GLP) at Fraunhofer Institute in Schmallenberg, Germany, on the 1-oxa-4,5-dithiepane compound as a representative of the cyclic HD degradation products. Test concentrations were analytically verified by gas chromatography mass spectrometry (GC-MS) with a limit of quantification (LOQ) of 0.10 mg/L.

In the algae test, the reproduction of algae was measured by determining fluorescence during an incubation period of 72 hr. The test was conducted under static conditions, applying a concentration series of 4.10, 5.12, 6.40, 8.00 and 10.0 mg test substance per litre. The analytically verified concentrations at test start and test end were 81 – 90% and 76 – 81% of the nominal, respectively. Due to stable concentrations during the test, the initial measured concentrations 3.33, 4.62, 5.66, 6.80 and 8.41 mg/L were used to calculate the NOEC (No Observed Effect Concentration) calculation, which is in accordance to Organisation for Economic Co-operation and Development (OECD) requirements. Evaluation was done for growth rate (r) and yield (y). Both endpoints showed no effects up to and including the highest concentration tested.

In the chronic Daphnia test, the growth, survival and reproduction of *Daphnia magna* were measured during an incubation period of 21 d. The test was conducted under semi-static conditions with three media renewals per week, applying a concentration series of 4.10, 5.12, 6.40, 8.00 and 10.0 mg test substance per litre. The analytically verified concentrations at test start and test end were 96 – 107% and 79 – 92% of the nominal, respectively. Due to decreased concentrations during the media renewal intervals, the time-weighted average (TWA) measured concentrations 0.263, 0.474, 0.825, 1.638, and 2.982 mg/L were applied for NOEC calculation, which is in accordance to OECD requirements. According to the guideline, the daphnids were fed during the test with suspensions of unicellular alga. Parent survival, offspring per females introduced and offspring per females survived were the most sensitive endpoints and showed comparable sensitivity.

Chemical analysis of groundwater samples was performed by filtering the water sample through glass fibre filters and extraction with dichloromethane. The combined organic extracts were dried with anhydrous sodium sulphate, reduced with nitrogen to a small volume and measured by electron ionisation (EI)-GC/MS in the combined SIM-/Scan-mode. Reference compounds were obtained commercially (1,4-dithiane and 1,4-oxathiane, Sigma-Aldrich) or were synthesised in-house at Envilytix GmbH (1-oxa-4,5-dithiepane and 1,2,5- trithiepane). The methods follow the methods used for the monitoring of groundwater for these compounds performed on behalf of Munster municipal utilities (Stadtwerke Munster – Bispingen) by the Dr. Nowak GmbH Institute (https://www.limnowak.com, 2019).

3. Results

3.1. Summary of existing knowledge about HD and its degradation products

We reviewed the available data and information, where Munro is a key reference (Munro et al., 1999), as well as TOXNET reviews for the compounds in Table 1. Significantly less data are available for the degradation products of Sulphur mustard than there is for it as a parent compound. Below, in Table 2, we compare the measured critical mammalian toxicity of HD and its degradation products from TOXNET (Toxicology Data Network, 2019). As HD is a strong carcinogen, we highlighted the genotoxicity and carcinogenicity of the compounds.

Table 3 describes the measured environmental toxicity of the detected HD degradation products summarised by Christensen (Christensen et al., 2016) and Storgaard (Storgaard et al., 2017). The toxicity of the contaminants is also described in the context of the Globally Harmonised System of Classification and Labelling Chemicals (GHS). The EC50 value for 1-oxa-4,5-dithiepane is considerably lower compared to 1,4 – dithiane and 1,4 – oxathiane. Moreover, according to the GHS systems 1-oxa-4,5-dithiepane is classified as toxic to the aquatic life in both chronic and acute conditions.

The measured toxicity data in Table 3 are mainly based on MicroTox analysis, as well as a 14-d Zebrafish test. Hence, the paucity in higher tier toxicity testing necessitated additional tests with a focus on the representative compound 1,4,5-oxadithiepane. The chronic no observed effect concentration (NOEC<sub>chronic</sub>) results of the GLP environmental toxicity tests conducted for algae and Daphnia for 1-oxa-4,5-dithiepane are showed in Table 4. The NOEC<sub>chronic</sub> data express toxicity to aquatic invertebrates (*Daphnia magna*) and algae (*Raphidocelis subcapitata)*.

Table 4 data provide a description of chronic exposure concentrations given in μg L<sup>−1</sup> unit, as well as the corresponding GHS classification. It is clear that *Daphnia magna* is more sensitive than algae, and also more sensitive than zebrafish, according to the 14-d chronic toxicity test, if we do not consider the behavioural endpoint.

The local health authority in Lower Saxony has derived provisional insignificance threshold values for groundwater (Environmental Quality Standards (EQS)) (EQS<sub>drinking water</sub>) for three of the mustard gas degradation products. The 1,4 – dithiane value is calculated
Table 2. Measured mammalian toxicity data profile of mustard gas and its degradation products, based on TOXNET (Toxicology Data Network, 2019).

| Compound          | Mammalian toxicity                                                                 | Genotoxicity, Carcinogenicity                                                                 |
|-------------------|------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|
| mustard gas       | Acute Apoptosis assay (lung): inhibitor concentration: 300 µmol/L/16h               | DNA lesion caused by mustard gas exposure observed in Iran-Iraq war victims. Underlying mechanisms were noted as gene p53 mutations within exons 5–8, primary G to A transitions. Other cases reported multiple p53 point mutations (Hosseini-khalili et al., 2009). |
|                   | In-vitro (human cell lines), MTT assay (skin); inhibitor concentration: 30 µmol/L/30 min. LD$_{50}$ guinea pig, intratracheal: 0.730 mg/kg | Genotoxicity mouse lymphoma assay based on OECD 476 guideline in the up to 5000 µg/mL showed no significant mutagenic effects. |
| thioglycol        | Sub-chronic: NOAEL: 500 mg/kg bw/day (Angerhofer, Michie, Leach, Johnson, & Reddy, 2014). LD$_{50}$ rat, oral 9900 mg/kg bw/day (OECD; Screening Information, 2006) | Not classifiable as human carcinogenicity based on supporting data of Ames test (Salmonella/mammalian microsome mutagenicity assay). The US Environmental Protection Agency established a NOAEL of 105 mg/kg/day for 1,4 dithiane in drinking water (Schieferstein, Sheldon, Cantrell, & Reddy, 1988). |
| 1,4 – dithiane    | LD$_{50}$ rat, oral 2768 mg/kg bw                                                  | Negative test result on mutagenicity based on supporting data of Ames test (Salmonella/mammalian microsome mutagenicity assay) range concentrations: 0.0015-Sul/plate |
| 1,4 – oxathiane   | NOEC: 2830 mg/kg bw                                                               | NA: not assessed                                                                            |

Table 3. Measured environmental toxicity of mustard gas degradation products (µgL$^{-1}$).

| Compound          | End point                                      | GHS Class                                                                 |
|-------------------|------------------------------------------------|----------------------------------------------------------------------------|
| 1,4 – dithiane    | A. fischer EC50 = 9970                         | Acute Category 2: toxic to aquatic life                                      |
| 1,4 – oxathiane   | A. fischer EC50 = 47,400                       | Acute Category 3: harmful to aquatic life                                     |
| 1-oxa-4,5-dithiepane | NOEC Chronic fish $14_d = 1533$                     | Chronic Category 2: toxic to aquatic life with long lasting effects          |
|                   | NOEC Fish behaviour study: 40.3 ± 2.9          | Chronic Category 2: toxic to aquatic life with long lasting effects          |

Table 4. 1-Oxa-4,5-dithiepane environmental chronic NOEC for Algae and Daphnia magna (µgL$^{-1}$).

| Compound          | Chronic toxicity                                                   | GHS Class                                                                 |
|-------------------|---------------------------------------------------------------------|----------------------------------------------------------------------------|
| 1-oxa-4,5-dithiepane | NOEC Algae$_{25uL} = 8410$                                           | Chronic Category 2: toxic to aquatic life with long lasting effects          |
|                   | NOEC Daphnia magna$_{24_1} = 825$                                    | Chronic Category 2: toxic to aquatic life with long lasting effects          |

Based on the more substantial available data, whereas the two other degradation products with fewer data are determined via a Toxicological Threshold of Concern (TTC) approach, as well as an environmental Predicted No Effect Concentration (PNEC), see Table 5 by Wollin (Wollin, 2018).

3.2. Exposure

Relatively little is known about the environmental exposure to the materials. A research team from France and Germany shared a summary of concentration ranges of HD degradation products found in the groundwater (Table 6) from the sites in Germany and France (Hubé 2018, unpublished data). Moreover, the highest porewater concentrations of the cyclic degradation products found from the measurements in sediment at the Bornholm Deep dumpsite (Söderstrøm et al., 2018, Storgaard et al., 2017) have been calculated based on equilibrium partitioning modelling (EqP). Table 6 summarises these currently known maximum environmental exposures. Regarding 1,4-dithiane, literature sources report that a concentration of 9,000 µg 1,4 dithiane/L has moreover been found at the Rocky Mountain Arsenal (Munro et al., 1999).

Table 5. EQS drinking water and PNEC environment for Lower Saxony, Germany.

| Compound          | EQS drinking water (µg/L) | PNEC (µg/L) |
|-------------------|---------------------------|-------------|
| 1,4 – dithiane    | 23.2                      | 23.2        |
| 1,4 – oxathiane   | 5.25                      | NA          |
| 1-oxa-4,5-dithiepane | 5.25                      | NA          |

Table 6. Maximum measured aquatic exposures of mustard gas cyclic degradation products (µg/L).

| Compound          | Groundwater; Germany (µg/L) | Baltic Sea porewater (µg/L) | Groundwater; France (µg/L) |
|-------------------|-----------------------------|----------------------------|---------------------------|
| 1,4 – dithiane    | 1                           | 3.4                        | 0.8                       |
| 1,4 – oxathiane   | 10                          | ND                         | 0.5                       |
| 1-oxa-4,5-dithiepane | 250                         | 0.89                       | 0.5                       |
| 1,2,5- trithiepane | 1                           | 0.76                       | < 0.2                     |
Measurements summarised in the tables above show that 1,4-dithiane was prominently observed in Baltic Sea porewater among other measured compounds listed. The 1-oxa-4,5-dithiepane concentration measured in groundwater indicates that this is a prominent compound of the measured HD cyclic degradation products. Moreover, its concentration measured in the groundwater was considerably higher, than concentration measured in the Baltic Sea pore water. There are no data available regarding 1,4-oxathiane concentration in Baltic Sea pore water.

Table 7 shows the concentrations of HD degradation products detected in a pool in the Verdun area in 2015 (see Figure 4).

4. Discussion

The highest detected surface water concentration of 1-oxa-4,5-dithiepane (0.89 µg/L) does not exceed an estimated PNEC. Calculated as follows, 825 µg/L divided by an assessment factor of 50 – for derivation of PNEC marine sediment from long-term sediment toxicity tests with species representing different trophic levels, which is in accordance with the EU Technical Guidance Document on risk assessment (2003) (EU Technical Guidance Document, 2003), PNEC equals 16.5 µg/L. The PNEC derived by Wollin (Stock & Lohs, 1997) of 23.5 µg/L for 1,4-dithiane is also not exceeded in the Baltic Sea with a maximum of 3.4 µg/L. These values suggest low risks for both of these. However, the EQS_Drinking water value is exceeded for both 1-oxa-4,5-dithiepane and 1,4-oxathiane in the worst-case scenarios suggesting that the risks need to be further assessed.

The occurrence of tertiary degradation cyclic products in the environment should be considered in the context of their chemical properties. It is known from the production processes that they tend to polymerise. For example, 1,2,5-trithiepane is polymerised at room temperature within 1 year to circa 30% into the white polymer which is insoluble in most solvents. As it is not stable, we can conclude that this compound could not have been formed over 100 years ago. 1-Oxa-4,5-dithiepane is more stable compared to 1,2,5-trithiepane. 1-Oxa-4,5-dithiepane polymerises circa 1% per year at the room temperature. Therefore, those cyclic tertiary degradation products can be used as indicators of HD contamination. The six-membered ring products are stable and are not suspected to exhibit the tendency to polymerisation. According to the literature 10,149 tons of HD were used during WW1 mainly by the Germans (3/4 of the total) (Haber, 1988) – the question is, how much is still available in buried munitions? We know that certain hotspots exist, like ammunition destruction sites, production sites, filling sites and testing sites. Bausinger and Hubé (unpublished) detected the tertiary degradation products mainly in such hotspots. The remaining HD is enclosed in the munition shell; nevertheless, these corrode over time and can then release their toxic content.

Presence of tertiary HD degradation products causes concern with regards to potential environmental and public health impacts and constitutes a key decision factor if a site remediation is needed. As indicated by the local

Table 7. Analytical results of the water sampled in the pool on the ammunition destruction plant of the interwar period near Verdun. Bausinger & Hubé, 2015 (unpublished).

| Compound            | Pool (µg/L) |
|---------------------|-------------|
| Diphenylarsinic acid| 20.4        |
| Triphenylarsine     | < 0.25      |
| 1,4-dithiane        | 0.46        |
| 1,4-oxathiane       | 0.80        |
| 1-oxa-4,5-dithiepane| 0.43        |
| 1,2,5-trithiepane   | < 0.25      |
| Chlorobenzene       | < 0.10      |

Figure 4. Inspection of the Head of the General War Department in the storage and testing facility near Munster on 12 April 1918 (Friedrich & James, 2017).
health authority in Lower Saxony, for these materials, EQS values were developed. Moreover, we know that Germans produced thickened mustard (winter mustard) in the times of WW II (Angerhofer et al., 2014). Thickening process increases Sulphur mustard persistency by mixing it with polymers. Verdun municipality is not an isolated case – for example, Munster, city in Germany struggles with drinking water resources safety uncertainties (Böhme Zeitung, 2019). Undoubtedly, many factors contribute to favour the necessity of further investigations in the context of environmental contamination with cyclic mustard gas degradation products. The toxicity of the degradation products needs further elucidation and EQS values need to be updated based on new derived and available data.
5. Conclusion

Based on this summarised data on the occurrence of HD tertiary degradation products and measured groundwater concentration we can conclude that further evaluation of those findings is needed. Due to the possible genotoxicity of compounds described in this paper, further toxicity data need to be generated. The EQS value for 1-oxa-4,5-dithiepane exceeds threshold value nearly 50 times. Since 2015 to June 2019 the monitoring results at Munster are below 0.1 µg/L (Bispingen, 2019). The lack of toxicological data mainly on this compound contributes to uncertainty related to public health risk, potentially posed by drinking water contamination with cyclic mustard gas degradation products. Furthermore, the environmental predicted No Effect Concentration value for 1-oxa-4,5-dithiepane value could be improved with more data.

Disclosure statement

No potential conflict of interest was reported by the authors.

Notes on contributors

Katarzyna Chmielinska is a MSc candidate in Environmental Science at Copenhagen University.

Daniel Hubé is a groundwater expert with the French Geological Survey.

Tobias Bausinger is an analytical chemist with 10+ years of expertise in CWAs.

Markus Simon is an ecotoxicologist and risk assessor at Fraunhofer Inst.

Gilles Rivière works for the French ANSES where he is the unit head of physicochemical risk assessment.

Patrik Fauser is a Sr Scientist at Aarhus University with expertise in exposure modelling and CWAs.

Hans Sanderson is a Sr Scientist at Aarhus University with expertise in ecotoxicology and risk assessment of CWAs.

ORCID

Gilles Rivière http://orcid.org/0000-0002-7317-8104
Hans Sanderson http://orcid.org/0000-0002-3765-4310

References

Angerhofer, R.A., Michie, M.W., Leach, G.J., Johnson, M.S., & Reddy, G. (2014). Oral toxicity evaluation of thiodiglycol in Sprague-Dawley rats. International Journal of Toxicology, 33 (5), 393–402. doi:10.1177/1091581814547541

Ashmore, M., & Nathaniel, P. (2008). A critical evaluation of the implications for risk based land management of the environmental chemistry of sulphur mustard. Environment International, 34(8), 1192–1203. doi:10.1016/j.envint.2008.03.012

Bausinger, T., Bonnaire, E., & Preuss, J. (2007). Exposure assessment of a burning ground for chemical ammunition on the great war battlefield of Verdun. Science of the Total Environment, 382, 259–271. doi:10.1016/j.scitotenv.2007.04.029.

Bausinger, T., Dehner, U., & Preuß, J. (2004). Determination of mono-, di- and trinitronaphthalenes in soil samples contaminated by explosives. Chemosphere, 57(8), 821–829. doi:10.1016/j.chemosphere.2004.07.018.

Beldowski, J., Klusek, Z., Szub ska, M., Turja, R., Bul czak, A.I., Rak, D., Brenner, M., Lang, T., Kotwick, L., Grzelak, K., Jakacki, J., Fricke, N., Östlin, A., Olsson, U., Fabisiak, J., Garnaga, G., Nyhol m, J., Majewski, P., Broeg, K., Söderström, M., Vanninen, P., Popiel, S., Nawala, J., Lehtonen, K., Berg lind, R., Schmidt, B. (2016). Chemical munitions search & assessment – evaluation of the dumped munitions problem in the Baltic Sea. In Deep-Sea research. Part 2: Topical studies in oceanography (Vol. 128, pp. 85–95) The Netherlands, Elsevier.

Bispingen, S.M. [assessed 20 June 2019]. Retrieved from https://ih-artstadtwerk.de/versorgung/wasser/downloads.html

Böhme Zeitung. [assessed 28 March 2019]. Retrieved from http://www.boehme-zeitung.de/lokales/news/artikel/lost- reste-gutachter-s

Christensen, I.M.A., Storgaard, M.S., Fauser, P., Hansen, F.H., Bastrup, E., & Sanderson, H. (2016). Acute toxicity of sea-dumped chemical munitions: Luminating the environmental toxicity of legacy compounds. Global Security: Health, Science and Policy, 1(1), 39–50.

Encyclopedia Britannica inc. 2019. [assessed 27 March 2019]. Retrieved from https://www.britannica.com/event/Battle-of-Verdun

EU Technical Guidance Document. (2003). [assessed 12 Nov. 2019]. Retrieved from https://ec.europa.eu/eur-lex/publisher/eur-scientific-and-technical-research-reports/technical-guidance-document-risk-assessment-part-1-part-2

Friedrich, B., & James, J. (2017). From Berlin-Dahlem to the fronts of world war I: The role of Fritz Haber and His Kaiser Wilhelm institute in German chemical warfare. In B. Friedrich, D. Hoffmann, J. Renn, F. Schmaltz, & M. Wolf (Eds.), One hundred years of chemical warfare: Research, deployment, consequences. Springer, Cham. Conference paper (pp.22–25) Springer Nature, New York, NY: USA.

Gorecki, S., Nesslany, F., Hubé, D., Mullot, J.U., Vasseur, P., Marchioni, E., ... Rivere, G. (2017). 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. Science of the Total Environment, 599–600, 314–323. doi:10.1016/j.scitotenv.2017.04.213

Guicherd, J., & Matriot, C. (1921). La terre des régions dévastées. Journal d’Agriculture Pratique, 34, 154–156.

Haber, L.F. (1988). The poisonous cloud: Chemical warfare in the first world war (1st ed., pp. 260–261). Clarendon Press Press, Oxford, UK.

Hosseini-khalili, A., Haines, D.D., Modirian, E., Sorouch, M., Khateri, S., Joshi, R., ... Giardina, C. (2009). Mustard gas exposure and carcinogenesis of lung. Mutation Research, 678(1), 1–6. doi:10.1016/j.mrgentox.2009.05.022
Hubé, D. (2016). Sur les traces d’un secret enfoui. Enquête sur l’héritage toxique de la Grande Guerre. Paris France, Michalon éditions.

Hubé, D. (2017). Industrial-scale destruction of old chemical ammunition near Verdun: A forgotten chapter of the Great War. Journal of First World War Studies, 1947–5020, 1947–5039. Online.

Jung, H., Kah, D., Lim, K.C., & Lee, J.Y. (2017). Fate of sulfur mustard on soil: Evaporation, degradation, and vapor emission. Environmental Pollution, 220(Part A), 478–486. doi:10.1016/j.envpol.2016.09.090

Lohs, K. (1991). Der Krieg endet nicht am tag des letzten Schusses. Spectrum, 2, 24–26.

Martens, H. (1990). Incineration plant for toxic waste of the federal armed forces defence science agency for NBC protection in munster. In F. Arendt, M. Hinsenveld, & W. J. Van Den Brink (Eds.), Contaminated Soil 90 (pp. 1441–1443). Dordrecht: Springer.

Munro, N.B., Talmage, S.S., Griffin, G.D., Waters, L.C., Watson, A.P., King, J.F., & Haushild, V. (1999). The sources, fate, and toxicity of chemical warfare agent degradation products. Environmental Health Perspectives, 107(12), 933–974. doi:10.1289/ehp.99107933.

OECD; Screening Information. (October 2006). Data Set (SIDS Initial Assessment Report for SIDS Initial Assessment Meeting (SIAM) 19, Thiodyglycol (CAS 111-48-8) p.13.

Sanderson, H., & Fauser, P. (2015). Environmental assessments of sea dumped chemical warfare agents. Aarhus University, DCE – Danish Centre for Environment and Energy, 116 pp. Scientific Report from DCE – Danish Centre for Environment and Energy No. 174

Schieferstein, G., J., Sheldon, W.G., Cantrell, S.A., & Reddy, G. (1988). Subchronic toxicity study of 1,4-dithiane in the rat. Fundamental and Applied Toxicology, 11, 703–714. doi:10.1016/0272-0590(88)90133-9

Söderström, M., Östin, A., Qvarnström, M.R., Rattflett-Nyholm, J., Vahe, M., Joul, P., Lees, H, Kaljurand M., Szubskia, M., Vanninen, P., Baldowski, J. (2018). Chapter 4: Chemical analysis of dumped chemical warfare agents during the MODUM project. In B. Baldowski (Ed.), NATO SPS series. Turmus.

Stock, T., & Lohs, K. (1997). The challenge of old chemical munitions and toxic armament wastes. SIPRI Chemical & Biological Warfare Studies, 16, 77–103.

Storgaard, M., Sanderson, H., Henriksen, P., G., Fauser, P., Östin, A., & Baatrup, E. (2017). Suppressed swimming activity in Zebra fish (Danio rerio) exposed to 1,4,5-oxadithiepane, a sulphur mustard degradation product. Global Security: Health, Science and Policy, 2(1), 22–28.

Toxicology Data Network. [assessed 5 March 2019]. Retrieved from https://toxnet.nlm.nih.gov

Van Meirvenne, M., Meklit, T., Verstraete, S., De Boever, M., & Tack, F. (2008). Could shelling in the first world war have increased copper concentrations in the soil around Ypres. European Journal of Soil Science, 59(2), 372–379. doi:10.1111/j.1365-2389.2007.01014.x

Wollin, K.-M. (2018). Geringfügigkeitsschwellen Grundwasser für metaboliten chemisher kampffstoffe. Hannover March 13, 2018.