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Environmental Remnants of the First World War: Soil Contamination of a Burning Ground for Arsenical Ammunition

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During World War 1 about 11.000 tons of arsenical warfare agents were produced in Germany and France. The most important compounds were diphenylchloroarsine (Clark 1), diphenylcyanoarsine (Clark 2), ethyldichloroarsine (Dick), phenyldichloroarsine (Pfiffikus) and arsenic(III)-chloride. The first 4 compounds were used by the German Army, arsenic(III)-chloride by the British, French and Russian troops in mixture with chlorine, phosgene and prussic acid (Hanslian 1937; Haber 1986). After the end of the war large amounts of filled and unfilled agents, unfired ammunition and duds remained in the hinterland of the belligerents and the former front in Belgium and France. Due to safety problems the munitions had to be destroyed as soon as possible. Some of the material was dumped into the sea but several hundred thousand tons of all ammunition types were destroyed in Belgium, France and Germany (Bausinger 2000). A common process for the destruction of ammunition filled with high explosives and arsenical warfare agents was burning out by very simple methods. At the „gas burning ground“ the arsenical munitions together with some fire wood were stacked in trenches and ignited, next day the casings were „clean“. Sometimes explosives were sprinkled on the wood to poke up the fire. During this process beside some arsenic(III)-oxide several tertiary arsines can be formed as pyrolysis products of Clark and Pfiffikus *(unpublished results)*. Pitten et al. (2000) postulated 32 aromatic arsenicals from studies of plant and soil samples taken at a German World War 2 chemical warfare agents destruction facility, however only triphenylarsine was used as authentic reference standard for the laboratory analyses.

The purpose of this study was to characterize the soil contamination of a former ammunition destruction facility in Belgium.

MATERIALS AND METHODS

At the investigated installation nearly all types of high explosive and chemical ammunition were handled around 1920. At least ammunition containing arsenicals and high explosives was burnt out. Therefore all soil samples were analysed concerning total arsenic, copper, lead, organoarsenicals, nitroaromatic explosives and sulfur mustard derivatives.

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Today the sampling area is used for agriculture. Certain places of the former burning ground lack vegetation and contain fragments of small bottles made from thick green glass. These types of bottles were used during World War 1 in Germany in chemical ammunition as receptacles for the nose-throat irritants Clark 1 and Clark 2 called „blue cross“ agents. This was a strong hint that arsenicals could play a major role as pollutants at this site.

A total of 20 soil samples was taken from 0-20 cm depth, some of them contained black ashes from the burning process and the above mentioned glass fragments. The origin of the investigated soil samples is specified in Table 3, some were taken directly at the gas burning ground (location=bg) but the majority at the surrounding delaboration area (location=dl) up to a distance of ~1000 m from the burning ground. All samples were dried at 30 °C, the fraction < 2 mm was separated and thoroughly homogenized in a mortar.

Total arsenic was determined photometrically after digestion with sulfuric acid/hydrogen peroxide according to a german standard method (DIN 1993). The recovery rates for arsenic acid, cacodylic acid and phenylarsine oxide were determined. Copper and lead were analysed by F-AAS after aqua regia digestion (DIN 1997). The recovery rate was controlled using two elemental standard solutions.

The investigation of sulfur mustard derivatives and organoarsenicals by GC/MS is described elsewhere (Bausinger 2000). Additionally the most important explosives and organoarsenicals were determined by HPLC-DAD after soil extraction with acetone in an ultrasonic bath: 2.5 g soil were mixed with 2.0 g anhydrous sodium sulfate and 10 mL acetone and treated for 2 h in an ultrasonic bath. To remove colloids aliquots of these extracts were mixed 1:1 (vol/vol) with calcium chloride solution ($c = 5\ g\ L^{-1}$), centrifuged 5 min at 3000 rpm and filtered through 0.45 μm PTFE membranes.

These solutions were injected into the HPLC system which was equipped with a pump M 480, an online degaser Degasys DG-1310, an autosampler Gina 50, a diode array detector UVD 340 S and a column oven STH (all parts Gynkothek, Idstein / Germany). The nitroaromatics were separated on a Nucleosil column 120-3 C_{18} 250 x 4 mm with a pre-column 8 x 4 mm packed with the same material (Macherey-Nagel, Düren / Germany). A methanol-water-gradient (methanol: 0-10 min → 40-50 % / 10-35 min → 50 % / 35-80 min → 50-80 % / 80-85 min → 80-100 % / 85-90 min → 100 %) was used at a flow rate of 0.45 mL min^{-1} and a column temperature of 10 °C. 100 μL were injected onto the column, the detection wavelength was 230 nm. The organoarsenicals were determined on a Nucleodur column 100-3 C_{18}ec 250 x 4 mm with a pre-column 8 x 4 mm (Macherey-Nagel, Düren / Germany) using an acetonitrile-water-gradient (acetonitrile: 0-60 min → 60-100 % / 60-85 min → 100 %) at a flow rate of 0.40 mL min^{-1} and a column temperature of 20 °C. The injection volume was 100 μL and the detection wavelength was set to 220 nm.

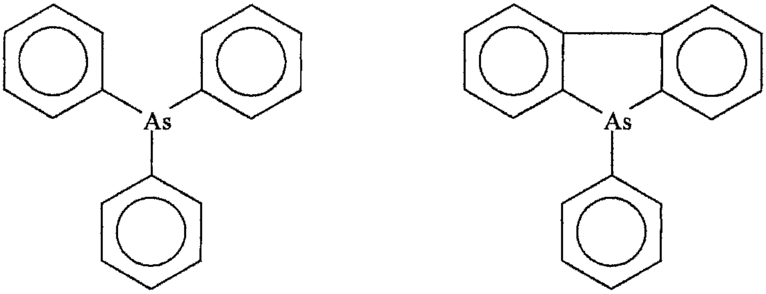
For both HPLC methods the limits of detection (LoD) and quantification (LoQ) were determined (DIN 1994). They were calculated from the standard deviations (s) of calibration curves close to the detection limit (LoD = 4s / LoQ = 11s, k = 3) for a level of significance of 0.01.

To test the extraction efficiency of the sonication process a spike/recovery study was performed: an unpolluted silty loamy sand (fraction < 2 mm) was fortified with solutions of all organic compounds listed in Table 2 at a concentration of 20 mg kg^{-1} for each compound. The soil characteristics were as follows: 40.5 % sand; 44.2 % silt; 15.3 % clay; pH 7.2; effective cation exchange capacity 11.2 cmol kg^{-1}; potential cation exchange capacity 22.8 cmol kg^{-1} and 7.2 % carbonate. This soil was dried at 105 °C to a constant weight and afterwards 100 g were separated. To this portion 10 mL water and the solutions of the organic compounds in acetonitrile were added. The fortified soil was air dried 4 days at room temperature in the dark to a constant weight. The soil was grind < 200 μm and thoroughly homogenized. An unspiked blank was treated in the same way. The dry mass was determined at 105 °C (~98 %) and sub-samples of this soil were extracted according to the method given above using 3 replicates. Another portion of this soil was spiked with bis(diphenylarsine) oxide (BDAO) at a concentration of 1 g kg^{-1} (100 g soil + 10 mL water + 100 mg BDAO dissolved in 10 mL acetone).

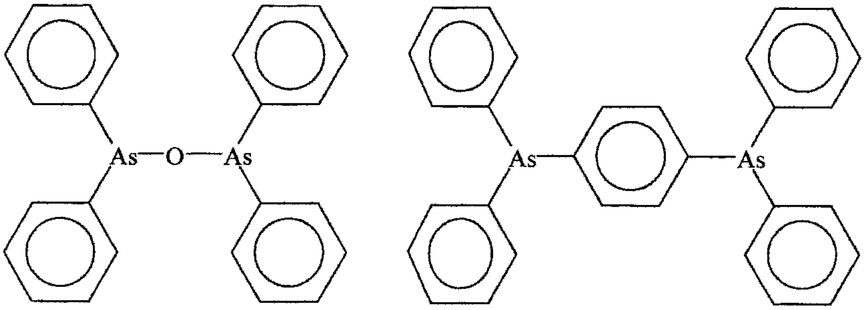
Four organoarsenicals were available as reference materials (see Figure 1): bis(diphenylarsine) oxide, the hydrolysis product of Clark, was synthesized after the method of Blicke & Smith (1929). 9-Phenylarsafluorene was prepared according to Blicke & Cataline (1938).

A new method was developed for the preparation of p-phenylene-bis-diphenylarsine from diphenylchloroarsine and p-phenylene-di-magnesium-bromide. The Grignard-reagent was obtained from 0.49 g (20 mmol) magnesium powder and 2.36 g (10 mmol) 1,4-dibromobenzene as described by Sander (1962). 5.29 g (20 mmol) diphenylchloroarsine in 20 mL benzene were added to the Grignard suspension at room temperature within ~30 seconds whereupon the temperature rised and the solution became clear. Afterwards it was refluxed for 3 h and the resulting greenish solution was hydrolysed with some ice, acidified with hydrochloric acid and the organic layer was separated. The aqueous phase was extracted twice with benzene (2 x 20 mL) and the collected extracts were dried over sodium sulfate. The solvents were evaporated at 60 °C and the residue was recrystallized from 20 mL benzene/n-propanol-mixture (50:50). After a second recrystallization from 10 mL of this solvent 1.98 g (37 %) brilliant-white crystals were obtained (corrected melting point: 148-149 °C / literature: 150 °C).

1,3,5-Trinitronaphthalene and 1,4,5-trinitronaphthalene were synthesized as described by Ward et al. (1959), 1,3,8-trinitronaphthalene was obtained after the method of Hodgson et al. (1945). The purity of all synthesized compounds was controlled by HPLC (> 98 %) and the identity was proven by melting point and EI-MS. All other chemicals were obtained commercially.



Triphenylarsine (TPA) 9-Phenylarsafluorene (PAF)



Bis(diphenylarsine) oxide (BDAO) p-Phenylene-bis-diphenylarsine (PDPA)

Figure 1. Formulas of the investigated organoarsenicals.

RESULTS AND DISCUSSION

The recovery rates for the two digestion procedures are given in Table 1. Inorganic and aromatic arsenic was determined quantitatively by the photometric method after H_2SO_4/H_2O_2 digestion. Cacodylic acid, a possible environmental metabolite (Sadiq 1997), is not mineralized and cannot be detected this way. The analysis of copper and lead caused no difficulties.

Table 1. Recovery rates (R) after digestion with H_2SO_4/H_2O_2 (arsenicals) or aqua regia (copper and lead).

Reference compound	R (%)	RSD	N
Arsenic (V) elemental standard	100	1	8
Cacodylic acid	3	2	3
Phenylarsine oxide	100	2	3
Copper elemental standard	96	3	8
Lead elemental standard	101	1	4

RSD=relative standard deviation; N=number of replicates

Regarding the recovery of the organic compounds after acetone extraction in most cases 50-85 % were achieved (Table 2). Only triphenylarsine, 3-nitroaniline and 1,4,5-trinitronaphthalene have a poor recovery. BDAO was totally lost in the 20 mg kg^{-1} soil. LWA (1994) reported similar findings for BDAO in underivatized extracts and attributed it to hydrolysis of this compound. In our opinion the main reason should be a strong interaction of the more polar BDAO to the soil matrix. To verify this, a high concentration soil was prepared (1 g kg^{-1}) and extracted in the usual manner. A BDAO recovery of 64.3 % was achieved and it could be shown that BDAO was only discriminated at low concentration levels. Regarding the whole extraction process it should be mentioned that the same procedure carried out with a solvent mixture of acetonitrile/methanol (50:50) gave 5-20 % higher yields for the nitroaromatics and therefore is superior to the acetone method when explosives have to be determined. On the other hand the recovery of arsenicals was 6-39 % lower when this mixture was used.

Table 2. Retention times (T_r), limits of detection (LOD) and quantification (LOQ) for the HPLC-methods and recovery rates (R) of the organic compounds from the spiked soil samples.

Compound	T_r (min)	LOD (ng)	LOQ (ng)	R (%)	RSD
Bis(diphenylarsine) oxide	16.0	0.3	1.0	0.0 / 64.3	0.0 / 0.7
9-Phenylarsafluorene	47.9	0.3	0.9	55.9	1.0
Triphenylarsine	51.1	0.4	1.0	31.3	0.5
p-Phenylene-bis-diphenylarsine	77.2	0.3	0.8	67.8	4.8
2-Nitroaniline	30.2	0.1	0.4	72.5	1.2
3-Nitroaniline	21.2	0.2	0.5	25.8	0.4
1,2-Dinitrobenzene	36.8	0.5	1.5	82.4	1.2
1,3-Dinitrobenzene	35.7	0.2	0.6	78.1	0.9
1,3,5-Trinitrobenzene	23.6	0.1	0.4	57.1	1.4
2,4-Dinitrotoluene	56.8	0.4	1.2	84.1	1.3
2,4,6-Trinitrotoluene	39.6	0.3	0.8	59.5	0.5
2-Amino-4,6-dinitrotoluene	54.9	0.3	0.8	70.5	1.4
4-Amino-2,6-dinitrotoluene	52.3	0.2	0.4	61.8	1.0
1-Nitronaphthalene	80.6	0.4	1.0	85.3	0.6
1,3-Dinitronaphthalene	81.4	0.2	0.6	73.1	0.3
1,5-Dinitronaphthalene	74.7	0.3	0.8	84.9	1.6
1,8-Dinitronaphthalene	61.0	0.2	0.6	69.2	0.5
1,3,5-Trinitronaphthalene	73.3	0.3	0.9	68.4	4.0
1,3,8-Trinitronaphthalene	65.3	0.1	0.3	54.9	4.2
1,4,5-Trinitronaphthalene	59.5	0.1	0.4	46.5	0.6

The most important contaminant of the burning ground is arsenic. Four of these samples contained high levels of this element (~1.1-2.6 g kg^{-1}) which should be responsible for the damaged vegetation. Organoarsenicals could only be found in these soils, the dominant compounds were triphenylarsine and 9-phenylarsafluorene (HPLC-results, Table 3). Both compounds are formed together with other tertiary arsines, e.g. p-phenylene-bis-diphenylarsine, during the pyrolysis of aromatic arsenical warfare agents like Clark or Pfiffikus. BDAO, the hydrolysis product of Clark, plays only a minor role as a pollutant at this site. Due to hydrolysis of Clark 1 and 2 in the aqueous mobile phase of the HPLC system it is not possible to differentiate between BDAO and Clark if HPLC is used for the analysis. For this reason Clark 1 and 2, bis(2-chloroethyl) sulfide (sulfur mustard) and some related compounds (1,3-dithiane, 1,4-dithiane, 1,4-oxathiane) were determined additionally by GC/MS, however no traces of these compounds could be found in any of the soil samples (Bausinger 2000).

Table 3. Amounts of total arsenic, copper, lead and organoarsenicals found in the Belgian soil samples (mg kg^{-1}).

Sample ID	Location	As	Cu	Pb	BDAO	PAF	TPA	PDPA
1	bg	13	27	61	< 0.10	< 0.10	< 0.10	< 0.10
2	dl	22	246	202	< 0.10	< 0.10	< 0.10	< 0.10
3	dl	9	27	258	< 0.10	< 0.10	< 0.10	< 0.10
4	dl	18	65	1359	< 0.10	< 0.10	< 0.10	< 0.10
5	dl	5	30	64	< 0.10	< 0.10	< 0.10	< 0.10
6	bg	1659	74	615	< 0.10	2.88	8.61	0.32
7	dl	7	18	34	< 0.10	< 0.10	< 0.10	< 0.10
8	dl	7	17	25	< 0.10	< 0.10	< 0.10	< 0.10
9	dl	10	24	24	< 0.10	< 0.10	< 0.10	< 0.10
10	dl	6	27	50	< 0.10	< 0.10	< 0.10	< 0.10
11	dl	5	26	69	< 0.10	< 0.10	< 0.10	< 0.10
12	dl	5	15	140	< 0.10	< 0.10	< 0.10	< 0.10
13	dl	13	24	49	< 0.10	< 0.10	< 0.10	< 0.10
14	dl	19	56	1451	< 0.10	< 0.10	< 0.10	< 0.10
15	dl	49	156	4331	< 0.10	< 0.10	< 0.10	< 0.10
16	bg	30	29	81	< 0.10	< 0.10	< 0.10	< 0.10
17	bg	2595	116	1284	1.42	3.67	12.20	0.73
18	bg	2193	82	643	< 0.10	3.00	7.90	0.83
19	bg	1120	369	945	1.50	2.92	39.97	0.41
20	bg	13	32	83	< 0.10	< 0.10	< 0.10	< 0.10

bg=burning ground; dl=delaboration area; BDAO, PAF, TPA, PDPA see Figure 1

Some soils contain high concentrations of lead and elevated amounts of copper. Both elements were used in small arms ammunition, shrapnel balls, brass cases, driving bands etc. Sometimes artillery shells, bullets or other metal fragments were found in the study area which is located at the former front. These remnants of war can be a source for arsenic and heavy metals.

The contamination by nitroaromatic explosives and metabolites was lower than expected. Only six samples contained small amounts of nitrobenzenes, nitronaphthalenes, nitrotoluenes and the corresponding reduced environmental metabolites. 1-Nitronaphthalene and 1,3-dinitronaphthalene could not be quantified because there were interferences with matrix components. The most important substances identified in the soil extracts were 1,3-dinitrobenzene, 1,5- and 1,8-dinitronaphthalene (Table 4). Other explosives which were used during the First World War, e.g. picric acid or 2,2′,4,4′,6,6′-hexanitrodiphenylamine, were not found in the soil samples.

Table 4. Concentrations of nitroaromatics detected in the Belgian soils (mg kg^{-1}).

	Sample ID					
Compound	**5**	**6**	**16**	**17**	**18**	**19**
2-Nitroaniline	< 0.10	0.20	< 0.10	0.37	IF	0.18
3-Nitroaniline	< 0.10	0.19	< 0.10	0.28	0.22	< 0.10
1,2-Dinitrobenzene	< 0.10	0.89	< 0.10	1.95	1.33	0.16
1,3-Dinitrobenzene	< 0.10	5.34	< 0.10	8.30	14.05	3.19
1,3,5-Trinitrobenzene	< 0.10	0.19	< 0.10	0.36	0.27	0.16
2,4-Dinitrotoluene	< 0.10	1.10	< 0.10	1.71	1.61	1.38
2,4,6-Trinitrotoluene	< 0.10	1.08	< 0.10	2.40	2.96	2.28
2-Amino-4,6-dinitrotoluene	< 0.10	0.38	< 0.10	0.92	0.54	0.48
4-Amino-2,6-dinitrotoluene	< 0.10	0.23	< 0.10	0.64	0.31	0.27
1-Nitronaphthalene	< 0.10	IF	< 0.10	IF	IF	IF
1,3-Dinitronaphthalene	< 0.10	IF	< 0.10	IF	IF	IF
1,5-Dinitronaphthalene	0.41	4.46	0.26	6.30	6.40	1.71
1,8-Dinitronaphthalene	0.21	4.82	0.12	7.44	6.45	3.43
1,3,5-Trinitronaphthalene	< 0.10	0.13	< 0.10	0.63	0.43	0.20
1,3,8-Trinitronaphthalene	0.14	0.56	< 0.10	3.31	2.22	0.68
1,4,5-Trinitronaphthalene	< 0.10	0.14	< 0.10	0.88	0.53	0.14

IF=chromatographic interference

Finally the following conclusions can be drawn from our study: There are abandoned delaboration sites around the former World War 1 front in Belgium and also in France which can be contaminated by arsenic, heavy metals, explosives and chemical warfare related compounds or other toxic substances. Until now the environmental science does not pay any attention to this question. The most important contaminants found during this investigation were arsenic and lead. Organic compounds were detected only in minor concentrations at certain hot spots which clearly demarcate from the (almost) unpolluted surrounding area. Chemical warfare agents were not found in any soil sample. The open burning out of arsenical gas shells produced mainly inorganic arsenic but also minor amounts of tertiary arsines, the most important being triphenylarsine and 9-phenylarsafluorene. It is advisable to use such areas not for agriculture. Further investigations of the whole subject are necessary.

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