



Heavy metals and organic pollutants in ammunition paints – a source of contaminants from disposed explosive ordnance

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Abstract

Background/aim: Paint components can contain various organic and inorganic substances that are harmful to human health and the environment. This can also be the case for ammunition paints. Therefore, improperly stored or abandoned ammunition can become a source of contamination. **Methods:** The presence of heavy metals, asbestos, polychlorinated biphenyls (PCB) and chlorinated paraffins was investigated in ammunition objects from different time periods. **Results:** No asbestos and only little chlorinated paraffins were found. 2 of 21 samples contained elevated PCB-concentrations >150 mg/kg. Most prominent metals found were Pb, Cr, Zn, Ba and Ti, reaching values of over 89 g/kg, 25 g/kg, 230 g/kg, 87 g/kg and 190 g/kg, respectively. The presence of PCBs and heavy metals can be historically explained with their prevalence in the paint industry and correlated to bans and the use of alternative products. Some concentrations were found to be high enough to raise concerns in terms of health effects and restrictions for disposal. Example calculations were done to evaluate the role of contaminants originating from paints. For this purpose, an actual ongoing ordnance remediation project in Switzerland was used and calculations were made for Pb, Zn, Ba and Cr. For these four elements, potential contamination proportions originating from paint were estimated to account for 0.06%, 0.4%, 40% and even 100%, respectively. **Conclusion:** Paint contaminants can play an important role in the overall material budget and should be accounted for during future ordnance-caused remediation projects.

1. Introduction

Remediation projects dealing with old ammunition need to consider a large spectrum of compounds originating from the explosives, such as organics, most prominently, TNT, and heavy metals, e.g., from primary explosives or luminescent substances [1]. But other ammunition components, such as paints, might pose a health risk as well but are not often considered.

Various potentially harmful substances were and are still used in paint components, such as pigments, plasticizers, fire retardants or other additives. In Switzerland, the disposal of painted mineral and metallic wastes is regulated to prevent the influx of polychlorinated biphenyls (PCB), heavy metals and in some rare cases also asbestos into the recycling, incineration or landfills [2, 3].

Due to reapplication/renewal of paints, older layers can be covered by new ones so that a stratigraphy forms with typical pigments and additives of that specific time. Investigation of such layers can be used to answer archeological

questions or for reconstruction purposes [4]. However, regarding remediation, such layering means that also newer appearing objects might carry older layers underneath with the respective contaminants of that time. The following substances are known to be present in various paint components:

- ★ **Asbestos.** Because of its thixotropic and flame-resistant properties, asbestos was mixed into paints and coatings. Earliest use of asbestos in colours comes from Cyprus in the year 1183 [5]. In more recent times, asbestos was used in coatings for wood and steel often in combination with lead oxide [6].
- ★ **PCB.** In Switzerland, for example, PCB were used from about 1946. Up to their ban in 1972 (some imports and limited uses till 1975 or 1986) they were added to various components including paints, where there mainly had a plasticizing role [3, 7]. The concentrations in paints can vary depending on date and application

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and can reach in extreme cases up to 50 g/kg or more. In the archived military documentation [8], no data specifically on PCB in military paints could be found. However, in the technical documentation on the Swiss military equipment from 1954, a reference to “Resista-Chlorkautschukemaille” (refers to a chlorinated metal varnish) can be found. Such additives were often used in paints and had up to 100 g/kg PCB [9].

★ **Chlorinated paraffins (CP).** In parallel to PCB and even more after their ban, CP were used for similar purposes [10]. Especially the short-chain CP (C10-C13) express high mobility and toxicity. Their use was later regulated, for example in Switzerland in 2018, which is not the case for other CP, the middle-chain (C14-C17) and long-chain (C18-30) ones [11]. Chlorinated paraffins can often be found in paint with concentrations reaching up to 50 g/kg [12].

★ **Heavy metals.** Many pigments have been made over hundreds of years of metal compounds, such as Pb oxide, various chromates, CdS or HgS [13, 14]. While some are now regulated, like Pb, others can still be found to this day (Ti). Some metals have not only a colour-giving property but are also used for corrosion resistance or as anti-fouling agents (Pb, Cu). In the Swiss military, historically various metal-based pigments are documented (Table 1).

★ **Per- and polyfluoroalkyl substances (PFAS).** Produced first in 1940s PFAS are also used as emulsifiers, dispersants, wetting agents or corrosion protectors [15]. Since perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) were regulated or banned, the short-chained (C4-C6) and long-chained (C9-C14) PFAS became widely used [16]. In paints, specific PFAS are used: PVDF, PTFE, FEVE, ECTFE, FEP.

Some of the above-mentioned contaminants can be expected to be present in ammunition paints. Improper storage, handling or disposal could lead to their release into the environment. A known example in Switzerland, although not related to ammunition but steel, was the improper handling of coated steel components which lead to the release of PCB into the river Birs, which flows through four cantons and enters the river Rhein [17].

A more relevant example is the intentional dumping of ammunition in Swiss lakes or the use of lakes for military target practice with planes and artillery [18]. Here, the released contaminants from paints are difficult to quantify, however some release is ongoing due to aerobic and anaerobic interactions in the lake sediments.

Another Swiss example, related to an accident that happened in the Mitholz underground ammunition storage facility will be used to estimate the pollution potential from ammunition paints. In Mitholz (Kanton Bern, Switzerland), during WWII, an underground storage facility was constructed. 1947 about seven explosions (some reaching 10 t and 30 t of TNT) caused its partial destruction, the collapse of the rock wall above and the death of 9 people [19, 20]. At the time of the accident, approximately 7,000 t of ammunition was stored of which about 3,500 t are estimated to remain inside the mountain and in the immediate

vicinity. 2020 an expert group concluded that only a cleanup with the removal of buried ammunition would sustainably reduce any explosive or contamination risks. 2023, the parliament accepted the cleanup enterprise, which is now in its planning stage and is supposed to be accomplished by 2045.

With this work, we attempted to make first estimates about the pollution potential originating from ammunition paints with a focus on PCB, CP, heavy metals and asbestos.

Table 1. Mentioned inorganic pigments in the Swiss military documentation.

Pigment	Formulas	Colour	Year of document(s)
Lead red / men-nige/minium	Pb ₃ O ₄ , PbO	Orange	1940
Zink white	ZnO (Pb as contaminant)	White	1940
Titan white	TiO ₂	White	1946
Lead white	PbCO ₃	White	1959
Zink green	ZnCrO ₄	Green	1940, 1947, 1958
Chrome yellow	PbCrO ₄	Yellow	1940, 1963
Anti-corrosion paint	Pb	Reddish brown / deep black	1944, 1945
Field grey	ZnO, ZnCrO ₄ , traces of Fe and Mn	Grey	1945, 1947
Opaque white lithopone	ZnS, ZnO, BaSO ₄	White	1959, 1963
Olive green	Not declared; without Pb and Cr	Olive green	1982, 1998

2. Materials and Methods

To obtain an overview of the presence of asbestos, heavy metals, PCBs and chloroparaffins in ammunition paints, 21 paints from 14 ammunition objects of different calibers and ages were analyzed. These pieces were provided from collections of the explosive ordnance disposal group of the Swiss armed forces (Kdo KAMIR) and the armasuisse WTE group (Table 2, Figure 1). Paint layers were removed with a utility knife down to the ammunition body surface (steel, plastic, aluminum) and the blade was cleaned with alcohol after extraction of each sample. Where possible, an area of 100 cm² was stripped from paint. The removed samples were collected in clean aluminum foil and then transferred into polypropylene or polycarbonate sample tubes for analysis.

Asbestos analysis was performed on 14 samples (objects 1-8 and 11) by scanning electron microscopy according to the norm ISO 22262-1 by a commercial laboratory (Analysis Lab SA, Biel, Switzerland). The other parameters were analyzed by a commercial laboratory (Bachema AG, Schlieren, Switzerland). Here the samples were finely ground in a ball mill to a particle size of <0.1

mm. The powder was transferred into a cuvette, covered with a Mylar foil and measured by energy-dispersive X-ray fluorescence under atmospheric conditions. Calibration was performed with a fundamental parameter method, supplemented with the use of various certified reference materials.

The powder was further used for extraction with acetone/cyclohexane (1:1) in an ultrasonic bath. PCB was then measured using a GC-MS/MS. A procedure according to the Swiss regulations was used to deduct the total PCB concentration. The typical 6 PCB-congeners 28, 52, 101, 138, 153 and 180 were analyzed and their sum was multiplied by 4.3 to extrapolate to the total PCB concentration according to Swiss governmental guidelines [2]. Another aliquot of the chemical extract was diluted and transferred into an Atmospheric Pressure Chemical Ionization (APCI) chamber without a chromatographic column and measured by LC-HRMS (QTOF) in a full scan mode. The individual congener groups in the chain length range from C10 to C27 with chlorination degrees between 30% and 70% were identified based on the exact masses of the respective $[M+Cl]^-$ adducts, which are formed during ionization in the APCI source by adding dichloromethane to the eluents. Quantification was performed by external calibration.

3. Results and Discussion

3.1. Contaminants found in the analyzed paints

No paint sample showed presence of asbestos. This was not very surprising because of the nature of the ammunition paints. The addition of asbestos in paints that were sometimes used on girders or tanks [6] lead to rough-textured paints (green or grey), properties, which are usually not favored for ammunition.

Chlorinated paraffins were found in grey paints from 1944 (likely from the newer top layer from revision in 1965) to 1983 and in newer paint from 1990 (Figure 2). However, the concentrations were very low (<10 g/kg), making them irrelevant in the view of the legislation for wastes in Switzerland (Table 3). Short-chained and middle-chained CP were found near the detection limit on the objects 1 (grey and yellow), 4 (blue) and 6 (yellow), however the values were much lower than the legal limit of 0.15% for the short-chained CP.

PCB mass fractions were generally low (<20 mg/kg). In terms of disposal, no specific decontamination measures for painted surfaces are necessary in Switzerland at concentrations <50 mg/kg [3]. High concentrations were found in the grey colour of object 6 (7.5cm PaG) and the black colour of object 8 (81mm Oe Rak) with 170 mg/kg and 150 mg/kg respectively (Table 3). Here, the composition of the PCB congeners suggested the products Aroclor 1260 or Clophen A60 for the grey colour. PCB in such paints can convert to polychlorinated dibenzodioxines and dibenzofuranes (dioxins) when exposed to temperatures >250 °C [3]. Therefore, the presence of PCB in the paints can even be relevant during ammunition use (firing) and troops may get exposed to dioxin vapors.

Table 2. Sampled ammunition objects (by production year). Paint samples analyzed for asbestos are marked with “*”. For all of them, the result was negative.

Object Nr.	Caliber	Type	Designation CH	Production / revisions	Colour
1	15cm	Artillery shell	StG	1944 / 1965	Grey* Yellow*
2	10.5cm	Artillery shell	Kan u Hb Nb G	1956	White*
3	10.5cm	Artillery shell	Kan u Hb Bel G	1970	Grey* Red*
4	3.5cm	Anti-air shell	Flab Kan U	1977	Blue*
5	8.1cm	Mortar round	WM	1943	Grey* Yellow*
6	7.5cm	Artillery shell	PaG	1955	Grey* Yellow*
7	-	Bomb	UeB 4kg	1990	Black*
8	8.1cm	Rocket	Oe (SNORA) Rak	1968	Grey* Black*
9	8.1cm	Mortar round	WG	1945 / 1969 / 1981 / 2004	Grey Yellow
10	-	Explosive pipe charge	SprR	1954	Grey
11	15.5cm	Artillery shell	Hb 66 Bel G	1975	Green*
12	15.5cm	Artillery shell	Hb 66	1983	Grey Yellow
13	8.1cm	Mortar round	WG Bel G	1987	Grey
14	15.5cm	Artillery shell	Hb 66 Bel G	1992	Green

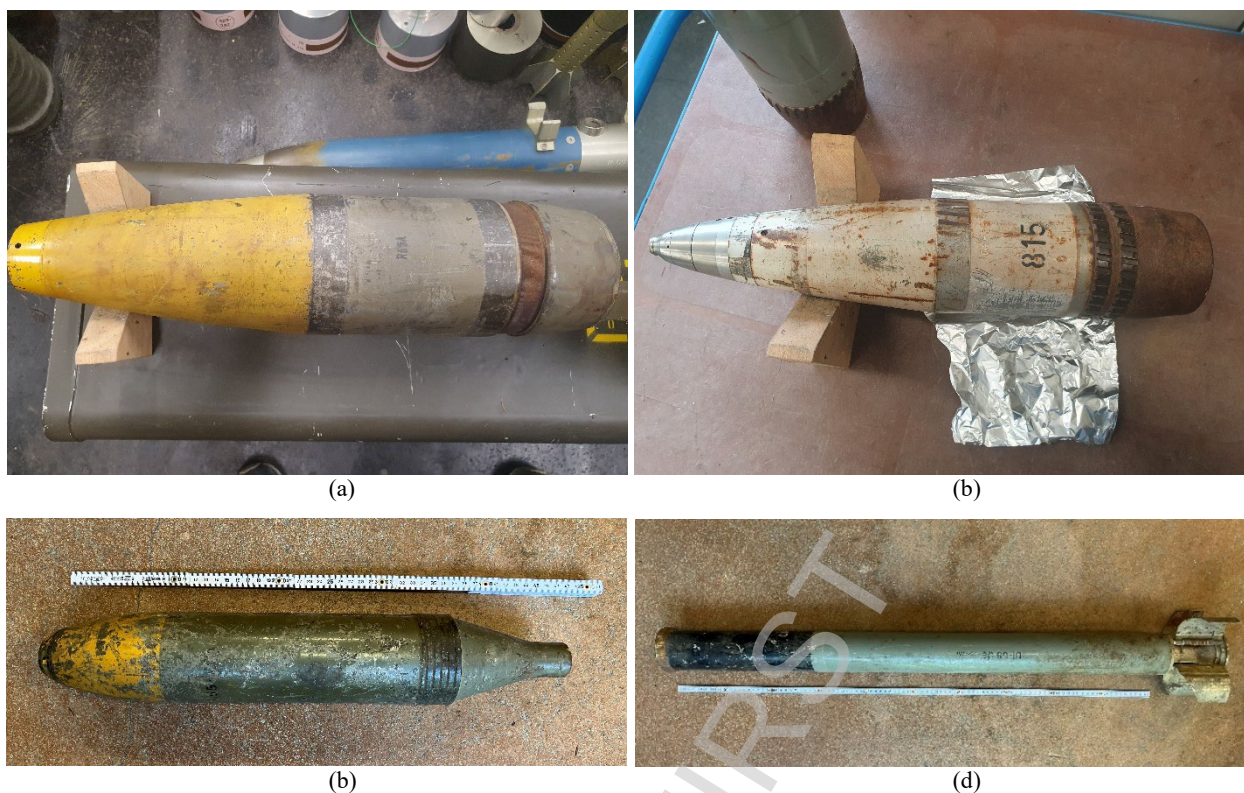


Figure 1. Examples of sampled ammunition. (a) 15cm artillery shell from 1944 (object nr. 1). (b) 10.5cm artillery shell from 1956 (object nr. 2). (c) 8.1cm mortar round ("Wurfmine") from 1943 (object nr. 5). (d) 8.1cm Oerlikon rocket from 1968 (object nr. 8).

Table 3. Results for PCB and CP in 21 sampled paints. The „Total“ for PCB was calculated according to the Swiss regulation with a multiplication factor of 4.3 [2]. The 6 considered congeners are: 28 (2,4,4'-Trichlorbiphenyl), 52 (2,2',5,5'-Tetrachlorbiphenyl), 101 (2,2',4,5,5'-Pentachlorbiphenyl), 138 (2,2',3,4,4',5'-Hexachlorbiphenyl), 153 (2,2',4,4',5,5'-Hexachlorbiphenyl), and 180 (2,2',3,4,4',5,5'-Heptachlorbiphenyl).

Object, colour	PCB (mg/kg)		CP (g/kg)			
	Sum of 6 congeners	Total	C10-13	C14-17	C18-27	Sum
1, grey	1.8	7.7	0.3	0.04	0.07	0.41
1, yellow	2.6	11	0.2	<0.02	0.03	0.23
2, white	2.4	10	<0.02	<0.02	0.03	<0.05
3, grey	0.9	3.9	<0.02	<0.02	0.04	<0.05
3, red	<0.2	-	<0.02	<0.02	<0.02	<0.05
4, blue	3.8	16	0.02	0.03	0.04	0.09
5, grey	0.8	3.4	<0.02	<0.02	<0.02	<0.05
5, yellow	2.9	13	<0.02	<0.02	<0.02	<0.05
6, grey	40	170	<0.02	<0.02	<0.02	<0.05
6, yellow	2.5	11	0.02	<0.02	0.04	0.06
7, black	<0.2	-	<0.02	0.12	0.07	0.19
8, grey	3.2	14	<0.02	0.03	0.23	0.26
8, black	34	150	<0.02	<0.02	<0.02	<0.05
9, grey	0.8	3.4	<0.02	<0.02	0.08	0.08
9, yellow	<0.2	-	<0.02	<0.02	0.05	0.05
10, grey	3.3	14	<0.02	<0.02	<0.02	<0.05
11, green	3.0	13	<0.02	<0.02	<0.02	<0.05
12, grey	0.6	2.6	<0.02	<0.02	0.06	0.06
12, yellow	<0.2	-	<0.02	<0.02	0.05	0.05
13, grey	<0.2	-	<0.02	<0.02	0.02	<0.05
14, green	1.9	8.2	<0.02	<0.02	<0.02	<0.05

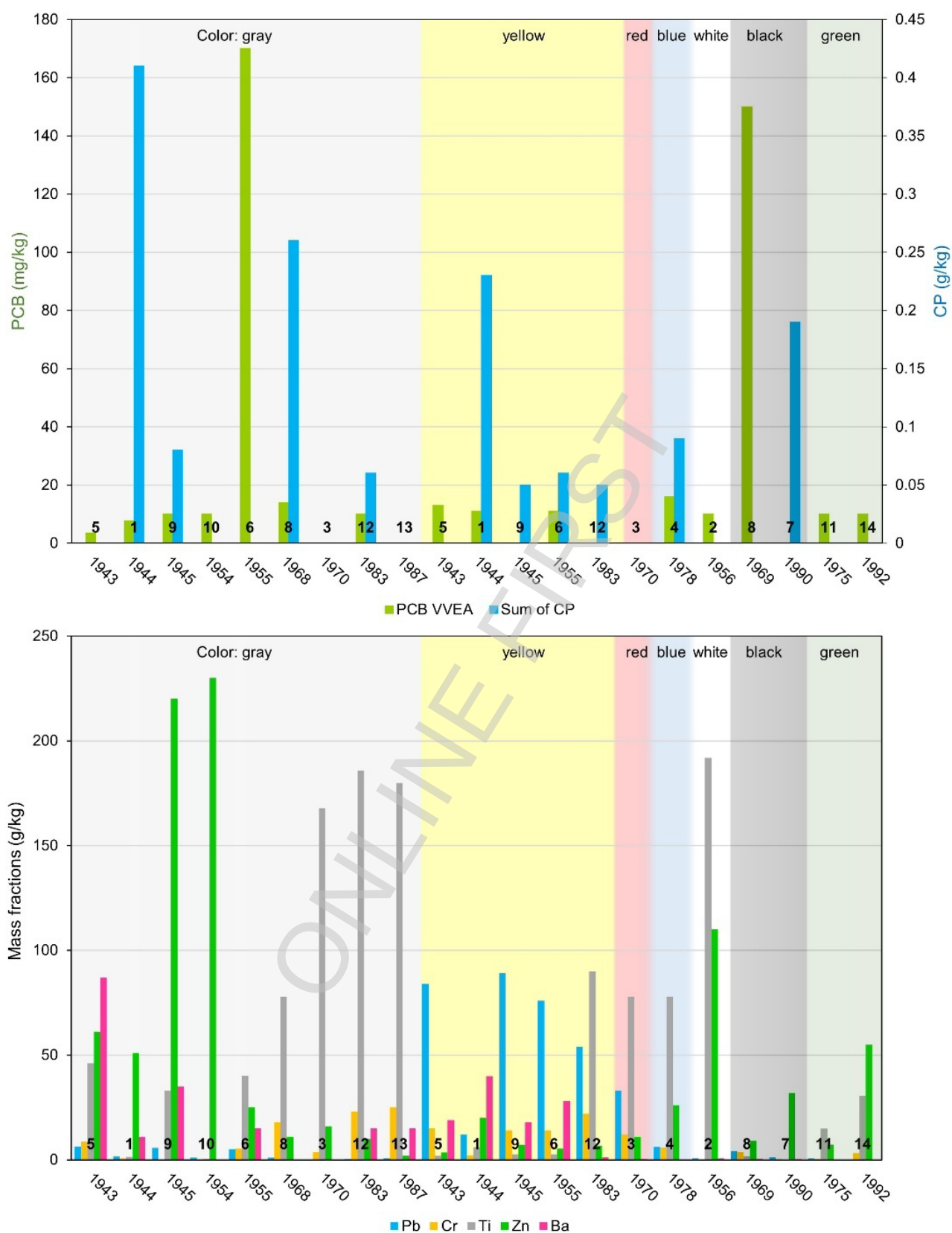


Figure 2. Mass fractions of contaminants in paints sorted by colour and production date. The object number is listed along the x-axis. Top: PCB and CP. Bottom: Pb, Cr, Ti, Zn and Ba.

We can also calculate the amount of PCB in the steel scrap [3], a procedure, which is required in Switzerland for disposal of steel contaminated with PCB. For this, an estimation formula below can be used:

$$\begin{aligned} & \text{PCB in steel} \left(\frac{\text{g}}{\text{t}} \right) \\ &= \text{PCB in paint} \left(\frac{\text{mg}}{\text{kg}} \right) \\ & \quad \frac{\text{Density of paint} \left(\frac{\text{kg}}{\text{m}^3} \right) * \text{Thickness of paint (m)}}{\text{Density steel} \left(\frac{\text{kg}}{\text{m}^3} \right) * \text{Thickness of steel (m)}} \end{aligned}$$

The density of steel and paint is estimated to be 7,850 kg/m³ and 1,400 kg/m³, respectively, and the average thickness of steel and paint 15 mm and 0.25 mm, respectively. The result is a PCB concentration of 5 g/t of steel, which is higher than the legal limit of 2 g/t. Therefore, such steel should not be directly disposed of regularly, e.g., in a smelting plant. Instead, the paint should be removed prior to recycling.

Four of the seven objects built after 1972 (date of PCB ban) still contained PCB in lower amounts. This could potentially originate from the use of leftover paint stocks or through indirect contamination from PCB vapors during storage, which could happen, if high PCB air-concentrations exist [21]. Such air contamination could originate from construction materials in the storage facilities, such as PCB-containing joint sealants and floor paints.

The most prominent heavy metals found were Pb, Cr, Zn, Ba and Ti (Table 4). Pb was detected in older ammunition but also in newer types with concentrations reaching >89 g/kg, especially in red paint. Likely it was present in such pigments like chrome yellow (PbCrO₄ and PbCrO₄·PbSO₄) and red lead or “minium” (Pb₃O₄) [22, 23]. Only in 2003, the members of the Association of Swiss Paint and Varnish Manufacturers (VSLF) volunteered to renounce the use of Pb in paints and coatings [24]. In 2005 a new regulation was released (“Chemikalien Risikoreduktions-Verordnung”), which limited the use of Pb. According to technical documents, the military appears to have turned away from Pb- and Cr-rich paints approximately around 1982 (Table 1). The technical documents further list various pigments such as chrome yellow and lead white/minium in 1940 and lead white in 1959.

In the grey colour, the transition from Zn to Ti and their co-existence can be seen (Figure 2). Important pigments were lithopone with ZnS and BaSO₄, its substitute zinc white ZnO and since 1950 widely used titan white TiO₂ [25-29].

Some heavy metal spikes can also be explained with pigments. For example for Sb (object 12, yellow) with >530 mg/kg: Naples yellow Pb₃(SbO₄)₂ or Pb(SbO₃)₂ [30, 31]; for Cd (object 8, black colour) with >130 g/kg: cadmium red CdS [32].

It is important to mention here that the original colouration was often renewed during revisions, and this is why the results do not always represent the original state of the heavy metal mass fractions. Furthermore, some of the detected elements could originate from the steel surface itself and were sampled together with paint by the applied method. According to technical documentation from 1968, this could concern metals like Mn, Cu, Ni, Cr, Al.

3.2. Example calculations: Mitholz underground ammunition depot

To demonstrate, which pollution potential could be contributed by ammunition paints, we can take a closer look at the ongoing remediation project in the village of Mitholz in Switzerland. Sampling done on recovered ammunition showed that under the corrosion layer some coloured layers can be found, which indicate the presence of minerals formed from Pb (Figure 3).

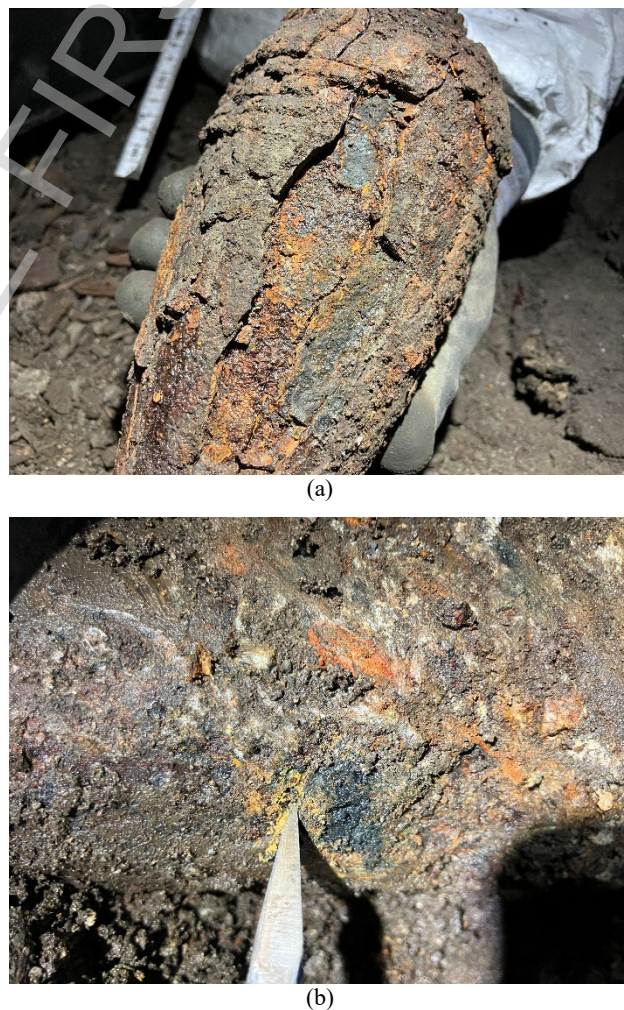


Figure 3. Examples of ammunition surface states seen in Mitholz. (a) 8.1cm mortar round with an 8 mm thick corrosion layer. (b) Surface of a 7.5cm artillery shell with yellow and black layers underneath the corrosion indicating paint remains.

Table 4. Heavy metal mass fraction summary for 21 paint samples determined by XRF. All values in mg/kg. Values below detection are marked with a „<“. Values above the calibrated range marked with a „>“. In this case the value is a good estimate. Values for As (<0.40-24 mg/kg), Co (<3.0->320 mg/kg), Ni (<0.50-220 mg/kg), Sn (<0.50-240 mg/kg) and Cu (<2.2-870 mg/kg) not shown. A comma („“,“) is used as thousands separator.

Object, colour	Sb	As	Pb	Cd	Cr	Co	Cu	Ni
1, grey	2.4	<0.40	>1,500	22	640	<18	300	30
1, yellow	<0.50	<0.40	>12,000	0.3	2,100	<3.0	290	24
2, white	34	12	>770	14	92	>180	230	200
3, grey	11	15	190	1	3,700	46	230	89
3, red	>230	<0.40	>33,000	<0.30	12,000	>170	55	5.1
4, blue	23	2.3	>6,200	1	5,900	>120	870	140
5, grey	<0.50	<0.40	>6,300	30	8,700	>220	160	49
5, yellow	<0.50	16	>84,000	5.6	15,000	<3.0	140	26
6, grey	2.6	5.3	>5,100	16	5,300	>320	260	96
6, yellow	<0.50	<0.40	>76,000	>1,200	14,000	>110	210	70
7, black	5.1	<0.40	>1,300	17	320	>110	96	46
8, grey	>62	12	>1,000	>490	18,000	48	130	58
8, black	<0.50	6.1	>4,000	>130,000	3,800	<22	41	50
9, grey	3.3	<0.40	>5,700	>96	220	>300	26	110
9, yellow	10	<0.40	>89,000	<0.30	14,000	>220	45	<0.50
10, grey	1.8	<0.40	>990	43	55	>310	<2.2	72
11, green	8.7	<0.40	>730	0.9	430	46	100	110
12 grey	6	<0.40	310	<0.30	23,000	30	260	84
12, yellow	>530	<0.40	>54,000	0.7	22,000	>280	130	53
13, grey	56	21	>770	<0.30	>25,000	28	410	170
14, green	13	24	240	0.5	3,200	>240	250	220

Table 4 (continued)

Object, colour	Hg	Zn	Sn	Ba	Se	Sr	S	Ti
1, grey	5.1	>51,000	33	>11,000	<0.20	460	9,300	1,400
1, yellow	6.1	>20,000	31	>40,000	3	600	11,000	6,000
2, white	<1.3	>110,000	48	700	<0.20	31	1,700	>190,000
3, grey	<1.5	>16,000	9.1	190	<0.20	12	740	>170,000
3, red	4.8	>11,000	7.4	360	>21	6.7	<20	>78,000
4, blue	6.4	>26,000	4.3	110	<0.20	9.1	1,800	>78,000
5, grey	<1.8	>61,000	<0.50	>87,000	<0.20	>2,800	>40,000	46,000
5, yellow	>55	>3,600	<0.50	>19,000	>70	310	8,200	1,900
6, grey	>12	>25,000	18	>15,000	7.6	380	16,000	40,000
6, yellow	>43	>5,300	33	>28,000	>260	1,300	16,000	2,600
7, black	2.9	>32,000	4.9	310	<0.20	36	1,100	180
8, grey	2.5	>11,000	5.7	130	<0.60	18	6,700	>78,000
8, black	>10	>9,000	240	520	3.4	17	9,200	1,800
9, grey	<0.70	>220,000	40	>35,000	<0.20	740	6,600	33,000
9, yellow	<0.70	>7,000	32	>18,000	>51	440	5,800	2,700
10, grey	<5.7	>230,000	<0.50	37	<0.20	13	750	380
11, green	<0.70	>7,200	<2.9	58	<0.20	9.8	1,500	15,000
12, grey	<0.70	>9,900	42	>15,000	<0.20	580	11,000	>190,000
12, yellow	>25	>6,700	5	1,200	>30	74	7,100	>90,000
13, grey	<0.70	>2,000	54	>15,000	<0.10	380	15,000	>180,000
14, green	<0.70	>55,000	55	120	<0.20	12	940	31,000

The stored ammunition list was worked up from historic documents [33] as a planning and safety assessment instrument. Luckily, the inventory was meticulously documented and archived

[19], so the stock from 1947 was known. The list was further supplemented by ammunition details and composition from technical documents, listing 94 individual ammunition articles [34]. This allowed to

estimate the pollution potential from the ammunition. Here, the focus was made only on heavy metals relevant to the analyzed paints described above, i.e. Pb, Cr, Zn, Ba.

With the available technical details, 3D models of each ammunition piece (see example in Figure 4) were prepared using the Measure tool in the SOLIDWORKS software package for teaching and identification purposes and using these models, surface areas of each painted piece were calculated.

Based on historic images, the painted areas (proportions) and their colours were determined and so the main pigments were determined based on the analyses described above. With the available information it was determined that 61 of 94 ammunition articles had relevant amounts of paint and were further considered for calculations. For these articles the mass fractions of metals in paints was estimated by considering the measured mass fractions in sampled objects with a production date close to the Mitholz incident. This included the objects 1, 5 and 9 (for the grey and yellow colours) and object 2 for the white colour.

Besides paints, sources of Pb in Mitholz are Pb azide, Pb dioxide and minium from priming charges and Pb materials in small caliber rounds and in detonators [33, 34]. Zinc is found in brass (in the Swiss case 28% Zn) and in luminescent fillings. Barium was used in priming charges such as Ba carbonate and Ba nitrate. For Cr, no other sources than paints could be determined so far based on technical ammunition data. Further, the following assumptions were made:

- ★ For surface areas the surfaces of the objects as usually found in the debris of Mitholz were used, i.e., for mortar rounds and bombs the wing surface was not included (usually aluminum or steel without paint).
- ★ Estimated an average paint density of 1.2 g/cm³ and an average thickness of 0.25 mm [35]

- ★ Where available, the paint composition for the corresponding ammunition type was taken, otherwise, the composition from object 1 and 2 was used for shells and the composition of object 9 was used for mortar rounds, hand grenades and bombs.

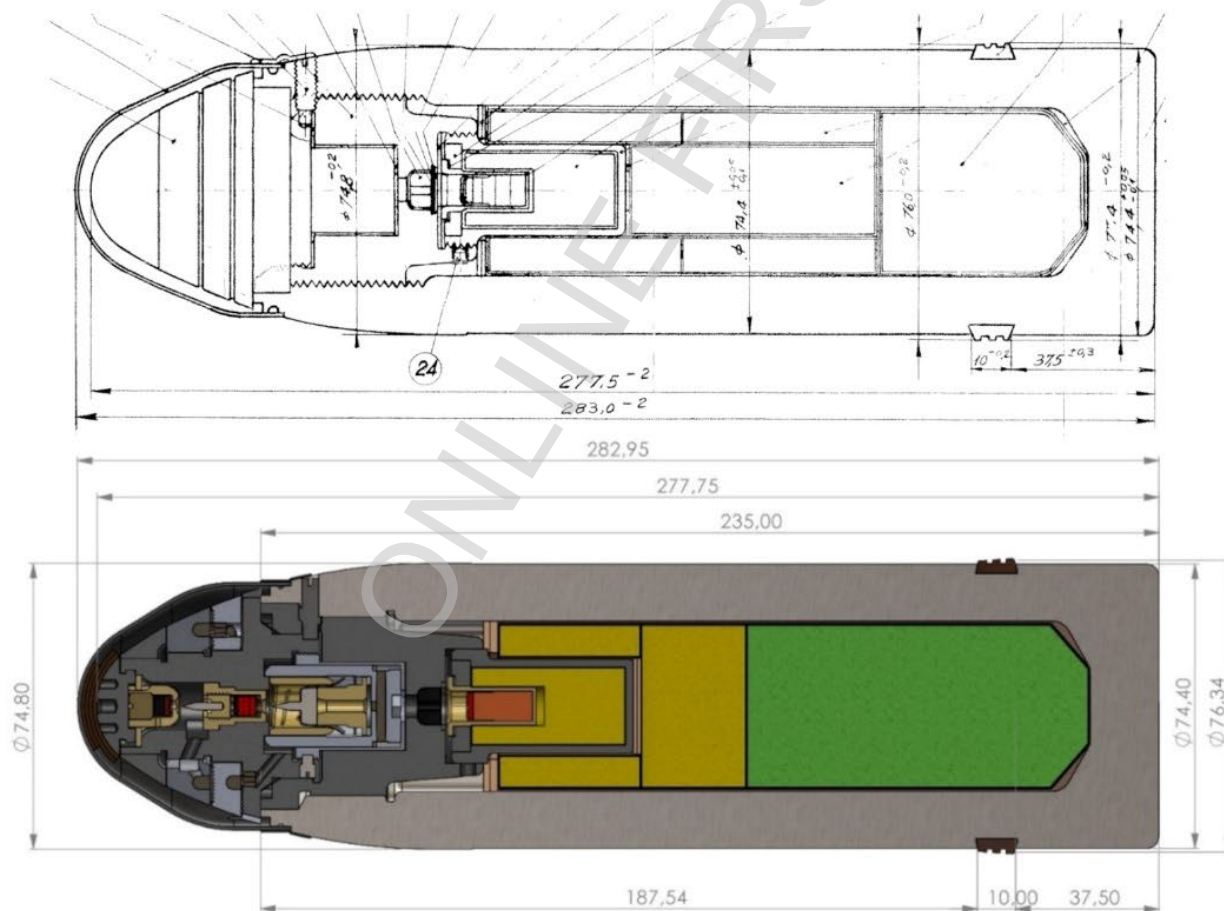
With this, the amounts of Pb, Zn, Ba and Cr were calculated (Table 5). It should be noted that the numbers in Table 5 are referring to the contamination potential. During the accident and through the input of heat, many of the contaminants were already released and later partially leached into the surrounding rock and soil. Part of the contaminated material and still intact ammunition was then removed during initial remediation activities in 1948 [36]. To this day, roughly 50% of this calculated potential is estimated to still be present within or in the immediate proximity of the former and partially collapsed Mitholz ammunition depot.

With this example it becomes clear that heavy metals in paint can play an important role. While the proportions of paint-originating Pb and Zn are rather low (0.06% and 0.4%, respectively) given the large quantities of Pb and Zn from the ammunition body materials, e.g. bullets and casings, for Ba and Cr, paints are likely to be the primary sources. Looking at the absolute numbers, the quantities originating from paint are impressive. In Mitholz we are potentially dealing with about 0.2 t of Pb, 1.4 t of Zn and 0.5 t of Ba from paints. For Cr, the amount is rather low, with about 40 kg.

These paint-bound contaminants can be released when in contact with water. For example, Pb and Zn from anti-corrosion are known to end up the highly mobile and bioavailable phases [37]. However, the water in the collapsed caverns is rather basic given the surrounding limestone rock and the fact that the former paint layers are covered or embedded in corrosion products can have a dampening effect on metal release due to the limit of diffusion of oxygen and moisture [38].

Table 5. Estimated pollution potential in Mitholz originating from ammunition paints for Pb, Zn, Ba and Cr. The column "others" includes detonators, small caliber rounds (≤ 7.5 mm), mines and various ammunition (e.g., ignition screws). Medium calibers 2-4.7 cm. Large calibers 7.5-15 cm. All numbers rounded to three significant digits. „n.p.“ = not painted.

Ammunition type	Medium caliber	Large caliber	Hand grenades	Bombs	Others	Total
Stock (number of pieces)	1.57 Mio.	630,000	176,000	25,500	66.1 Mio.	68.5 Mio.
Total area of paint [m ²]	14,300	45,000	3,340	4,420	n.p.	68,700
Total weight of paint [kg]	4,300	13,500	1,000	1,330	n.p.	20,600
Average proportions yellow/grey/white [%]	25/36/7	19/38/27	28/60/0	21/80/0	n.p.	-
Total Pb [kg]	219	3,490	136	38.8	344,000	347,000
Pb from paint [kg]	17.5	140	14.7	31.4	-	203
Pb from paint [% of Pb _{tot}]	7.97	4.00	10.8	81.1	-	0.0585
Total Zn [kg]	56,500	32,500	257	257	247,000	336,000
Zn from paint [kg]	112	944	70.1	231	-	1,360
Zn from paint [% of Zn _{tot}]	0.198%	2.90%	27.3%	89.7%	-	0.403
Total Ba [kg]	95.6	353	13.6	41.5	697	1,200
Ba from paint [kg]	68.0	351	13.6	41.5	-	475
Ba from paint [% of Ba _{tot}]	71.1%	99.4%	100%	100%	-	39.5
Cr from paint [kg]	3.67	29.9	2.10	4.24	-	40.0
Cr from paint [% of Cr _{tot}]	100	100	100	100	-	100



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4. Conclusion

Analysis of 21 samples indicated the presence of various heavy metals, PCB and CP. In some samples PCB, Pb, Cr, Zn and Ba, concentrations were high enough to raise concerns in terms of possible health effects and restrictions for disposal/recycling.

Example calculations with an actual ongoing remediation case in Switzerland and with a focus on heavy metals showed that paint contaminants can play an important role in the overall material budget.

It is also important to mention the limitations of XRF for metal analysis. This analytical method is recognized and accredited for regulatory work and is in Switzerland the major methodology applied during the decommissioning of shooting ranges or for the determination of contaminants in paints (during building renovations). While relatively inexpensive and fast, the results are rather semiquantitative and can show strong variations depending on the sample matrix. Future studies should consider using wet chemistry techniques even that the organic paint matrix might present difficulties during sample preparation.

More studies would be necessary to further determine important contaminants in ammunition paints, e.g., including PFAS. Also ammunition packaging could contain significant amounts of PCB, heavy metals and even wood preservatives, such as pentachlorophenol (PCP). For decommissioning projects dealing with ammunition, our recommendation is that paints should not be forgotten as a possible sources of contamination found in soils and water.

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Teški metali i organski zagađivači u bojama za municiju – izvor kontaminanata iz odbačene eksplozivne municije

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Apstrakt

Uvod/Cilj: Sastojci boja mogu sadržati razne organske i neorganske supstance koje su štetne po ljudsko zdravlje i životnu sredinu. To može biti slučaj i kod boja za municiju. Stoga nepravilno skladištena ili napuštena municija može postati izvor zagađenja. **Metode:** Istraživano je prisustvo teških metala, azbesta, polihlorisanih bifenala (PCB) i hlorisanih parafina u objektima municije iz različitih vremenskih perioda. **Rezultati:** Nije pronađen azbest, a uočena je samo mala količina hlorisanih parafina. U 2 od 21 uzorka utvrđene su povišene koncentracije PCB >150 mg/kg. Najzastupljeniji metali bili su olovo (Pb), hrom (Cr), cink (Zn), barijum (Ba) i titanijum (Ti), sa vrednostima preko 89 g/kg, 25 g/kg, 230 g/kg, 87 g/kg i 190 g/kg, respektivno. Prisustvo PCB i teških metala može se istorijski objasniti njihovom rasprostranjenošću u industriji boja i povezati sa zabranama i upotrebom alternativnih proizvoda. Neke koncentracije su bile dovoljno visoke da izazovu zabrinutost u pogledu zdravstvenih posledica i ograničenja u uklanjanju. Izvršene su primerne proračune kako bi se procenila uloga kontaminanata koji potiču iz boja. U tu svrhu korišćen je stvarni tekući projekat sanacije municije u Švajcarskoj, a proračuni su izvršeni za Pb, Zn, Ba i Cr. Za ova četiri elementa procenjeno je da potencijalni udeo kontaminacije koji potiče iz boja iznosi 0.06%, 0.4%, 40% pa čak i 100%, redom. **Zaključak:** Kontaminanti iz boja mogu igrati važnu ulogu u ukupnom materijalnom bilansu i treba ih uzeti u obzir tokom budućih projekata sanacije uzrokovanih municijom.

Originalni naučni rad

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Ključne reči:

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