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Secondary mineral phases of metallic lead in soils of shooting ranges from Örebro County, Sweden

Abstract In some countries Pb-containing shotgun pellets have become one of the sources of soil contamination in shooting range areas. Pb pellets from eight shooting ranges in central Sweden were mineralogically analysed and the results show that when the Pb pellets come into contact with soil, about 10% of them are decomposed and transformed into secondary lead minerals as encrustations. The encrustation consists of two concentric rims: a 50 to 150 μm wide outer rim of hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) and a 10 to 30 μm wide inner-rim of massicot (PbO). Anglesite ($PbSO_4$) occurs locally in the inner rim. The growing relationship between lead mineral phases suggests that replacement took place. The podzols of the shooting ranges studied are favorable for the formation of lead carbonate. Lead carbonate provides effective controls on the retention of lead in the upper soil layers.

Key words Shooting range soils · Hydrocerussite · Massicot · Anglesite · Lead · Podzols

Introduction

The pollution of shooting range soils has received much attention in recent years. In some of the Scandinavian countries, the use of lead pellets as shotgun ammunition has been recently reported as another significant source of lead pollution to soils. Jørgensen and Willems (1987) reported that amounts Pb used as shotgun ammunition in Denmark to 800 tons annually, compared with 250 tons of Pb used annually as additives in automobile fuel. In 1990, about 563 tons of Pb were used as shotgun ammunition in Finland (T Mukherjee unpub.data). It is estimated that 500–600 tons of Pb are used annually as shotgun ammuni-

tion in Sweden (B Comet unpub.data). The annual load of lead to the soils in shooting range areas is a remarkably high figure. For example, about 100,000 shotgun cartridges are fired annually in the Munkatorp shooting range in Örebro county, Sweden. Each cartridge with 28 g of lead pellets, the annual load of lead from these firing activities on the soils, is estimated at 2800 kg. It is not a small figure if the contribution of all cartridges, including bullets from rifles, in Sweden is considered.

When the Pb pellets come into contact with soil they are readily decomposed. The concentrations of lead in the shooting range soils are obviously elevated as compared with the reference soils (not loaded by Pb pellets). The chemical analysis of some shooting range soils indicates that total Pb concentrations are significantly elevated, in some cases exceeding 10,000 ppm (Tanskanen et al, 1991. Engström 1993). Most of the lead can remain in the soils. The principal mechanisms of Pb retention in soils involve adsorption with organic complexes, clay minerals, Fe-, Mn- and Al-hydrous oxides (Jørgensen and Willems, 1987; Lin et al, 1994). The secondary lead minerals forming encrustation on Pb pellets is a significant Pb retention process. From the environmental point of view, secondary lead minerals have a potential impact on the concentration of soil lead. The present study is aimed at the identification of the mineral phases of Pb pellet encrustations using X-ray diffraction, electron microprobe and scanning electron microscopy.

Site description and laboratory work

The shooting ranges studied are located in Örebro county, Sweden (Fig. 1). They are called Bofors, Brostugan, Gyttorp, Höghult, Ingvaldstorp, Karintorp, Munkatorp and Munkhyttan. Skeet training is the primary activity at these shooting ranges. These shooting ranges have been used since the early 1970s, with 10,500 to 100,000 firings annually. In the shooting range areas, the average temperature in January is minus 4.1 °C and the average tempera-
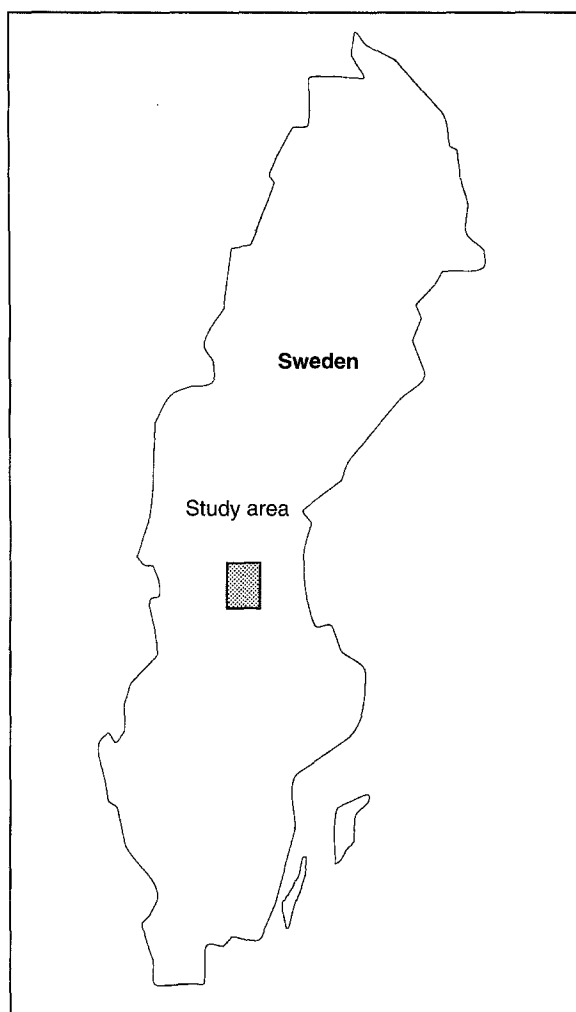
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Fig. 1 Map showing the study area

Table 1 Pb concentrations in the A-horizons of eight shooting range soils

Shooting Range	Reference soil mean (mg/kg)	Shooting range soil	
		max. (mg/kg)	min. (mg/kg)
Bofors	127	24500	5340
Brostugan	23	2090	767
Gyttorp	150	3410	305
Höghult	63	690	102
Ingvaldstorp	41	1780	1040
Karintorp	191	3040	—
Munkatorp	40	687	71
Munkhyttan	78	5610	4560

Data from Engström (1993)

ture in July is 16.3 °C. The annual precipitation is 614 mm (Alexandersson, 1991).

According to the FAO Soil Classification (Driessen and Dudal, 1991), the soils of these ranges are classified as haplic podzols which are developed from glacial till. The haplic podzols consist generally of an A, E, B and C horizons. The A horizons are 5–10 cm thick, dark gray in color and composed of quartz, feldspars, chlorite, muscovite, hornblende, kaolinite and Al hydroxides, they are often overlain by a 3–7 cm thick layer of plant residues. The E horizons are eluvial horizons, about 5 cm thick, light gray or white in color, and consist of quartz and feldspars. The B horizons are illuvial horizons, more than 40 cm thick, brown in color, and rich in iron hydroxides. The C-horizons are parent glacial till.

In 1993 soil samples containing Pb pellets from the eight shooting ranges were collected, and the Pb pellets separated, and then soil samples were chemically analyzed (Engström, 1993). The Pb pellets were principally found in the A-horizons. Some pellets were associated with the overlying poorly decomposed plant residues. No Pb pellets were found in E and B horizons. The pH values of A horizons are between 2.9 and 4.5 in the shooting range

soils. The highest concentrations of lead are found in the A horizons. The total lead concentrations are shown in Table 1.

The selected Pb pellets are about 2–2.5 mm in diameter, visibly corroded, and encrusted with yellowish gray colored materials. For the present mineralogical study, the Pb-pellet crust materials were obtained by the following procedure: a small batch of the corroded pellets from each shooting range was suspended in distilled water and treated in an ultrasonic bath (20 treatments for 3 min. each, 30 kHz). The resulting suspension was decanted and dried at room temperature. X-ray diffraction analysis (XRD) was used to determine the mineralogy of removed crust materials. Random orientation specimens were scanned from 4 to 70° (2°/min., CuKα).

For electron microprobe analysis (EMPA), corroded pellets without any treatment were cemented by epofix resin, flat polished, coated with carbon, then analysed using a CAMECA SX-50 electron microprobe with three X-ray spectrometers (LIF, PET and TAP crystals). Beam resolution is 1 μm and working potential is 20 kV. The morphology of the pellet crust materials was observed using an XL 30 scanning electron microscopy (SEM) operated at 15 kV.

Results and discussion

The mineralogical composition of crust material was semi-quantitatively determined by measuring the intensity of diagnostic peaks of hydrocerussite, anglesite, and massicot. According to the XRD analysis, the encrustation of Pb pellets from eight shooting ranges is primarily hydrocerussite $[Pb_3(CO_3)_2(OH)_2]$, with small amounts of anglesite $(PbSO_4)$ and massicot (PbO). As shown in Figure 2a, the XRD pattern for a crust sample from Bofors shooting range is composed of sharp peaks of hydrocerussite at 2.62 Å, 3.29 Å and 3.61 Å. Less intense peaks for anglesite at 2.07 Å and 3.33 Å, and for massicot at 3.07 Å, 2.95 Å and 2.74 Å are identified as well. The diffraction peak of cerussite $(PbCO_3)$ overlaps that of plattnerite (PbO_2)
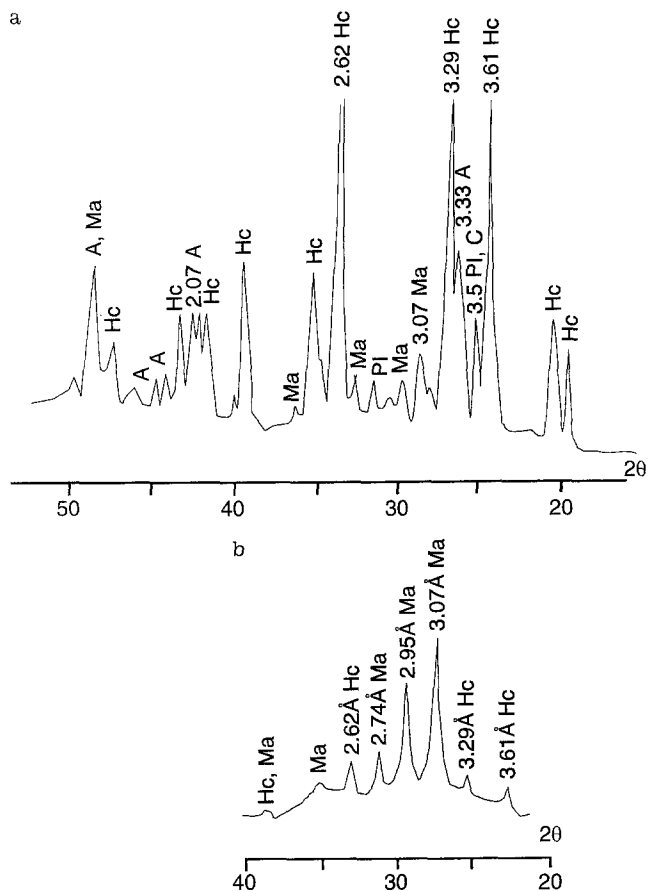
a

b

Fig. 2 a XRD pattern of the crust materials of Pb pellets from the Bofors shooting range. b XRD pattern of yellow film from pellets after removal of encrustation and exposed to air for five months A Anglesite, C cerussite, Hc Hydrocerussite, Ma Massicot, Pl Plattnerite

Fig. 3 a Photomicrograph of hydrocerussite crystals from the encrustation of Pb-pellets, b spectrum of crust composition of the pellets

at 3.5 Å, and an additional peak at 2.79 Å suggests the presence of plattnerite. The mineral content of the pellet crust is roughly the same for all eight shooting ranges, semi-quantitatively determined as 75–80% hydrocerussite, around 10% anglesite, 5–10% massicot, 5% cerussite and less than 5% plattnerite. Generally a new pellet contains 97% Pb, 2% Sb, sometimes 0.5% As and 0.5% Ni (Tanskanen, 1991). However, no secondary antimony mineral phase could be idendified by XDR, probably because they are poorly crystalline or present in small in amounts.

Figure 3 shows the SEM image of lead minerals in the encrustation separated from Pb pellets. Prior to the SEM photomicrograph, EMPA examinations show that the very fine grained platelets were predominantly hydrocerussite.

Using reflected microscopy, the pellet presents a rim about 200 μm wide. The images obtained by EMPA show that the pellet exhibits two concentric rims, i.e., the inner rim and the outer rim. The inner rim is a light gray, narrow, discontinuous concentric ring and 10–30 μm wide. The outer rim is a dark gray, continuous, concentric ring and 50–150 μm wide (Fig. 4). The pellets were qualitatively analyzed to identify their major element composition. The qualitative analysis shows that the two rims and
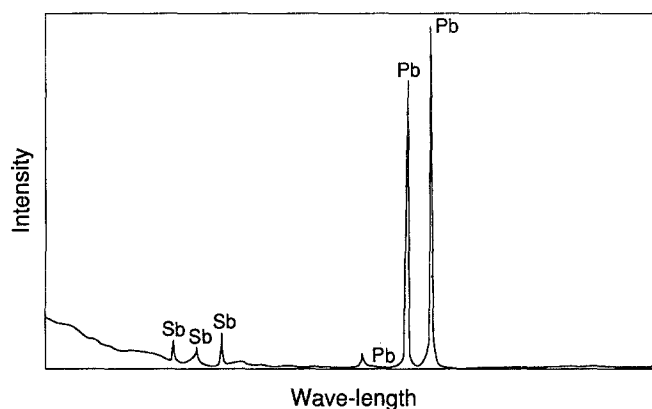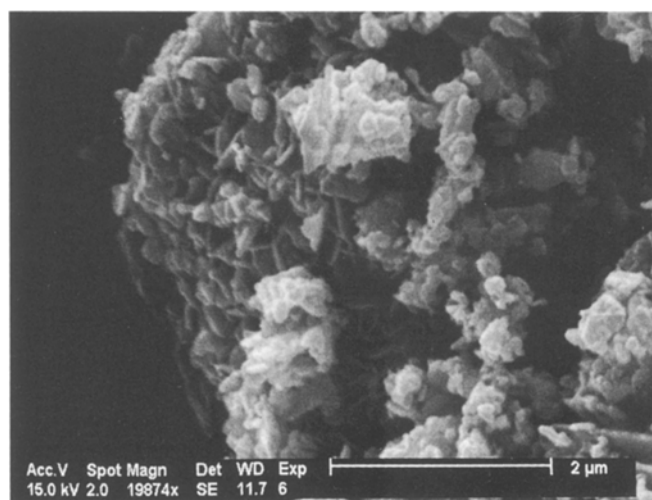
the pellet core consist predominantly of lead, with minor amounts of antimony. Traces of sulfur occur in the inner rim (Fig. 5). A quantitative analysis, including traverse and spot analysis, was conducted to determine the concentrations of Pb, Sb and S in pellet cores and rims (Fig. 6).

Results of EMPA show a decrease in concentration of Pb from the pellet core outward. The decrease results mainly from the formation of the secondary mineral phases having lower lead stoichiometry. Figure 5 shows the intensities presented as counts of Pb, Sb and S in the core, inner rim and outer rim, respectively. These intensities are independent and demonstrate obviously that the outer rim contains the lowest Pb concentration and the core contains the highest Pb concentration. The weight percent of Pb, Sb and S related to the amounts of total elements is exhibited in Fig. 6, from which a negative correlation of Pb and Sb was found. This negative correlation may result from irregularly distributed and relatively concentrated antimony, which is an additive during pellet manufacture. Although this negative correlation of Pb and Sb causes a decrease in Pb concentration as well, in general, the average concentration of lead is decreasing in the order core > inner rim > outer rim (Table 2).
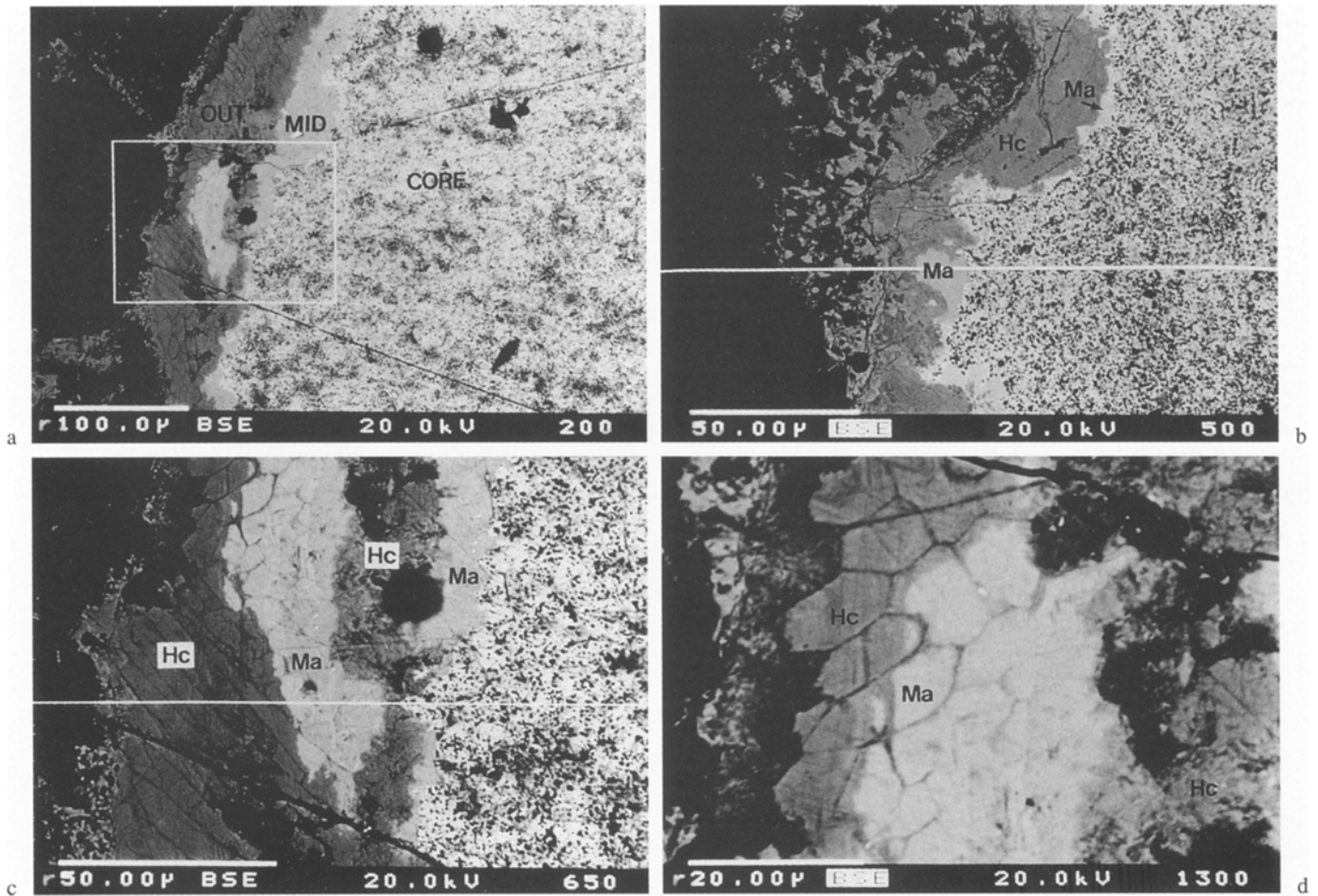
Fig. 4a–d Backscattered electron images of Pb-pellets and traverse location (white line), **a** OUT the outer-rim, MID the inner-rim, CORE the metallic lead core of pellet; **b** Pb-pellet from Gyttorp shooting range; **c** Pb-pellet from Bofors shooting range; **d** The replacement of hydrocerussite for massicot along the fractures. Hc Hydrocerussite, Ma Massicot
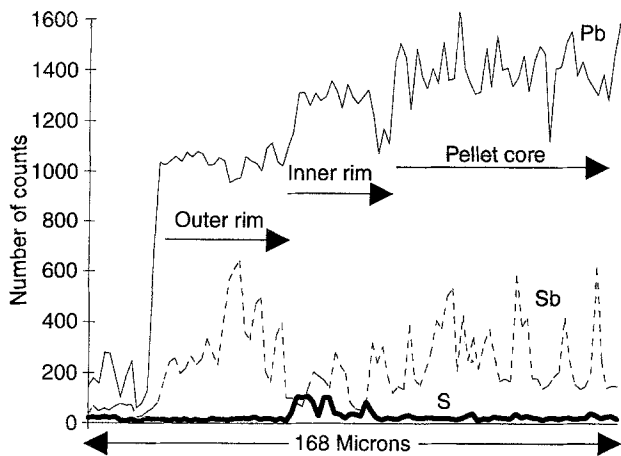

Fig. 5 Qualitative scanning traverse of Pb-pellet from Bofors shooting range. Traverse length 168 microns (see Figure 5c for traverse location)
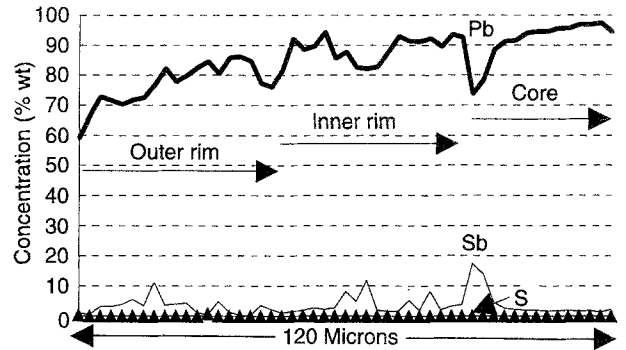

Fig. 6 Quantitatively scanning traverse of Pb-pellet from Gyttorp shooting range. Scanning length 67 microns (see Figure 5b for traverse location)

Table 2 EMPA of Pb-pellets from shooting ranges in Örebro county, Sweden

	Pb	Sb	S	Sum
		wt %		
Pellet core	96.0	1.9	—	97.9
Mid-rim	87.6	3.9	2.3	93.8
Out-rim	76.9	3.1	—	79.6

The average concentration of the core is 96% Pb and 1.9% Sb, which is quite well consistent with composition of a new pellet that contains generally 97% Pb and 2% Sb. The EMPA images show that the pellet core consists of dark spots and light matrix. The dark spots are irregularly distributed in the light matrix (Fig. 4). The light matrix contains average 96.5% Pb, 1.8% Sb. The dark spots contain relative higher antimony, ranging from 2.3 to 17.9%. As antimony is a primary constituent of the pellets, it is possible that the higher Sb concentrations may be caused by the originally irregular distribution of this additive.

The lead concentrations of the inner rim range from 88 to 92%, suggesting that the inner rim consists of massicot, and probably also plattnerite. Massicot (PbO) contains 92% Pb by stoichiometry, and plattnerite (PbO$_2$) contains 86% Pb by stoichiometry. Figure 5 exhibits a fluctuation of lead concentrations. This fluctuation is comparable with the change in mineral phases (Fig. 4c). The relatively low Pb concentrations correspond to the dark gray part and relative high Pb concentrations represented by the light gray part on the EMPA image.

Lead concentrations of the outer-rim range from 72 to 84%, indicating that the outer rim consists of hydrocerussite Pb$_3$(CO$_3$)$_2$(OH)$_2$ which contains 80% Pb by stoichiometry. The outer rim makes up about 80% of the crust, which can account for the case with which hydrocerussite as dominant mineral in the encrustation is identified by XRD.

The growing relationship between the rims can suggest that replacement of lead oxides by lead carbonates takes place as the pellets remain in the soil. Figure 4d shows that the replacement first takes place along the fractures. The fracture fillings appear dark gray, with a lead concentration of around 80%, indicating hydrocerussite composition. A few residuals of the inner rim mineral (lighter spots) are isolated in the darker outer rim. These lighter spots have a relatively higher lead concentration of around 90%, representing massicot composition. The replacement of one mineral by another has been studied extensively by economic geologists and can be compared with the replacement of lead oxides by lead carbonates in the shooting range soils studied. One of the hypotheses for the mineral replacement is that when the temperature of a mineral is raised, a point is reached at which the atomic structure is disordered but loosely tied together, allowing ions to diffuse through the crystal with ease (Park and MacDiarmid 1970). It is assumed that when the pellets are fired the rising temperature creates a disordered and loosely tied atomic structure, allowing organic carbon to diffuse through and form lead carbonates.

After removing encrustation pellets were exposed to air for about five months, and then examined using a binocular microscope. A translucent, reddish yellow, discontinuous thin film was observed. The reddish yellow film was interspeised with some gray-white fine crystals. The reddish yellow film is identified as massicot and the white fine crystals as hydrocerussite (Fig. 2b). It seems that when the pellet is exposed to air, lead oxides form readily at the

surface of pellet. In addition, the atmospheric CO$_2$ may contribute to the formation of minor amounts of lead carbonates.

In soils, lead oxides (PbO) are the most soluble minerals, but lead carbonates are considerably more stable. Cerussite (PbCO$_3$) and hydrocerussite [Pb$_3$(CO$_3$)$_2$(OH)$_2$] have identical solubilities at 0.0003 atm of CO$_2$ and increasing CO$_2$ causes lead carbonates to be more stable (Lindsay, 1979). The present study shows that the conditions of the shooting range soils are favorable for the formation of lead carbonates. The podzols contain relatively high organic carbon in the A horizon, which is rich in plant litter and plant residue, but rarely more than 1% organic carbon in the E and B horizon (Drissen and Dudal, 1991). The oxidation of organic compounds in plant residues produces abundant CO$_2$. The results of chemical analyses have shown that high concentrations of lead were mainly found in the A horizons with corresponding relatively high organic carbon concentration, ranging from 6 to 12%, in the shooting range soils (Engström, 1993). When the Pb-pellets come into contact with the soils, the more soluble lead compounds, i.e. lead oxides could convert to more stable lead compounds, i.e. lead carbonates. The amounts of anglesite identified by XRD average around 10%. Small amounts of lead sulfate can form in the studied shooting range soils because the soil sulfur content is low. The ratio of organic carbon to sulfur in podzols is 132:1.2 (Whitehead, 1964). Park and MacDiarmid (1970) pointed out that lead sulfate can be replaced by lead carbonates according to following chemical reaction:

$$PbSO_4 + H_2O + CO_2 \Rightarrow PbCO_3 + SO_4^{-2} + 2H^+$$
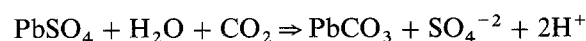
Figure 5 shows that a relatively high concentration of sulfur was found in the inner rim. The occurrence of lead sulfate indicates that the conversion of anglesite to hydrocerussite may also take place. Figure 6, however, shows no obviously high concentration of sulfur in the inner and outer rims. Accordingly, the replacement of lead sulfate by lead carbonate seems to proceed toward a complete replacement, i.e. in some pellets lead sulfate could be completely replaced by lead carbonate. It is assumed that there is probably little or no lead sulfate in the outer rim owing to this replacement, and it is likely, therefore, that present soil conditions cannot influence lead sulfate directly.

The secondary Pb-bearing minerals become sinks for lead. Their solubilities are of great significance in controlling Pb concentrations in the soil solution of the shooting range areas. The soil solution as defined by Brady (1990) contains small but significant quantities of soluble inorganic and organic compounds. At equilibrium the lead concentration of the soil solution is determined by the least soluble lead compound. In the shooting range soils studied, the solubility-limiting lead mineral phase is likely hydrocerussite in the encrustation. If hydrocerussite determines Pb concentrations of the soil solution, at pH 6–7.5 the equilibrium concentration of lead may range from 2 to 2000 μg L^{-1} (Lindsay, 1979), depending on

organic carbon concentration. The concentration of dissolved lead decreases with the increasing concentration of carbon dioxide in the soil, i.e. when the organic carbon concentration increases, more lead will be retained by forming lead carbonate and less lead will be released into soil solution. In the shooting range soils studied the total concentrations of lead in the E and B horizons are about two orders of magnitude lower than that of the A horizon (Lin et al, 1993), owing to the great amounts of lead carbonate whose low solubilities inhibit the downward movement of dissolved lead.

The solubilities of lead compounds can be influenced by pH as well. Generally anglesite is more stable below pH 6, whereas cerussite is more stable at higher pH (Lindsay, 1979). The pH of the shooting range soils studied is around 4. The images of EMPA show the dissolution of lead carbonates, which produce the porous fragmentary morphology of the outer rim (Fig. 4). (The fragmentary morphology may be partially due to thin section polishing as well). However, all pellets collected from eight shooting range soils contain 75–80% hydrocerussite, but about 10% anglesite. Although the crust materials of Pb pellets collected from some shooting ranges seem to be containing slightly more anglesite (12%), e.g., Brostugan and Munkhyttan shooting ranges, which have relatively low soil pH (about 3), the relationship between pH and lead sulfate is not very clear. This fact suggests that the organic carbon content governs the formation of lead carbonate in the studied shooting range soils. It seems that under such conditions, lead carbonates are the more stable mineral phases even when the pH value is lower than 6.

Jørgensen and Willems (1987) calculated that within 6–13 years 5–17% of metallic lead was transformed in Dannish shooting ranges.

The growing relationship between the two rims suggests that the replacement reactions between lead mineral phases proceed when the pellets remain in the soils. Lead oxides and lead sulfate could be replaced by lead carbonates. Lead oxides could form when pellets are exposed to air. After pellets were fired and landed in Örebro county, Sweden, the podzols are favorable for the replacement of lead oxides by lead carbonate. The podzols enrich plant litter and plant residues in the A horizon. The oxidation of organic compounds in plant residues generates abundant CO_2. The CO_2 content in the soils governs the formation of lead carbonate. The high ratio of organic cabon to sulfur in the soils contributes to the small amounts of lead sulfate. Hydrocerussite is the solubility-limiting mineral phase to control Pb concentration of soil solution.

The occurrence of secondary lead mineral phases has an environmental significance. The inner rim of massicot and anglesite have less direct impact on the concentrations of lead in the soil as compared to the outer rim of hydrocerussite. Although hydrocerussite is dissoluble at the pH range of the shooting range soils studied, the enrichment of organic carbon in the soil can lower its solubility, which provides effective controls on the retention of lead in the upper soil layers.

Conclusions

It has been clearly demonstrated that Pb pellets falling on soils are decomposed and transformed into secondary lead minerals as encrustation on the pellets. The encrustation consists of two concentric rims: the outer rim of hydrocerussite and the inner rim of massicot, associated locally with anglesite. The outer rim is much wider than the inner rim, which correspondes to the predominance of hydrocerussite in the pellet crust as identified by XRD. The shooting ranges in Örebro county have been used since early 1970s. According to the ratio of rim width to the pellet diameter, it is estimated that within 20 years, about 10% of Pb pellets were transformed into secondary lead compounds. As the shooting activities are continuing in these shooting ranges, it is rather difficult to distiguish the residence time of individual pellets in the soils. Time to forming the pellet encrustation was not determined in the study. The above estimation, therefore, is general. Based on this discomposing rate, it is predicted that all the metallic lead pellets currently present in the shooting range soils studied would be transformed within about 200 years.

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