Research Article

Lead Shot Pellets as Soil Pollutants in the Maltese Islands.

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Summary. *The fate of lead shot in Maltese soils is investigated. The study shows that soil lead levels are directly proportional to the exposure of the region to bird and clay pigeon shooting. The dispersed lead shot subsequently undergoes weathering effects with the rate of erosion of the shot being dependent on the soil type. The mobility of the soil lead is shown to be dependent on the soil type, salinity and the use of chemical artificial fertilizers.*

Keywords: lead, soil, pollution, fertilizers

The Maltese population has been found in various studies to have high blood lead levels at various stages of life (Bruaux et al, 1983; Sammut and Savona-Ventura, 1996; Savona-Ventura et al, 1994), though educational and legislative measures instituted in the last decade appear to have had a positive role in decreasing the mean blood lead levels in the population (Savona-Ventura et al, 1997). There are many potential sources of lead contamination in the Maltese environment, the main ones being petrol lead (Sammut and Savona-Ventura, 1996), and the use of leaded paint with subsequent use of painted wood as fuel in bakeries. Another potential source of lead in the Maltese environment is the use of lead shot pellets for bird and clay pigeon shooting. The annual lead shot importation to Malta amounts to about 100 metric tonnes or the equivalent of about 0.5g of lead per square metre of agricultural and countryside areas per year (Dept of Statistics, 1987-89). Lead shot pellets settling on the soil are subjected to various weathering factors enhancing the spread of lead in the soil environment through the production of fine particles and the possible mobilization in the form of ions or complexes. In as far as we know, the potential hazard of lead shot contamination in the local environment has never been assessed. While lead shot cannot be considered a major source of lead pollution, the amount is constantly increasing and is accumulative. This study attempts to quantify soil lead levels from various sites in Malta and Gozo, and to determine the fate of these lead pellets in Maltese soils under different circumstances under laboratory conditions similar to environmental conditions to which the pellets are possibly exposed.

Material and Methods

Different surface soil samples were obtained from twelve sites in Malta and Gozo. The sites were classified according to the authors' estimated popularity with bird or clay pigeon shooters, thus reflecting exposure of these sites to lead shot deposition (Table I). Each soil sample collected was sieved on site through a 2 mm mesh and after air-drying stored in plastic bags at -20°C. The twelve samples were analyzed using a flame atomic absorption spectrometer (AAS) for the total lead content after digestion with concentrated nitric acid. Six of the samples (I-IV, VIII and X) were repeatedly assayed for five times enabling a mean and standard deviation result. The other six samples (V-VII, IX, XI-XII) were assayed once. The four soil samples obtained from sites quantified as having low exposure to lead shot deposition (samples I-IV) were further analyzed chemically.

In vitro studies to determine mechanical and leaching effects on lead pellets were further performed on the two soil samples representing Carbonate Raw soils and Terrarossa soils obtained from sites quantified as having a low exposure to lead shot pellets (samples II & IV). The mechanical erosive effects of the two soil types on lead pellets was assessed after continuously shaking two sets of nine soil sample tubes for 4 hours per day. Each tube contained 5 g of soil and one lead pellet (average weight 0.06g). The sample tubes were shaken for 3, 7 and 14 days, respectively. After each time-point determination, three sample tubes of each set were analyzed for total lead content using AAS. This analysis was performed after removing the lead pellet and digesting with concentrated nitric acid.

Sample	Lead shot dispersion	LOCATION
I	Low exposure	*Ghar Ilma, Gozo*
II		*ByPass, St.Paul's Bay, Malta*
III		*Buskett, Malta*
IV		*Qajjenza, Malta*
V	Moderate exposure	*Madliena, Malta*
VI		*Ghalis, Malta*
VII		*Bidnija, malta*
VIII		*Delimara, Malta*
IX	High exposure	*Mizieb, Malta*
X		*Fanal tal-Gordan, Malta*
XI		*Mellieha Ridge, Malta*
XII		*Bidnija Shooting Club, Malta*

Table 1. Soil samples.

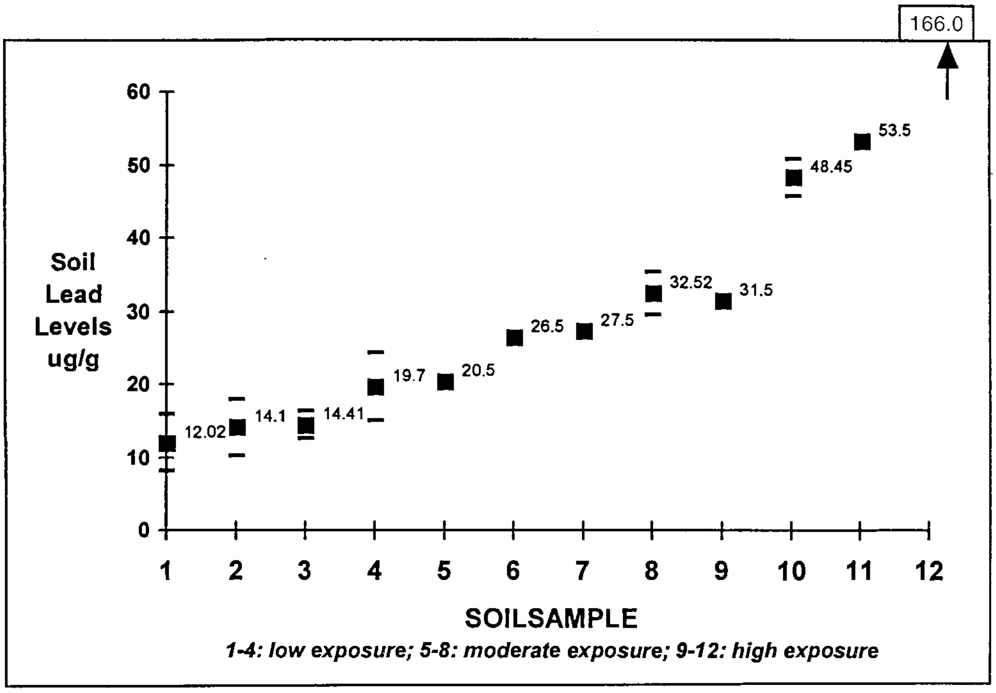

Figure 1. Soil lead levels.

estimated as having a very high exposure had a soil lead level of 166.0 ug/g (Figure 1).

The soil lead levels in samples obtained from low exposure sites (samples I-IV) appeared to be inversely dependent on the chloride and conductivity (salinity) levels of the soil samples. There appeared to be no further correlation with other chemical constituents of the soil (Figure2/Table II).

Lead pellets in the soil are apparently eroded gradually by the mechanical abrasive effects of the soil. Thus, the dry shaking experiment in vitro suggests that in both soil types (samples II &IV), pellet erosion was marked by Day 3, increasing mean soil lead content by 28.9 ug/g in sample II and 26.6 ug/g in sample IV. Further prolonged shaking continued the erosive mechanism which was reflected in an increase in the mean soil lead content by a total of 41.5 ug/g in sample II and 36.6 ug/g in sample IV by day 14. The rate of abrasion was apparently greater in sample II irrespective of the duration of shaking. The mean soil lead levels were overall higher in sample IV, but only showed a significant increase prior to shaking and after day 7 of shaking. This difference seems to suggest that abrasive properties are dependent on the soil characteristics and are different for Carbonate Raw soils and Terrarossa soils, the former showing the higher rate (Table III).

The leachability of lead from soil samples II & IV was assessed by preparing soil sample tubes containing 5 g of soil with/without a lead pellet and adding 10 ml of tap water. Further soil samples containing natural fertilizers - manure and primary effluent sludge - and artificial fertilizers - ammonium sulphate and water soluble NPK: F1, F2, F5 - were also prepared in a similar manner. These tubes were mechanically shaken for 18 days at 25°C for 4-hour intervals per day. After centrifugation, the supernatant was digested with concentrated nitric acid and the lead leachate level was analyzed with single readings using Anode Stripping Voltameter (ASV).

Results

The total soil lead levels appeared to be proportional to the estimated degree of lead shot deposition at the various sites. Thus, those sites estimated to have a low exposure to lead gave a mean soil lead level in the range of 12.02-19.70 ug/g, while those with a moderate and high exposure gave a mean soil lead levels in the range of 20.5-32.52 and 31.5-53.5 ug/g respectively. The site

Tap water added to the soil sample helps to mobilize the intrinsic soil lead salts and particles as lead leachates. The amount of lead leachate increases minimally by 3.7 ug/g in sample II and 6.9 ug/g in sample IV in the presence of a lead pellet, an approximate 1.25 fold increase. The addition of primary effluent sludge or

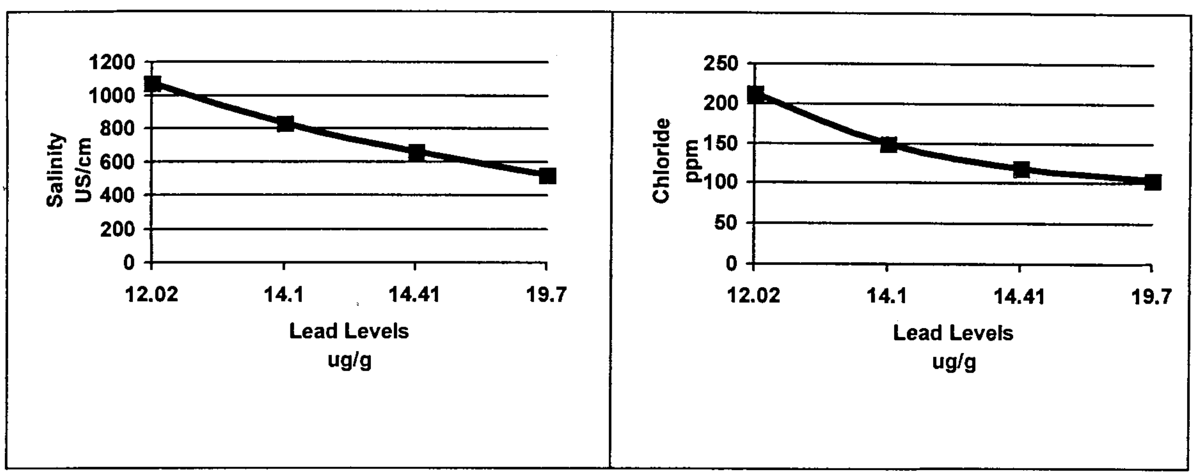

Figure 2. Soil lead levels by soil salinity.

SOIL SPECIMEN	I	II	III	IV
SOIL TYPE	*Carbonate Raw*	*Carbonate Raw*	*Xerorendzina*	*Terrarossa*
Soil lead ug/g (mean+sd)	12.02+3.9	14.1+3.92	14.41+1.9	19.7+4.7
Salinity US/cm	1070	833	660	519
pH	7.13	7.41	7.05	7.26
Phosphorus ppm	8000	7000	9500	9000
Potassium ppm	84	32	72	8
Chloride ppm	213	149	119	105
Sodium ppm	204	68	160	84
Nitrogen %	0.316	0.246	0.221	0.285
CaCo3 %	29.1	36	51.57	22.5
Organic matter w/w %	8.1	4.7	5.0	6.0

Table 2. Chemical analysis of soil types.

ammonium sulphate fertilizer minimally increased the amount of lead leachate by approximately 1.36- and 2.07-fold, respectively. Manure increased the lead leachate by 7.8-fold, while NPK water soluble fertilizers increased the lead leachate by 62.05-305.2-fold depending on the NPK values (Table IV).

Discussion

The presence of lead in soil may theoretically pose a serious health hazard since soils are considered to be strong accumulators of lead. Lead incorporated in alkaline soil is usually of very low mobility and thus once contaminated, a soil is liable to remain polluted with lead for a long time. Lead shot is irretrievably dispersed in the environment. The amount of lead shot dispersion in the Maltese agricultural countryside approximates 0.5g of lead per square metre annually (Dept of Statistics, 1987-89). However, the lead shot dispersion is not even, but depends on the use of the locality for bird or clay-pigeon shooting by enthusiasts. This varied dispersal is further reflected in the difference of soil lead levels from various sites in Malta and Gozo The present study confirms that soil lead levels are directly dependent on the popularity of the site with shooting enthusiasts, being very markedly elevated at 166.0 ug/g levels at the Bidnija Shooting Range and lowest at 12.02 ug/g levels at Ghar Ilma, a site not particularly popular with shooting enthusiasts.

MECHANICAL SHAKING	SOIL SAMPLE II [mean+sd, n=3]	SOIL SAMPLE IV [mean+sd, n=3]	significance
Day 0 (n=5)	14.10+3.92	19.70+4.70	t=2.046 p<0.05
Day 3 (n=3)	43.00+2.00	46.33+5.51	t=0.984 p> 0.5
Day 7 (n=3)	45.33+3.51	53.33+1.53	t=3.619 p<0.001
Day 14 (n=3)	55.67+4.16	56.33+5.03	t=0.175 p>0.5

Table 3. In-vitro mechanical abrasion.

The dispersed lead shot in the soil is gradually eroded by weathering forces reflecting mechanical and chemical factors. The extensive weathering and erosion processes that the lead shot is subjected to at the topsoil tend to encourage the spread of lead as a result of the physical transformation into finer particles (Mudge, 1984). The rate of mechanical erosion of lead shot pellets is apparently dependent on the soil type. This study has shown that the finer particled Pliestocene Terrarossa soil deposits had poorer abrasive properties when compared to the relatively younger Carbonate Raw soils. The chemical and organic constituency of the different soils did not generally appear to influence the soil lead levels, though an inverse relationship between soil lead levels and the soil salinity measured directly or as a function of chloride level has been shown in the present study. Lead in Maltese soil has been shown to be present in a free uncomplexed form. Consequently, soil lead levels would be governed by the solubility product of Lead Chloride ($PbCl_2$), thus explaining the observed inverse relationship (Vella, 1997).

The high alkaline pH of Maltese soil types and the high calcareous content tends to render the eroded particulate lead immobile as a result of the formation of insoluble compounds such as $PbCO_3$, $Pb_3(PO_4)_2$ and $PbSO_4$ (Zimdahl, 1977). The high clay content of Maltese soils further contributes towards lead immobilization possibly through the high adsorptive powers of clay. The adsorptive properties of clay and probably iron oxide were demonstrated by the lower lead leachate obtained after the soil sample was added to the Terrarossa soil in contrast to the Carbonate Raw soil. The addition of a lead pellet did not seem to have much effect on the amount of lead leached by tap water. Similarly, very minimal differences could be noted when the soil was leached in the presence of primary effluent sludge or ammonium sulphate used as fertilizers, though a two-fold increase in leachate was observed with the latter. Significant changes in lead mobility were observed when the soil samples were leached in the presence of manure or water soluble NPK fertilizers, being very marked at

CHEMICAL EROSION	SOIL SAMPLE II	SOIL SAMPLE IV	mean increase
Tap water alone	24.2	18.8	-
In presence of lead pellet	27.9	25.7	x 1.25
Primary effluent sludge	27.3	31.0	x 1.36
Manure	170.9	164.5	x 7.8
Ammonium sulphate	38.0	51.2	x 2.07
F1 [NPK:11,0,30]	1504.0	1164.3	x 62.05
F2 [NPK:30,3,11]	1941.4	3300.0	x 121.9
F5 [NPK:25,5,30]	7775.0	5350.0	x 305.2

Table 4. Chemical soil leaching of lead.

approximately three hundred fold with F5 NPK[25,5,30] fertilizer. The mobilization of lead from soil may possibly be due to the formation of soluble organic and inorganic lead species, thereby enhancing mobilization in the aqueous medium. These soluble species may include the formation of soluble organic complexes or chelates, inorganic ion pairs or free metal ions. Once mobilized, these soluble lead species may be made available to vegetation thus entering the food chain.

The mechanism of lead uptake by plants is still not clear and disagreement exists as to the proportion and the form in which lead is taken up from the soil system. The relationship between the lead content of certain plant species such as lettuce, oats, grain and radish grown in contaminated soils and the concentration of lead in soils has been determined (Harrison and Laxen, 1984; Bolt and Bruggenwert, 1978). The lead content of most plant species is normally in the range 0.5-3.0 ppm. Plant toxicity generally occurs above this concentration. However, certain species of plants can withstand high levels of lead without showing any toxic effects. This high concentration of lead is, however, toxic to humans if consumed.

Conclusion and Recommendation

Lead shot dispersion is a minor lead additive in the Maltese ecosystem, more important factors in the process being vehicular lead and the burning of old wood painted with leaded paint products. However, the continuous dispersion of lead shot, particularly in agricultural areas, may pose a long-term hazard since soil lead tends to be accumulative. By virtue of their carbonate content and alkalinity, Maltese soils generally limit lead mobility and restrict uptake by vegetation. The use of fertilizers, particularly the NPK water soluble fertilizers, significantly mobilizes the soil lead making the ion available for uptake by vegetation and for the subsequent introduction of lead in the food chain. The introduction of steel shot or non-toxic tungsten polymer shot as an alternative to lead shot for birdshooting in agricultural areas should be considered. Lead shot should be restricted for use in clay shooting on suitable grounds where spent pellets could be collected and where agriculture is not practised.

References

Bolt GH and Bruggenwert MGM. (1978) *Soil Chemistry, Basic Elements.* Elsevier Scientific Publishers, London.

Bruaux P, Claeys-Thoreau F, Ducoffre G, Lafontaine A, Grech A and Vassallo A. (1983) Exposure to lead and cadmium of the general population of Malta. *International Archives of Occupational and Environmental Health,* 53, 119-125.

Dept. of Statistics. (1987-89) Trade Statistics, 1987-1989. Government Press, Malta, 3 vols., 1987:p.120,211; 1988:p.124,218; 1989:p.124,219.

Harrison RM and Laxen DPH (1984) *Lead Pollution, causes and control.* Chapman and Hall, London.

Mudge GP (1984) Densities and settlement rates of spent shotgun pellets in British Wetland soils. *Environmental Pollution,* (ser.B) **8**, 299-318.

Sammut M and Savona-Ventura C (1996) Petrol lead in a small island environment. *International Journal of Risk and Safety Medicine,* **9**, 33-40.

Savona-Ventura C, Sammut M, Ducoffre G and Claeys-Thoreau F (1994) Chronic lead exposure and pregnancy. *International Journal of Risk and Safety Medicine,* **6**, 25-33.

Savona-Ventura C, Sammut M, Licari L and Vassallo A (1997) Blood lead levels in pregnant women and the neonate. *Maltese Medical Journal,* **9**, 42-45.

Vella J (1997) Heavy Metals in Soils amended by composed municipal waste. Thesis M.Sc. (Agri. Sc.), University of Malta.

Zimdahl RL and Skogerboe RK (1977) Behaviour of lead in soil. *Environmental Science and Technology,* **11**, 490-497.