Potential for PAH contamination from clay target debris at shooting sites:

Review of literature on occurrence of site contamination from clay targets

Environment Canterbury
Your regional council

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Report No. U06/81

Prepared for Environment Canterbury by

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June 2006

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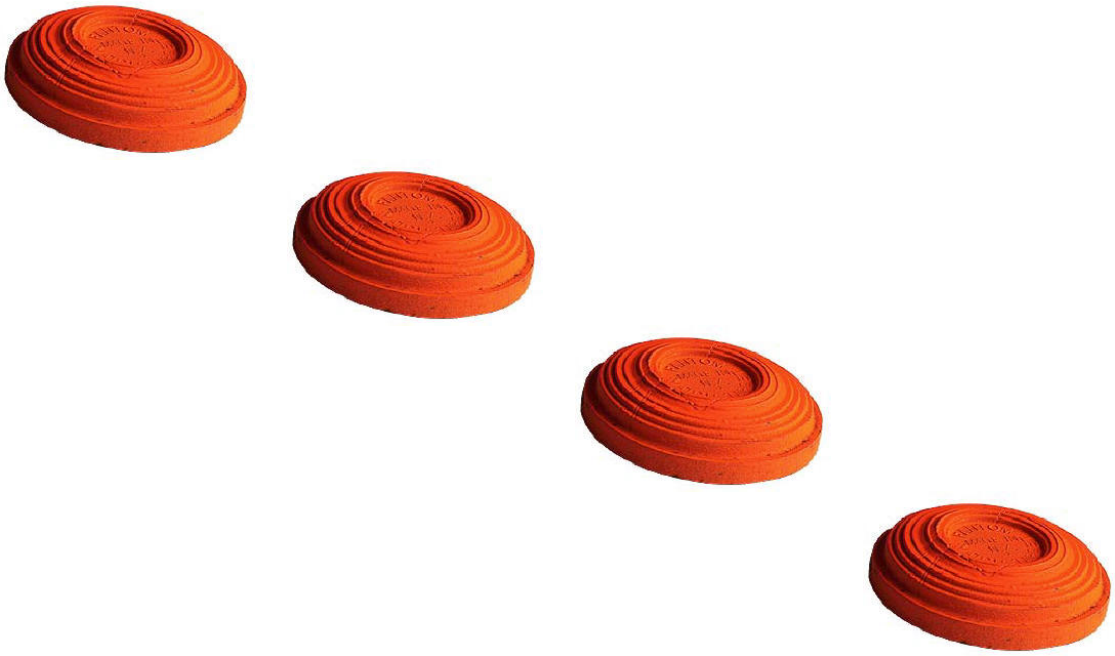
Potential for PAH Contamination from Clay Target Debris at Shooting Sites: Review of Literature on Occurrence of Site Contamination from Clay Targets



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Disclaimer:

The conclusions and recommendations are the opinion of the author, based on the information in the available literature review, prior experience of investigations and responses for the sites, and the current national and regional management regime in place for sites known be contaminated or at risk of contamination. By providing these conclusions and recommendations the author accepts no responsibility or liability for any past, current or future consequences of contaminants at the sites, or of contaminants entering the environment from these sites. In the event that new literature becomes available indicating contrary findings to those reported here, and/or the management regime changes, the recommendations should be re-evaluated by Environment Canterbury. Best endeavours were used to identify appropriate literature for this survey. The author accepts no responsibility or liability for omissions resulting from literature that was not identified during the project.

1.0 Introduction

Lead contamination of land and water associated with lead shot from clay target shooting is now documented in New Zealand and international studies. Questions have been raised about the potential for other contaminants to enter the environment from the other types of debris at shooting sites. In particular debris from clay targets which are known to contain a group of toxic hydrocarbons called polycyclic aromatic hydrocarbons (PAHs).

Figure 1 is taken from a technical guide[1] prepared by a US intergovernmental body (the Interstate Technology and Regulatory Council (ITRC) and illustrates the range of materials that are deposited at trap and skeet shooting sites. It shows a zone where target fragments and unhit targets fall, from approximately 50 to 90 metres from the shooting position.

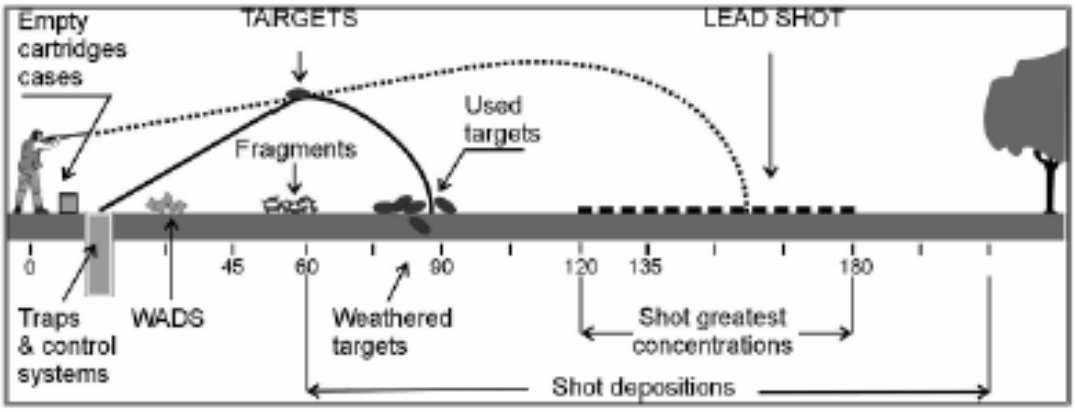

Figure 1: Schematic diagram showing distances of fall-out of shooting debri and lead shot. Taken from ITRC Technical Guide (2005) Figure 2-12.

In 1996/97 Environment Canterbury investigations of clay target shooting sites in Canterbury targeted lead contamination from lead shot, the issue of PAH contamination was not included. This report has been commissioned by Environment Canterbury to gather information regarding the potential for PAH contamination of sites. This has been carried out by surveying available and applicable literature on clay targets, shooting sites and associated contamination.

2.0 Research Method

This project involved research of readily available literature and information on clay target composition and the behaviour of clay targets in the environment at shooting sites. The aim of the research was to determine whether clay targets contained contaminants that could present a risk to people or the environment, if or when targets degraded over time or through environmental processes occurring at sites. The internet was used to locate documents, and both broad (i.e., investigations and management of clay target shooting sites) and specific (i.e., PAH contamination, PAH leaching etc) parameters were used in the searches undertaken.

This documentary research has shown that generally investigations of soil contamination at clay target shooting clubs is only reported to a small degree in scientific literature and is very minor in comparison to other types of contamination investigation, including in New Zealand. Within this limited pool, information on contamination arising from degradation of clay targets is even more scarce. However, several documents contain analytical information on PAH concentrations as well as others that address the issue as part of a broader range of contamination and waste management issues for sites.

[1] Environmental Management at Operating Outdoor Small Arms Firing Ranges, Technical Guideline, February 2005.

3.0 Clay Target Composition

Clay targets are typically composed of limestone (70%) and a binding material (30%) – pitch[2], bitumen or other organic material (ITRC 2005). The limestone and pitch are mixed then press moulded to form the designed shape. The final targets are sometimes left black, and other times painted white or fluorescent colours (depending on the type of background they will be used against). Figure 2, taken from a european manufacturer's website (Laporte[3]), shows the typical range of colours for clay targets.

Figure 2: Photographs of targets showing varying colours

It is the binder material in targets that can contain a range of hazardous components that may be a potential risk in the environment. If the binder is derived from tar or pitch, it may contain a complex mix of a group of hydrocarbons called polycyclic aromatic hydrocarbons (PAHs), some of which are known to be toxic.

The PAH content varies depending on the type of binder used. A 1998 report of German State Ministers for the Environment[4] (referred to as the Laender Ministers report) describes studies showing the PAH content of clay targets ranging from 3,000 to 40,000 mg/kg PAH[5], depending on the manufacturer. Table 3.4 of that report (Table 1 here) shows what they consider to be a representative analysis of typical clay targets.

Low-Polluting Clay Targets

In recent times an awareness of the polluting effects of clay target shooting has prompted development of targets with reduced or no PAH. The Laender Ministers report also identifies that clay target manufacturers are producing low-PAH targets (3 to 70 mg/kg[5]), and that there are options for PAH free targets being developed (tree resin produced in Finland and gypsum based produced in Australia).

Relevance to Canterbury Shooting Sites

Because of the age of the shooting sites in Canterbury it is considered highly likely that the clay targets used over the life of the clubs would predominantly be those containing high levels of PAH, even if in more recent years low PAH or PAH free targets have been used. It is therefore

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[2] Petroleum or Coal Tar Pitch: Petroleum pitch is a "…residue from heat treatment and distillation of petroleum fractions. It is solid at room temperature, consists of a complex mixture of numerous predominantly aromatic and alkyl-substituted aromatic hydrocarbons…" (IUPAC Compendium of Chemical Terminology, 2nd Edition 1997, sourced on internet at www.iupac.org/goldbook/P04523.pdf); Coal tar pitch is a semi-solid hydrocarbon formed as a residue from the distillation of coal tar, which itself is a product of the high temperature treatment of coal to make coke or natural gas (ATSDR Toxicity Assessment, sourced on the internet at www.atsdr.cdc.gov/toxprofiles/tp85.pdf)

[3] http://www.laporte-shooting.com/index.php?page=11

[4] *Soil Contamination at Shooting Ranges*, Report by the Work Group of the Conference of the (Laender) Ministers for the Environment, November 1998. Available on the internet at www.wfsa.net link to Environment.

[5] Sum of 16 EPA-PAH.

appropriate that the potential for leaching of PAH and other contaminants from clay targets is considered further.

Table 1: Typical PAH and metal content in clay targets. Source Table 3.4, Laender Ministers for the Environment, November 1998

PAH	(mg/kg)	PAH	(mg/kg)
Naphthalin	n.a.	Benzo(a)anthracen	1736
Acenaphthylen	n.a.	Chrysen	1764
Acenaphthen	257	Benzo(b)fluoranthen	1852
Fluoren	370	Benzo(k)fluoranthen	832
Phenanthren	1781	Benzo(a)pyren	1764
Anthracen	712	Dibenzo(a,h)anthracen	487
Fluoranthen	2881	Benzo(g,h,i)perylen	1543
Pyren	2058	Indeno(1,2,3 cd)pyren	n.a.
Sum of 16 EPA-PAH			**18037**

Heavy metals	(mg/kg)
Lead	49,9
Cadmium	0,66
Chromium	3,3
Copper	2,4
Nickel	7,3
Mercury	0,02
Zinc	28,8
Arsenic	n.a.

4.0 Degradation, Leachability & Toxicity of Contaminants in Clay Targets

The potential for leaching of contaminants, in particular PAHs, from clay targets is addressed in a number of the documents researched. Two (the ITRC and NSSF reports) of the guidance documents on best management practices (listed in Appendix 1) at shooting sites refer to a 1995 paper by Baer et al. This paper reports on toxicity and leachate toxicity testing of crushed clay targets (both aged and new targets) on a selection of freshwater and marine organisms.

The Baer et al findings were that the target materials showed very low acute toxicity to the organisms tested, even when the concentrations tested were much greater than the concentrations usually used for such tests (concentrations determined: 52,000 to >600,000 mgl^{-1}) range. They also showed that for the species tested (mysid shrimp) the leachates were not acutely toxic and relatively non-toxic to marine shrimp in a chronic bioassay. This compared with information available at the time that showed the acute toxicity saltwater aquatic organisms for PAH occurred at concentrations as low as 0.30 mgl^{-1}. Baer et al concluded that while PAH was not measured in the water during the toxicity testing undertaken, it was unlikely that the PAHs had leached from the target materials in any significant amounts based on the results of the toxicity tests.

The Baer paper also reported on findings from a 1990 report on an investigation and remediation of shooting site (the Remington Gun Club in the US in a report by Battelle Ocean Sciences), in

which they determined the concentrations of PAHs in targets, sediments and organisms at the shooting range. The findings of that investigation were that the PAH concentrations in sediment and marine animals were no higher (and often lower) than would be expected for the area in general.

The Baer findings also demonstrated no significant difference between the PAH concentrations of aged and new targets. Baer et al therefore concluded that since the hydrocarbons in the pitch component of the clay targets are bound under heat and pressure with the limestone, that they will be relatively inert and it would therefore be unlikely that the PAHs would leach into the environment.

Despite the Baer et al findings on the relative immobility of the PAH components of clay targets, several more recent documents report elevated PAH concentrations in soils and sediments associated with clay targets:

- Laender Ministers report – PAH in soils up to 1,000 mg/kg (analysis methodology and soil fraction not reported);
- San Francisco Bay remediation order for shooting site, from an area where clay target debris were stockpiled – PAH in soils ranging from anthracene at 22 mg/kg up to pyrene at 370 mg/kg, with benzo(a)pyrene at 350 mg/kg (total for 12 of 16 PAHs 2,431 mg/kg) (analysis methodology and soil fraction not reported);
- Florida Best Management Practices – reports PAH concentrations in soil and sediments above Florida standards.

By way of comparison of these reported concentrations, New Zealand soil acceptance criteria[6] for some PAH compounds from petroleum sourced contamination are given in Table 2 below. It is clear that the PAH concentrations reported, would exceed current land use standards in New Zealand. However, this can only be used as a simplistic guide, because the hydrocarbons in clay targets will be in different phases to those in liquid hydrocarbons, and therefore exhibit different fate and transport characteristics. In addition, it is uncertain what soil fraction is reported in the analyses, that is whether the quantities represent PAHs bound within soil itself, or whether the soil concentrations are influenced by fragments of clay targets themselves. Whatever the relevant standards in New Zealand, it is clear that in the countries where these sites are found, the concentrations exceed the relevant standards.

Land Use	Naphthalene mg/kg	Pyrene Mg/kg	Benzo(a)pyrene Equivalent mg/kg
Agricultural	7.2	160	0.027
Residential	58	1600	0.27

Table 2: New Zealand Soil Acceptance Criteria for PAHs.

Relevance to Canterbury Shooting Sites

Limited information on leaching potential and toxicity exists for PAH compounds within clay targets, and the commonly reported research indicates that the compounds are tightly bound within the targets and present a low risk. However, there are reports of elevated concentrations of PAHs in soils associated with clay target debris. It is therefore considered appropriate that the potential for soil contamination in Canterbury be assessed.

[6] Guidelines for Assessing and Managing Petroleum Hydrocarbon Contaminated Sites in New Zealand, Ministry for the Environment, June 1999

5.0 Volumes of Target Debris

Various estimates of the quantity of target material deposited onto shooting clubs has been reported. The Laender Ministers report has estimated 11,000 kg of targets for a yearly shoot of 130,000 rounds (or 1.5 rounds per clay). They have estimated for a single shooting site in Germany, there could be between 1.6 to 1,600 kg of PAH deposited in a year.

Given the length of use of sites in Canterbury it is anticipated that comparable volumes of targets would have been deposited. However, the 1997 investigation did not assess management practices for clay target debris at the Canterbury sites. The quantities involved are therefore unknown, and whether the target debris was gathered to stockpile on-site or disposed of off-site is also unknown. Assessment of the management of target debris and estimates of the quantities involved in Canterbury is discussed below.

6.0 Other Debris & Site Management Issues

While this report is focussed on PAH contaminants, the documents researched identify other debris and contaminants that may be present at shooting sites. These would typically be (as reported in the Laender Ministers report):

- Alloy components in lead shot – antimony (2-3%), arsenic (2-3%), copper;
- Cadmium and/or chromium may be associated with clay target debris;
- Cartridge cases;
- Wads (partly made of PVC) and sometimes burnt to dispose of waste, so chlorine compounds may be present in the soil;
- Lead from ignition of the ammunition.

Where contaminants are not of direct concern to the environment, waste management and compliance with the relevant waste legislation is one of the main issues for clay target and other debris in the international site management guidance.

Relevance to Canterbury Sites

The investigations undertaken in Canterbury focussed on lead contamination associated with lead shot deposition at sites. The potential for other contaminants was not considered, therefore the potential for these contaminants to be present at sites in Canterbury cannot be discounted, and requires further assessment.

Waste management legislation in New Zealand is not likely to impose as stringent controls for management of shooting debris (e.g., wads or targets) as in Europe or the United States. However, landfill acceptance criteria and landfill classifications would now make it important that any off-site disposal of waste, particularly clay targets, be undertaken at an appropriate facility.

7.0 Conclusions & Recommendations

Conclusions

Limited research is available on the leaching and toxicity of contaminants from clay targets. The research and investigation reports available suggest that the PAH compounds are tightly bound within the targets and therefore present little toxicity risk to aquatic organisms where the targets are present in aqueous environments, including sediments in such environments.

However, soil analyses from shooting sites required to undergo remediation have shown PAH concentrations, above the applicable guidelines for the location, to be present. This may indicate that in soil under particular conditions, the targets may degrade such that the components are mobile and available to soil particles. It may also be attributable to small intact fragments of clay targets being present in the soil samples analysed. Further research is required to determine whether targets degrade in soil, and if during that decomposition PAH compounds are released as leachate.

The recommendations below identify the type of research considered necessary to determine the impacts of clay target deposition into soil. Of two key approaches – investigations of soils at clubs to identify the presence of specific contaminants at sites, and analytical research replicating soil and leaching conditions. The analytical approach is preferred in the first instance. This is based on the experiences from the 1997 investigative work and responses to this work, which has resulted in site management approach to the contamination being adopted, unless there is a change in land use proposed for a given site. As well as being tempered with the clear scale and significance differences between the clay target and other debris, and the lead contamination at sites. The preference for analytical work as the first step in follow-up is also conditional on the appropriate information being gathered during site investigations at the time of proposed land use changes, including that the range of additional contaminants that may be present on site other than lead, be tested for, affected areas being appropriately delineated and remediated or managed, and the potential for leaching of any of the contaminants at the site is adequately assessed.

Other contaminants, particularly those associated with leadshot, i.e., arsenic, antimony and copper, were also not tested for in the 1997 investigations. While likely to be minor in scale in relation to lead or these types of contaminants from other sources, the potential for arsenic contamination of groundwater in particular is of concern. Given the estimated quantity of lead shot deposited on sites in Canterbury (table 3.1, Environment Canterbury 1997), the relative quantities of arsenic and antimony could be a maximum of 11 up to approximately 1960 kilograms per year at each club. The recommendations below identify the need for these additional contaminants to be included in further investigations at the sites, particularly when assessing the potential for lead to leach into groundwater, and when considering investigation, remediation or management at the sites.

Recommendations

Clay Target Debris:

- Research on fate and transport of targets and their constituent components for typical soils and conditions in Canterbury be carried out to determine whether clay targets degrade and PAHs or other contaminants become available to soil or mobilise as leachate (note it is envisaged that this may involve collection of soil samples from several sites in the region);

If results of this research show PAHs or other contaminants bind to soil or mobilise in leachate, undertake the following:

- quantify the area and scale of potential contamination at the shooting site sites in the region;
- identify clay targets and their constituent components as contaminants of concern at such sites and require investigation, management and/or remediation options for these

contaminants be evaluated when change of land use at a site, or whenever site investigation is being carried out;
- evaluate the potential risk to groundwater at sites in the region.

Additional Components of Lead Shot:
- Ensure that an evaluation of the potential for contamination of groundwater from the other contaminants associated with lead shot, particularly arsenic, at the sites is included in any evaluation of lead leaching to groundwater at the sites;
- Where the potential for lead contamination of groundwater has already been assessed, evaluate the potential for contamination of groundwater from the other contaminants associated with lead shot, particularly arsenic, separately;
- If groundwater contamination is of potential concern, quantify the scale of the threat at the sites in the region and develop a management approach for these additional contaminants to be incorporated with the recommended management strategies for lead;
- Whatever the outcome of the evaluation of the risk to groundwater, ensure that the additional contaminants are included in the determinands investigated and included for management and/or remediation when a change of land use or site investigation is being carried out at any sites in the region

Other Waste Debris:
- These are likely to be minor in scale and significance, but at least should always be included in the assessment, management and/or remediation programmes for sites in the region.

These recommendations take a pragmatic approach to the nature of the assessment required because it is considered that lead is the most significant toxic contaminant at the sites and the management regime in place for these sites at present is that these risks can be managed on site, unless there are off-site effects or the land use is to be changed. It is expected that when site investigations and appropriate management or remediation options are required, the additional contaminants would be identified, evaluated and appropriate options for their management or remediation would be adopted.

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United States Environmental Protection Agency, 2005: Best Management Practices for Lead at Outdoor Shooting Ranges. Available on internet at http://www.epa.gov/region2/waste/leadshot.

APPENDICES

Best Management Practice Guidelines identified in internet research

Source:	Title:	Website Address:
Laender Ministers 1998	*Soil Contamination at Shooting Ranges*, Report by the Work Group of the Conference of the (Laender) Ministers for the Environment, November 1998	www.wfsa.net link to Environment
ITRC 2005	*Environmental Management at Operating Outdoor Small Arms Firing Ranges, Technical Guideline,* prepared by Interstate Technology and Regulatory Council (ITRC), Small Arms Team, February 2005	www.itrcweb.org link to Guidance Documents, Small Arms Firing Ranges
Florida DEP 2004	*Best Management Practices for Environmental Stewardship of Florida Shooting Ranges,* Florida Department of Environmental Protection, Bureau of Solid and Hazardous Waste, 2004 Edition	http://www.dep.state.fl.us/waste/categories/hazardous/pages/lead.htm
NSSF 1997	*Environmental Aspects of Construction and Management of Outdoor Shooting Ranges,* National Shooting Sports Foundation, 1997	www.rangeinfo.org link to Range Resources, Environmental Management
USEPA 2005	*Best Management Practices for Lead at Outdoor Shooting Ranges,* United States Environmental Protection Agency, June 2005	http://www.epa.gov/region2/waste/leadshot

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