KEY WORDS

Transition environment
Heavy metal pollution
Clay pigeon shooting

Examination and evaluation of a coastal environment contamination at a former shooting area.

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INTRODUCTION

In the recent past a very beautiful area along the shore of Venice lagoon (Venice, Italy; see Fig. 1) was used as a *clay pigeon shooting* for a long time.
The sport of *clay pigeon shooting* (see Fig. 2) involves using a shotgun to shoot at and breaking a circular flying target made of a fragile material (*clay*). It is released from a *trap* positioned in front of, or at the back of, a shooter; then, a typical target (*clay pigeon*) flight area characterizes each shooting site, where pellets (*leadshot*), shot cartridge, clay pigeon fragments and generic ammunition residues are found in a large quantities.
This process causes soil/sediment (especially by the used leadshot, clays and other ammunition parts), atmospheric and (ground)water contaminations (see Tab. 1).
The deposition areas of the above materials can, in general, be defined at the individual shooting ranges. Whereas the deposition areas of clays and wads are, as a rule, easily to perceive, the areas of leadshot impact are distributed more widely and can only be defined in exact local knowledge of the shooting ground's morphology.
Given the partly considerable soil contaminations by heavy metals and PAH in the shooting ranges' areas of impact, a lot of effects on the protected resources have to be looked at (see Box 1, *on the right*).
So, it is really evident that if a clay pigeon shooting area was realized (it has been allowed!) in a transition environment (as the Venice Lagoon) soil/sediment treatment, waste removal and potential re-use of the area are extremely delicate processes.
In this poster, only the first step of our work was presented, *i.e.* monitoring of heavy metal (Pb, As and Sb), studying their potential release and following leaching event occurred.

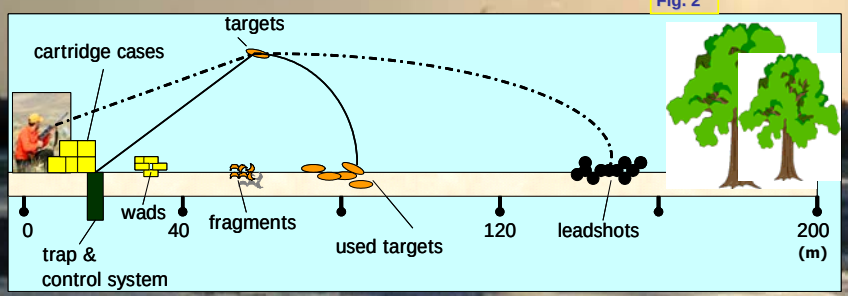
Fig. 1

BOX 1
Major known effect paths following pollution in a shooting area moving of pollutants with seeping water.
✓ Soil - Surface Water direct input or washing away, which, for example, may lead to contaminations of waterfowl by direct ingestion.
✓Soil - Plant effects on the vegetation as food source for wild animals, in certain cases also on food and forage plants, if there is agricultural use in the impact areas of shooting ranges.
✓Soil - Humans effects in case of direct ingestion, especially if shooting ranges are accessible for playing children.

EXPERIMENTAL DESIGN

- Geological soil/sediment profiles in three sites (named A, B, C; see Fig. 1) of the target flight area has been performed.
- These sampling points have been picked out considering both local morphology of the fall-out zone and different levels of water saturation into sediment.
- So, site A is almost dry, whereas B and C sites are located in typical transition environment, *barena* called, *i.e.* sediment left dry at low tide only. Furthermore, C site lies in the middle of leadshoot fall-out zone.
- Into A, B and C sites 6 cm layers has been collected, carefully removing targets, leadshoots, and other related materials eventually present.
- As well, grassy layer coating sampling sites and organisms living into has been picked, in order to verify a potential uptake and bioaccumulation (*data here not showed*).
- On sediment heavy metal content by ICP/MS (see below), both total and geochemical phases have been determined (*but only total data here not showed*), in order to verify a leaching process and to quantify heavy metal's bioavailability fraction.

Fig. 2



RESULTS & DISCUSSION

Between different contaminants detectable in the clay pigeon shooting area (see Tab. 1), Pb, As and Sb contents are here pictured as total heavy metal concentration (see Figg. 3, 4 and 5). Resulting data for each contaminant metal have been grouped for each sampling site. [Please, note different concentration scale!]. In this examination, clearly decreased contents of lead and antimony were mainly found in soil depths of up to ≈30 cm from superficial layer. It is really interesting to note for these two metals the same matched trend (although there are obviously different concentration range).

Tab. 1

CONTAMINANTS IN A SHOOTING AREA	PRINCIPAL COMPONENTS	NOTES
leadshot	~ 95 % Pb	more than 90 % of the ammunition used
	~ 2 to 3 % As	
	~ 2 to 3 % Sb	as alloy additives
clay pigeon (target)	~ 70 % stone powder	- up to 30 % stone coal pitch or petrol pitch are used as binders - both materials contain, to a different extent, polycyclic aromatic hydrocarbons (PAH) - PAH contents in clays are indicated with 5,000 to 25,000 mg/kg
	additives	to facilitate processing and forming
other ammunition parts	propellant charges	- nitrocellulose-powder - nitrocellulose : nitroglycerine / 40 : 60 - nitroguanidin
	initializing explosives	either lead-containing primers or the so-called „*reduced-toxic ammunition*" containing primers without lead additives
	wads	contaminated, among others, by small quantities of lead residues, which adhere to the wads when the leadshot leaves the barrel
	cartridge	leadshot cartridges have 24 - 32 charge g of leadshot
	cartridge cases	

Fig. 3

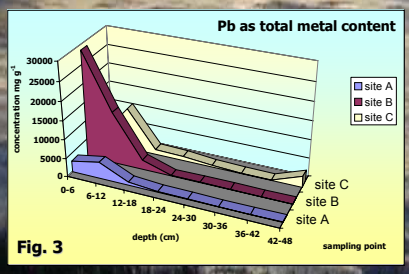


Fig. 4

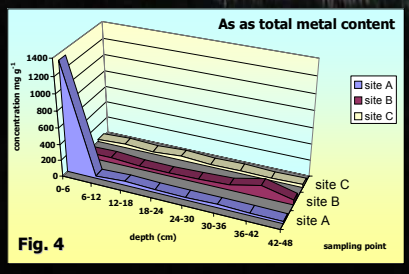
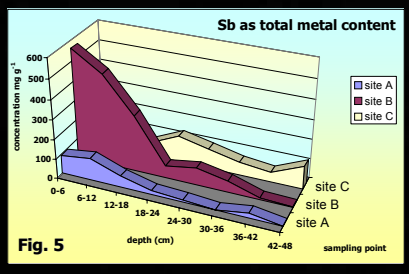


Fig. 5



Sediment has been digested using microwave digester (ETHOS 1600) with :

- 5 mL of MilliQ water,
- 1,5 mL of hydrofluoric acid
- 3 mL of Acq*ua Regia* (3:1/HCl:HNO_3)
- 3 replicates /layer (*n*=3)

ICP-QMS (Agilent 7500, Agilent Technologies, U.S.A.)	
Forward Power	1450 W
Plasma gas flow	15 L min^{-1}
Auxiliary gas flow	1 L min^{-1}
Carrier gas flow	1.09 L min^{-1}
Sample depth	8 mm
Monitoring masses (As, Sb, Pb)	*m/z* 75 ; 121 ; 208
Acquisition mode	Peak hopping
Integration time per mass	0.1 – 0.5 sec
Spray chamber temperature	2 °C

CONCLUSIONS

It is obviuous that a clay pigeon shooting area, lying in a brackish water contest, soil/sediment treatment, waste removal and potential re-use are extremely delicate processes.

Long detention periods, high acidity of the sediment (soil), input of acid radicals and acid-forming substances with the atmospheric deposition, as well as a high level of organic substance (*i. e.* moor soils) cause an increasing mobilization of lead. For this reason, it cannot be excluded that in future, other compartiments will be damaged by these concentrations of pollutants in the sediment. Decisive factors are mainly sediment pH-value, texture, iron and manganese contents, clay content and the content of sediment organic matter.

The danger of lead and other heavy metals entering the food chain via grazing has been referred.
About requirements on recycling, it is clear that the re-processing of the waste (sediment material mixed with leadshot) at the shooting range, however, is relatively expensive particularly in a transition environment, with the consequence that the proceeds of the lead sale do not always cover the costs. But it should be clear in wetlands (moors, wetland biotopes) shooting ranges must not be built (!). The same applies for high-water and flood areas.
In cases that shooting ranges were operated in wetland areas the planning and carrying out of remediation measures require a close cooperation and coordination with the responsible nature conservation authority.

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