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The influence of environmental conditions on lead transfer from spent gunshot to sediments and water: Other routes for Pb poisoning

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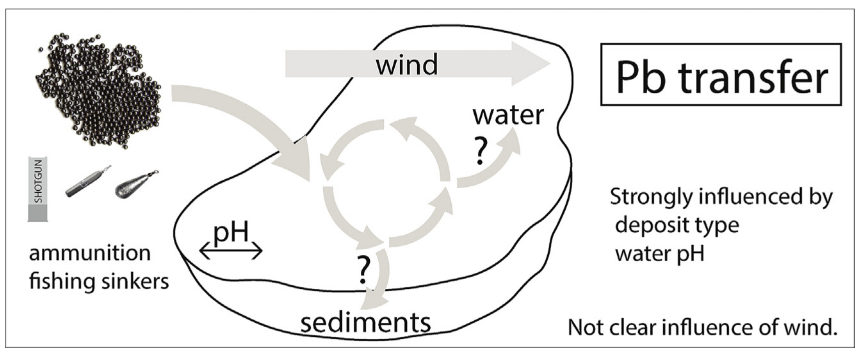
HIGHLIGHTS

- Sediment type and water pH visibly influenced Pb transfer to water and sediments.
- Simulated wind conditions were a significant factor more often in gravel sediments.
- The highest deposit to water and sediments occurred in acidic mud microcosms.
- The relative higher deposits to water and sediments occurred in gravel microcosms.
- Pellet erosion did not differ much between sediment types in microcosms.

GRAPHICAL ABSTRACT



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ABSTRACT

Lead (Pb) from spent gunshot and fishing sinkers is recognized as the main source of Pb poisoning among waterfowl. It is also suspected to directly pollute water and sediments, but no appropriate, comprehensive evaluation of this issue has so far been carried out. An experiment on Pb pellets in microcosms ($n = 160$) with two sediment types (mud and gravel), three water pH values (4, 7 and 9) and two wind levels (wind and windless simulation) was therefore run. Substantial differences in Pb transfer (measured with ICP-OES) between sediment types and pH levels of water were observed. Simulated wind conditions were a significant factor only for some variables and circumstances. The strongest Pb deposit to water and sediments occurred in mud microcosms with water of pH value of 4. Median pellet erosion during the experiment differed little between sediment types. The experiment revealed that Pb transfer from spent gunshot to the environment occurs only in specific environmental conditions.

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1. Introduction

Lead (Pb) poisoning of waterfowl has long been a major threat in wetland areas all over the world (Binkowski and Sawicka-Kapusta, 2015; Friend, 1999; Mateo et al., 1998; Matz and Flint, 2009; Sanderson and Bellrose, 1986). There is a connection between the lead poisoning of waterfowl and the prevalence of spent gunshot (pellets) and fishing sinkers in waterfowl habitat, where the number of spent gunshot per square meter sometimes reaches 288

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or even 370 000 (in shooting ranges) (Mateo et al., 1998; Stansley et al., 1992). Birds may mistake Pb elements for stones when foraging (Scheuhammer and Norris, 1996). The acidic nature of the gizzard and its grinding mechanism dissolve pellets and Pb enters the bloodstream. The highest Pb concentrations are noted in bones (long after the exposure) which are where the Pb finally deposits. High concentrations are also found in kidney, liver and blood tissues where a rapid turnover is observed. The exposure causes neurotoxic effects, anemia due to the decrease of ALA-d activity and even death (Binkowski and Sawicka-Kapusta, 2015). Poisoned birds, if they do not die, are vulnerable to predators and this leads to transfer of the poison (in meat, organs and even organic lead chemical species deposited in fat) to higher levels of the trophic chain and add the ecotoxicological importance of the problem (Clark and Scheuhammer, 2003).

Most investigations link the poisoning with nothing but the ingestion of spent pellets by birds. There are, however, suspicions that, due to mechanical corrosion and chemical reactions, Pb pellets may be transferred to water and sediments which may then become further carriers of Pb to the whole ecosystem (Binkowski and Rzonca, 2014; Rooney et al., 2007). Experiments on Pb transfer from bullets into the soil of shooting ranges (purpose-built or adapted) bearing in mind various environmental factors have already been carried out and they suggest a significant transfer (Hardison et al., 2004; Rooney et al., 2007). There is, however, no such data for water, except for a study that denies the link between hunting activity and Pb concentrations (Binkowski and Rzonca, 2014). Studies undertaken on waterfowl hunting areas where pellets rather than bullets are used are scarce. Discrepancies between them (in Pb content, additives, and hardness) may be significant regarding their fate in the wild. The surface of Pb elements in water may be covered by a light layer of Pb oxide reducing its initial reactivity, unless it is broken due to acidic dissolution or mechanical friction. Despite the fact that transfer efficiency has so far not been thoroughly evaluated, some reports took it for granted that the pollution of environment by the pellets occurs which may be incorrect.

Research that verifies the Pb transfer from pellets into sediments and water in controlled conditions is therefore crucial. The experiment, which included not only the evaluation of Pb deposit in water and sediments, but also environmental factors, such as water pH, differences in the sediments and simulated wind conditions, was carried out. This allowed an evaluation of the conditions in which Pb transfer happens and those levels at which it is higher and lower. This is critical in areas rich in spent gunshot and fishing sinkers, where recognizing cases with water and sediments as Pb carriers is extremely important. This knowledge may also be helpful in preparing the protection and restoration plans for hunting wetlands.

The main aim of the study was to verify in controlled conditions the influence of a wind, water pH levels (4, 7 and 9) and types of sediments (gravel and mud) on Pb transfer from spent gunshot to water and sediments. Variables, such as Pb concentrations, Pb deposit and pellet erosion, were calculated in the inquiry. As well as evaluation of influence, relationships between variables were also investigated.

2. Materials and methods

The experiment was carried out in the Laboratory of the Institute of Biology (Pedagogical University of Cracow, Poland) in 2015. For the models of fish ponds, microcosms (500 mL glass jars; $n = 160$) filled with the tap water (previously adapted) were used.

2.1. The microcosms

The sediments used in the preparation of microcosms were of two different types: gravel and mud. They were chosen since both of them may be found on wetland hunting areas. Gravel was collected from the river San near Jaroslaw city in south-eastern Poland and mud was collected from fish ponds near Zator city in southern Poland. Both materials were collected in places where there was neither hunting nor fishing, so Pb pollution from either pellets or sinkers was out of the question.

Materials were firstly air-dried, cleaned of larger stones, and organic fragments. Sediments were then thoroughly mixed to obtain a homogenous portion of each type and sampled for Pb and basic analyses (Table 2) (Karczewska and Kabała, 2008). Since the values measured were in line with what was typical, prepared sediments were transferred to microcosms.

The tap water used in the microcosms was firstly poured into the 100 L glass container (microbiologically and chemistry clean) and mixed. Initial pH was then measured (value obtained 6.5; CX-505, Elmetron) and samples for physicochemical and for Pb analysis were taken (Table 3). The water was then divided into three glass containers and pH was adjusted by adding nitric acid (65% Ultranal, POCH, Gliwice), sulfuric acid (95% Ultranal, POCH, Gliwice), sodium hydroxide (30%, POCH, Gliwice) and calcium hydroxide (99.995%, Sigma-Aldrich, Munich).

In each microcosm 100 mL of dry sediment samples and 400 mL of water were put. All the microcosms were distributed according to the statistical model into groups and left for 24 h for the internal conditions to stabilize (Table 3). During the next five days the pH was adjusted in the microcosms and they were then left for another week for the conditions to stabilize.

Four shotgun Pb pellets (diameter 3 mm) of common manufacture on the Polish market were used in each microcosm. Each of the four pellets in the sample was weighed (accuracy to 0.0001 g, laboratory balance RadWag WPA 60/C) before and after the experiment to calculate the pellet erosion expressed by a standardized subtraction.

During the experiment all the microcosms were stored in the room with natural photoperiod at 19°C. The pH of the water was checked in every microcosm every two days and, if needed, adjusted to desired values (the maximum pH drift observed was at the beginning and reached 0.5 unit). The experimental group with simulated wind conditions were shaken every two days for 30 s to mix the water. The experiment lasted 30 days.

Table 1
Parameters of the sediments used in the preparation of the experiment (density, pH and shares were measured in air-dried samples).

Parameter	Mud sediment	Gravel sediment
Dry weight content [%] at 105 °C	97.57	97.77
Ash content [%]	93.25	97.02
Density [g/ml]	1.34	1.81
pH in water (electrochemical method)	6.4	7.6
pH in KCl (electrochemical method)	5.4	6.6
Pb concentration [μg/g]	25.7	<0.05
Share [%] - gravel very fine	0.00	4.71
Share [%] - sand very coarse	0.00	27.70
Share [%] - sand coarse	0.00	60.96
Share [%] - sand medium	0.00	5.59
Share [%] - sand fine	0.16	0.75
Share [%] - sand very fine	10.99	0.03
Share [%] - Silt very coarse	33.04	0.11
Share [%] - Silt coarse	26.74	0.10
Share [%] - Silt medium	14.14	0.04
Share [%] - Silt fine	7.48	0.02
Share [%] - silt very fine	3.36	0.01
Share [%] - clay	4.07	0.00

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