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Lead pollution from waterfowl hunting in wetlands and rice fields in Argentina

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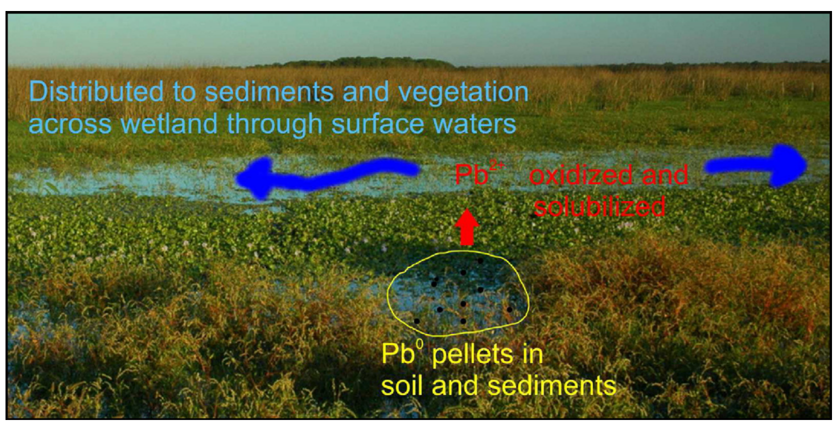
HIGHLIGHTS

- Soil pellet density shows high variability between sites.
- Site Pb(II) concentrations in soil and waters do not correlate with site pellet density.
- Site Pb(II) concentration in grasses does not follow site Pb(II) content in soil.
- Pellet Pb is oxidized, solubilized and distributed over the site by surface waters.

GRAPHICAL ABSTRACT



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ABSTRACT

The pollution of wetlands by lead derived from waterfowl hunting with lead shot was investigated. We determined soil pellet density and Pb concentration in soil, water and vegetation in natural wetlands and rice fields in central-eastern Santa Fe province, Argentina. Pellet density varied greatly among hunting sites (between 5.5–141 pellets/m^2) and pellets were present in some control sites. Soil Pb concentration in most hunting sites (approximately 10–20 mg kg^{-1}) was not much higher than in control sites (~5–10 mg kg^{-1}), with the exception of the site with highest pellet density, which also had a high Pb soil concentration. In water, on the other hand, Pb concentration was similar in all sites (~4–7 μg L^{-1}), both control and hunting, and higher than reference values for aquatic media. Lead was also present in vegetation, including grasses and rice crops, in almost all cases. Most soil-collection sites were slightly acidic, and were frequently flooded. These results strongly suggest that metallic Pb from spent shot is oxidized and dissolved due to wetland conditions. Thus, the pollutant is readily mobilized

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and distributed across all wetland areas, effectively homogenizing its concentration in locations with and without hunting activities. The replacement of lead by nontoxic materials in pellets appears to be the only effective way to prevent Pb pollution in wetlands.

1. Introduction

Lead poisoning of waterbirds due to spent shot ingestion has been widely reported around the world (Pain, 1992; Guitart et al., 1994; Friend, 1999; Fisher et al., 2006; Pokras and Kneeland, 2008). Before the substitution of lead shot by non-toxic alternatives, 1.5–3 million waterfowl were annually lost in the U.S.A. (U.S. Fish and Wildlife Service, 1990), and about one million in Europe (Mateo, 2009). High-risk sites are those where intense hunting occurs and uncountable lead pellets are introduced to the environment over many years (Kendall and Driver, 1982; Pain, 1990, 1991; Guitart et al., 1994; De Francisco et al., 2003; Mateo et al., 2007). Lead pellets can remain between 15 and 300 years in soil, depending on physicochemical conditions (Jorgensen and Willems, 1987). In Denmark, pellet decomposition rate is about 1% per year (Jorgensen and Willems, 1987), but under environmental conditions common in tropical and subtropical regions, such as high temperature, moisture and rainfall, the decomposition rate increases, as well as with mechanical soil tillage in crop fields (Cao et al., 2003).

In contact with soil, lead in shot is oxidized from metallic Pb to Pb(II) by abrasion and weathering processes. In soil, Pb(II) soil is present in the form of different chemical species of increasing stability until reaching highly stable mineral forms (Lin et al., 1995; Cao et al., 2003; Vantelon et al., 2005; Jensen et al., 2006; Torri and Lavado, 2008; Ferreyroa et al., 2014). The most commonly found mineral forms are massicot or litharge (PbO), cerussite ($PbCO_3$) and hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) (Cao et al., 2003; Vantelon et al., 2005; Hashimoto et al., 2011; Hashimoto, 2013). These transformation processes result in an important increase of the pollutant in soil, water, and vegetation (Cao et al., 2003), often making it totally or partially bioavailable for its incorporation into the food chains (Guitart and Thomas, 2005; Dickerson et al., 2007). In general, it is assumed that the bioavailable part of Pb is the soluble and interchangeable fraction (Magrisso et al., 2009; Osakwe, 2013), but other Pb chemical species can also be bioavailable, depending on the biological species considered.

Both spent lead pellets and leached Pb(II) can be incorporated into living organisms through several pathways (Čelechovská et al., 2008). Pellet ingestion is, however, the most common way of exposure in waterbirds (Behan et al., 1979; Eisler, 1988; Beyer et al., 1994, 1997; Scheuhammer and Norris, 1995; Farag et al., 1998; Mateo, 2009; Burco et al., 2012). Notwithstanding, estimating lead concentrations in environmental compartments such as soil, wetland sediments and surface water, as well as that adsorbed by vegetation, allows for the evaluation of added indirect exposure risk for wildlife, domestic animals and people associated with these environments (Braun et al., 1997; Rooney et al., 1999; Guitart and Thomas, 2005; Romero et al., 2007; Pain et al., 2010; Pareja-Carrera et al., 2014).

Central-eastern Santa Fe province is one of the most significant hunting sites for wild ducks in Argentina, attracting hunters from all around the world (Ferreyra et al., 2014). Hunting has been ongoing for over 20 years on a wide mosaic of natural and artificial wetlands (e.g. rice fields) (Zaccagnini, 2002). Cartridges normally used in Argentina for waterfowl hunting are caliber 12 with a mass of 30 g (24 to 36 g range). The number of pellets per cartridge varies by pellet size (160 N°3 pellets of 3.3 mm, 199 N°5 pellets of 2.9 mm, or 339 N°7 pellets of 2.5 mm) (Tagliafico, 2014). Pellets are composed of 97% metallic lead (Pb), 2% antimony (Sb), 0.5% arsenic (As) and 0.5% nickel (Ni) (Industrias Deriplom, 2014). Even though there is a restriction to using lead pellets in Santa Fe wetlands since 2011 (Gobierno de Santa Fe, 2011), hitherto this type of ammunition remains the only available option locally.

In spite of recent studies showing high levels of lead exposure in waterfowl from spent shot in the provinces of Santa Fe and Corrientes (Ferreyra et al., 2009, 2014, 2015), there is still no information about the presence, concentration and distribution of Pb in other elements of these ecosystems. The objective of this study is to estimate the density of spent lead pellets in the soil, and to assess the presence of lead in different biotic and abiotic components (soil, water, and plants) of natural wetlands and rice fields where waterfowl hunting occurs.

2. Materials and methods

2.1. Study area

The area under study encompasses natural wetlands (W) and rice fields (RF) located in San Javier and Garay departments, central-eastern Santa Fe province, where waterfowl hunting regularly occurs. These sites are located in an old alluvial plain molded by the Paraná River, as well as by different geomorphologic forces during the Quaternary period (Ramonell et al., 2013). Seventy percent of the plain is occupied by wetlands (Pilatti et al., 2002), where several plant communities grow, dominated by hygrophilous species like *Luziola peruviana*, *Ludwigia peploides*, *Schoenoplectus californicus*, *Typha domingensis*, *Eichhornia* sp., *Polygonum* spp., as well as free-floating species like *Azolla* sp. *Limnobium* sp., *Nymphaea* sp., *Pistia* sp., *Salvinia* sp., among others (Hilgert et al., 2003). Wetlands are mainly used for cattle grazing (Ramonell et al., 2013) though many are presently being drained and converted to crop fields. Rice crops alternate flooding and dry periods (summer and winter, respectively), generating, together with natural wetlands, a landscape that favors the establishment of several species of waterbirds, particularly large populations of wild ducks (Blanco et al., 2006). These birds are considered pests for rice crops due to their trampling and consumption of shoots and grains (Bucher, 1983; Zaccagnini, 2002). This is one of the reasons why sport hunting is allowed in these habitats, though damage from birds has not yet been quantified. The climate of this area is humid or subhumid, with 19–20 °C mean annual temperatures, 900 to 1100 mm mean annual rainfall, concentrated in the summer (Hilgert et al., 2003).

2.2. Sampling and analysis

Six sites within natural wetlands were chosen for this study: four with sport hunting (W-H1, W-H2, W-H3, and W-H4) and two without hunting, as controls (W-C1 and W-C2). Similarly, three rice fields were chosen: two where hunting occurs (RF-H1 and RF-H2) and one where it does not (RF-C) (Fig. 1).

According to data from INTA (http://geointa.inta.gov.ar/visor/), the soil of sites W-C1 and W-H1 are Typic Haplaquolls (USDA Soil Taxonomy); W-C2, RF-C, and RF-H1 are Thapto-argic Udipsamments, W-H2 is a Typic Natraqualf, W-H3 is a Typic Natraquoll, whereas sites W-H4 and RF-H2 are considered undifferentiated complexes, without classification, as these are water runoff areas. Table A1 (Appendix A, Supplementary Material) summarizes the main characteristics of the upper horizons (0–20 cm) of these types of soils.

Table A2 (Appendix A, Supplementary Material) details sampled sites according to year and season. Sediment cores were sampled all years, while soil and rice plants from rice fields were collected in 2009