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

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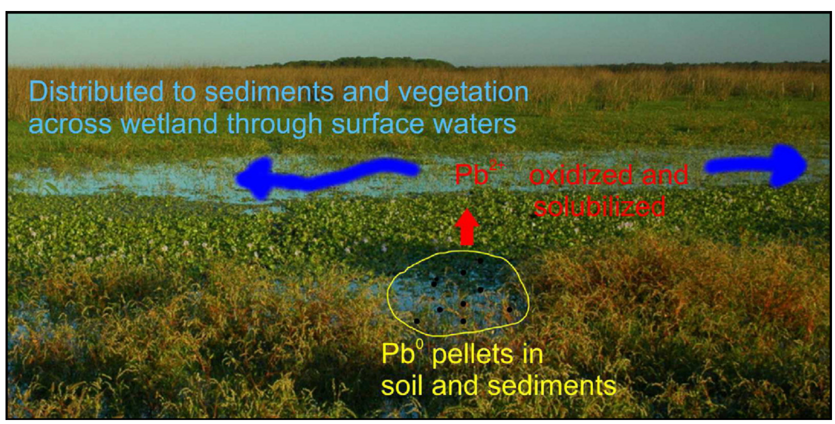
HIGHLIGHTS

- 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

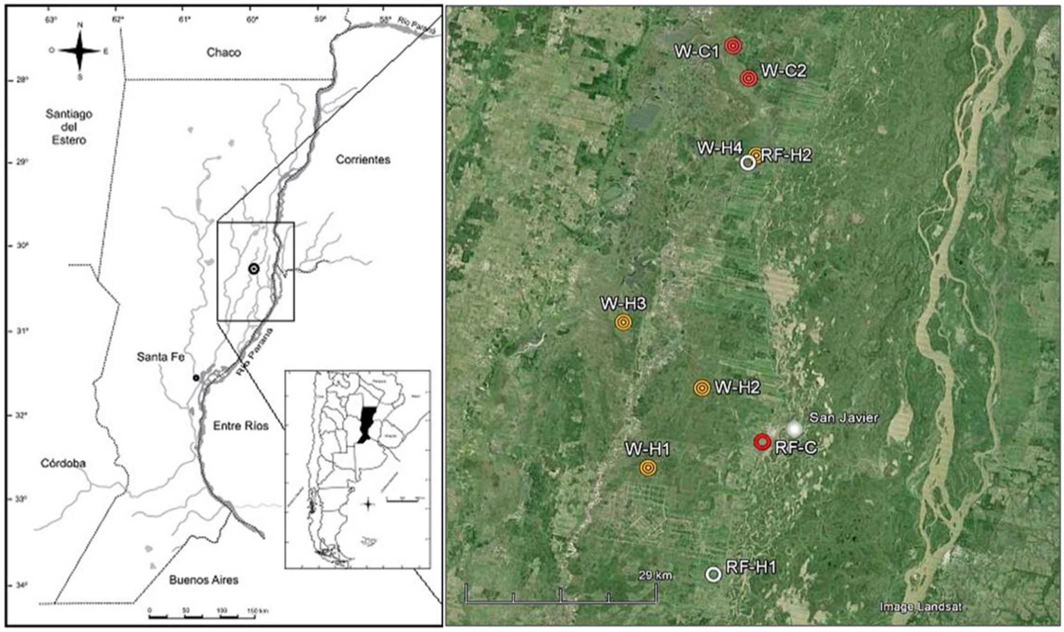

Fig. 1. Study area and sampling sites. ◎: wetland-control sites, ◎: wetland-hunting sites, ◎: rice field-hunting sites and ○: rice field-control site.

and 2010, and soil, water and plant samples were collected in natural wetlands in 2011 and 2012.

At each site, two parallel 500 m long transects were defined, located perpendicularly to, and at a distance between 30 and 60 m, of the shooting line. From a randomly selected point within each transect, ten sampling points separated by 50 m were set up. These sampling points were georeferenced.

2.2.1. Lead pellets in soil

Samples were taken with a soil core sampler 16 cm in diameter and 15 cm in depth. Soil samples were air-dried at room temperature, and later analyzed by radioscopy to detect the presence and location of images compatible with lead pellets, which were later confirmed by manual recovering. Radioscopy was performed on a Siemens Vertix U (500 mA–500 kV) with an exposure dose of 90 kV, 64 mA/s × 320 ms, and a distance focus-plaque of 1 m. Images were processed with a Fuji Film FCZ equipment with a digital capsule, using K-Pacs software from Image Information Systems Ltd. Fig. B1 (Appendix B, Supplementary Material), shows some examples of radioscopic images of lead pellets within soil cores.

2.2.2. Lead determination in soil

From the same sampling points in the transects used for soil cores, a second sample, 2.2 cm in diameter × 5 cm deep was taken, according to EPA Standard Procedure SOP 2012 (02/18/2000) for lead determination (i.e. 20 soil samples per site). Each single sample was divided in two aliquots, one of which was submitted for analysis while the other was conserved as backup. Samples from natural wetlands were oven-dried at 40 °C during 48 h until constant weight; all soil compositions reported are referred to dry weight. The dry samples were passed through a 2 mm stainless steel sieve and then digested with a MARS-5 Microwave Digestion System, CEM Corporation, USA, using nitric acid Pro Analysis Merck®, according to Method US EPA SW 846-3051 (power: 400 W; pressure (max.): 800 psi; temperature (max): 200 °C; time: 30 min). Lead analyses were conducted by inductively coupled plasma-atomic emission spectrophotometry (ICP-AES) (Shimadzu 9000, Shimadzu Corporation, Kyoto, Japan), following 200.7 EPA standards (U.S. Environmental Protection Agency). Standard Reference Materials were used in 2011 and 2012 to validate results from soil (RTC-Trace Elements on Fresh Water Sediment, CNS 392-050, certified value of lead: 121 mg/kg, DL: 0.5 mg/kg). Samples from rice fields were processed by graphite furnace at STPGFAA conditions according to EPA 600/R-94/111, 200.9 standards, with a Perkin Elmer AAnalyst 800 Atomic Absorption Spectrometer (Detection Limit (DL): 0.4 mg/kg).

2.2.3. Lead determination in water

Water samples were collected only from natural wetlands, following standard method 3010B (Clesceri et al., 1999). At each sampling point where surface water was found, 200 cm^3 of water were collected in plastic vials previously washed with distilled water and 0.5 M HCl. Single samples were kept at pH 2 with high purity HCl (SUPRAPUR; Merck Labs). In a preliminary study, ten randomly selected unfiltered water samples were microwave-digested according to US EPA SW-3052 standard. Then, lead was quantified in aliquots of the digested and non-digested samples, filtered through 2.0 μm membranes and the results were contrasted. No significant differences were found; thus, sample digestion was not further conducted. Lead analyses were carried out on samples filtered as above with the same methods used for soil samples of natural wetlands as described in 2.2.2, at DL: 2 μg/L. Standard Reference Materials (RTC-Trace Metals by AA-2, Constant Value QCI-049, certified value of lead: 51.2 μg/L ± 1.49 μg/L/obtained value 49.9 ± 2.2 μg/L) were used.

2.2.4. Lead determination in vegetation

At each soil sampling point in natural wetlands the aboveground vegetation biomass present in a 0.5 × 0.5 m area was collected. Samples were repeatedly rinsed with collection-site water, and finally with distilled water. Then, plants were identified at family, genus or species level. When the harvested dry biomass was not enough to perform Pb determinations, plants of the same species, genus or family from two or more sampling points from each site were pooled. Plant samples were oven-dried at 60 °C during one week. Then, they were digested and analyzed as in 2.2.2, together with a Certified Reference Material. In all cases, the determinations were done with external calibration using certified standards Chem-Lab, Zedelgem B-8210, Belgium (Aquatic plant (*Lagarosiphon major*), Certified Reference Material BCR-060, certified lead value 64.0 mg/kg. Institute for Reference Materials and Measurements, Joint Research Centre, European Commission (Feb 08, 2011), Retieseweg 111, 2440 Geel, Belgium) (DL: 0.25 mg/kg).

Rice plants ($n = 18$) were only collected in the rice fields subjected to sports hunting (RF-1 and RF-2). Samples were oven-dried at 60 °C for a week. Then, they were microwave-digested in Milestone START D. Pb determinations were done by electrothermal atomization at STPF conditions. External calibration curve with certified aqueous standards was employed. A Perkin Elmer AAnalyst 800 Atomic Absorption Spectrometer was used (DL: 0.2 mg/kg).

2.3. Statistical analyses

Statistical analyses were carried out with Infostat software (available at http://www.infostat.com.ar). The Kruskal–Wallis test was used to analyze differences in pellet density, Pb in soil, Pb in water, and Pb in vegetation among sites. For each sampling date, when significant differences were detected a *post hoc* pair comparison analysis was carried out.

3. Results

3.1. Site scale analysis

3.1.1. Pellet soil density

A total of 441 soil cores were analyzed, distributed in 126 from control and 315 from hunting sites. Control site samples were 123 in W and 3 in RF, whereas those of hunting sites were 252 in W and 63 in RF. Pellets were found in 98 samples, 4 from W control sites and 94 from hunting sites (73 in W and 21 in RF). The average number of pellets per core was 1.63 (range 1–5). Recovered pellets showed different conditions depending on the collection site. Most presented a clean surface whereas others appeared eroded and coated with a layer of white. We found pellets in soil from all natural wetlands sampled; however there were significant differences between sites and sampling dates (Fig. 2). The site W-H2 registered the highest densities at all dates.

Pellets were also found in hunting RF soil cores at all sampling dates, being higher for RF-H1 than for RF-H2 (Fig. C1, Appendix C, Supplementary Material).

3.1.2. Lead in soil

A total of 390 soil samples were collected, 123 from control sites (all in W) and 267 from hunting sites (240 in W and 27 in RF). Significant differences were observed in the Pb content between sites, at all sampling dates (Fig. 3). Control site W-C1 showed significantly lower Pb values than all hunting sites, except in May 2012 when its Pb values resulted similar to hunting sites W-H3 and W-H4. On the other hand, site W-C2 presented Pb contents higher than W-C1, and did not significantly differ from hunting sites (Fig. 3). Thus, site W-C2 was considered an inadequate control site. Among hunting sites, site W-H2 presented the highest lead content, which was about 450% higher than W-C1.

In hunting RF sites, Pb contents were similar to values found in natural wetlands with hunting (Fig. C2, Appendix C, Supplementary Material compared with Fig. 3). In February 2010, site RF-H1 presented higher lead content than site RF-H2.

3.1.3. Lead in surface waters

Water samples were mainly collected in July 2011 due to an extended drought registered in 2012. Thus, a total of 109 water samples from natural wetlands were obtained, distributed in 59 samples in July 2011, 36 in May 2012 and 14 in July 2012. In Table D1 (Appendix D, Supplementary Material), the water physicochemical parameters registered at the sampling sites between 2009 and 2012 are presented. pH values in most cases ranged between 5.5–7.6, with some exceptions in 2011 and 2012 when higher values, up to 10.4, were found in some sites. Oxygen content was very low in most cases, except when high pH values were recorded, and where higher O_2 concentrations (up to 19.3 mg/L) were found. Due to the aforementioned drought which hampered the collection of representative water samples in 2012, only Pb concentrations for July 2011 are presented (Fig. 4); a high dispersion of values was found in most cases, with sites W-H2 and W-H4 showing the highest Pb concentrations.

3.1.4. Lead in vegetation

Fifty three percent (173 out of 360) of the vegetation samples collected in natural wetlands (formed by either one or more species per sample) had grasses (Poaceae). The most representative grass species

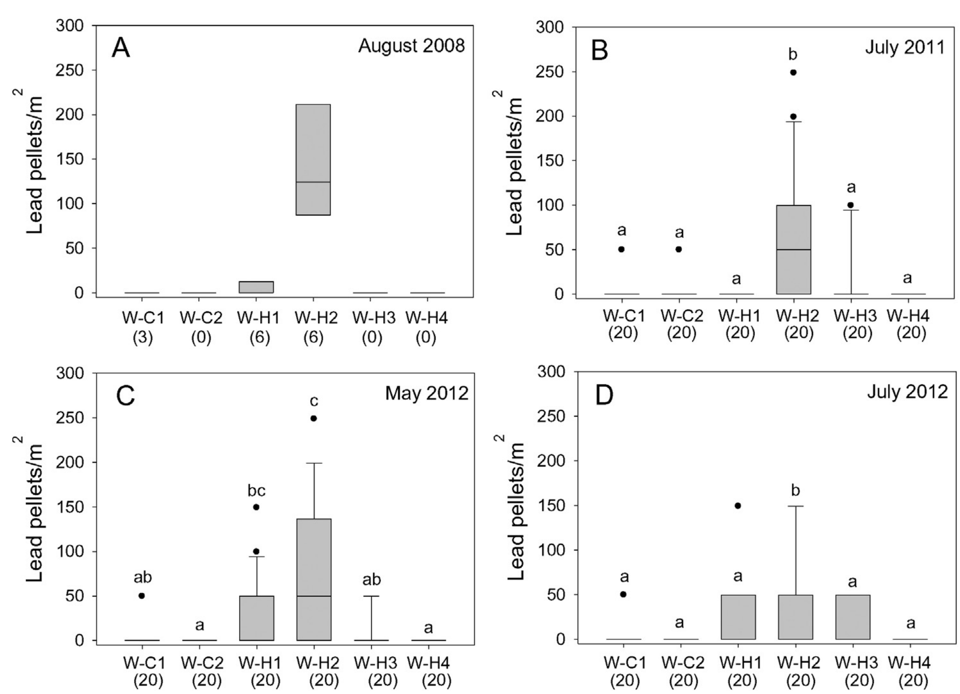

Fig. 2. Pellet density (number of pellets/m²) in natural wetlands, both control (W-C) and hunting (W-H) at different sampling dates. For each case different letters indicate significant differences ($p < 0.05$). Boxplots embrace 25th and 75th percentiles, the median being shown. Whiskers show 10th and 90th percentiles. Numbers in brackets show the sample size for each site.

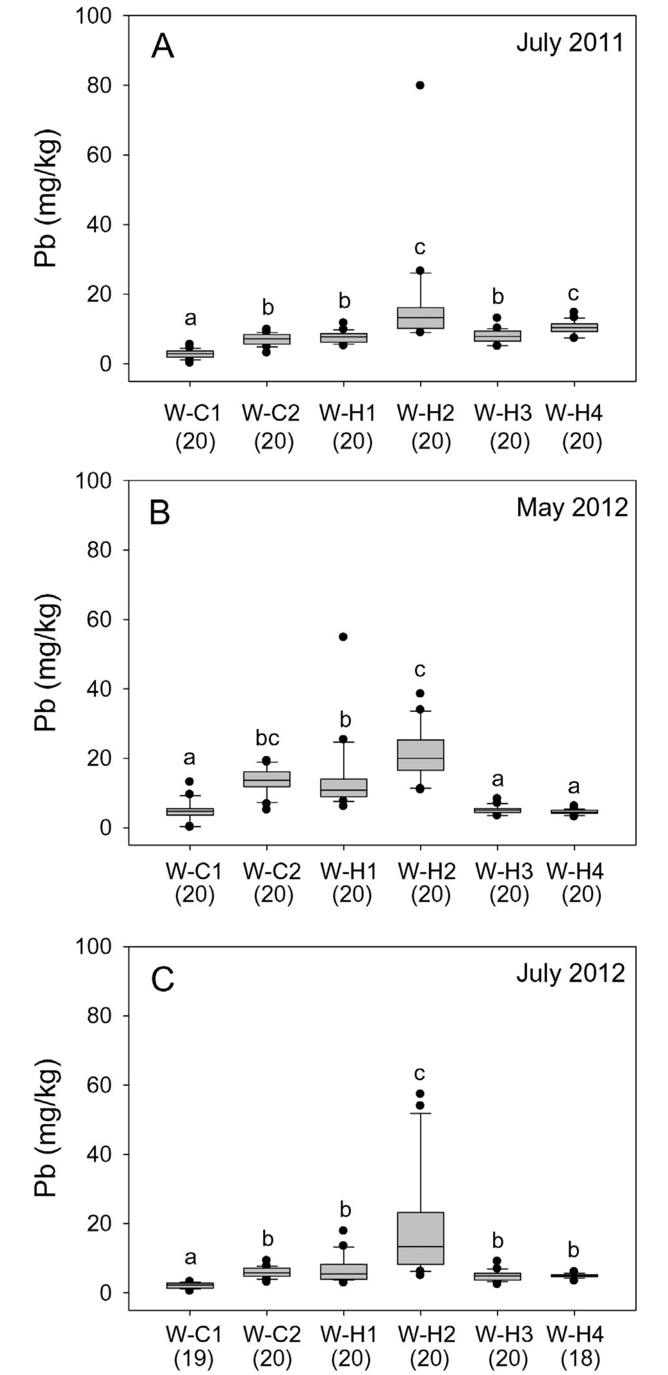

Fig. 3. Pb soil contents in natural wetlands control (W-C) and hunting (W-H) sites at different sampling dates. For each case different letters indicate significant differences ($p < 0.05$). Boxplots embrace 25th and 75th percentiles, the median being shown. Whiskers show 10th and 90th percentiles. Numbers in brackets show the sample size for each site.

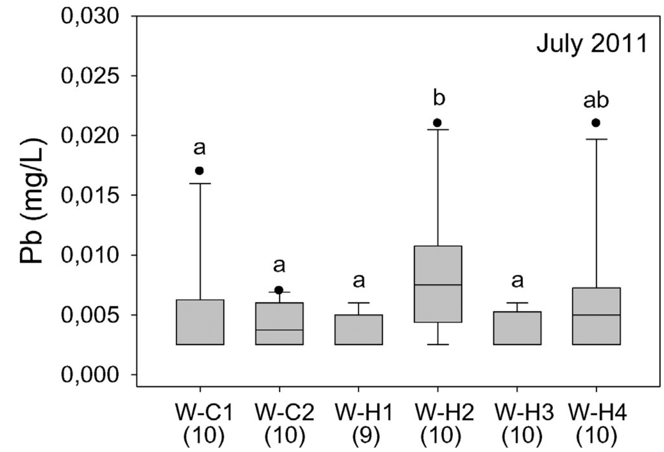

Fig. 4. Pb concentrations in water at natural wetlands sites, both control (W-C) and hunting (W-H) in July 2011. For each case different letters indicate significant differences ($p < 0.05$). Boxplots embrace 25th and 75th percentiles, the median being shown. Whiskers show 10th and 90th percentiles. Numbers in brackets show the sample size for each site.

were *L. peruviana*, *Cynodon dactylon*, *Echinochloa* sp., whereas the most common non-grass species were *L. peploides*, *Polygonum* spp., *S. californicus*, *Azolla* sp., *Salvinia* sp. *Nymphaea* sp., among others. Table E1, Appendix E (Supplementary Material) shows several plant species in which Pb was recorded that are commonly eaten by waterbirds and cattle. For the analysis of the relationship between soil and plant Pb contents, only grass samples were considered. In natural wetlands Pb was recorded in all grass samples (Fig. 5). In July 2011 and May 2012, Pb concentration in grasses from site W-H2 was higher than in all other sites (Fig. 5A and B). In July 2012, grass samples from sites W-H2 and W-H3 had higher lead contents than all other sites (Fig. 5C).

In hunting RF sites, Pb content in rice plant stems (Fig. E1, Appendix E, Supplementary Material) was similar to that of grasses from hunting W sites (compared with Fig. 5). Site RF-H1 presented higher Pb content than site RF-H2.

3.1.5. Relationship between pellet density and Pb contents in all environmental compartments

Fig. 6 shows the relationship between lead concentration in soil, water and grass samples (Poaceae) and pellet density. In spite of an apparent increasing trend, a general correlation between pellet density and soil Pb (Fig. 6A) was not observed. For instance, in control site W-C1 no pellets were found, yet the average Pb concentration was the same as site W-H1, which had an important pellet density. On the other hand, at RF sites, the pellet density in RF-H1 was noticeably higher than in site RF-H2, whereas Pb content was only slightly higher. In site W-H2 both pellet density and Pb concentration were the highest of all sites studied, being the only case where an apparent correlation was observed; moreover, this site also presented the highest Pb concentrations in water (Fig. 6B) and plants (Fig. 6C). Site RF-H1 had a pellet density considerably higher than RF-H2, whereas Pb content did not follow the ratio observed in pellets. Finally, in both wetland-control sites, W-C1 and W-C2, Pb was found in soil in different concentrations, albeit pellet density was similar in all cases.

Likewise, no correlation was found between Pb in surface water and pellet density (Fig. 6B), nor between Pb in grasses and Pb in soil (Fig. 6C). For example, Pb soil concentration in site W-H2 was considerably higher than in sites W-H1 and W-H3; however, the mean Pb content in grasses did not follow the same order, being 2.61, 0.79 and 2.21 mg/kg, respectively.

3.2. Analysis at the wetland scale

3.2.1. Pellet density and lead content in environmental compartments

Fig. 7 compares results at the wetlands scale. In all hunting sites, both natural wetlands and rice fields, pellet density was significantly higher than in control sites (Fig. 7A). In natural wetlands, Pb contents in soil and grasses were higher in hunting sites than in control ones (Fig. 7B and D), whereas Pb values in hunting RF were similar to hunting W sites (Fig. 7B and D). Finally, in W, Pb content in water was similar in hunting and control sites (Fig. 7C).

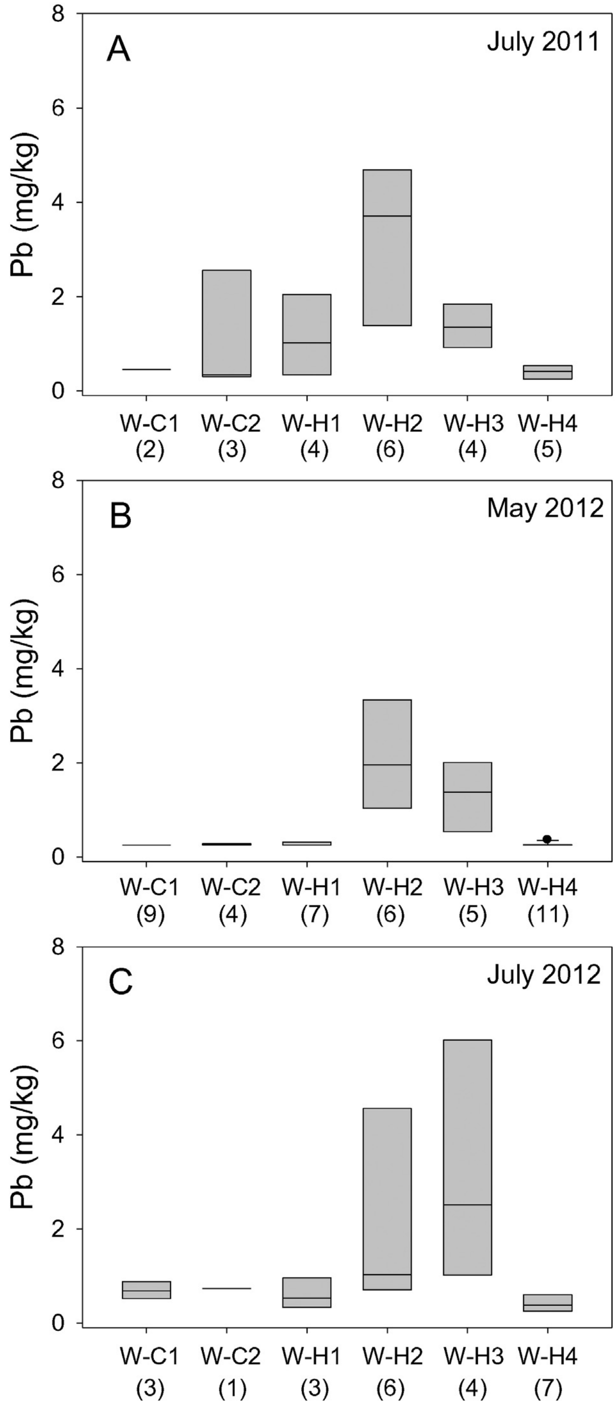

Fig. 5. Pb contents in grass samples from natural wetlands in control (W-C) and hunting (W-H) sites at different sampling dates. Boxplots embrace 25th and 75th percentiles, the median being shown. Whiskers show 10th and 90th percentiles. Numbers in brackets show the sample size for each site.

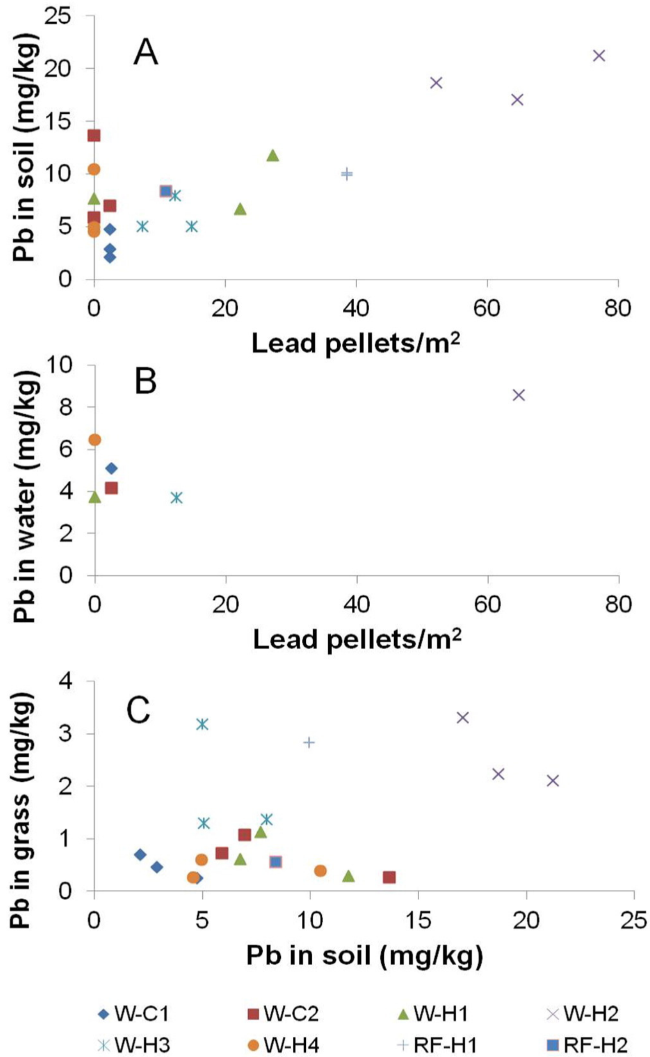

Fig. 6. Plots of soil Pb concentration as a function of pellet density (A), water Pb concentration against pellet density (B) and Pb in grasses (C) against Pb in soil, for all sampling dates together. W and RF indicate natural wetlands and rice fields, respectively; C indicates control sites, and H hunting ones.

4. Discussion

This study shows for the first time important Pb levels in soil, water and vegetation from hunting areas, both in natural wetlands and rice fields, of central-eastern Santa Fe province, Argentina. The high pellet density observed in soil at hunting sites suggests that Pb of hunting origin generates or contributes to those pollution levels. Furthermore, we found broad Pb bioavailability in the environment, which implies risk of long term exposure to this toxicant for wildlife and other species. The relative isolation of most study sites support this hypothesis, as the distance from alternative lead sources (urban areas, roads, etc.) seems to rule out these options.

4.1. Pellet density and Pb contents in soil and water

Pellet densities ranged from 7.5 to 141 and 5.5 to 38.7 pellets/m^2 in hunting W and RF sites, respectively. As the pellet density is usually very heterogeneous, concentrated nearby the shooting points, extrapolation to higher areas could be inaccurate. Nevertheless, we scaled the present results from square meters to hectares to allow comparisons with other studies. Thus, the high level of site W-H2 of 1.41×10^6 pellets/ha is similar to the highest densities found in French wetlands of about 2×10^6 pellets/ha (Taris and Bressac-Vaquer, 1987; Pain, 1990), and higher than values reported in USA and several European countries, in the range of 2×10^4 to 5.4×10^5 pellets/ha (Guitart et al., 1994). These last values are comparable to the results obtained in rice fields in our study (5.5×10^4 to 3.9×10^5 pellets/ha). Concurrently, previous studies in our study area reported high levels of pellet ingestion and Pb tissue accumulation in wild ducks (Ferreyra et al., 2009, 2014, 2015). In similar environments, pellet densities comparable to those found in our study have been associated with high pellet ingestion and mortality of ducks and swans (Kendall and Driver, 1982; Guitart

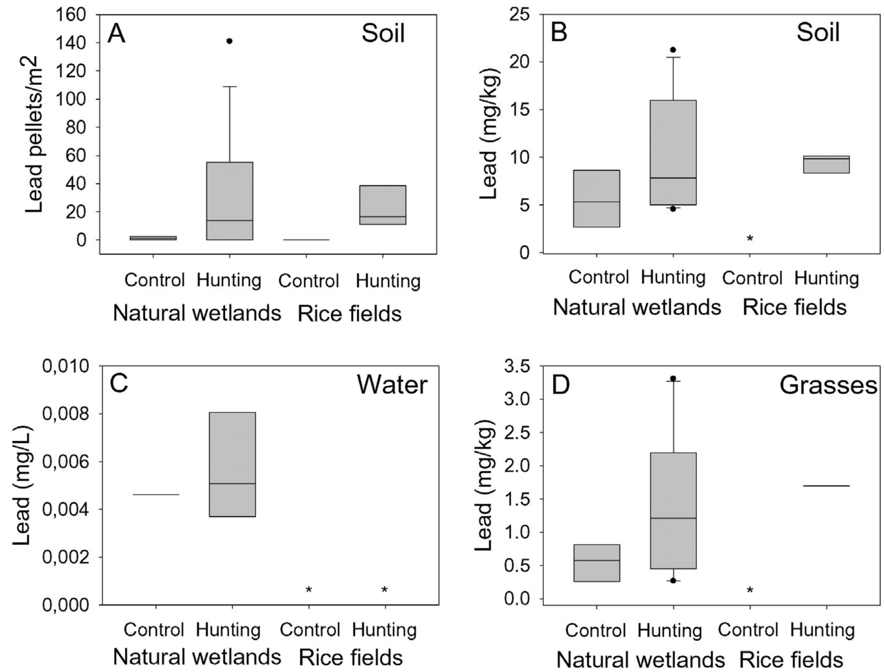

Fig. 7. Pellet density (A), Pb concentration in soil (B), Pb concentration in water (C) and Pb contents in grasses (D), in natural wetlands and rice fields, both hunting and control sites. Boxplots embrace 25th and 75th percentiles, the median being shown. Whiskers show 10th and 90th percentiles. Symbol * indicates a non-sampled site.

et al., 1994), flamingos (Mateo et al., 1997), as well as prey and carrion birds (Jacobson et al., 1977; Lambertucci et al., 2011), among others.

Of notice is the presence of spent pellets in control sites WC-1 and WC-2, and of Pb in soil, water and vegetation in all sites. While poaching can't be ruled out as a source, the half-life of pellets is much higher than that of hunting restrictions in these areas (about 20 years). Thus the pellet levels found could well be from previous hunting activities. Water birds, like ducks, can also transport pellets. It was shown that ingested pellets can remain in the duck's digestive tract for up to 30 days, and that 10% are expelled, with different erosion levels, within 10 days following ingestion (Stendell et al., 1979; Brewer et al., 2003; Rodríguez et al., 2010). Lead pellet ingestion by ducks in our study area varied between 7.6–50%, depending on species, site and year (Ferreyra et al., 2009, 2014). Thus, it is conceivable that ducks could act as pellet spreaders transporting them from areas with high level of pellets to non-hunting sites (Calabuig et al., 2010; Don Pablo Res.T., 2012).

In contrast to published reports from other areas, we did not find a clear correlation between Pb concentration in soil and pellet density (Cao et al., 2003; Vantelon et al., 2005; Perroy et al., 2014). However, most published studies were conducted in fields polluted by mining activities or in shooting ranges, which have very different environmental and soil conditions than our study area, and tend to have a very high content of metallic lead. Notwithstanding, the lack of correlation in our study could be due to oxidation of metallic Pb through abrasion and weathering processes, resulting in dissolution and, eventually, precipitation of Pb(II) in mineral forms.

In most soils under normal humidity regimes, metallic Pb is oxidized and evolves through several chemical species, of increasing stability, reaching finally stable mineral forms (Lin et al., 1995; Cao et al., 2003; Vantelon et al., 2005; Vodyanitskii, 2006; Ferreyroa et al., 2014). However, in soils of wetland areas, which are frequently flooded, there is an increased possibility of mobilization for soluble pollutants, increasing bioavailability. In the present study, the Pb content in soil of most hunting sites was only slightly higher than in control sites, with the exception of site W-H2, where the highest values of pellet density (Fig. 2) and Pb soil concentration were found. Despite the evidently higher hunting activity at this specific site, there are clear differences in soil with other sites: this soil is a Typic Natraqualf, with a high pH (10.1) and presence of calcite (Table A1). All other sites, including RF, had considerably lower pHs, between 5.6 and 6.8. Low pH values decrease or directly inhibit precipitation of common Pb(II) soil minerals, namely massicot and litharge (PbO), cerussite ($PbCO_3$) and hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) (Hashimoto et al., 2011):

$$PbO(s) + 2H^+ \rightleftharpoons Pb^{2+} + H_2O \tag{1}$$

$$PbCO_3(s) + 2H^+ \rightleftharpoons Pb^{2+} + CO_2 + H_2O \tag{2}$$

$$Pb_3(CO_3)_2(OH)_2(s) + 6H^+ \rightleftharpoons 3Pb^{2+} + 2CO_2 + 4H_2O \tag{3}$$

Reactions (1–3) suggest that in acidic medium Pb(II) can be brought to solution, as long as, for reactions (2–3), the CO_2 concentration can be kept low. In flooded soils like those studied here the dissolution of CO_2 is clearly hampered, thus favoring Pb(II) dissolution. Thus, it can be expected that in slightly acidic wetland soils Pb^0 can be oxidized and solubilized; this is supported by chemical speciation calculations (Appendix F, Supplementary Material). This is also consistent with the macroscopic condition of many pellets recovered, which appeared eroded and uncovered, whereas in the literature (studies on soils under a normal hydrological regime), pellets are found covered with a crust formed by some of the above mentioned minerals (Cao et al., 2003; Vantelon et al., 2005; Hashimoto, 2013). In the case of rice fields, constant plowing further modifies the soil structure and the location of remnant pellets.

More thorough estimates of pellet density, Pb concentration and the correlation between pellet density and Pb contents in the different environmental compartments, would require a study period comparable with the mean life of pellets in the environment, especially in stable locations where plowing and other land labors are not performed. Furthermore, the soil processes leading to Pb(II) fixation in soil should also be considered (Jensen et al., 2006; Vodyanitskii, 2006), as well as those causing metal mobilization (Shahid et al., 2012; Klitzke and Lang, 2009). It would also be important to analyze the chemical speciation of the metal in soil (Ferreyroa et al., 2014). As this information is not known, the comparison at the same sampling time is valid under the assumption that hunting activities and plowing operations (in cultivated areas) are constant in time.

In view of the aforementioned findings, our results strongly suggest that pellets undergo oxidation and solubilization processes. In an environment such as a wetland, with frequent flooding, it is expected that Pb(II) will be mobilized relatively easily (Yin et al., 2010), leading to a relative homogenization of Pb(II) water concentrations, explaining its relative uniformity in the different sampling sites, including those where pellets were not found (W-H4), or those without hunting history. This Pb(II) homogenization is also consistent with the lack of correlation between Pb contents in soil samples and plants, as the soluble Pb(II) present in water would clearly be preferably incorporated.

4.2. Pb incorporation in vegetation

Several studies have shown Pb incorporation in crops and pastures growing in polluted substrates (Beyer et al., 1997; Braun et al., 1997; Guitart and Thomas, 2005; Čelechovská et al., 2008; Salazar et al., 2012; Rodriguez et al., 2014), as well as in different elements of the food chain (Vighi, 1981; Eisler, 1988; Henny et al., 1991; Laskowski and Hopkin, 1996; Darling and Thomas, 2005). This is in agreement with the present findings of Pb contents in grasses of natural wetlands, as well as in rice plants. Moreover, in some sites (RF-H1, W-H2 and W-H3) the metal concentration was higher (2.83, 2.61 and 2.21 mg/kg, respectively) than baseline values reported for grasses and clovers in other areas of the world (2.1 and 2.5 mg/kg, respectively) (Kabata Pendias and Pendias, 1992).

In both rice plants and wetland grasses there was no apparent relationship between plant and soil Pb contents. In particular, it should be noted that even though site W-H2 had the highest Pb concentration in soil and considerably higher levels than sites W-H1 and W-H3, the lead contents in grasses did not follow soil concentrations; in most cases Pb in plants only presented small differences between sites. There is one exception, site W-H3 at the last sampling time (July 2012), when a high Pb level in grasses was found in comparison with other sites (except W-H2). These results show that soil Pb concentration is not determinant for plant Pb uptake, and is thus consistent with Pb(II) mobilization in the aquatic medium and homogenization across flooded areas. The increase observed in site W-H3 in July 2012 could be attributed to occasional changes in flooding and water movement (an extended drought in October 2011 was followed by an important flood a few months later) which could have carried Pb-concentrated water to this site. It could also be related to random differences in the vegetation sample pools collected.

4.3. Environmental concern

The Pb levels found in this study are below the limits established for agricultural soils in Argentina (Ley Nacional de Residuos Peligrosos N° 24.051), and are similar to the baseline values reported for the Pampas region (Lavado et al., 2004). However, the above reference values refer to non-wetland or non-flooded agriculture lands. Wetlands are more comparable to waterways, in which case reference levels for protection of aquatic life in surface waters (1 μg/l and 10 μg/l for fresh and salty waters, respectively) apply. The values of Pb in water found in our study are well above the limit for freshwater. Regarding international standards, according to the Criteria for Priority Toxic Pollutants (EPA, 1992), the values found here for wetlands are above the acceptable basal level in most cases. In the specifications of the EPA — Water Quality Standards, "Natural soils may contain as much as 10 ppm total lead and normal lead levels in various plants range from 0.5 to 3 ppm". Considering the highest concentration of a material in ambient water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable adverse effect, lead concentration could range between 1.3 to 7.7 μg/l depending on the water hardness.

Several plant species in which lead was detected (Appendix E, Supplementary Material) are eaten by ducks and other wildlife, as well as domestic animals like cows and horses. Moreover, the presence of lead in natural wetlands under agriculture raises the need to intensify research, especially regarding Pb mobility in the different physical and biological environmental compartments (Braun et al., 1997; Rooney et al., 1999; Guitart and Thomas, 2005). Likewise, it is advisable to increase research on lead incorporation in rice and the possible consequences for consumers (Ok et al., 2011). Finally, the impact of Pb on each part of the food web in polluted environments, as well as on consumers of hunted meat potentially polluted with Pb(II) or carrying metallic pellets, should also be addressed.

In contrast to other environmental pollution problems, contamination due to hunting activities is reversible. The substitution of lead ammunition by nontoxic materials can lead to significant reductions in the damage to wildlife in a short time (Moore et al., 1998; Anderson et al., 2000; Samuel and Bowers, 2000; Mateo et al., 2014). This study contributes essential information for the application of precautionary measures based on scientific arguments in Argentina, and highlights the importance and urgency to substitute lead shot when hunting occurs in wetlands and other aquatic environments.

5. Conclusions

The following conclusions stem from the present work:

1. High pellet density and high Pb levels in soil, water and vegetation were found in hunting areas, both in natural wetlands and rice fields, of central-eastern Santa Fe province, Argentina.
2. Pb was found in both rice plants and wetland grasses, but no apparent relationship was observed between plant and soil metal contents.
3. The results strongly suggest that pellets undergo oxidation and solubilization processes, with the consequence of mobilization and homogenization through the wetland.
4. This study contributes essential information for the application of precautionary measures based on scientific arguments, and highlights the importance and urgency to substitute lead shot when hunting occurs in wetlands and other aquatic environments.

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Appendices A–F. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.12.075.

References

Anderson, W.L., Havera, S.P., Zercher, B., 2000. Ingestion of lead and nontoxic shotgun pellets by ducks in the Mississippi flyway. J. Wildl. Manag. 64 (3), 848–857.

Behan, M.J., Kinraide, T.B., Selser, W.I., 1979. Lead accumulation in aquatic plants from metallic sources including shot. J. Wildl. Manag. 43 (1), 240–244.
Beyer, N.W., Blus, L.J., Henny, C.J., Audet, D., 1997. The role of sediment ingestion in exposing wood ducks to lead. Ecotoxicology 6, 181–186.
Beyer, W.N., Cormor, E.E., Gerould, S., 1994. Estimates of soil ingestion by wildlife. J. Wildl. Manag. 58, 375–382.
Blanco, D.E., López-Lanús, B., Dias, R.A., Azpiroz, A., Rilla, F., 2006. Uso de arroceras por chorlos y playeros migratorios en el sur de América del Sur. Implicancias de conservación y manejo. Wetlands International, Buenos Aires, Argentina.
Braun, U., Pusterla, N., Ossent, P., 1997. Lead poisoning of calves pastured in the target area of a military shooting range. Schweiz. Arch. Tierheilkd. 139, 403–407.
Brewer, L., Fairbrother, A., Clark, J., Amick, D., 2003. Acute toxicity of lead, steel, and an iron-tungsten nickel shot to Mallard ducks (*Anas platyrhynchos*). J. Wildl. Dis. 39 (3), 638–648.
Bucher, E.H., 1983. Las aves como plaga en la Argentina. In: Elias, D.J. (Ed.), Simposio: Zoología económica y vertebrados como plagas de la agricultura. IX Congreso Latinoamericano de Zoología, Octubre 9–15 — 1983, Arequipa, Perú, pp. 74–90.
Burco, J., Myers, A.M., Schuler, K., Gillin, C., 2012. Acute lead toxicosis via ingestion of spent ammunition in a free-ranging cougar (*Puma concolor*). J. Wildl. Dis. 48 (1), 216–219.
Calabuig, C.P., Green, A.J., Menegheti, J.O., Abad, R.M., Patiño, J., 2010. Fenología del Coscoroba (*Coscoroba coscoroba*) en el sur de Brasil y sus movimientos hacia Argentina. Ornitol. Neotrop. 21, 555–566.
Cao, X., Ma, L.Q., Chen, M., Hardison Jr., D.W., Harris, W.G., 2003. Weathering of lead bullets and their environmental effects at outdoor shooting ranges. J. Environ. Qual. 32, 526–534.
Čelechovská, O., Malota, L., Zima, S., 2008. Entry of heavy metals into food chains: a 20-year comparison study in northern Moravia (Czech Republic). Acta Vet. Brno 77, 645–652.
Clesceri, L.S., Greenberg, A.E., Eaton, A.D. (Eds.), 1999. Standard Methods for Examination of Water & Wastewater, 20th ed. American Public Health Association, Baltimore, Maryland.
Darling, C.T.R., Thomas, V.G., 2005. Lead bioaccumulation in earthworms, *Lumbricus terrestris*, from exposure to lead compounds of differing solubility. Sci. Total Environ. 346, 70–80.
De Francisco, N., Ruiz Troya, J.D., Agüera, E.I., 2003. Lead and lead toxicity in domestic and free living birds. Avian Pathol. 32 (1), 3–13.
Dickerson, K., Farag, A., Gray, A., Harper, D., Brumbaugh, W., 2007. Lead shot availability to birds using the North Platte River near a trap and skeet range. Contaminants Report Number: R6/722C/06. U.S. Fish & Wildlife Service, Environmental Contaminants Program, p. 52.
Don Pablo Research Team, 2012. Movements and resource utilization of four species of ducks captured in the mid-Parana River Basin, Corrientes Province, Argentina. Final Report, Tudor Farms, Cambridge, Maryland USA.
Eisler, R., 1988. Lead hazards to fish, wildlife, and invertebrates: a synoptic review. Biological Report 85(1.14). U.S. Fish and Wildlife Service, p. 94.
EPA, 1992. Guide to site and soil description for hazardous waste site characterization. Volume 1: Metals. EPA's Section 304(a) criteria for Priority Toxic Pollutants.
Farag, A.M., Woodward, D.F., Goldstein, J.N., Brumbaugh, W., Meyer, J.S., 1998. Concentrations of metals associated with mining waste in sediments, biofilm, benthic macroinvertebrates, and fish from the Coeur d'Alene River Basin, Idaho. Arch. Environ. Contam. Toxicol. 34 (2), 119–127.
Ferreyra, H., Beldomenico, P., Marchese, K., Romano, M., Caselli, A., Correa, A., Uhart, M., 2015. Lead exposure affects health indices in free-ranging ducks in Argentina. Ecotoxicology 24, 735–745.
Ferreyra, H., Romano, M., Beldomenico, P., Caselli, A., Correa, A., Uhart, M., 2014. Lead gunshot pellet ingestion and tissue lead levels in wild ducks from Argentine hunting hotspots. Ecotoxicol. Environ. Saf. 103, 74–81.
Ferreyra, H., Romano, M., Uhart, M., 2009. Recent and chronic exposure of wild ducks to lead in human modified wetlands in Santa Fe province, Argentina. J. Wildl. Dis. 45 (3), 823–827.
Ferreyroa, G.V., Montenegro, A.C., Tudino, M.B., Lavado, R.S., Molina, F.V., 2014. Time evolution of Pb(II) speciation in Pampa soil fractions. Chem. Speciat. Bioavailab. 26 (4), 210–218.
Fisher, I.J., Pain, D.J., Thomas, V.G., 2006. A review of lead poisoning from ammunition sources in terrestrial birds. Biol. Conserv. 131, 421–432.
Friend, M., 1999. Lead. In: Friend, M., Franson, J.C. (Eds.), Field manual of wildlife diseases. General field procedures and diseases of birds. USDIUSGS Biological Resources Division Information and Technology Report 1999–001, Madison, pp. 317–334.
Gobierno de Santa Fe, 2011. Caza deportiva, Resolución N° 036, 5 MAYO 2011. http://www.santafe.gov.ar/index.php/web/content/download/113452/557097/file/Temporada%20de%20caza%202011.
Guitart, R., Thomas, V.G., 2005. ¿Es el plomo empleado en deportes (caza, tiro y pesca deportiva) un problema de salud pública infravalorado? Rev. Esp. Salud Pública 6 (79), 621–632.
Guitart, R., To-Figueras, J., Mateo, R., Bertolero, A., Cerradelo, S., Martinez-Vilalta, A., 1994. Lead poisoning in waterfowl from the Ebro Delta, Spain: calculation of lead exposure thresholds for mallards. Arch. Environ. Contam. Toxicol. 27 (3), 289–293.
Hashimoto, Y., 2013. Field and laboratory assessments on dissolution and fractionation of Pb from spent and unspent shots in the rhizosphere soil. Chemosphere 93, 2894–2900. http://dx.doi.org/10.1016/j.chemosphere.2013.08.095.
Hashimoto, Y., Takaoka, M., Shiota, K., 2011. Enhanced transformation of lead speciation in rhizosphere soils using phosphorus amendments and phytostabilization: an X-ray absorption fine structure spectroscopy investigation. J. Environ. Qual. 40, 696–703.
Henny, C.J., Blus, L.J., Hoffman, D.J., Grove, R.A., Hatfield, J.S., 1991. Lead accumulation and osprey production near a mining site on the Coeur d'Alene River, Idaho. Arch. Environ. Contam. Toxicol. 21, 415–424.
Hilgert, N.I., Pensiero, J.F., Marino, G., Lewis, J.P., D'Angelo, C., 2003. Vegetation of the Saladillo area (province of Santa Fe) in the South of the Chaco, Argentina. Interciencia 28, 512–520.
Industrias Deriplom, 2014. Searched on 25 May, 2014 http://www.deriplom.com.ar.
Jacobson, E., Carpenter, J.W., Novilla, M., 1977. Suspected lead toxicosis in a bald eagle. J. Am. Vet. Med. Assoc. 171, 952–954.
Jensen, P.E., Ottosen, L.M., Pedersen, A.J., 2006. Speciation of Pb in industrially polluted soils. Water Air Soil Pollut. 170 (1–4), 359–382.
Jorgensen, S.S., Willems, M., 1987. The fate of lead in soils: the transformation of lead pellets in shooting range soils. Ambio 16, 11–15.
Kabata Pendias, A., Pendias, H., 1992. Trace elements in soils and plants. CRC Press, Florida.
Kendall, R.J., Driver, C.J., 1982. Lead poisoning in swans in Washington State. J. Wildl. Dis. 18 (3), 385–387.
Klitzke, S., Lang, F., 2009. Mobilization of soluble and dispersible lead, arsenic, and antimony in a polluted, organic-rich soil — effects of pH increase and counterion valency. J. Environ. Qual. 38 (3), 933–939.
Lambertucci, S.A., Donázar, J.A., Delgado, H.A., Jiménez, B., Sáez, M., Sanchez-Zapata, J.A., Hiraldo, F., 2011. Widening the problem of lead poisoning to a South-American top scavenger: lead concentrations in feathers of wild Andean condors. Biol. Conserv. 144 (5), 1464–1471.
Laskowski, R., Hopkin, S.P., 1996. Accumulation of Zn, Cu, Pb and Cd in the Garden Snail (*Helix aspersa*): implications for predators. Environ. Pollut. 91 (3), 289–297.
Lavado, R.S., Zubillaga, M.S., Alvarez, R., Taboada, M.A., 2004. Baseline levels of potentially toxic elements in Pampas Soils. Soil Sediment Contam. Int. J. 13, 329–339. http://dx.doi.org/10.1080/10588330490500383.
Ley Nacional de Residuos Peligrosos N° 24.051, Decreto 831/93. Bs. As., 23/04/1993. http://infoleg.mecon.gov.ar/infolegInternet/anexos/0-4999/450/texact.htm
Lin, Z., Comet, B., Qvarfort, U., Herbert, R., 1995. The chemical and mineralogical behaviour of Pb in shooting range soils from Central Sweden. Environ. Pollut. 89 (3), 303–309.
Magrisso, S., Belkin, S., Erel, Y., 2009. Lead bioavailability in soil and soil components. Water Air Soil Pollut. 202 (1–4), 315–323.
Mateo, R., 2009. Lead poisoning in wild birds in Europe and the regulations adopted by different countries. In: Watson, R.T., Fuller, M., Pokras, M., Hunt, W.G. (Eds.), Ingestion of Lead from Spent Ammunition: Implications for Wildlife and Humans. The Peregrine Fund, Boise, Idaho, USA http://dx.doi.org/10.4080/ilsa. 2009.0107.
Mateo, R., Dolz, J.C., Aguilar Serrano, J.M., Belliure, J., Guitart, R., 1997. An epizootic of lead poisoning in Greater Flamingos (*Phoenicopterus ruber roseus*) in Spain. J. Wildl. Dis. 33 (1), 131–134.
Mateo, R., Green, A.J., Lefranch, H., Baos, R., Figuerola, J., 2007. Lead poisoning in wild birds from southern Spain: a comparative study of wetland areas and species affected, and trends over time. Ecotoxicol. Environ. Saf. 66, 119–126.
Mateo, R., Vallverdú-Coll, N., López-Antia, A., Taggart, M.A., Martínez-Haroa, M., Guitart, R., Ortiz-Santaliestra, M.E., 2014. Reducing Pb poisoning in birds and Pb exposure in game meat consumers: the dual benefit of effective Pb shot regulation. Environ. Int. 63, 163–168.
Moore, J.L., Hohman, W.L., Stark, T.M., Weisbrich, G.A., 1998. Shot prevalences and diets of diving ducks five years after ban on use of lead shotshells at Catahoula Lake, Louisiana. J. Wildl. Manag. 62 (2), 564–569.
Ok, Y.S., Usman, A.R.A., Lee, S.S., El-Azeem, S.A.M.A., Choi, B., Hashimoto, Y., Yang, J.E., 2011. Effects of rapeseed residue on lead and cadmium availability and uptake by rice plants in heavy metal contaminated paddy soil. Chemosphere 85 (4), 677–682.
Osakwe, S.A., 2013. Chemical partitioning of iron, cadmium, nickel and chromium in contaminated soils of South-Eastern Nigeria. Chem. Speciat. Bioavailab. 25 (1), 71–78.
Pain, D.J., 1990. Lead shot ingestion by waterbirds in the Camargue, France: an investigation of levels and interspecific differences. Environ. Pollut. 66, 273–285.
Pain, D.J., 1991. Lead shot densities and settlement rates in Camargue marshes, France. Biol. Conserv. 57 (3), 273–286.
Pain, D.J., 1992. Lead poisoning of waterfowl: a review. In: Pain, D.J. (Ed.)Lead Poisoning in Waterfowl, Special Publication Nº 16. International Waterfowl and Wetlands Research Bureau, Slimbridge, Gloucester, UK.
Pain, D.J., Cromie, R.L., Newth, J., Brown, M.J., Crutcher, E., Hardman, P., Hurst, L., Mateo, R., Meharg, A.A., Moran, A.C., Raab, B.A., Taggart, M.A., Green, R.E., 2010. Potential hazard to human health from exposure to fragments of lead bullets and shot in the tissues of game animals. PLoS One 5, e10315.
Pareja-Carrera, J., Mateo, R., Rodríguez-Estival, J., 2014. Lead (Pb) in sheep exposed to mining pollution: implications for animal and human health. Ecotoxicol. Environ. Saf. 108, 210–216.
Perroy, R.L., Belby, C.S., Mertens, C.J., 2014. Mapping and modeling three dimensional lead contamination in the wetland sediments of a former trap-shooting range. Sci. Total Environ. 487, 72–81. http://dx.doi.org/10.1016/j.scitotenv.2014.03.102.
Pilatti, M.A., D'Angelo, C., Marano, R., Pensiero, J., Potente, H., López Calderón, A., 2002. Ordenamiento territorial de la cuenca de Los Saladillos (Santa Fe) Estudio de prefactibilidad del uso actual y potencial de los recursos naturales. Ediciones UNL, Santa Fe, Argentina.
Pokras, M.A., Kneeland, M.R., 2008. Lead poisoning: using transdisciplinary approaches to solve an ancient problem. EcoHealth. http://dx.doi.org/10.1007/s10393-008-0177-x.
Ramonell, C.G., Marchetti, Z.Y., Barberis, I.M., Giraudo, A.R., 2013. Sistema de Humedales del Bajo de los Saladillos. In: Benzaquen, L., Blanco, D., Bó, R., Kandus, P., Lingua, G., Minotti, P., Quintana, R., Sverlij, S., Vidal, L. (Eds.), Inventario de los Humedales de Argentina. Sistemas de paisajes de humedales del Corredor Fluvial Paraná-Paraguay. Secretaría de Ambiente y Desarrollo Sustentable de la Nación, Proyecto GEF 4206 PNUD ARG 10/003, Buenos Aires, pp. 177–185.

Rodríguez, J.J., Oliveira, P.A., Fidalgo, L.E., Ginja, M.M.D., Silvestre, A.M., Ordóñez, C., Serantes, A.E., Gonzalo-Orden, J.M., Orden, M.A., 2010. Lead toxicity in captive and wild Mallards (*Anas platyrhynchos*) in Spain. J. Wildl. Dis. 46 (3), 854–863.

Rodriguez, J.H., Salazar, M.J., Steffan, L., Pignata, M.L., Franzaring, J., Klumpp, A., Fangmeier, A., 2014. Assessment of Pb and Zn contents in agricultural soils and soybean crops near to a former battery recycling plant in Córdoba, Argentina. J. Geochem. Explor. 145, 129–134.

Romero, D., Peñalver, J., García Fernández, A.J., 2007. Perdigones de plomo y aves cinegéticas: un problema de salud pública. Inf. Vet. 2007, 11–15 (Abril).

Rooney, C.P., Mclaren, R.G., Cresswell, J.R., 1999. Distribution and phytoavailability of lead in a soil contaminated with lead shot. Water Air Soil Pollut. 116, 535–548.

Salazar, M.J., Rodriguez, J.H., Nieto, G.L., Pignata, M.L., 2012. Effects of heavy metal concentrations (Cd, Zn and Pb) in agricultural soils near different emission sources on quality, accumulation and food safety in soybean [*Glycine max* (L.) Merrill]. J. Hazard. Mater. 233, 244–253.

Samuel, M.D., Bowers, E.F., 2000. Lead exposure in American Black Ducks after implementation of non-toxic shot. J. Wildl. Manag. 64 (4), 947–953.

Scheuhammer, A.M., Norris, S.L., 1995. A review of the environmental impacts of lead shotshell ammunition and lead fishing weights in Canada. Canadian Wildlife Service, Occasional Paper 88, p. 56.

Shahid, M., Pinelli, E., Dumat, C., 2012. Review of Pb availability and toxicity to plants in relation with metal speciation; role of synthetic and natural organic ligands. J. Hazard. Mater. 219/220, 1–12 (June).

Stendell, R.C., Smith, R.I., Burnham, K.P., Christensen, R.E., 1979. Exposure of waterfowl to lead: a nationwide survey of residues in wing bones of seven species, 1972–73. U.S.Fish and Wildlife Service Special Scientific Report — Wildlife No. 223, Washington, D.C.

Tagliafico, D., 2014. Sector de Tiro. Searched on 25 May, 2014. http://www.sectordetiro.com/cartuchos.htm.

Taris J.P., Bressac-Vaquer Y. (1987). Oiseaux migrateurs transcontinentaux: cas particulier de la Barge à queue noire, *Limosa l. limosa* (L.), en Camargue. Office National de la Chasse, Arles. Unpublished report.

Torri, S.I., Lavado, R.S., 2008. Dynamics of Cd, Cu and Pb added to soil through different kinds of sewage sludge. Waste Manag. 28 (5), 821–832.

U.S. Fish and Wildlife Service, 1990. Lead Poisoning in Waterfowl. U.S. Fish and Wildlife Service, Washington, D.C., pp. 1–15.

Vantelon, D., Lanzirotti, A., Scheinost, A.C., Kretzschmar, R., 2005. Spatial distribution and speciation of lead around corroding bullets in a shooting range soil studied by micro-X-Ray fluorescence and absorption spectroscopy. Environ. Sci. Technol. 39, 4808–4815. http://dx.doi.org/10.1021/es0482740.

Vighi, M., 1981. Lead uptake and release in an experimental trophic chain. Ecotoxicol. Environ. Saf. 5, 177–193.

Vodyanitskii, Y., 2006. Arsenic, lead, and zinc compounds in contaminated soils according to EXAFS spectroscopic data: a review. Eurasian Soil Sci. 39 (6), 611–621.

Yin, X., Gao, B., Ma, L.Q., Saha, U.K., Sun, H., Wang, G., 2010. Colloid-facilitated Pb transport in two shooting-range soils in Florida. J. Hazard. Mater. 177, 620–625. http://dx.doi.org/10.1016/j.jhazmat.2009.12.077.

Zaccagnini, M.E., 2002. Los patos en las arroceras del noreste de Argentina: ¿plagas o recursos para caza deportiva y turismo sostenible? In: Blanco, D.D., Beltrán, J.J., de la Balze, V.V. (Eds.), Primer Taller sobre la Caza de Aves Acuáticas. Hacia una estrategia para el uso sustentable de los recursos de los humedales. Wetlands International, La Plata, Buenos Aires, pp. 35–57