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After the Aznalcóllar mine spill: Arsenic, zinc, selenium, lead and copper levels in the livers and bones of five waterfowl species

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Abstract

In April 1998, a holding lagoon containing pyrite ore processing waste, failed and released 5–6 million m^3 of highly polluting sludge and acidic water. Over 2650 ha of the internationally important Doñana Natural Park became contaminated, along with <100 ha of the more pristine Doñana National Park. In order to assess the affect of the spill on waterfowl from Doñana, bone and liver samples from 124 individuals have been analysed for As, Pb, Cu, Zn and Se. Five species have been studied, from the Rallidae (rails), Anatini (dabbling ducks) and Aythyini (pochards) families. Geometric mean bone concentrations 2–3 months after the spill were in the order of Zn > Cu > Pb > Se > As, while liver concentrations were in the order of Zn > Cu > Se > Pb > As. Dry weight bone concentrations ranged from n.d-1.76 mg kg^{-1} As, 109.4–247.6 mg kg^{-1} Zn, 0.06–1.27 mg kg^{-1} Se, n.d-134.11 mg kg^{-1} Pb, and 2.18–8.92 mg kg^{-1} Cu. Wet weight liver concentrations ranged from n.d-0.34 mg kg^{-1} As, 29.8–220.1 mg kg^{-1} Zn, 0.15–0.85 mg kg^{-1} Se, n.d-3.80 mg kg^{-1} Pb, and 7.30–742.96 mg kg^{-1} Cu. The most important factor related to the accumulation of these metals was commonly species; however, location and sex also had important effects on liver As levels, location and age affected Cu levels, while Zn and Pb were affected by age, sex and location. Birds from Natural Park areas were found to have significantly higher levels of bone Zn, Pb and Cu, and liver As and Cu than birds from National Park areas. Female birds had higher liver As, Zn and Pb than males; whilst adults appeared to have lower bone As and Zn but higher liver Pb than chicks/juveniles. Although metal concentrations were elevated in certain individuals, in the majority of birds studied, they did not reach levels widely considered to be toxic. However, it would appear that As and Cu liver levels (which may be indicative of short-medium term pollutant exposure) were elevated in waterbirds which died in the spill contaminated Natural Park, 2–3 months after the disaster.

Keywords: Arsenic; Heavy metals; Aznalcóllar; Waterfowl; Liver; Bone

"**Capsule**": 2–3 months after the Aznalcóllar mine spill, Cu and As appeared to have entered the waterfowl food chains of the Doñana Natural Park.

1. Introduction

On the 25th of April 1998, a massive holding lagoon containing pyrite ore processing waste failed, and released an estimated 5–6 million m^3 (Vidal et al., 1999; Galán et al., 2002) of acidic, metal rich sludge and water into the Rio Guadiamar, SW Spain. The Rio Guadiamar flows through Doñana, one of the most important conservation areas for birds in Europe (partly protected as a World Heritage Site, Biosphere Reserve

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and Ramsar Site), in which 70% of all European bird species can be found. Despite rapid emergency response to the disaster, some 2754 ha of the Doñana Natural/National Park sustained some degree of contamination. The Natural Park areas suffered the greatest impact, with 2656 ha affected (Grimalt et al., 1999). Of this, a 900 ha area known as the 'Entremuros' was most heavily impacted (Meharg et al., 1999; Taggart et al., 2004, 2005). An extremely important Natural Park zone (Fig. 1), this area acts as a seasonal wetland and therefore a rich breeding ground for many bird species, including some (i.e, marbled teal (*Marmaronetta angustirostris*)) that are globally threatened (Pain et al., 1998).

Waste from the spill entered the Entremuros, a 22 km long and 1 km wide 'bunded' area (within which water levels can be partially controlled) from the north. Although sludge impacted only the most northerly reaches of this feature, contaminated water reached as far south as Dam 2 (see Fig. 1). The sludge component of the waste contained 0.4–0.6% As, 0.8–1.3% Pb, 0.5–0.9% Zn, 0.1–0.2% Cu and 0.001–0.002% Se (Galán et al., 2002; Pain et al., 1998; Alastuey et al., 1999). The acidic, metal rich waters of the spill were stored temporarily, in the Entremuros (protecting more pristine National Park areas further south). The pH of the waters in this important wetland environment fell from 8.5 to 4.5, and in open water, Zn levels were recorded up to 270 mg L^{-1}, Pb up to 2.5 mg L^{-1}, Cu <0.01 mg L^{-1}, As up to 0.011 mg L^{-1} and Se <0.005 mg L^{-1} (Pain et al., 1998; Garralón et al., 1999). Fish and invertebrate populations were decimated, and valuable habitat, especially for waterfowl, was destroyed. Emergency clean-up operations began immediately, sludge was removed, and contaminated water treated and discharged. However, the scale of the disaster meant that residual contamination inevitably remained (Galán et al., 2002; Taggart et al., 2004, 2005), and the longer term impacts on the ecosystems of Doñana are yet to be determined.

Doñana is considered to be a very important haven for resident and migratory bird species. Of those birds, waterfowl, which feed in the wetlands contaminated by the Aznalcóllar spill, are perhaps at greatest risk from the longer term transfer of metal contaminants through the Doñana wetland food chains. Herbivorous waterfowl may be especially susceptible, as they have a tendency to consume significant amounts of soil/sediment associated with their food (Beyer et al., 1994, 1999; Beyer, 2000). Beyer et al. (1999) reported that soil ingestion by herbivorous grazing ducks was 3%, and higher than in granivorous filtering species, which ingested <1%. Waterfowl may serve as important bioindicator species, useful in terms of monitoring the long term impacts of the spill. They are also important, in that certain species (e.g, greylag geese (*Anser anser*)) are a key food source, not only for predators such as the highly endangered Spanish Imperial Eagle (*Aquila adalberti*), but also for humans who hunt and consume ducks, geese and rallids in the area.

Prior to the spill, a number of studies determined metal and organochlorine levels in bird eggs in Doñana, (González et al., 1984; Hernández et al., 1986, 1987,

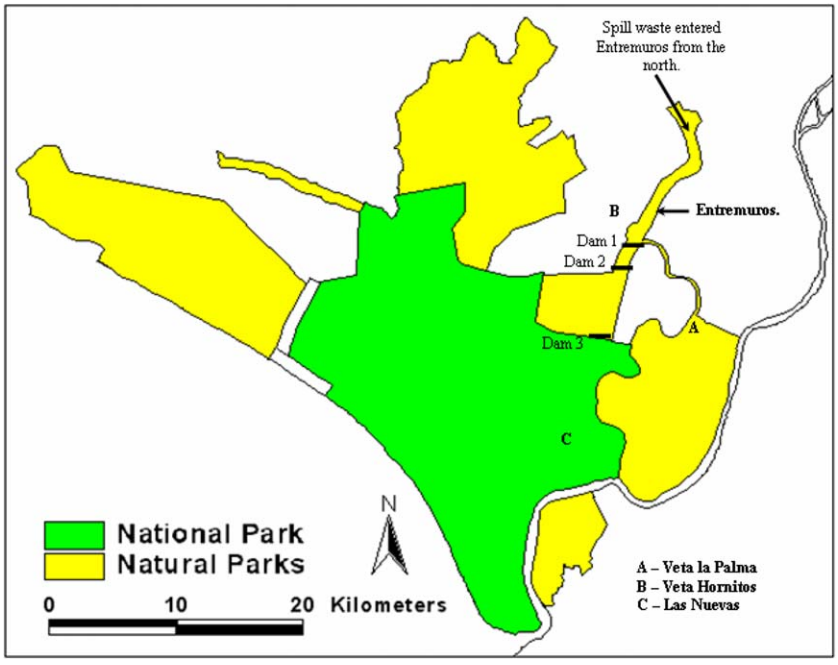

Fig. 1. Map of Donana Natural/National Park areas showing the location of the Entremuros and the areas from which the majority of samples were collected.