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Lead emissions from lost fishing sinkers

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Lead sinkers used in salmon fishing in river mouth areas are lost in amounts of up to 200 tonnes year^{-1} in Sweden. An experimental field investigation has shown that the dissolution rate is about 20 mg cm^{-2} yr^{-1}. No secondary corrosion coating has been observed except when the sinkers were fully or partially buried in fine sediments. The loss is larger in fast running waters, but there is no obvious relation between the loss and the water quality within the range present in the field sites. Approximately 1% of the deposited lead is dissolved yearly, provided it is not buried. An alternative to lead sinkers could be concrete sinkers with magnetite as a filler.

Introduction

The use of lead in fishing sinkers has long been known to be a threat to wildlife, especially waterfowl. Investigations have shown that the deaths of swans (*Cygnus olor*) can often be attributed to lead poisoning from fishing sinkers ingested by the birds (Sears 1988, Kirby *et al*. 1994). The common loon, *Gavia immer*, has also been found to be affected by its ingestion of lead sinkers (Locke *et al*. 1981, Pokras and Chafel 1992, Twiss and Thomas 1998). In places where angling and loon populations co-occur lead poisoning accounts for 10%–50% of the adult loon mortality (Scheuhammer and Norris 1996). Mallards, *Anas platyrhynchos*, are often found to ingest lead bullets from hunting at shore sites (Rocke and Samuel 1991). Cases of small children being poisoned by ingested lead fishing weights are also recorded (Fergusson *et al*. 1997, Mowad *et al*. 1998).

The picture in the Nordic countries is somewhat different. The lead sinkers are usually lost in deep running water where they are not accessible for waterfowl. Swedish rivers have been housing migrant salmon populations. The construction of hydropower-plants has obstructed the migration, and the salmon fishing is nowadays practised in the lower portions of regulated rivers where salmon are introduced from hatcheries. The area of active fishing is usually restricted to a few kilometres below the lowermost hydroelectric power station. Heavy lead sinkers, weighing from 30 g up to as much as 140 g, are used to take the bait into local hollows as the fish in the running water seek shelter to save energy. The bottoms are generally stony and there is a considerable risk that the fishing line will get stuck. As the lead weights are cheap, it is usually arranged so that in such instances the bait can be recovered while the lead sinker is lost. In Sweden, as much as 100–200 tonnes of lead metal used in fishing sinkers are lost yearly (Swedish Chemicals Inspectorate, pers. comm.). In Canada, 125 to 187 million lead sinkers are deposited annually (Twiss and Thomas 1998) which means losses at least ten times those in Sweden. The lead sinkers can be buried in the sediment or they can remain exposed in the running water.

If they are buried, the dissolution of the lead weights will be limited, as they will generally be protected by secondary coatings of cerrusite ($PbCO_3$), hydrocerrusite ($Pb_3(CO_3)_2$ $(OH)_2$) or anglesite ($PbSO_4$) (Storgaard Jörgensen and Willems 1987). The corrosion in soil proceeds as pit corrosion. Lead deposited from the atmosphere seems to be almost completely retained in the soil zone (Borg and Johansson 1989, Wang *et al.* 1995).

The sediments in the fishing areas are generally coarse due to the rapid flow of the water and there is a considerable likelihood that the lead weights will not be buried but will remain exposed between the stones. Lead immersed in water has a considerable solubility, as is shown by the numerous problems in connection with lead piping especially in Anglo-Saxon countries. The solubility increases with decreasing pH and decreasing alkalinity (Schock and Wagner 1985).

The aim of this investigation was to assess the emission of lead from lead sinkers and the fate of the emitted lead.

Material and methods

The investigations were conducted in the lower parts of the rivers Lagan, Dalälven and Indalsälven, all which are active fishing areas. The bottom sediments in the Lagan river downstream of Laholm are mostly sandy with smaller areas of silt and gravel. The flow rate is fairly gentle. The bottom sediments in the Dalälven river downstream of Älvkarleby are gravelly and sandy. The same applies to the Indalsälven river east of the Bergeforsen power plant. Additional investigations have been undertaken in the Ådran brook south of Stockholm.

Selected water quality parameters for the rivers in which test sinkers were immersed during the investigation period from May to November 1994 are listed in Table 1.

The investigations have been carried out by exposing lead weights for a period of 1–6 months in running water. Lead sinkers purchased on the market were used, and also lead sheets 50 × 50 × 1 mm were used to increase the ratio of the exposed surface area to the weight. Test objects were exposed both in running water (0.1–1 m s^{-1}) and in backwater positions (0–0.1 m s^{-1}). The sinkers were weighed before and after exposure and the weight loss was calculated as a loss per surface area.

To detect metals in the water, we used mosses of the *Fontinalis* spp. type, either natural or transplanted, which were supposed to take up dissolved metals. The mosses were washed in distilled water before drying and 1 g was digested in 7 M HNO_3. The lead contents in the digests were analysed with ICP-IES.

Lead isotope analysis with ICP-MS has been done on three polycarbonate filters (0.45 μm) from the Lagan river used to collect suspended matter. Twenty litres of water were pumped through the filters which has a diameter of 80 mm. One sample was taken upstream of the

Table 1. Hydrology and water quality in the investigated sites (*Bergström 1993; **Dept. of Environmental Analysis, Swedish University of Agricultural Sciences).

Watercourse	Mean flow m^3 s^{-1}*	pH**	Alkalinity mM**	TOC mg l^{-1}**	Length of fishing area km
Lagan	75	6.5–6.8	0.13–0.19	8–12	6 km
Dalälven	344	7.0–7.1	0.17–0.21	5–6	2 km
Indalsälven	445	7.2–7.5	0.40–0.45	3.2–4.5	4 km
Ådran brook	0.2	6.5	0.15	ca. 10	no fishing

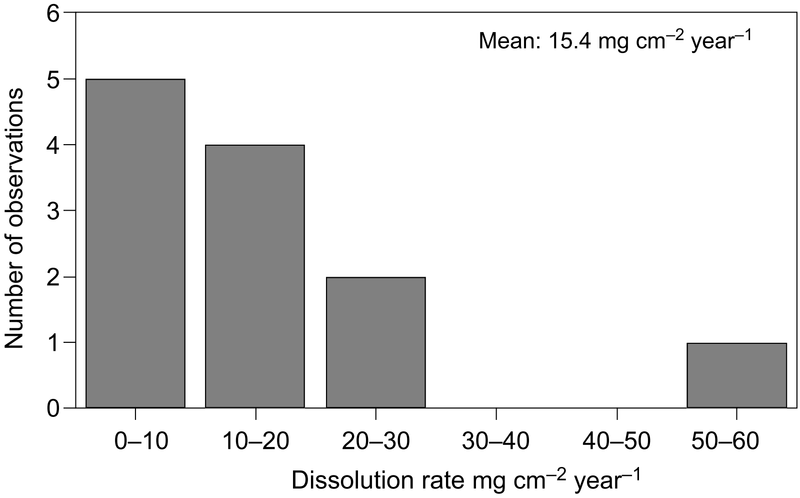

Fig. 1. Distribution of weight loss of lead sinkers in the Lagan river.

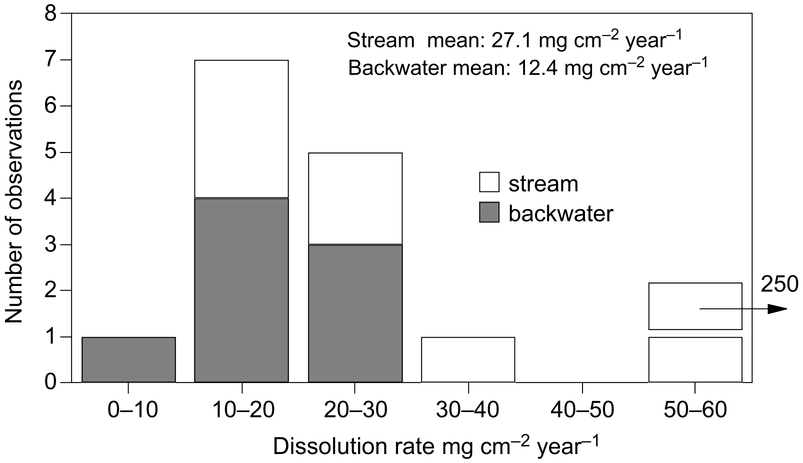

Fig. 2. Distribution of weight loss of lead sinkers in the Dalälven river in backwater positions and in flowing water.

fishing area and two samples in the fishing area.

Coatings on stones were collected, as they were considered to contain some humic matter which might contain lead. Stones were taken up and dried, and the coatings were brushed off. The coatings were digested in 7 M HNO_3 and digests analysed for lead on AAS. The coatings were also analysed for organic carbon with a Shimadzu 5000 TOC.

To trace the dissolved metals, we have searched for undisturbed sediments. In none of the above sites have we been able to detect such sediments because of the generally high flow rates especially in the autumn and spring.

Results

Lead sinkers

About 75% of the lead weights were recovered in the Lagan and Dalälven rivers. The high water level at the time of collection allowed only four out of 20 to be recovered in the Indalsälven river. The results from the Lagan and Dalälven rivers are shown in Fig. 1 and Fig. 2 respectively. The weight losses are extrapolated to a period of one year. In Dalälven, the sinkers placed in rapidly flowing waters show larger weight losses. The outlier in the

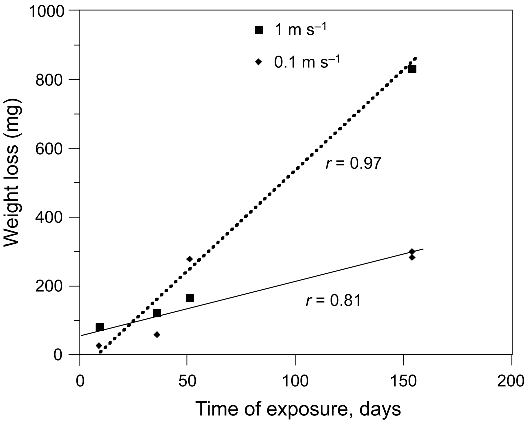

Fig. 3. Weight loss of lead sinkers in the Ådran brook over 160 days.

Dalälven data was placed below a small rapid. The recorded corrosion rate is about 50% to 100% higher than the value for natural waters in general (Smith 1985).

There was no visible corrosion coating on the sinkers except in a couple of cases when the sinker was partly buried in silt. The sinkers from the Lagan river had a partial humic coating.

Table 2. Content of lead in *Fontinalis* from three rivers. L = Lagan, D = Dalälven, I = Indalsälven.

Sample	Position	Pb mg kg^{-1}
L 1	Upstream	50
L 3	Downstream	40
L 4	Downstream	49
D 1	Upstream	16
D 3	Upstream	14
D 4	Downstream	25
D 5	Downstream	18
D 6	Downstream	34
D 7	Downstream	23
D 8	Downstream	16
I 2	Downstream	16
I 3	Downstream	27

Two sinkers exposed at the mouth of Lagan, where brackish water entered at times of high tide, showed extensive corrosion amounting to 23 and 52 mg cm^{-2} year^{-1} (Fig. 1). There were also signs of the beginning of pitting corrosion on the sinkers exposed to brackish water.

The lead weights exposed in the Ådran brook showed a linear rate of dissolution with respect to time over a study period of 160 days (Fig. 3). Unfortunately, we lost several sinkers in the high speed site. However, the dissolution rates are in the same range as those found under similar conditions in the Dalälven river i.e. 10 mg cm^{-2} year^{-1} at a flow rates of 0–0.1 m s^{-1} and 37 mg cm^{-2} year^{-1} at a flow rate of 0.1–1 m s^{-1}.

Moss analysis

Reference samples were taken upstream of the fishing areas, but too few reference samples were collected to make the analysis conclusive (Table 2). In general, the flow is too slow upstream of the power plants to suit colonisation by *Fontinalis* spp. The lead content in mosses from the Lagan river is generally high but it does not show any gradient downstream. These mosses were transplanted. The mosses from Dalälven show moderately high contents of lead, but again there was no gradient downstream (Table 2). In the Dalälven river, there is a background load of lead from mining activities (Ingri *et al*. 1993).

Lead in suspended matter

The lead isotope investigations showed that the ^{207}Pb/^{206}Pb ratio was 0.850 upstream of the fishing area and 0.859 in the fishing area (Table 3). The humic coatings on stones, presumably formed by settling from the water, had high contents of

Table 3. Lead isotope ratios in suspended load upstream of fishing area and in fishing area.

Sample	207Pb/206Pb	S.D.	208Pb/207Pb	S.D.	208Pb/206Pb	S.D.
Upstream	0.8497	0.0007	2.4348	0.0017	2.0791	0.0019
0.5 km into fishing area	0.8593	0.0012	2.4266	0.0018	2.0954	0.0036
1.5 km into fishing area	0.859	0.0006	2.4338	0.0035	2.1008	0.0033

lead but there was no obvious gradient downstream in the few samples taken (Table 4).

Discussion

The results do not indicate any pronounced dependence of dissolution rate on the water quality. In fact, the dissolution rate is higher in Dalälven than in Lagan in spite of the lower pH, lower alkalinity and higher TOC content in the latter, which should favour more rapid dissolution (Schock and Wagner 1985). At a slightly acid pH and a TOC content of 10 mg l^{-1}, about 90% of the lead is present in humic complexes (Lindsay 1979). Most corrosion investigations are made in connection with the distribution of drinking water, where relatively more lead metal is exposed and dissolved concentrations are closer to the solubility of compounds like cerrusite or hydrocerrusite. Humic matter should promote dissolution (Shock and Wagner 1985). However, the Lagan river with the highest total organic carbon concentrations does not show higher dissolution rates. In these rivers, the dissolved background concentrations of lead are of the order of less than one μg l^{-1} and the suspended load is slightly higher (Pontér *et al.* 1990). This means that the factor limiting dissolution is the oxidation of the lead metal, not the diffusion through a protective coating. The fact that the measurements were made during the warm season from May to October might thus have increased the corrosion. However, laboratory tests did not show an enhancement when the temperature was increased from 4 °C to 20 °C. The increased weight loss in fast flowing water may be due to a faster oxidation and dissolution. However, it is more probably due to erosion by small sand grains. Traces of erosion caused by scratches were seen on some of the sinkers exposed to rapid flow. In winter, the flow in Lagan river is larger, and there is a pronounced spring flood in both Dalälven and Indalsälven with elevated flow. This may mean that the larger water velocities in the winter may increase the weight losses.

The moss analysis did not reveal any significant increase in the lead load in the water of the fishing areas. Lead has a high affinity for organic ligands (Lindsay 1979) and this would decrease the uptake of lead by the mosses. Such lead-humic compounds were probably removed by the washing in distilled water. That the lead is largely present in the suspended phase is supported by the lead isotope investigation, which indicated the addition of lead with a different isotopic signature in the fishing area. Although the lead content in organic matter in stone coatings was moderately high, there was no obvious gradient downstream. However, the number of samples were few. The most convincing evidence of any dissolution of lead sinkers are the isotopic data. There is a clear difference between upstream and downstream ratios of ^{207}Pb/^{206}Pb indicating that lead with a different isotopic signature has been added downstream pointing to the dissolution of lead sinkers (Table 3). The upstream ratio of 0.850 is in the order of what has been found in the soil mor layer (Renberg *et al.* 2000).

The present results indicate a mean dissolution rate of the order of 20 mg cm^{-2} $year^{-1}$. If the results are extrapolated to the ca 200 tonnes of annual loss and in the form of 80 g weights with 25 cm^2 surface area the dissolution will be 1.25 tonnes per year. The fact that this type of fishing has been going on for about 20 years means that the total amount of lead deposited is about 4000 tonnes, and the current yearly dissolution is probably in the order of 25 tonnes. This figure is highly speculative as many of the sinkers may have been buried in sediments. On the other hand, pit corrosion may have increased the exposed surface. In the Lagan river, the total concentration of lead may be approximately doubled by emission from the deposited lead sinkers. This is difficult to verify by measure-

Table 4. Lead in stone coatings in Lagan river.

Site	Pb mg kg^{-1}	Org. C%	Pb/Org. C mg kg^{-1}
Upstream 1	22	8.1	272
Upstream 2	24	4.9	489
Upstream 3	44	6.2	710
Fishing area 1	23	4.0	575
Fishing area 2	16	2.9	552
Fishing area 3	15	2.7	556

ments, in view of the natural variability.

There is currently no evident effect of lead emission from the dissolution of lead sinkers in the Lagan river. The dissolved lead probably ends up in marine or brackish water sediments in the sea. The possible effects depend on the concentration and on the local ecosystems, and they are difficult to assess without a detailed investigation. In any case, the handling of 100–200 tonnes of lead per year involves risks which should be avoided. Alternatives for the lead sinkers are available in the form of plastic-coated iron sinkers. The coating is provided to avoid corrosion and rust stains on the fishing utensils. In Canada, bismuth or tin sinkers are recommended (Seed *et al*. 1995). These alternatives are more expensive. A possible alternative would be to use concrete sinkers with magnetite or chromite as filler (Prof. Alf Björklund, Åbo Akademi, Åbo, Finland, pers. comm.). They do not corrode but will necessarily be larger than those made of metallic materials.

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