ENVIRONMENTAL RISK ASSESSMENT OF ZINC ARISING FROM DISPOSAL OF USED BATTERIES WITH MUNICIPAL SOLID WASTES

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Executive Summary

Batteries are an indispensáble requirement of modern daily life supplying the portable energy required to service societies ever growing medical, social and communication needs. Watches, hearing aids, heart pacemakers, smoke detectors, telephones, ... are some of the appliances which are dependent on battery technology.

In the absence of suitable recycling technology, the disposal of household batteries in municipal solid wastes (which are either directly landfilled or landfilled after incineration) do not pose nor increase any significant risk to human health or to the environment at large. The quantity of zinc thus added to the environment through direct landfilling of batteries, through landfilling of flying or bottom ashes from MSW incinerators or from zinc compounds escaping the gas washing process of these incinerators is quite acceptable in view of

i) the current sources of zinc in the environment,
ii) the low solubility at neutral pHs of zinc compounds adsorbed on soil material (especially clay, iron-manganese oxydes and hydroxides and humic acids) and
iii) the near absence of toxicity of zinc at the level of concentration presently observed in soils and rivers of West European countries : 100 to 200 mg/kg in most non-sandy soils with a bio-disponibility of around 30 percent, and 50 to 100 µg/l in most surface or river waters with a proportion of 50 percent soluble zinc.

The estimation of normal household battery use in Europe per year is 4,6 manganese-alkaline batteries and 4,3 zinc-carbon/zinc chloride batteries per person, resulting in 29 g zinc compounds disposed of per year and per person in our countries. A Dutch study estimates to 30 g zinc per kg dyr MSW the part of household batteries in the MSW burden of zinc.

These figures are compared in this report to other inputs of zinc into the environment and after a specific review of the toxicity of zinc, the conclusion is that the classification of household batteries as hazardous material or material imposing specal legislative requirements over their use or their disposal is arbitrary and without scientific justification.

1. Introduction

The purpose of this study is to investigate the environmental impact in Western Europe of zinc from household batteries. The family of batteries considered are the alkaline (manganese), the zinc-carbon and zinc chloride of the following formats : AAA, AA, C, D and 9 volts. It takes also account of the fact that, over the last ten years, European battery manufacturers have taken environmentally responsible measures through the stepwise reduction in the mercury and cadmium content of household primary batteries and in the subsequent decrease of toxicity of the possible effluents generated by the disposal of these batteries. Under a voluntary battery industry initiative from 1 January 1994, mercury and cadmium have been totally eliminated from alkaline manganese and zinc carbon batteries.

Environmental impact studies reviewed by the Federation of Electricity and Electronics (FEE, asbl) on the disposal of dry-cell batteries in municipal waste management system do not indicate that such disposal or incineration practices pose, at the time being and for the foreseeable future, significant threats to the environment.

The fundamental purpose of all environmentally motivated taxes and deposits (eco-taxes, eco-redevances) is the development of public and industrial awareness about prevention of avoidable pollution. It centered rapidly on the protection of the environment, immediate and at large, e.g. protecting the whole planet from excess CO_2, avoiding the presence of excess nitrates and pesticides in our drinking waters or our foods, or caring about a too large emission of exhaust gases in town air, about the production of too much waste or about an excess toxic heavy metals in our soils.

Soon after this first view, the problem of ecotaxes was mixed and sometimes aggravated by the new concept of "sustainable development" put forward in 1988 by the Brundtlandt report at the UNO Conference in Rio. In Belgium, the ecotaxes were introduced in the law of 16.07.93, modifying the perception of taxes in the different regions of the newly federalized nation. The purpose of the ecotaxes was defined as : "to modify the behavior of producers and consumers in order to generate a better environment" and thus, ecotaxes will "levy a duty on a list of consumer products that are demonstrated to generate a nuisance". The word "ecological" was added to nuisance when the official text of the law was printed, on 20.07.93, in the Official Journal (art. 369).

Batteries of any type were included in the products to be "ecotaxed" because of their content in toxic heavy metals (mercury and cadmium mainly), of their widespread uses (resulting in their increased presence in municipal solid waste) and of the absence of any feasible recycling method. In counterpart, industry studied the possibilities of modifying the design of the batteries in order to decrease their content in mercury and cadmium. That decrease is specially marked in zinc dry batteries, the most common in domestic uses : their mercury content has decreased to zero. Cadmium followed the same evolution.

However zinc dry batteries are still considered by some persons as made of toxic metals, those persons even having a tendency to consider zinc itself as a toxic metal (ICDI, 1992) and to include zinc dry batteries in the items to be ecotaxed.

This report is centered on the issue of zinc omnipresence in the environment, on its lack of toxicity for humans and the environment at large at any concentration following its normal use under the present commonly adopted national or international regulations. It is based mainly on figures collected in Belgium and in the Netherlands and on scientific documentation from Canada and the United States.

2. Environmental status and significance of zinc

Zinc is present everywhere. It is estimated to represent 40 mg/kg (ppm) of the earth substance and 70 mg/kg in the earth crust (Table 1). It is 25 th chemical element in order of occurrence, approaching that of iron. Its content in vegetables is 1 to 10 mg/kg and up to 140 mg/kg in dry cereals. It has been shown to be an essential plant nutrient and an element indispensable to the activity of more than 200 important enzymes.

Zinc is present in larger concentrations in urban and industrial environments, due to anthropogenic pollution. Its mean concentration in loamy garden soil in Liege and Charleroi is 1800 mg/kg dry weight (n = 56), of which 22 % is bioavailable to vegetation, whereas in Engis (20 km SW of Liege), where zinc industry was until recently very active, the garden soil concentration was 2900 mg/kg DW and its bioavailability 31 %. In Balen (Belgian Limburg, 100 km NW of Liege) however, where zinc industry is still very active, but with an acidic and sandy soil, the zinc concentration lies around 250 mg/kg only with a 35 % bioavailability (SCOKAERT, 1983). Thus, many natural and anthropogenic factors play a large role in the inhomogeneity of the concentrations of the ubiquitous element zinc, its salts and its complexed forms. In Belgian agricultural soils the normal concentrations lie around 250 - 300 mg/kg DW.

2.1. Zinc in spent batteries

The typical composition of spent batteries is given in table 2, in percents of the total weight of the batteries. Although about 50 % of the disposed batteries are not fully spent they rapidly discharge in aqueous surroundings and convert the residual zinc metal to zinc oxide.

The number of household batteries sold per capita according to data compiled by the EPBA. It amounted to 4,6 alkaline-manganese batteries plus 4,3 zinc-carbon/zinc chloride batteries per person per year in Europe in 1993, and was considered to be disposed of on the same year.

The balance of zinc from batteries in municipal solid wastes (MSW) is difficult to assess. These fluxes are calculated on inconsistent bases (weight of zinc or weight of batteries, weight of zinc or of total heavy metals, weight of MSW or MSW + industrial waste, ...) and most cited numbers are calculated from ratios, interpolations, European extrapolations from national figures, or from occasional measurements.

From the European Zinc Institute, we quote that the consumption of zinc in Europe amounts yearly to $1,9.10^6$ T, of which 1,3 % enters in various forms of batteries, i.e. 25.10^3 T per year.

From the OECD report in 1991, we see that MSW production in Europe is 136.10^6 T per year and data from TREDI in France show that (ROUSSEAUX, 1990) zinc accounts for 0,06 % in that total (= 82.10^3 T/year) and that 32 % of the zinc in MSW (figure corrected from the original paper) originate in batteries, amounting to $26,2.10^3$ T per year. However, data from Germany (TABASARAN, 1990) give lower figures and show that zinc makes 0,2 % of the total municipal plus industrial waste and that batteries contribute to 1,7 % of that zinc burden (1,3 % if we take the RIVM) which would result in the deposit of $4,6.10^3$ T per year for zinc from batteries in European dumping sites.

The gap between these figures (half an order of magnitude) can probably be attributed to the quality of the raw data used, but the French output is very near the OECD calculated input.

2.2. Physical state and solubility from spent zinc batteries

In spent batteries most of the zinc (mean 92 %) is in the form of solid or pasty zinc oxide mixed with other solid constituents. The remaining portion of the zinc (mean 8 %) is in a soluble form and will be more rapidly leached after breakage of the metallic case; the residual power of those batteries makes those more susceptible to corrosion and thus to breakage but partially discharged batteries will rapidly fully discharge from short-circuiting after disposal. It is however generally expected that active and capped landfills have a low compressibility and that loads on battery cases are too small to damage them.

There is a great uncertainty over the timescale for the battery zinc to be leached out and released : assuming the landfill to be hydrologically stabilized after a residence time of 10 years, IRR (1992) calculated a transfer coefficient of 2.10^{-4} for zinc into the leachate (battery case and content combined).

Figures from the literature confirm the low yield in soluble zinc in MSW, even if one supposes an appreciable complexing effect for zinc, of organic acids resulting from anaerobic degradation of MSW. In a US-EPA TCLP test on completely shredded zinc-carbon/zinc chloride batteries, the zinc content of the experimental leachate was 1970 mg/l and 1190 mg/l for alkaline batteries (IRR, 1992). In an untreated leachate of a 2 years old UK dumping place (2 Ha of shredded and compacted MSW), ROBINSON (1983) measured 17,6 mg/l raw leachate (pH 5,95) and 0,9 mg/l after aerobic treatment and 10 days settling time. In USA, RADI (1987) measured 326 mg Zn/l in the leachate (pH 7,8) of a 30 years closed landfill of a town of 60.000 in habitants. In seven core samples in an industrial waste deposit in South Belgium, we found after nitric acid attack zinc concentrations varying between 44 and 7800 mg/kg (IGRETEC, 1993); three successive TCLP tests of a composite sample gave non-detectable concentrations in water (less than 0,25 µg/l). In a sample of another industrial liquid waste treated by an immobilization-solidification technique in a cement/lime based mixture, the material crushed after 4 weeks solidification time gave for the TCLP test zinc concentrations of 43 µg/l, 36 µg/l and 32 µg/l in three successive tests, showing thus a low but continuous solubility.

These few examples show the great variability of zinc compounds and ashes solubility in complex matrices. We can thus summarize zinc solubility in MSW as

- maximum solubility : 2000 mg/l in a TCLP test on shedded batteries;
- normal solubility : 300 mg/l at pH 7,8 in an old MSW landfill;
- reduced solubility : less than 1 mg/l in a TCLP test of industrial waste treated by a solidification technique

We can also summarize the input into the environment from household batteries on the basis of figures collected in Europe in 1993 : alkaline batteries have over 52 % of the household market share and the zinc-carbon/zinc-chloride about 48 %. The most popular battery size is AA, 1,5 V, 23 g total weight. Per year and per person, the use amounts to 4,6 manganese-alkaline batteries (= 3,2 g zinc x 4,6) and 4,3 for the zinc-carbon/zinc chloride (= 3,4 g zinc x 4,3) and should result in 29 g Zn disposed of per year and per person in our countries. An estimation by VAN DE BEEK in the Netherlands estimates to 106 g/kg dry municipal waste the weight of batteries present in MSW (i.e. 30 g zinc per kg dry MSW), partly sent to the landfill and partly to the incinerator.

2.3. Fate of zinc from dumping places

The solubility of zinc from batteries inside the landfill is one problem; the fate of that solution is another.

If the landfill is perfect and maintained as such, the liquids will be totally collected, their concentrations will be nearly constant and they will be treated. The results of ROBINSON show that the zinc problem can be solved and we are then left with another pollution : the zinc is immobilized in a liquid sludge that can be spread on the landfill top, or on agricultural soils at short distance. The sludge can also be thickened, dried and either used as a commercial compost base (if the metal content allows it) or be burned in an incinerator. In this last case, the dust or smoke generated is discharged from the stack and part of the zinc will be dispersed on a soil area larger than would have been by dispersion of the liquid sludge and contribute to the turnover of zinc by the vegetation.

Or the landfill is smaller or in use since a longer time : its "juices" are not collected and run freely to the local surface waters and then to the nearest river, where zinc compounds react with carbonate or hydrocarbonate ions or adsorb on clay particles and partly sédiment (ca 50 %) with river sludge, resulting in total river zinc concentrations of 0,2 mg Zn/l from all sources (Table 3).

Or the landfill was prepared and maintained without care, long ago or recently. It is leaking on all sides and no liquid is visible, because it escapes continuously in the ground with a flow proportional to rainfall. If the soil is sandy or gravelly, the flow is rapid and the zinc concentrations do not decrease notably. The solute will in a short time reach the water table or the nearest river or lake. If on the contrary the soil contains various amounts of clay or loam, the flow of liquids will be slower and the exchange of metals with clay micelles, or with iron and manganese oxydes and hydroxydes will be greatly enhanced (depending on pH of the soil, its cation exchange capacity, its saturation in phosphates, the types and concentrations of the metals present, the particle dimensions of the clay, the presence of organic matter, ...). Many prediction models exist that give a good idea of the mechanisms of these exchanges but none is practically able to predict the fate of solutes of variable composition.

2.4. Zinc from manure and other sources

The important for us is that most often soluble zinc concentrations will decrease slowly with its trajectory in the soil but we do not know its limits or how long it will be immobilized. We may also ask the question in another manner : in that vast reservoir with very slow movements, what is the part of zinc from batteries and the part of zinc from other sources like manure discharge over fields and grass, corrosion of galvanized structures (electricity pylons, crash barriers or lampposts along the motorways (one lamppost every 100 m on all motorways in Belgium), car tyres). Table 4 gives an estimation of these flows of zinc per year to the soil in the Netherlands. Similar figures can be obtained in Belgium, especially on zinc from motorways. The sludge of motorway storm basins contains 1000 to 2000 mg zinc per kg dry sludge and zinc decreases rapidly in the soil : at 50 cm beneath the basin bottom (loam) its concentrations are only 30 (background) to 600 mg/kg dry soil (VERNIERS, 1985). The total emission of zinc from the motorway into the soil is estimated to 10 to 20 g/day/km. These figures show also that the mobility of zinc in the soil from the motorway emissions is reduced, at least in the vertical direction in the soils studied.

2.5. Fate of zinc from incinerators

The Dutch RIVM report states that in the Netherlands 40 % of used household batteries are dumped, 20 % are incinerated and 40 % are stored. Public concern about MSW incinerators is about airborne emissions and the risks that can arise in the proximity of the stack, under the large area of dispersal from the plume and, again, from the solubility in water of the fly-ash disposed of in one or a few landfills.

Incineration of batteries does not destroy the heavy metal contained in them. Thermal processes transfer heavy metals either to stack gas as fine particles or to the bottom ash. The bottom ash falls through the grates of the incinerator while the fly ashes rise through the smokestack and may be trapped by a washing or a collection device. Lime scrubbing systems using filter fabric typically remove 99,9 % of the fly ash. They remove 99 % of the zinc, 95 % of the cadmium and 90 % of the mercury, due to the higher volatility of this last metal. We are not concerned here with cadmium and mercury, which have been eliminated at the battery production process and are left with the sole problem of zinc emissions. This problem is poorly documented because zinc being not considered as a toxic heavy metal, most studies do not mention zinc concentrations in the results of the analysis of stackgases. Zinc however is a low temperature smelting metal; it could thus partly vaporize in the combustion process and condense on the warm inorganic particles on cooling (in the same time it can be oxidised to zinc oxide). A part of it could still be in the vapour state in the last portion of the stack where temperatures still reach 150°C in many cases. For these reasons it is reasonnable to believe that most of the zinc will be found in the fly ash and very little in the bottom ash, which contains most of the iron, manganese and aluminosilicates. Given also the temperature characteristics of the MSW incinerators one can tentatively predict that the zinc case of zinc-carbon batteries (anode) will in great part remain in the bottom ash : only the zinc present in the electrolyte will be well mixed with the shredded MSW and will be transformed into particles tending to escape with the combustion gases.

In a Belgian report on metal emissions from an RDF heating plant, the zinc content of bottom ash was 750 mg/kg, that of fine dust on the fabric filter 6700 mg/kg and for raw dust arrested in cyclones 3300 mg/kg. In another Belgian incinerator burning "fluff" only, equipped with a semi liquid treatment gas cleaner, the total concentration of dust in the chimney after cleaning was 5 to 7 mg particles/Nm^3 of which 0,4 mg/Nm^3 was zinc respirable particules, resulting in a concentration in breathed air at 1 km of the chimney of 1.10^{-6} mg Zn/m^3 and a wet deposition at the same place of 0,13 mg Zn/m^2/year, when the total normal zinc wet deposition in Liege is of the order of 160 mg/m^2/year.

In another older incinerator south of Brussels burning only MSW, the bottom ashes contain 7.000 mg Zn/kg while fly ash contains 11.900 mg Zn/kg. A Canadian report (IRR, 1992) gives more details about a large incinerator burning MSW with a content of 500 to 3500 mg Zn/kg dry waste : fly ashes contained 2800 to 152.000 mg Zn/kg; bottom ashes, 200 to 12.000 mg/kg; cleaned flue gas, 1 to 10 mg/Nm^3. As far as these incinerators are concerned with heavy metals emissions, they have not to bother about exceeding the national rules for zinc : table 5 shows that zinc was not retained in any country on the list of toxic metals to be limited. Thus the burning of household batteries containing zinc and devoid of Cadmium and Mercury are not any longer of concern for atmospheric pollution.

The fate of the collected ashes is normally a closed landfill where precautions are taken for the collection of percolates. Fly ash especially is made of very small particules which favor the solubility in water of zinc compounds. Most TCLP tests of fly ashes show a solubility of 30 to 50 % for zinc residues. This is very high and results probably from the presence of excess lime present in the cleaning process of the combustion gases. While most other metals are then insolubilized as oxides or hydroxides, lime at high pHs favors dissolution and formation of soluble zincates. Such effluents have then to fulfill specific requirements concerning industrial water pollutants concentration in residual water (0,8 to 8 mg total zinc per L residual water in Belgium in most cases) and the part of batteries in the quality of these effluents is proportional to the quantity of battery zinc in the total MSW. We are taken back to the preceding case where the fate of zinc from batteries through landfill disposal was the surface and shallow ground water and then the soil itself.

Atmospheric pollution from incinerators contributes extremely little, as far as zinc is concerned, to health or ecological problems, be it through inhalation or contamination of the ground or of vegetables.

3. Zinc toxicity

3.1. Toxicity to humans and mammals

Zinc is normally not considered as toxic to humans and mammals (MARQUIS, 1993) but, on the contrary, as an essential element for life. Zinc deficiency (at daily intakes of less than 0,05 to 0,1 mg/kg body weight/day) is perhaps more frequent than zinc overdose. Moreover zinc benefits an excellent regulation system in our body and does not accumulate. This is in fundamental opposition with toxic heavy metals like mercury, cadmium and lead, whose excretion is much lower, regulation inexistant and toxic character appreciably more irreversible.

Toxic zinc compounds however exist but their toxicity is always linked to the anion moiety of the molecule and not to zinc itself. The pigment zinc chromate is carcinogenic like all chromates, zinc phosphide liberates easily the deadly phosphine gas like all phosphides and is used as a raticide and zineb or zincbisdithiocarbamate is a toxic fungicide like other metallic dithiocarbamates.

Most zinc salts are also skin and eye irritants due partly to the metal itself and partly to the strong acid properties of the anions.

At very high doses only, are zinc soluble salts toxic, like other metal sulfates, i.e. copper sulfate and ferrous sulfate, with respective LD50 of 300 mg/kg and 320 mg/kg for the rat. The acute toxicity of zinc is mainly an irritation of the digestive tract. The LD50 for the rat by oral route amounts to 2460 mg/kg body weight for the acetate and to 2000 mg/kg for the sulfate. Zinc chloride has a lower LD50 (350 mg/kg) because of its very high acidity and the consequent caustic properties on biological tissue.

At lower doses and repeated exposures, the same soluble zinc compounds show a chronic toxicity at 0,4 mg Zn/kg/day for 10 weeks, characterized by a decrease in copper body burden and the consequent copper deficiency.

At normal dietary and environmental zinc levels and doses (15/20 mg per day, i.e. 0,25 mg/kg/day), humans like most mammals can maintain constant the zinc levels in the various tissues. The sites of regulation of zinc metabolism are : the absorption of zinc from the gastro-intestinal tract and rejection in the faeces of the non-absorbed zinc portion (10 mg/day), the excretion of zinc in urine (300-600 µg per day), in sweat and in the biliary fluids, the exchange of zinc with erythrocytes, the release of zinc from tissue (especially liver and muscles) and the secretion of zinc into the gastro-intestinal tract. Regulation of gastro-intestinal absorption and secretion probably contributes the most to zinc homeostasis.

Zinc is known to induce a specific protein (metallothionein) production in the mucosal cells lining the intestine; it binds to the metallothionein which remains in the mucosal cells and the metallothionein-zinc complex is excreted from the body upon sloughing of the cells.

In spite of that mechanism for whole-body zinc homeostasis and the relative large amount of zinc in tissue, a regular exogenous supply of zinc is necessary to sustain our physiological requirements and the limited exchange of zinc between tissues; 10 to 15 mg zinc are needed each day by an adult.

The zinc body burden of an adult ranges from 2 to 4 g, of which more than 95 % is intracellular zinc. The blood contains 0,5 to 1 % of that total : 80 % in the red blood cells and 20 %, or 0,8 to 1 mg/l, in the plasma (THYS, 1992) which is usually considered as reflecting the zinc status of a person (Table 6). The highest concentrations are found in bone (100 to 200 mg per kg, 20 % of the body burden), in hair (150 mg per kg) and in prostate (100 mg/kg) on a fresh weight basis. The concentration in muscle is lower but the total quantity in muscle mass represents 60 % of the body burden. These levels can vary with age.

Under normal conditions, the biological half-life of absorbed zinc ranges from 70 to 400 days following the organ. Large losses of zinc occur only on very special occasions (up to 30 mg per day) as liver cirrhosis, leukemia and post-surgical shock.

The information on mutagenicity of heavy metals is controversial. On the basis of chromosome aberrations found in cultured lymphocytes of zinc and cadmium workers, DEKNUDT (1975) stated that zinc was a potent mutagen whereas cadmium was not. A few years later however he discovered that the methodology used was not perfect but subject to some artifacts, first of all the calcium level in the diet of experimental animals (DEKNUDT, 1979). Today one may safely state that zinc is not a significant mutagen, nor a carcinogen in situations encountered by man, although zinc levels may affect (enhance) the growth of existing tumors, particularly when zinc intake is abnormal.

3.2. Zinc daily intake

The daily normal intake of zinc through food is estimated to 8-14 mg in the Netherlands (RIVM 1992) and to 14,7 ± 7,9 mg in Belgium (BUCHET, 1981), while the intestinal absorption of tha daily zinc is estimated at 20 % of the ingested quantities.

Most foods contain between 10 and 30 mg zinc per kg dry weight; exceptions are mussels (up to 200 mg/kg DW) and oysters (up to 1000 mg/kg DW).

Outside food, environmental zinc is not very important for humans. Zinc concentration in ai (respirable dust) vary in most Belgian towns between 300 and 800 ng/m³ (KRETZCHMAR, 1980) and between 1000 and 3000 ng/m³ in towns with huge industrial sources (mainly steel and non ferrous industries); water soluble zinc accounts for 25 % of the total particulate concentration and we are supposed to breathe 15 m³ a day. There is no rule in Belgium and the Netherlands as far as zinc immissions are concerned.

Zinc fallout (non respirable settled dust) was very important before 1976 in some places i.e. around non-ferrous industries : in Engis it amounted in 1975-80 to 30 mg/m²/day and from 1983 decreased to 3 mg/m²/day on a tri-monthly basis. It is not the object of an official norm either in the Netherlands or in Belgium but is indirectly regulated by various rules on industrial stack emissions. It should however be noted that these rules do not take into account the zinc fallout from corrosion of galvanized iron.

Concentrations of zinc in drinking water are negligible (under 0,15 mg/l in Belgium) and we drink two liters water a day. A considerably higher zinc content (up to 2 mg/l) has however been recorded as the result of the passage of water through zinc coated steel pipes. Water containing 3 to 5 mg zinc per liter is found by most people to have a bitter taste. Drinking water standards are 0,1 mg/l in the Netherlands, 0,2 mg/l in Belgium, and 5 mg/l in both countries after standing for 16 h in a galvanized pipe.

Finally, a last source should perhaps be mentioned in human intakes. It is presently quite frequent, specially among the old and the children, to be prescribed by the doctor tonic pills containing vitamins and trace metal. Zinc is among these at levels varying between 1 and 15 mg per tablet. As these mixtures are considered non toxic, their sale is considered free and their use escapes medical supervision (too much, too often or for too long).

Farm animals receive every day large amounts of zinc added to their food as a growth stimulant. The requirements in zinc vary following the animal : poultry, 20 mg/kg body weight/day; ruminants 25 to 50 mg/kg and pigs 50 to 100 mg/kg. Their food is often overdosed, resulting in high concentrations of zinc and other metals in manure.

3.3. Aquatic toxicity

If we generally say that zinc is not toxic to man and mammals we should be much more cautious for aquatic life. Many fishes and invetebrates are very sensitive to soluble zinc concentrations in waters but the subject is much more complex than for humans and the scattering of toxic or lethal doses among species is very wide. This scatter shows in itself that zinc is not the sole variable in the problem.

a. Water hardness is surely one of the important points

Presence of calcium and magnesium ions, divalent like zinc, play an important role in the permeability of inner or outer membranes to the divalent zinc. Saturation mechanisms like facilitation systems seem to exist.

b. Presence of other toxic metals

This is also very important due to the fact that aquatic organisms are completely exposed (by the food, by the skin and by their gills, (the organs of oxygen intake) to the full composition of their full environment. All these metals act together and it is impossible to say if cadmium increases the toxicity of zinc or if zinc decreases the toxicity of cadmium, when the toxicity index is of low specificity as is the lethal concentration : the LC 50, 24 h for Daphnia at pH 6,2 is 25 mg/l for zinc and 0,21 mg/l for cadmium; for a mixture of the two metals in equal proportions and at pH 6,2 the LC 50, 24 h is 1,2 + 1,2 mg/l. The presence of a third metal, copper for example, makes the situation still more difficult.

c. Enormous quantity of soluble zinc in rivers

Another important fact in zinc aquatic toxicity is the enormous quantity of soluble zinc transferred to rivers from factories and thus from country to country (e.g. from industrial or agricultural countries or regions to fisher countries or regions). Even if these quantities have decreased sharply since the beginning of the seventies from 0,25 mg/l to less than 0,05 mg/l (figure 1, table 7), they continue to bring large amounts of metals to the estuaries. The amelioration seen in the last ten years is the consequence of the environmental rules becoming more and more strict, especially those about industrial residual waters released by industries employing much zinc like metal surface coating, paint industry, pesticide industry, rubber industry, alloys industry, metals recycling, ceramics and frits, landfills, MSW incineration and sewage treatment plants. All these industries must now obey specific norms where zinc release in water are heavily limited. This fact underlines clearly the difference in aquatic, atmospheric and food toxicity of zinc : only concentrations in water are subject to strict rules and this has not to do with an eventual bioconcentration of zinc in fish. This factor remains low (except for mussels and oysters) : it ranges between 100 an 1000, those for fish being lower than for invertebrates.

Not withstanding the number and strength of these factors, zinc is thus toxic to aquatic life and known with some detail (short-term exposure vs semi-chronic or chronic exposure, freshwater vs salt water organisms, fish vs invertebrates or microorganisms, ...). Zinc is more toxic in soft or acidic waters; it does not seem to be more toxic to salmonids than to other fish, generally less sensitive. It is however more toxic to fish eggs, pups or growing organisms. Lowest effects begin at levels of 0,05 mg/l dissolved zinc; lethal effects begin at 1 mg/l in soft water or at 30 mg/l in hard water. Crustaceans and fishes are less sensitive. Large differences in toxic concentrations or lethal concentrations exist sometimes for species being physiologically very near or being from the same taxonomic group. Zinc toxicity for fish is easily demonstrated in the laboratory. It is much more difficult to demonstrate in the open field or to assess the importance of zinc in river mortality of fish or in fish disappearance from some rivers or places. The phenomena themselves are well identified but the factors of influence are not.

3.4. Plant toxicity

Toxicity of zinc to plants and vegetation is well known experimentally in the laboratory or in field experiments, as well as its essentiality as growth factor. Its toxicity is also well known in fields and forests around zinc smelters but in this case attention should be paid to the simultaneous atmospheric pollution by other metals (lead, cadmium, ...) and particularly sulfur oxide which is emitted in large quantities from the smelters and has a very toxic effect in vegetation in periods of thermal inversions.

The resorbtion of zinc by the vegetation is double :

a. direct fallout of zinc particles on leaves and in the cracks of tree barks and we do not worry very much here about that source;

b. radicular resorbtion of soluble zinc from the ground and of the zinc added to the ground by atmospheric pollution and rain (reduced quantities : 60 to 300 mg/m²/year) and by manure tipping of agricultural soils (resulting in a zinc concentration in soil after a few years of 150 to 300 mg/kg dry soil instead of 20 to 60 mg/kg dry soil in untreated areas).

Many studies of soil properties have shown that resorbtion of metals from the soil into the roots and the green tissues of vegetation depends from a multitude of factors, some depending on the vegetal species (it is well known that spinach and tobacco accumulate metals), some on the climatology and many on the properties of the soil, among these :

- the type of soil (sandy, sandyloam, sandy clay, and heavy clay) is the most important, including the mean dimension of clay particles;

- pH of the soil (Table 8) : solubility of zinc is the lowest at normal soil pH and zinc will dissolve only at pH below 5, whereas cadmium does at pH below 6;

- organic matter content of the soil;

- cation exchange capacity of the soil (high concentration of calcium carbonate and phosphate are characteristic of low zinc availability)

All these variables play a role on the availability of zinc from soils and they are rarely described in totality in experiments describing the toxicity of added zinc to soils.

Zinc deficient soils have zinc concentrations ranging from 1 to 20 mg/kg; normal values are in the range 20 to 200 mg/kg; near toxic values, measured by yield decrease, are spread from values of 500 mg/kg to 1500 mg/kg but already visible in some cases at 50-100 mg/kg. The content of zinc in vegetation can also be taken as a sign of toxicity but does not seem to increase very much with the concentration in soil : it does not increase more than 3 times the normal value and therefore has never been the base of a judgement of the quality of the resulting food. Truly toxic values (causing for exemple chlorosis of wheat leaves) were obtained at 3000 mg/kg but without effect on yield. Beside this general situation, it must be said that some species are more sensitive to zinc, that some others are resistant to zinc (and it has been shown that this resistance is attached to a specific gene), and that some other are accumulating zinc.

Soil zinc toxicity can also be measured on other organisms living in the soil like microorganisms or arthropods or earthworms : the same toxic levels of zinc were described in these studies as well as the same levels of bioconcentration (less than 10) in the populations grown in presence of added zinc. Some adverse effects on microbial processes can however be expected at levels of 50-70 mg/kg dry soil.

The authorities of some countries are presently very attentive to the problems of metals in the soil in relation to the new concept of multifunctionality of former industrial soils and to the possibilities of remediation of the contanmination in a number of industrial sites. In the Netherlands especially, the tendency is to decrease the permitted limits of metals in soil, on the basis of experimental results, factors of uncertainty and statistical limits of confidence. This process of interpretation of results and extrapolation to existing situation will lead to very difficult positions of the authority and time will show if they are really applicable or if they are pure theoretical considerations. At the present time, the maximum tolerated concentration in soil is 300 mg/kg. The background level should not be higher than 140 mg/kg for a certain type of soil; a content of 500 mg/kg means a polluted soil and one of 3000 mg/kg would have to be treated.

In Germany, the background level should not be higher than 150 mg/kg, agricultural land 300 mg/lg, playgrounds 300 mg/kg and industry grounds 1000 mg/kg. Interventions should occur at respectively 600, 2000 and 3000 mg/kg (KLOKE, 1991).

4. Risk assessment analysis of zinc from disposed batteries

Household battery useage and disposal practice currently in place result in some additional load on the environment with potential detrimental effects. Risk assessment methods can predict the risks associated with various disposal options for dry cell batteries that become part of household waste streams. It consists of several steps. The first, **hazard identification**, is the qualitative evaluation of the potential adverse health/environmental impact of chemical on potential receptors. The second, the **exposure assessment** phase includes the identification of significant migration pathways and potential receptors. It estimates the rates at which chemicals are absorbed by organisms (by skin contact, by oral ingestion, by inhalation or any possible other route) and tries to determine wether any threats exist, based on quantified exposure conditions from a potentially contaminated media. It may then, in a third step, compare feasible disposal options and in the best case indicate the least harmful. It should be understood that the words **hazard** or **exposure** relate here most often to human life or human health, but could also mean other precise forms of life like forests or earthworms. The present report is concerned by effects on human health.

4.1. Hazard identification

In general, the hazard identification starts on a theoretical basis : the risk associated with a substance depends largely on its biological and physico-chemical properties; their study decides if the risk induced by the substance is worth considering and if, in a second step, more data have to be generated in order to prepare a quantitative assessment of the exposure and compare this figure to existing data on ADI, acceptable daily intake, or LOAEL, lowest observed adverse effect level. In that context, the risk R of a chemical compound is considered as the sum, or the product, of the toxicity T of the compound studied (acute or chronic toxicity or a combination of both), its persistance P or its degradation in the environment, its bio-accumulation potential A, its fugacity F and, naturally, the quantity Q produced or used per year in the country and Q', the percentage of Q really released to the environment. Each of these variables can be measured and condensed into scores, as was shown by KONEMANN (1983). Other variables can be added and treated the same way or adapted to the case, without disturbing the whole process, the higher scores meaning always the higher risks. In practice for zinc :

- T = 1 because the LD 50 for zinc is between 250 and 2500 mg/kg
- P = 0 because the half-life of zinc in the environment is shorter than 1 year

- A = 0 because log BCF (bioconcentration factor) is smaller than 1,5
- F = 0 because zinc has no tendancy to evaporate and a reduced tendancy to dissolve into water from spent household batteries
- Q = 3 because zinc use from batteries amounts to 100 and 1000 tons per year for whole Belgium; i.e. 650 t/y
- Q' = 1 because zinc will be dispersed from a limited number of places and at a rate of between 3 and 30 %.

In the case of zinc from batteries, the combination of all scores (plus eventually others added to make the picture more complete or more relevant) will give a very low degree of priority to the problem and the conclusion is immediate : disposal of zinc from household batteries either by landfill or by incineration does not pose a significant health problem.

4.2. Exposure assessment

If however we consider it necessary to complete the exposure assessment phase and quantify the exposure we adopt a similar process as the preceding one, for example that adopted by USEPA (1989), designed to calculate the daily intake of zinc from the compound studied and compare it with the ADI for zinc, following the generic equation for calculating chemical intakes :

$$I = C \times CR \times CF \times FI \times ABS_s \times EF \times ED \times 1/BW \times 1/AT$$

where

I = intake, adjusted for absorption (mg/kg-day)
C = chemical concentration in media of concern (e.g. mg/kg)
CR = contact rate (e.g., mg soil/day; liters water/day)
CF = conversion factor (to account for consistency in units used)
FI = fraction of intake from contaminated source (unitless)
ABS_s = bioavailability/absorption factor (%)
EF = exposure frequency (days/years)
ED = exposure duration (years)
BW = body weight (kg)
AT = averaging time (period over which exposure is averaged -- days)

This equation is adapted to estimate actual exposure intakes by potential receptors as a results of releases of metals into various environmental media from the battery disposal practices.

On the base of all the figures cited or calculated in this report, the daily intake of zinc for man resulting from the disposal of spent household dry batteries will be absolutely negligible, given the existing daily normal intake of zinc, its large variability and the absence of any case of bioaccumulation. The same yields for fish, for the final fate of zinc after many years will be the rivers, and the concentration of zinc in the rivers will never decrease under a certain high background value due to normal erosion of agricultural soils.

5. Conclusions

Regulations governing waste disposal practices attempt to distinguish between hazardous and non-hazardous materials. Materials are determined to be hazardous based on a set of tests that examine their toxicity, flammability, explosivity, corrosivity, and/or infectiousness. Dry-cell batteries are themselves not affected by hazardous waste regulations, since all household wastes entering the MSW stream are generally classified as non-hazardous.

It is true that in the past, batteries were associated with the presence of toxic metals, notably mercury and cadmium, and that their increased use followed by their careless disposal had stirred the fear of ecologists for the liberation or accumulation of heavy metals in waters, air and soils. The responsability of the batteries industry corrected the situation in the best way on one side by reducing to zero the quantities of cadmium and mercury added or present in the household batteries and on the other side by developping very small and light weight rechargeable batteries for long term household use.

Zinc toxicity cannot be compared to toxicity of heavy metals in general. Human and mammals physiology shows that, contrarily to mercury, cadmium and lead, concentrations of zinc in the body are precisely regulated by biological mechanisms of resorbtion and excretion and that there is no long-term accumulation of zinc, nor any cumulative lesion (except copper depletion in experimental caser) resulting from the increased presence of zinc in the ingested food.

Indisputable biochemical evidence shows also that, on the contrary to the three other heavy metals, zinc is an essential element for the activity of a great number of enzymes and natural processes like alcohol and glucose metabolism, skin healing and sexual maturation of young male adults. From the LD 50 figures we see distinctely that zinc sulfate is ten times less toxic (acutely) than ferrous sulfate or copper sulfate.

To aquatic organisms however, zinc shows a certain degree of toxicity at doses that can commonly be met in the environment in industrial zones. Experiments with zinc compounds show widely different results for different organisms or even different species of the same family. Zinc concentration is very clearly not the sole responsible variable for the observed effects : salinity and hardness of the water, as well as the presence of other metals (in traces or in larger quantities) play also a very direct role in the penetration of zinc in these organisms or in its action on important physiological targets inside the aquatic organism. Also, zinc toxicity cannot be explained by the accumulation of the metal in the organism, for its bio-accumulation factor remains very low (between 3 and 5, except for filtering molluses like mussels and oysters) and can never be considered as a factor of risk in human food. On the basis of IC 50 for Daphnia, zinc toxicity is generally estimated to be hundred times lower than cadmium toxicity and two hundred times lower than copper toxicity.

Synergies and antagonisms are difficult to detect or to analyse except for specific cases and without generalization. Research on the essentiality of zinc for aquatic organisms is nearly inexistant but no available argument could deng it.

In large rivers, about half of the zinc is in an either insoluble or adsorbed form and does not seem to participate to metal toxicity. It contributes however to the toxicity of rivers and estuaries sludges because of their unstability.

To plants and vegetation, zinc is also toxic at high concentrations in soil and essential as growth element at low concentrations. Background zinc concentrations in Belgian soils are between 200 and 300 mg/kg but bio-availability of zinc to plants depends on the physico-chemical properties of the soil. Soil contents of 1000 to 2000 mg/kg around ferrous and non ferrous metal factories are not seldom and toxicity to plants is noticeable at 3000 mg/kg. Some plants are more sensible, some other are more resistant. Development of soil micro-organisms is inhibited by lower concentrations of zinc of the order of 100 mg/kg and this situation could be caused in some parts of the country by the disposal of cow and pig manure (by field spreading) which contains a high percentage of the zinc added to the food supplements of those animals.

In that summarized picture of zinc toxicity, zinc from household batteries plays a reduced role due to its presence in small quantities in relation to the soil background, to the other souces of environmental zinc and to its reduced solubility and mobility in the soil.

Concerns about battery disposal practices stem from the possibility of hazardous materials/chemicals leaching from landfills or entering the atmosphere through incineration of MSW. On the one hand, the amount of household battery usage seems to be going up which augments the concern about its impact when disposed together with MSW. On the other hand, some of the amounts of more toxic chemicals used in some of the batteries are going down and/or being substituted with potentially less toxic ones, thus minimizing potential impacts of the presence of dry-cell batteries in MSW.

Most used household batteries become an integral part of the municipal solid waste stream. In practice, all solid waste is either landfilled or incinerated, with recycling becoming an integral component. Several conclusions may be drawn based on this investigation :

- The dry-cell batteries investigated (i.e. the alkaline, zinc-carbon/zinc chloride) do not generally represent a concentrated source of heavy metals in MSW.

- Risks to the environment from battery disposal by landfilling and incineration are not likely to be significant. Thus, most household batteries may be safety disposed of in municipal landfills or municipal incinerators.

- At present "recycling" of non-rechargeables is more likely to present significant risks. There appear to be significant health-related problems associated with the separate collection, storage and disposal of most household batteries. During storage in a dry place short circuits could occur resulting in fires or explosions, during disposal of very large numbers of batteries without care in a landfill, significant concentrations of zinc could escape the place, not finding suitable neutral or inert material to be completely adsorbed or complexed, having thus greater opportunity to leave the landfill. However, with the elimination of Hg in most primary cells (especially the alkaline and zinc-carbon/zinc chloride batteries), recycling of alkaline and zinc-carbon/zinc chloride cells is not necessary or needed.

Soil type	Number	Mean	Maximum
peat	68	78	1200
sand	340	104	2900
sandy loam	11	108	470
not known	10	48	120
total	694	88	2900

Table 0 - The mean and the maximum of the zinc concentration in groundwater (µg.l^{-1}) per soil type

Mean	Percentile				
	10	25	50	75	95
48,1	8,1	14	32	67	130

Table 1 - The mean and percentiles of the zinc concentrations in dried soil (mg/kg) from the Netherlands (n = 1067; RIVM, 1993)

	Spent alkaline manganese	**Spent zinc-carbon**	**Spent zinc chloride**
Zinc oxide	20	26	30
Manganese oxide	33	29	27
Ferrous metal	19	4	4
Non-ferrous metal	2	-	-
Carbon	4	10	10
Non metals	5	8	7
KOH solution (33 %)	17	-	-
Zinc-ammonium chloride solution	-	22	21

Table 2 - Composition of spent zinc batteries, in percents of the batteries total weight (MAROLIA, 1994)

Mean	Percentile					
	10	25	50	75	95	number
88	2,5	10	29	84	360	569

Table 3 - The mean and percentiles of the zinc concentrations (µg/l) in shallow groundwater in the Netherlands in 1989, mean of the whole country (RIVM, 1993)

Source	Amount (in tonnes)	Comments
animal manure	1450	minimum estimate based on Zn content of animal feed
sevrage sludge	93	based on a Zn content of ca 1300 mg/kg dry weight
chemical fertilizers	135	-
pesticides	60	-
atmospheric deposition	250	based on particles deposition in rural areas
corrosion	2025	based on table 2-6, p. 26 of the RIVM document; specially high in winter
traffic	127	based on concentration of Zn in lubricating oil (1000 mg/kg), in the concrete (400 mg/kg) and in tires (16.000 mg/kg)
households	5	based on 40 % dumping of MSW
batteries	110*	based on the canadian consumption per capita and 40 % dumping of MSW

* This figure does not take into account the solubility of the zinc present in batteries (which has been estimated to 1-10 % per year)

Table 4 - The annual zinc input to agricultural soil; in tons of zinc per year, in the Netherlands, industrial sources excepted (RIVM, 1993)

France (law of 25.01.91 on MSW incinerators)			
Grouped metals	Pb + Cr + Cu + Mn	Ni + As	Cd + Hg
Admitted concentrations (annual means)	1	1	0,2
Netherlands (Richtlijn Verbranden, 1989)			
Grouped metals	Sb + Pb + Cr + Cu + Mn + V + Sn + As + Co + Ni + Se + Te	Cd	Hg
Admitted concentrations (hourly means)	1	0,05	0,05
Germany (17 Blm Sch V, 1990)			
Grouped metals	As + Co + Ni + Sn + Sb + Pb + Cr + Cu + Mn + V	Cd + Tl	Hg
Admitted concentrations (sample mean)	0,5	0,5	0,05
European Directive 89/369/CEE			
Grouped metals	Pb + Cr + Cn + Mn	Ni + As	Cd + Hg
Admitted concentrat. (mean on 7 days)	5	1	0,2
USA (Fed. Reg. vol. 54, n°243, 20 dec. 1989 : 40 CFR par 60)			
Grouped metals	As, Cd, Pb	Be,Cr,Ni	Hg
Min. cleaning efficacy	97 %	99 %	30 %

Table 5 - National rules for the emission of toxic metals at the chimney of MSW incineration plants, in mg/Nm³

Mean	Percentile				
	10	25	50	75	95
856	677	750	836	931	1023

Table 6 - The mean and percentiles of the zinc concentrations in µg/l in blood plasma in Belgium (n = 2129)

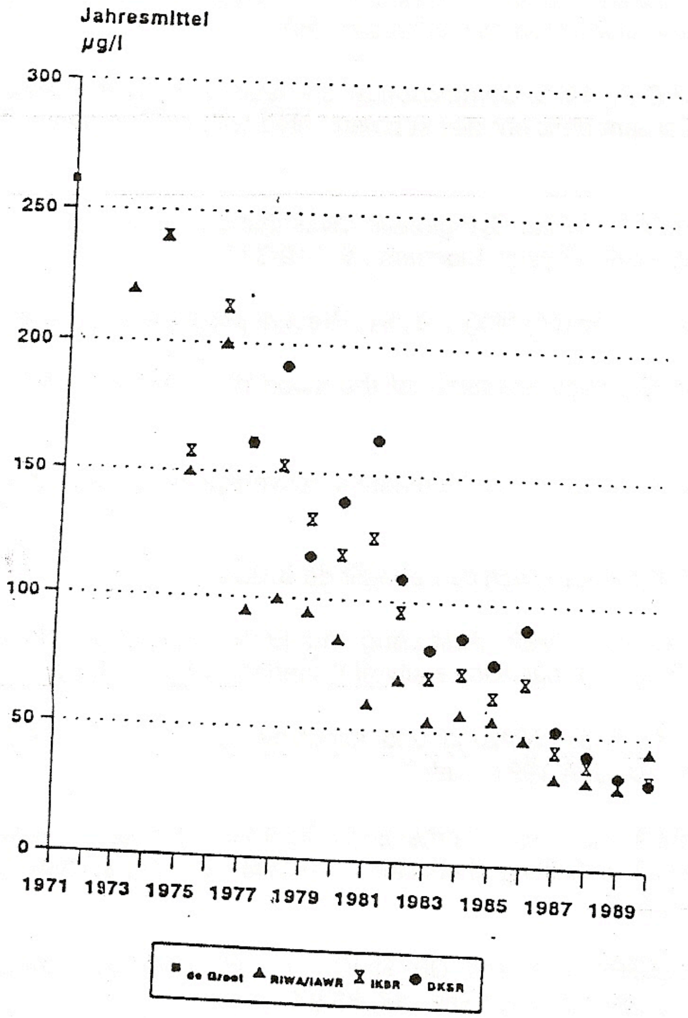
	1981-1983	1984-1986	1989
Rhine River	6500	4200	1625
Meuse River	2200	1500	375

Table 7 - Transboundary zinc transported by the Rhine and Meuse Rivers in tonnes per year into the Netherlands (RIVM, 1993)

pH of the suspension	Soluble + adsorbed Zn (in mg/kg or mg/kg soil)									
	Herentals	Peruwelz	W.-Lede	Glabbeek	Ath	Merendree	Waarschoot	Proven	Kieldrecht	Pervijze
0,5	6,51	13,47	12,59	13,99	25,15	7,73	9,86	13,06	13,74	13,50
1	7,67	13,32	12,77	15,49	25,00	7,90	10,72	14,24	14,85	14,52
2	5,82	11,50	9,20	13,00	17,25	6,12	10,52	9,75	10,50	5,75
3	4,77	6,60	6,35	8,15	15,82	2,85	6,80	5,12	8,20	1,80
4	3,05	5,20	4,80	6,37	4,50	2,95	5,20	2,35	5,25	1,75
5		3,45	2,90	4,35	1,75	1,62		1,45	2,52	1,40
6					1,95			1,15	2,25	1,12
7								0,62	1,35	1,25
at soil pH	2,27	3,97	3,55	3,57	2,37	1,00	3,22	1,50	2,35	0,75

Table 8 - Sum of soluble and adsorbed Zn extracted from 9 soils at different pH-values (VERLOO, 1973)

Figure 1 - Decrease of zinc concentration in the Rhine at Lobith (yearly means of monthly samples, by four different laboratories), Malle, 1992



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