

Zinc spread in the environment

- A literature study

GOODPOINT AB

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Summary

Zinc is one of our most common and most occurring metals. The metal is very useful and is used to prevent corrosion. Zinc is toxic to water living organisms when it occurs in concentrations above 20 µg / l. The metal affects the aquatic organism's reproduction, survival and growth negatively. It is especially young individuals and embryos who will be affected by enhanced concentrations of zinc. The toxicity for zinc is determined by its bioavailability and is affected by its metal form, pH, redox ratio, DOC etc. The largest emissions of zinc occur to water followed by emissions to air. Within both categories diffuse emission is most dominated. The biggest zinc emission source is leakages from wooded ground followed by atmospheric deposition on the water surface. Industries is the greatest point source. The leakage from wooded ground is derived from atmospheric deposition of zinc. This report has chosen to focus and examine three types of human activities that causes zinc emissions. The activities which has been chosen for more extensive studies are artificial turfs with rubber granulates, traffic related emissions and emissions from goods. The traffic causes zinc emissions around the roads and the pollutant is usually not spread far from the road. Locally high levels of zinc along the roadside can therefore occur. Galvanized goods are believed to be a major

secondary emission source even in places other than the traffic environment. Negative effects on aquatic or soil environment due to enhanced concentrations of zinc in Sweden is considered low. Generally, the chemical status in surface water in watercourses are good. Despite this, the risk of environmental impact due to zinc should not be underestimated. Zinc have been accumulated in the soil for a long time. If the soil or sediments characteristics changes it could lead to devastating effects on nearby recipients.

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Purpose and boundaries

The purpose of this report is to conduct a literature study and to compile data from various sources monitoring programs. The report aims to compile information on emission sources, to which medium in which emissions occur and its size. Furthermore, the report aims to determine how zinc is spread in the environment. Based on questions about potential sources of zinc derived from previous studies and experience, three diffuse sources of zinc emissions were selected for deeper studies.

Delimitations in surface have been made to Sweden's borders with the exception of zinc emissions that come via atmospheric deposition.

Background

Zinc is one of the most commonly used metals in industry and our environment. Every year 13 million tons of zinc are consumed in the world (Kwon et al., 2017). They are the construction and infrastructure industry largest end consumers of zinc. The automotive and electronics industries are also major end users of zinc (Boliden, 2017). Zinc is also used in the production of rubber, tires, and pesticides (Danielsson & Phil Karlsson, 2016). Zinc is also used in ointments and as a UV filter in sunscreen. IN sunscreen contains zinc as zinc oxide (Läkemedelsverket, 2016).

The metal has many uses in the metal industry. Zinc is used for, among other things galvanizing and as an alloying element in brass and bronze materials (Kwon et al., 2017). Through a surface treatment in the form of galvanizing or galvanizing, rust in steel structures can be counteracted in up against 100 years (Danielsson & Phil Karlsson, 2016). 60% of the zinc consumed goes to galvanizing of products (Boliden, 2017).

Metals occur naturally in our environment. They are found in our bedrock, soil and water. The most common form of zinc is zinc sulfide, ZnS (Kwon et al., 2017). The slow one The weathering that releases zinc from natural sources rarely becomes a problem for health and the environment then the process is slow and the zinc concentration in rocks is usually low. It is the zinc that is released from anthropogenic sources such as mining, smelting and processing that cause zinc to be redistributed to the environment, where it is enriched and accumulated in matrices available for biota which in turn can affect our health and the environment negatively (Walker et al., 2012).

The metal can spread at different stages in the life cycle. A contamination of metals can occur at the breaking of them. The refining of the metal is another step where there is a risk of metal contamination arises. The manufacture of products that contain metals can give rise to metal contaminants.

Metals can also be spread when the end product is used. During the life of the product zinc emissions occur via wear or corrosion. Areas of use that can result that zinc is spread to the environment is, for example, wear of brake linings and tires, or construction materials exposed to corrosion. Finally, when the product becomes waste and / or landfilled, a final discharge may occur arise (SOU 200: 23).

Zinc emission sources

Zinc released into the environment comes from either point sources or diffuse sources. To the point sources sewage treatment plants and industries are counted. Diffuse sources include stormwater, traffic, atmospheric

deposition, leaching from forest land and other land, agricultural land and individual sewers. To diffuse Sources in this report also include small industries or industries that do not emit pollutants above a threshold value and therefore do not have to report their emissions (Ejhed et al., 2010).

The major routes of distribution of zinc are to air or to water. Zinc is added via the wastewater

the sewage treatment plant where the majority is separated by means of the sludge which is then deposited or spread as fertilizer. Zinc that is not separated via the sludge passes through the sewage treatment plant and reaches recipients. Zinc is released into the air through, among other things, the burning of biomass (Swedish Environmental Protection Agency, 2017d). Sewage treatment plants are included in the point sources, even though it is actually a spreading route as it is zinc which accumulate and are measured here often are the result of emissions from diffuse sources upstream. In this report, only municipal sewage treatment plants are included in the result. To the diffuse sources upstream include smaller businesses such as dentists, car washes, households and the stormwater that reaches them municipal pipes and which later come to the sewage treatment plant (Ejhed et al., 2010) . Industries are the largest point sources for zinc. In the emission register "Emissions in figures", on The Swedish Environmental Protection Agency can see which industries report emissions of metals. Emissions are shared up on different industries and to what medium they release their pollution. Only industries like exceeds a threshold value must report their emissions (Swedish Environmental Protection Agency, 2017). Less industries that do not reach the threshold value are counted here as diffuse emissions. Stormwater is the water that comes from rainwater and meltwater that flows over surfaces and roads in densely populated areas. Land use, ongoing human activities and the catchment area determines which pollutants are found in the stormwater (Hjortenkrans, 2008). Atmospheric deposition of zinc is also considered a diffuse source. It can happen in the form of wet or dry deposition and is linked to the combustion of biomass, coal and oil (Ejhed et al., 2010). The deposition of zinc affects the whole of Sweden (Danielsson & Phil Karlsson, 2016). Although the fallout of zinc has decreased since the 1970s, the metal continues to accumulate in the marble layer, but not in the same pace as before. The deposition of zinc from atmospheric deposition is so large that it can not is explained only by Swedish emissions but probably originates from central parts of Europe (Hansson et al., 2012). Land use and the chemical properties of the soil affect how much zinc that will become mobile and reach the recipient (Ejhed et al., 2010). Pollutants can also be spread to the environment in other ways, for example through wear or when using goods and products. Corrosion or the use of solvents are examples of others emission sources of zinc (Hansson et al., 2012). Galvanizing is common to prevent corrosion steel products. This method is widely used in Sweden on, for example, poles, handrails, downpipes etc. Zinc from goods is today a large secondary source that is very difficult to estimate (Ejhed et al., 2010) . Individual sewers are also included in diffuse sources. Many diffuse sources are difficult to categorize

and to measure. In addition, it is difficult to know where a measured contamination from a diffuse source comes from actually originated.

[What happens to zinc in nature?](#)

Forests and other land receive their supply of metals from the atmosphere via atmospheric deposition. Since metals are not degraded and are persistent, these will accumulate in the soil. Metals such as falls down over the ground accumulates mainly in the upper parts of the ground, the marten layer which is rich in organic material. Because zinc is mobile at lower pH, it will move at a lower pH down into the soil layer or out into watercourses. In the marten layer, the pH is around 4 (SLU, 2017a). This makes that zinc, which is a relatively mobile metal, moves down the soil layer sequence or out to watercourses. Atmospheric precipitation is the largest source of zinc in forest land (Ejhed et al., 2010). Other land includes mountain environment, bog, open land and other land (Ejhed et al., 2010). Supply of metals to agriculture comes mainly from commercial fertilizers, manure, atmospheric precipitation and via liming. Leakage of metals from agricultural land is considered low. This is because high pH of agricultural land, which results in a low leakage of zinc. Plants also take up zinc as then the harvest is removed. Agricultural land therefore contributes little to the leakage of zinc. (Propriety et al., 2010) Wetlands are an important source of water purification as they store metals in the sediment. Through education of metal sulfides and binding of zinc to humus material reduces the bioavailability of zinc. If the wetland has natural redox conditions and a neutral pH metals will be stored in the sediment where they remain relatively permanent until conditions change (Ejhed et al., 2010) The form of zinc affects bioavailability. In the environment, zinc can occur in, for example, these forms: zinc ions Zn^{2+} , hydrated zinc, zinc sulfide, zinc oxide and zinc chloride. Zinc sulfide and free ions have highest bioavailability (Wallberg et al., 2016).

Toxic properties

Many metals are essential and vital for animals and plants. Zinc is a trace element and necessary for all life in small quantities. The metal is needed, for example, to create 150 different kinds of enzymes in our body (Walker et al., 2012). People ingest zinc mainly through food. Animal foods such as fish and meats are rich in zinc. Foods such as nuts and foods high in whole grains are also rich in zinc (Livsmedelsverket, 2016). A small portion of the population is exposed to zinc via occupational Contact.

Like several essential metals, zinc also has toxic properties in too high concentrations. Certain organisms are also more sensitive.

The toxic mechanism of metals is poorly understood (Söderqvist, 2007). Metal molds covalent bonds which give them toxicological properties. By binding covalently to organic compounds, the metals can form lipophilic substances and ions that can be taken up by animals and plants (Walker et al., 2012). This can cause biological functional groups to be blocked by the metal. It can too cause metal ions to bind to an enzyme or protein and thereby replace the metal ion that

previously sat there (Söderqvist, 2007). Another way that allows metals to become toxic is by bind to non-metallic constituents such as cellular macromolecules (for example, metals bind to sulfhydryl groups on the protein) (Walker et al., 2012). By binding to cellular molecules, it can

the conformation of the molecule changes, which in turn causes it to lose its function and this can lead to toxicity (Söderqvist, 2007).

pH affects the solubility of zinc, a lower pH makes zinc more soluble and thus more bioavailable. Zinc can occur bound to clay or oxides but may also occur in suspended forms such as colloids and particles containing metals (Huser et al., 2011). Organic material such as humus can affect the availability of metals as they bind to them and form strong bonds which decreases bioavailability (Huser et al., 2011). Zinc has a relatively high mobility in soil compared to others metals, especially at a lower pH. This allows zinc to be easily moved through the soil to the surface and groundwater under acidic conditions. Zinc in ionic form is very toxic to aquatic organisms (SOU 2000: 53). For zinc in water, bioavailability varies with pH, redox ratio, cation exchange, calcium content, presence of clay mineral, organic material, inorganic oxides and organic complexing agent (Swedish Maritime Administration, 2016). pH is believed to be one of the most important factors (Folkesson, 2005). For zinc, toxicity also depends on the degree of hardness of the water (the concentration of calcium ions). Hard water provides lower bioavailability than soft water. The presence of larger Organic particles such as humus also give it a lower bioavailability as zinc forms complexes with this makes it more difficult for the organism to absorb zinc. In addition to the previously mentioned factors affect also the structure of zinc toxicity (Folkesson, 2005).

Determining how much zinc accumulates can be difficult as it occurs in different shapes and it is the shape that determines the degree to which the metal can be accumulated and taken up. When In the case of essential metals, organisms can partially regulate this as they actively take up the metal and tend to have the same concentration in the body regardless of environment. Like other metals such as mercury and lead, zinc can affect organisms by inhibiting the functions of enzymes. Excessive levels of zinc often lead to zinc competing with chromium and copper by binding the body's molecules that really need chromium or copper. This causes symptoms that are similar lack of chromium and copper occurs. An excess of metals is most harmful to organisms in the early stages stage such as embryos and young individuals (Folkesson, 2005). Algae, zooplankton and fish are affected negative by elevated concentrations of dissolved zinc in the water. Algae are most sensitive followed by invertebrates animals, fish are least sensitive (SAC, 2018.) Toxicity to aquatic animals is concentration dependent because it disturbs the ion balance in the organism (Irwin, 1997).

Regulations and regulations covering zinc

Zinc is not subject to any regulatory restrictions or information requirements then the substance occurs in goods. Only two zinc-containing compounds are listed the list of candidates and which are thus subject to the obligation to provide information if they appear in goods over 0.1%. These are two specific zinc-chromate compounds that have carcinogenic properties. For chemical products that contain zinc, labeling and classification obligations apply to the majority zinc compounds. Zinc in powder form (EC no: 231-175-3) has a harmonized classification according to CLP as environmentally hazardous (H400, very toxic to aquatic organisms, and H410, very toxic to

several zinc-containing compounds such as zinc oxide and more.

Zinc is included in the Swedish Marine and Water Authority's regulations on classification and environmental quality standards

regarding surface water (HVMFS 2013: 19) where zinc is taken up as a particularly polluting substance in inland surface water. In order for an inland water to be classified as good chemical surface water status must not

the zinc concentration exceeds an annual mean of 5.5 µg / l. The value specified here is calculated on the bioavailable concentration of zinc, ie the content of dissolved zinc in water that is expected to be taken up of aquatic organisms. To obtain a correct value for the bioavailability concentration

the hardness of the water, dissolved organic carbon, pH and background levels of zinc have been taken into account (Sea and

water authority, 2016).

Zinc is also included in the regulation as a special pollutant in coastal waters and waters in the transition zones. To be classified as good status, the North Sea must have an annual average value of no more than 3.4

µg / l while the annual average value for the Baltic Sea may not exceed 1.1 µg / l. The value refers to dissolved concentration

of zinc in water (Swedish Maritime Administration, 2016).

According to the report "Proposed limit value for particularly pollutants" has the limit value for zinc calculated at 8 µg / l for water with a hardness > 24 mg CaCO₃ / l. Water with lower hardness than this has a limit value of 3 µg / l. The concentrations are based on dissolved zinc in the water, ie which is bioavailable. It is also calculated on an additive risk, the level that occurs above the background levels (Naturvårdsverket, 2008). For sediments, a limit value has been calculated at 860

mg / kg dry weight, this value also takes into account the background levels but also one equilibrium distribution calculated on the limit value in water. Zinc ion is toxic to aquatic life organisms and the EC / LC50 value is between 0.07–7.8 mg / l (Swedish Environmental Protection Agency, 2008). Already at

concentrations above 20 µg / l zinc is expected to have negative effects on the growth of aquatic organisms, survival and reproduction. The natural unaffected content of zinc in Swedish lakes and watercourses is on average 3 µg / l (SLU, 2017b).

Secondary poisoning for predator or human is not relevant as zinc is an essential substance and in to some extent can be regulated by the body (Naturvårdsverket, 2008).

Results and discussion

Zinc emissions in numbers

Water is the medium where the largest proportion of zinc emissions end up. The diffuse emissions stand for the majority of zinc emissions. Leaching from forest land and atmospheric deposition on water surfaces are by far the largest diffuse emission sources to water. Point emissions are too small more than 10% of total discharges to water. The point emissions include industries and municipal sewage treatment plants where the industries are predominantly the heaviest part (Naturvårdsverket, 2016). Diffuse sources of water are greater than diffuse sources of air. For both medium water and air it applies that

diffuse sources are much larger than the point sources of the respective medium. 846,000 kg of zinc is released annually

out to water and 160,000 kg / year zinc is released annually into the air in Sweden (Hansson et al., 2012) . In total

1023,000 kg of zinc was released into the environment every year. The size of emissions from diffuse sources and point sources

to air and water are shown in Table 1. Some double counting may occur when atmospheric deposition ends up in the aquatic environment due to land use and its leakage as well as deposition directly above the water surface (Hansson et al., 2012). An example is zinc that falls over forest land where it is counted As an atmospheric deposit, this zinc then accompanies the runoff and ports lakes are one counts again.

Table 1 shows a comparison between diffuse sources and point sources (Hansson et al., 2012).

Emission source zinc

(Kg)

Point discharge to water

86 000

Diffuse emissions of water

760 000

Total emissions of water

846 000

Point emissions to air

17 000

Diffuse air emissions

160 000

Total air emissions

177 000

Total zinc emissions

1 023 000

Discharge to water

Diffuse sources are a major emission source for zinc and it can be difficult to determine where the zinc is emitted comes from. The report "Diffuse emissions to air and water" (2012) written by Hansson et al. has investigated where the diffuse emissions come from. Through calculations, the study has taken produce data on diffuse emissions in Sweden. From these calculations, they have made an estimate of how a lot of zinc that comes from various diffuse sources. Of emissions from diffuse sources to water it was largest source of emissions of forest land, which annually emits 324,000 kg. Other large diffuse sources to Zinc emissions are atmospheric deposits on lake surface equivalent to 145,000 kg / year and stormwater as annually contributes 110,000 kg of zinc. The diffuse emission sources of zinc are shown in Figure 1.

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Figure 1 describes the distribution of diffuse emissions to water of zinc (Hansson et al., 2012).

To gain an understanding and relate the point emissions and the diffuse emissions to water in relation to each other, the size of the zinc emission is presented in Figure 2. For point sources, lineage can also be read out. For the origin of diffuse sources, see Figure 1. In the case of point sources, the majority come from zinc emissions from industries, industries emit 191,000 kg / zinc annually. Kommunala sewage treatment plant is a smaller source and emits 21,880 kg / zinc year, municipal sewage treatment plants therefore make up only a small part of the total emissions.

Forest land

Deposit on lake surface

Stormwater

Mountain

Agriculture

Mire
Open ground
Other land
Individual drains
Diffuse industries

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Figure 2 Comparison between diffuse sources and point sources of water (Ejhed et al., 2010; Hansson et al., 2012). For the point sources are those from industries with orange color and those from sewage treatment plants as gray.

The problem has shifted from point sources to diffuse sources as a result of the measures taken made to reduce emissions of metals from point sources (SOU 2000: 53). This make the contribution from diffuse sources is becoming increasingly important and is something that must be given priority. For zinc

goods that are in use and exposed to corrosion are probably a major secondary source of zinc emissions. First

when you know where you have elevated levels of zinc and where these emissions come from, you can take measures to limit the spread to the environment. The spread of metals is greatest around urban areas, zinc is around 4 times elevated around Stockholm. The levels are so high that effects on the environment

can not be ruled out.

Hansson et al. (2012) have calculated the gross load of zinc for each diffuse emission source and how large their contribution is to each water district. The figures from the study are shown in Table 2. The study

concluded that the North Sea has the largest gross load of zinc of 222,570 kg / zinc year followed by

The Bothnian Sea, which receives an average of 186,220 kg / zinc per year, and the Gulf of Bothnia with 183,150 kg / zinc

year. The Southern Baltic Sea received an average of 93,800 kg / zinc per year and the Northern Baltic Sea 73,300 kg / zinc

year. The figures for the load on the water districts are based on assumptions and calculations catchment area, land area, point sources and leakage content for the land type.

755 000

21 880

191 000

0

100,000

200,000

300 000

400 000

500 000

600 000

700 000

800 000

Diffuse sources

Point sources

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Table 2 Load of zinc from diffuse sources distributed on source and water district (Ejhed et al., 2010; Hansson et al., 2012)

Gross load
 (kg zinc / year)
Stormwater Agricultural land Skogsmark Fjäll
Mire
Open land Other
Deposit
on sea surface
Individual
drain
Kommunala
sewage treatment plant Industri Summa
Gulf of Bothnia
 8 700
 1 800
 88 000 22 000 15 000
 3 900
 1 900
 34 000
 350
 1 500
 6 000 **183 150**
The Bothnian Sea
 16 000
 3 700
 93 000
 9 500 11 000
 6 800
 2 200
 37 000
 910
 5 400
 710 **186 220**
Northern Baltic Sea
 23 000
 5 300
 23 000
 710
 1 100
 2 600
 14 000
 1 200
 2 600
 290
73 800
Southern Baltic Sea
 23 000
 10,000
 35 000
 1,000
 1 600
 6 900
 11 000
 1 300
 3,000
 1,000
93 800
The North Sea
 41 000
 18,000
 85 000
 770
 7,000
 3,500 13,000
 49 000
 2 100
 2 100
 1 100 **222 570**
Amount
 111 700
38 800
 324 000 32 270 34 710
 16 900 26 600
 145 000
 5,860
 14 600
 9 100 759 540

As we see from Table 2, the North Sea, the Gulf of Bothnia and the Bothnian Sea receive the greatest load while

The northern and southern Baltic Sea receives only a small part of the zinc. The reason why the North Sea gets one

a large load can be that it has a large catchment area and the proportion of forest land is large.

The catchment area to the North Sea is also exposed to a lot of atmospheric deposition that makes that the levels of zinc in the forest land are higher and there with a greater risk of leakage. Gulf of Bothnia and

The Bothnian Sea is located in northern Sweden, where the land type forest land dominates. In addition, these two have water districts a very large catchment area. Their catchment area extends from Uppsala and up.

The northern and southern Baltic Sea have a higher proportion of agricultural land with a higher pH and therefore less leakage of zinc. However, it is the forest land that makes the largest contribution here as well. The area of the catchment area for these two is also smaller, which in its entirety means less catchment area. In the case of individual sewers, it as a whole contributes little to the release of zinc. The reason it is higher contributions from individual sewers in the southern regions than in the northern ones are believed to be the population and population density. The same applies to stormwater, as the stormwater comes from urban areas and there are more and larger urban areas in the southern parts of Sweden. Note that the contribution from stormwater is as high as the contribution from forest land in the northern Baltic Sea.

Emissions to air

Zinc occurs in the air due to anthropogenic sources. A large part of the zinc that is emitted to air comes from the combustion of biomass. The biomass that is incinerated is used to produce heat and electricity (Swedish Environmental Protection Agency, 2017d). Emissions to air also come from industries such as zinc smelters, chemical industries coal incineration plants and waste incineration plants. Zinc is also emitted to air from the transport sector via wear of tires and brakes. In the air is zinc bound to particles that are added to the ecosystem via wet deposition or dry deposition. Point emissions, diffuse sources and long-distance atmospheric transport are all important routes of transmission of airborne zinc (Danielsson & Phil Karlsson, 2016).

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Atmospheric deposition of zinc

According to a study done by Danielsson and Phil Karlsson (2016), it has atmospheric The deposition of zinc in Sweden has decreased since 1975. The study studies mosses that have been measured the metal content in every 5 years since 1975. The study shows clearly downward trends of zinc contents which comes via atmospheric deposition. In 1975, the average concentration of zinc in moss was 63 mg / kg dry weight, in 2015 the concentration had decreased to 35 mg / kg dry weight. Since the saturations began the deposition of zinc from air has decreased by 50% (Danielsson & Phil Karlsson, 2016). The study shows also on a gradient in precipitation where Sweden has a higher concentration of zinc in southwest Sweden and between Sweden and a lower concentration in northern Sweden and the mountain areas. Figure 3 shows how the metal contents have changed since the measurements started in 1975. In the figure you can also see the gradient in concentration (Danielsson & Phil Karlsson, 2016).

Figure 3 Concentration of zinc in moss between 1975–2015 in mg / kg dry weight (Danielsson & Phil Karlsson, 2016).

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Furthermore, the report has compiled how much zinc comes via air transport to Sweden between in 1990 and 2014. Data come from CLRTAP (Convention on Long-Range Cross-Borders) air pollution). Since the measurements started in 1990, zinc emissions have decreased by 20% for Sweden, see Figure 4. For the whole of Europe, zinc emissions had decreased by the equivalent of 36% during the same period.

Figure 4 Emissions of zinc into the air for Sweden between 1990–2014.

The deposition of zinc via atmospheric deposition has decreased from 1975 to 2015 as a result of having got better treatment plants in industries such as, this applies to the whole of Europe because we partly get in atmospheric deposition from industries in Europe.

Zinc is one of the topics covered in the BREF document COMMISSION IMPLEMENTING DECISION (EU) 2016/1032 of 13 June 2016 establishing BAT conclusions for the non-ferrous metal industry, in accordance with Directive 2010/75 / EU of the European Parliament and of the Council of the European Commission. LETTER

the purpose of the document is to establish the best possible technology for current industrial sectors. The document takes

also up environmental performance and what environmental performance can be achieved if you use the best possible

technique. In the document, zinc is mentioned many times with suggestions on how emissions can be reduced

the best possible technology is used in each sector (Swedish Environmental Protection Agency, 2017f).

The European Commission's work on emissions and the use of the best possible technology seems to have paid off

results. Emissions of zinc in Sweden have decreased by 20% during the measured 24 years. Corresponding for Europe was 36%. The reason for a lower rate of decline for Sweden may be that Sweden

was / is at the forefront when it comes to purifying emissions from industries and therefore had already arrived

longer in the emission reduction when the measurements started. If you look at other metals, these have one more

drastic reduction in emissions. For example, emissions of lead decreased by 97%, chromium by 79% nickel with 73%, cadmium with 75% and copper with 46% during the same period (Danielsson & Phil

Karlsson, 2016). Why then do we see such a big difference between the different metals? Adjustments have been made for

0

50

100

150

200

250

1985

1990

1995

2000

2005

2010

2015

2020

Zinc emissions in

tons

Year

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to reduce emissions of, for example, lead, by legislating against lead-containing petrol. The measure which was taken gave great results on the emissions. When it comes to zinc, it is not considered as toxic compared to lead and cadmium and therefore not as great measures have been taken to reduce the emissions.

All zinc that is added to the soil via atmospheric deposition will eventually form part of it the leakage to water visible for different soil types in Figure 1.

Zinc status in water.

Zinc is regularly measured at coast and water. In order for freshwater to be classified as “good chemical surface water status” for zinc, the annual average value must not exceed $5.5 \mu\text{g} / \text{l}$. The value applies to its bioavailable fraction of zinc, ie the proportion of dissolved zinc in the water (Sea and water authority, 2015). Aquatic organisms are affected by low levels of zinc. Already at $10\text{--}25 \mu\text{g} / \text{l}$ negatively affects aquatic organisms (Wallberg et al., 2016). This figure is above “good chemical surface water status” regarding zinc according to the guidelines of the Swedish Maritime Administration.

In Sweden, zinc has generally decreased in the last 10 years in its occurrence in watercourses and lakes (Swedish Environmental Protection Agency, 2017b). This is believed to be partly due to reduced atmospheric precipitation but also due to reduced acidification leading to reduced leaching of zinc (Huser et al., 2011). In most cases is zinc content very low or low in Sweden (Naturvårdsverket, 2017b). It is difficult to predict the risks of elevated zinc in aquatic systems. Moderate increases in zinc will occur unlikely to cause unacceptable effects (Kemakta Konsult AB & the Institute for Environmental Medicine, 2016).

If we look at Sweden, this study has compiled data between the years 2010–2017 in four different places in Sweden from the database land - water and environmental data that has SLU as data host. The places selected

out were places with many sampling points and long time series, as well as partial geographical spread. An annual average was then calculated and plotted in a chart. The places selected were Ljusnan Röbbjörkeby, Viskan Daltorp, Bällstaån-Travbron, Märstaån outlet. Because the annual average value of “good

chemical surface water status” regarding zinc is based on soluble (bioavailable) content of zinc in the water was chosen

the filtered content of zinc in the water because it was considered most representative of the bioavailability the part zinc in the water. Values are also available for the total zinc content (unfiltered water) for a row different waters in the database managed by SLU.

Viskan Daltorp and Märstaån outlet achieves “good chemical surface water status” regarding zinc for all measure years while Ljusnan Röbbjörkeby reaches “good chemical surface water status” regarding zinc from 2014. Bällstaån Travbron, does not achieve “good chemical surface water status” regarding zinc but is assessed as

moderate status, this is illustrated in Figure 5. Worth mentioning when compiling data for Figure 5. is that the zinc content fluctuated a lot during the year and that the amount of zinc at some saturations had a lot high value. Figure 6 which illustrates how zinc fluctuates in Bällstaån Travbron during 2012–2017 shows such fluctuations in zinc during the year. What the fluctuations are due to is difficult to say and also how such high values affect the aquatic organisms when exposed to high concentrations of zinc for a short time. One explanation for the high concentrations could be that zinc follows with stormwater during snowmelt or heavy / prolonged rain and that the recipient for a short time

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then receives a lot of water with high concentrations of zinc, alternatively that other parameters so as the solubility of zinc varies.

Figure 5 annual average value of zinc in $\mu\text{g} / \text{l}$ (filtered water) for different watercourses in Sweden.

Figure 6 Levels of zinc in Bällstaån Travbron in $\mu\text{g} / \text{l}$ (filtered water).

A study done by Huser et al. (2011), have studied trends in zinc between the years 1996–2009. Between 1996–

In 2009, zinc content decreased by 67% in water and watercourses in Sweden (Huser et al., 2011). Overall is

the status of surface water is good for zinc. It is around cities that pollution causes elevated

0

2

4

6

8

10

12

14

2009

2010

2011

2012

2013

2014

2015

2016

2017

2018

 $\mu\text{g} / \text{l}$

year

LJUSNAN, RÖBJÖRKEBY

VISKAN, DALTORP

BÄLLSTAÅN-TRAVBRON

MÄRSTAÅN OUTLET

0

5

10

15

20

25

30

35

40

2010-11-18 2012-04-01 2013-08-14 2014-12-27 2016-05-10 2017-09-22 2019-02-04

 $\mu\text{g} / \text{l}$

year

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levels of zinc may affect the status of the surface water. It is especially the polluted stormwater which is a problem for the recipient as it contributes to elevated concentrations of contaminants which can reach critical levels when they reach the recipient. Furthermore, the zinc content in the Stockholm area in 2000 was elevated compared with nearby areas. Lake Mälaren and the Baltic Sea closest to Stockholm had 3-4 times higher levels of zinc in the sediment than the background value (SOU 2000: 53). Against this it can be said that the levels were further elevated in the 70s (SOU 2000: 53) but is today believed to be somewhat lower than when the report was written in 2000. A major improvement in groundwater has occurred since 1990 when the distribution in groundwater resources was following; 25% had a very low zinc content, 17% had a low zinc content and 52% had a moderately high zinc content. In 2016, a significant improvement had taken place and the distribution was instead that 61% had a very low content of zinc, 16% had a low content and 22% had a moderately high content. The big improvement is believed to be due to reduced atmospheric deposition of zinc (Swedish Environmental Protection Agency, 2017c). In the future, it is expected that the oceans will become more acidic due to more carbon dioxide in the atmosphere and changed pattern in catchment area and smaller catchment water is expected to come from the south the parts and more from the northern parts of Sweden. The water from the southern parts has a buffering property as the catchment area consists of calcareous soil, compared with the northern parts where the catchment area goes through calcareous soils. This means that the buffering capacity will be weaker (Swärd et al., 2014). With the reduced acidification (acid rain), less zinc will become bioavailable and thus, a smaller proportion of zinc is removed with run-off water to nearby watercourses and groundwater. But with a constantly accumulating metal content and lower leakage, the problem may well be moved. With increasing amounts of zinc in the soil, the content can reach critical limits that affect the market. If the grounding is affected, the nutritional cycles will go slower and we will have an accumulation of organic material in the soil (SOU 2000: 53).

Industries and emissions of zinc

The industry has previously been one of the major sources of emissions of zinc, but after pressure and improved treatment equipment, they have today reduced their emissions. Industries, however, are the largest the point sources of zinc emissions. In 1990, industries accounted for 73% of total emissions to air, today they account for industries only 24% of emissions (Swedish Environmental Protection Agency, 2017d). A total of 192,000 kg of zinc was released each year 2007 from industrial plants around Sweden. 240 plants in Sweden reported emissions of zinc to the Swedish Environmental Protection Agency's emission database "Emissions in figures" (Ejhed et al., 2010). A specific dark numbers exist as only industries that are above a threshold value for zinc emissions such as need to report. Industries that produce paper and wood dominate emissions to water. Zinc as an air pollutant from industrial industry comes mainly from the metal industry, chemical industry, coal incineration plants and waste plants (Swedish Environmental Protection Agency, 2017d). A compilation of zinc emissions from various industrial sectors in Sweden has been made. Data has been retrieved from "Emissions in figures" for emissions of zinc to water and emissions of zinc to air for 6 different industrial sectors between the years 2007–2016. The compilation of the industrial sectors that emit zinc to water is presented in figure 7 and industrial sectors that emit zinc to air are presented in figure

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8. For the release of zinc into water, the industrial sector dominates Production and processing of paper. Emissions to air are dominated by the industrial sector Production and processing of metals.

Figure 7 discharges to water distributed in each industrial sector between the years 2007–2016 in Sweden.

Figure 8 emissions to air distributed in each industrial sector between the years 2007–2016 in Sweden.

As can be seen in Figure 7, we see that discharges to water from the sector Production and processing of paper

decreases with time. For other sectors, emissions are at a constant level / slightly declining. For emissions to air there is no clear trend for production and treatment of metal, nor for others sectors appear to be a clear trend.

0

10000

20000

30000

40000

50000

60000

70000

80000

2006

2008

2010

2012

2014

2016

2018

The energy sector

Production and treatment of metal

The mineral wool industry

chemical industry

waste management and sewage treatment

production and processing of paper

0

5000

10000

15000

20000

25000

2006

2008

2010

2012

2014

2016

2018

The energy sector

Production and treatment of metal

The mineral wool industry

chemical industry

waste management and sewage treatment

production and processing of paper

Selected diffuse sources

Zinc and traffic

Metal emissions from traffic are affected by speed, acceleration, deceleration and traffic density. The zinc emissions come from zinc which is released during braking from wear of brake linings and wear of tires containing zinc. For zinc, emissions increase with speed. Another important source of zinc emissions from traffic is road equipment and this is probably the largest source of emissions of zinc from the traffic environment. Emissions from galvanized road equipment are greater than emissions of zinc from deceleration (Hjortenkrans, 2008). Road equipment near the ground emits more zinc than others zinc-coated surfaces. This is because the ground-level zinc equipment around roads is exposed in higher extent to corrosion (Hjortenkrans, 2008; Folkesson, 2005) and has a large surface area in relation to its weight (Sörme et al., 2001). The exposure comes from dirt from the traffic and salt from winter road maintenance. Splashes from the cars make the surface damp long after the rain has stopped and thus the surface becomes more susceptible to corrosion leading to zinc emissions (Folkesson, 2005). During winter time with flame temperatures and road maintenance show studies on clearly elevated levels of zinc in stormwater in environments close to roads (Folkesson, 2005). The road's upper soil layer contains three times higher metal levels in southern Sweden compared with the background levels. It is mainly the upper 10 cm of the soil layer that contains high levels of metals. The 10 meters closest to the road are the ones where the highest levels of zinc and other metals are measured, here you can concentrations of up to 350 mg zinc / kg are measured (Hjortenkrans, 2008). After 10 meters from the way is the zinc concentration in the soil at the level of the background levels, as in Hjortenkrans study (2008) was 48 mg / kg. A typical road profile is shown in Figure 9, at most metal concentrations are found within them 7 first meters from the roadside, ie next to the road and probably in the ditch next to the road (Hjortenkrans, 2008). One reason why zinc from traffic is no longer spread may be that they are associated with coarse and medium coarse particles that are not spread so far with air (Folkesson, 2005).

Figure 9 typical road profile

Since zinc from traffic is spread a short distance, the design of the ditch plays a major role in how large the leakage is of zinc will be. The design of the ditch, traffic volume, topography and soil conditions play a role in how much zinc will reach the recipient. How much zinc reaches the recipient also depends on how effective water treatment the ditch is, if there are treatment dams nearby and how close and sensitive recipient is. The contribution of traffic to the amount of zinc in stormwater is a significant factor.

(Hjortenkrans, 2008)

As previously mentioned, zinc is a relatively mobile metal and should disturbances or changes occur occur in the roadside, the accumulation of zinc can become mobile and move downwards in the soil layer sequence or out to watercourses (Hjortenkrans, 2008). Critically high concentrations could then arise in nearby watercourses. The same applies to heavy rain or melting snow that brings with it a lot of zinc with the stormwater to the recipient, which can get a large addition of zinc (Folkesson 2005). This is because zinc mainly occurs in the upper soil layer and if there is a heavy rain this would come with the stormwater to the environment. How much is bioavailable is difficult to say determine. It is mainly watercourses that are very close to major roads that are in the risk zone for elevated values of zinc or watercourses that receive large amounts of stormwater from major roads. This because the radius of spread of zinc from a road is very small.

A study conducted by Sörme et al (2001) has calculated the emissions of zinc from traffic in the city of Stockholm. The has estimated the use of zinc in the city of Stockholm is 28,000 tonnes. Of these, 28,000 tonnes are used were 14% related to traffic. However, 49.5% of zinc emissions from the city of Stockholm are believed to be due to emissions from traffic. This means that despite the low weight percentage of zinc in traffic-related products, the use of the product results in greater emissions. The emissions come from wear and tear tires and brakes, the vehicle itself containing zinc which is released in the event of corrosion and road equipment.

Impact from traffic is somewhat difficult to predict as it is a diffuse source. A study done by Folkesson (2005) believe that wear of tires that contain about 2% zinc is a major source of emissions of zinc. In total It is estimated that 150 tonnes of zinc / year are emitted as a result of tire wear in Sweden. Furthermore, it is estimated that brake pads add 50 tons and corrosion of vehicles would amount to as much as 250 tons zinc emissions / year. Ejhed et al. (2012) estimated that state roads contribute 15,000 kg zinc / year to the stormwater.

What do the emissions from zinc traffic look like in Sweden? The study has taken Skåne as an example. Through

Emissions in the figures database A map has been created that describes the emissions of zinc from transport.

Elevated zinc concentrations can be seen around major roads and urban areas. Figure 10. shows emissions of zinc to air in 2015 from Skåne County. In 2015, this database estimates that 4 tonnes of zinc were added the air in Skåne from the transport sector.

Figure 10 zinc emissions to air in 2015 (Swedish Environmental Protection Agency, 2017e).

Although traffic is a major source of emissions of zinc, there is a risk of ecological or health effects. due to high zinc levels low, even near major roads (Folkesson, 2005). This may have to do with that the zinc due to particle size falls out quickly and that we therefore get a local pollution that is relatively stable as long as conditions do not change (Folkesson, 2005). It can also be due to the roads where the pollution spreads constitute relatively large areas (Hjortenkrans, 2008). Can be added to others substances can contribute to an ecological and harmful environment around major roads (Folkesson, 2005). The tire industry has tried to find other compounds that could replace the zinc oxide but without major success (Wallberg et al., 2016).

Because zinc but also many other metals and hazardous substances are found in elevated levels around larger roads, a risk analysis should be made when constructing new roads. If recipients in the vicinity of the intended the road is sensitive, the construction of the road should be questioned and measures to reduce the metal load as well as other dangerous substances that may affect the recipient are taken if the road is nevertheless to be built.

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Artificial greens

Another source of zinc emissions are sports facilities with artificial turf or rubber mats such as tennis courts, football pitches and playgrounds where the rubber granules that are often used have been recycled tires (Magnusson et al., 2016). Rubber granules can also be used as a bottom layer for riding arenas for softer surfaces (Swedish Equestrian Federation, 2014). The advantage of artificial grass / rubber granules instead of ordinary grass on the football pitches, you get a longer playing season when the pitches are not the same sensitive to weather like ordinary grass. The playgrounds will be more hygienic (no animals will be able to dig down feces and in case of precipitation they are flushed clean) and accessible to people with disabilities. It is disputed whether the risk of injury is reduced when using rubber mats instead of sand playgrounds (Goodpoint, 2016). The infiltration capacity of the artificial surfaces is high and the water as flows through these ports into the stormwater (Magnusson et al., 2016). The materials used as rubber granules are Styrene-Butadiene rubber, SBR rubber which usually comes from recycled tires, Ethylene-propylene-diene rubber (EPDM) or Thermoplastic elastomers (TPE). In some cases, natural rubber (latex) is also involved in the granules (Goodpoint, 2016). The granules contain around 2% zinc. Zinc has been calculated for the metal in the granules that has the greatest potential to be leached out of SBR rubber from recycled tires (Magnusson, 2017). The leaching speed increases as the material gets older (Goodpoint, 2016). On a football pitch that is 7881m², 51 tonnes of SBR rubber, 61 tonnes of EPDM or 81 tonnes of TPE granules are needed to fill the plan. In addition, some granules disappear during use and the recommendation is that filling of 2–5 tonnes / year should be done. The granules that disappear can accompany the players home with shoes and clothes where they can end up in the washing machine which then reaches the sewage treatment plant. The granulate follows even with the stormwater down into the stormwater wells near the sports facilities, or disappear / spread in nature during snow removal at sports facilities (Magnusson et al., 2016). In 2016, Sweden had 1336 artificial football pitches. Of these, 1255 are outdoors, this corresponds to an area of 5,845,980 m². For every square meter, between 0.28–0.42 kg disappears the granulate / year that needs to be replaced. This means that Sweden emits 1638–2456 tonnes of granules a year

(Magnusson et al., 2016). Assume that two percent is zinc, then we have an outflow of 33–49 tons of zinc / year from sports facilities in Sweden annually.

Furthermore, Wallberg et al. (2016) on behalf of the Swedish Environmental Protection Agency investigated how much zinc is leached out of the respective rubber type. The leaching is greatest from EPDM granules followed by SBR granules. TPE from Europe and China has a slightly lower leaching content, the results are presented in Table 4.

(Wallberg et al., 2016). The leaching is calculated on a leaching test where a container was shaken with 1 liter of water and 100 g of granules and then measured the leaching of zinc. pH or in which chemical form in which zinc occurred was not apparent. The chemical form is essential information to predict the potential leaching and the bioavailability of the leached zinc.

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Table 3 Leaching from different granules

SBR granules

5.6 mg Zn / l

EPDM granules

6.4 mg Zn / l

TPE Europe

0.012 mg Zn / l

TPE China

0.058 mg Zn / l

Studies from Sweden on artificial turf show that zinc leaching is much higher from SBR rubber and EPDM rubber. For SBR, the leaching of zinc from artificial turf has been measured at 90 /g / L and For EPDM 80 /g / L. The study still points out that zinc leaks from all tested materials (SBR, EPDM TPE and natural materials). SBR and EPDM have a high content of zinc oxide, a form of zinc that does not occur dissolved in water unless the environment is acidic, this should mean that the zinc from these materials has a lower

bioavailability (Wallberg et al., 2016).

Studies have been done on leaching from SBR rubber. These show that emissions of zinc can take place then

the rubber granules are exposed to weather and wind. Emissions occur via leachate and can provide a local environmental impact. Due to the large surface area of the granules, the leaching from the granules will be greater than

leaching from tires (the original product).

When constructing new artificial turf, great emphasis should be placed on designing a good one drainage system. The design of the stormwater system is decisive for how much zinc reaches recipients (Wallberg et al., 2016). Furthermore, one should take into account nearby recipients at planning the construction of a new artificial turf. If nearby recipients are sensitive or already have elevated levels of zinc, measures should be taken to limit the impact of artificial turf or move the plans for artificial turf to a less sensitive area.

Articles containing zinc

In the case of zinc in goods, this is a major secondary source of zinc emissions into the environment. Zinc is used

much in our urban environments and the use of zinc has increased sharply in the urban areas during the 20th century

the environments. Leaching of zinc from road equipment such as galvanized road barriers and posts is taken into account

take into account when calculating emissions of zinc from traffic (Hjortenkrans, 2008), emissions due to of zinc from corrosion in our urban areas and state roads is partly taken into account as a diffuse emission source for stormwater (Ejhed et al., 2010).

Many of the metals and zinc we use are protected or indoors and are therefore not exposed to corrosion. This zinc has a low risk of leaking into the environment and causing problems there. The part of The products that are at risk of corrosion often have large surfaces in relation to their weight. This are products such as poles, roofs or tap water systems, due to the large areas there is a risk of larger amounts of zinc are released (Sörme et al., 2001).

In a study done by Sörme et al (2001), it has been estimated that there are a total of 28,000 tonnes of zinc in products / goods / goods in the city of Stockholm. Of these, 33% of zinc-containing articles are in protected environments and will thus not be exposed to corrosion. Remaining items such as will be exposed to corrosion can cause emissions of zinc to the environment. Zinc comes from articles

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such as taps, galvanized goods and unpainted zinc ceilings. Painted goods should not generate any zinc emissions (Sörme et al., 2001).

Sörme et al. (2011) estimates that in the city of Stockholm there are 5,600 tonnes of galvanized steel sitting on

buildings and other structures. Of these, 2.1 tonnes of zinc are estimated to leak from buildings and 5 tons from other galvanized steel structures. Tap water systems are estimated to release around 720 kg zinc / year. Other sources that could be a potential source of zinc emissions are taps, chemicals, cars and PVC where zinc has been used as a stabilizer (Sörme et al., 2001).

In the study done by Ejhed et al (2010) it was calculated that zinc in urban areas that reach the stormwater corresponds to

97,680 kg / year in Sweden. Zinc comes from diffuse sources such as road equipment, roofs and hoods. The does not go from this study to deduce exactly where the zinc comes from but is likely to some comes from galvanized products, but also artificial turf and playgrounds with rubber granules as foundation. In the study, Ejhed et al. Point out that diffuse emissions from goods and products are large secondary source of emissions of metals and that emissions from products and goods are difficult to calculate.

In an urban environment, leakage from zinc-coated surfaces can be a significant source. Solutions should be discussed for

to reduce emissions in the future or to ensure that the pollutants do not reach sensitive recipients.

Furthermore, there are problems when an item goes from being an item to being waste. If not zinc recycled, the metal is finally deposited. When deposited, the metal becomes a local pollutant that reaches it exposed to corrosion spreads to soil, groundwater and watercourses in their surroundings. At a landfill can metals lie for a long time and leak to the environment.

Conclusion

Sweden has large amounts of zinc stored in the soil after many years of emissions, storage and accumulation. This means that we have a large depot of zinc lying in the ground. Largest contribution of zinc to

the aquatic environment is the leakage of zinc from forest land followed by direct atmospheric deposition of zinc on

the water surface. How much zinc will be mobilized and travel deeper into the ground or out into

watercourses depend on the properties of the soil. Above all, the pH controls how much of the zinc comes in to become bioavailable. Lower pH means that zinc becomes mobile and bioavailable. Diffuse emissions of zinc are greater to both air and water than point emissions. Diffuse emissions are difficult to appreciate. Traffic and galvanized road equipment are believed to be a major source of zinc emissions. Zinc has elevated levels around major roads and urban areas where galvanized road equipment, traffic and galvanized goods are common. Artificial greens with rubber granules are also a secondary source of emissions. Because zinc is toxic at low concentrations, elevated levels in areas near the road or artificial turf can lead to sensitive recipients being harmed. Atmospheric precipitation of zinc occurs throughout Sweden with a gradient with higher precipitation in southwest Sweden. This is partly due to emissions from Central Europe and Western Europe. The fallout has decreased since 1975 but the decrease has stopped in recent years. Despite the levels of atmospheric precipitation has decreased, the risk of impact on ecosystems and health cannot be ruled out.

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The status of water regarding zinc is generally good in Sweden today. Despite this, the risk should not be negative consequences due to zinc are excluded in the future. Accumulation of zinc still occurs although in lower rate. A continued accumulation of zinc is associated with a risk when conditions change in pH (acidification) could lead to the release of problematic levels of zinc to watercourses and lakes. Locally, surface water with elevated zinc levels occurs in concentrations so high that the recipient does not can be classified as "good chemical surface water status" for zinc according to the Water Framework Directive. This means that future expansions of, for example, roads, construction of artificial turf or construction of buildings with zinc-coated materials within the recipient's catchment area, risks to violate the Directive and therefore can not be implemented. Locally, high levels of zinc in surface water have one potential environmental impact and the high levels affect the opportunities for expansion of certain social functions unless site-specific adaptations are implemented.

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