LEACHING OF METALS FROM PAINT AND RUBBER PARTICLES

Environmental Engineering 4th semester

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Title:

Leaching Of Metals From Paint And Rubber Particles

Project:

Master's thesis

Project period:

February 2018 - June 2018

ECTS

30

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Number of pages: 17

Appendices: 2 electronic

Completed: 1st of June 2018

Abstract:

Rubber and antifouling paint particles leach metals such as Zn an Cu in water, which were linked to environmental toxicity. Leaching experiments were done using 4 rubbers and 3 paints of size fractions 1-2 mm, 200-500 µm and 40-80 µm in miliQ water with agitation for 72 hours or longer at a low relative concentration of sample 0.52 mg/mL, and some additionally at 5.22 mg/mL to determine the influence of particle size, relative concentration, and duration of leaching on leaching rate. Digestion of rubber and paint was done to obtain info on total metal content, link it to total leaching, and estimate necessary time to leach 50% of containing Zn. Specific surface area of samples was calculated using data obtained from particle size validation microscopy, and used for correlation with the mass transfer rate of metals.

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Reading guide

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Electronic appendices containing raw data are submitted separately.

Throughout the report, related figures, tables or equations are referenced. These are numbered in order of appearance within a chapter.

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1 Introduction

1.1 Leaching from rubber particles

Tires have been used in traffic for more than 100 years, and their usage continues to this day in everyday traffic. Rubber particles in the environment are generated mainly from abrasion during traffic, and are usually deposited alongside the road or end up in stormwater runoff. It is estimated that about 5×10^8 kg of tire wear and debris is generated in the U.S. annually, and about one tenth of that amount in larger developed European countries, which usually ends up deposited in vicinity of the road (Wik, 2009). Worn-out tires, have found a large scale application in sports and playground surfaces in the form of rubber granulate (Rhodes, Ren and Mays, 2012). Rubber particles are known to leach metals, mostly Zn, and organic constituents in water (Wik, 2009).

Rubber tread is usually composed of styrene butadiene rubber, polybutadiene, and natural rubber compounded with carbon black or silica, oils and vulcanizing chemicals. (Wik, 2009). Rubber in tires contains approximately 1-2% Zn by mass, which is added to aid in the vulcanization process (Rhodes, Ren and Mays, 2012). Studies of ecotoxicity of rubber leachate were done involving aquatic organisms and found that its toxicity is mainly attributed to Zn and certain organic compounds (Nelson, Mueller and Hemphill, 1994; Wik, 2007). In addition to Zn, smaller quantities of S, Fe, Mg, Pb and trace amounts of other metals have been detected in rubber ash and digestion tests (Bocca *et al.*, 2009; Selbes *et al.*, 2015).

Additionally, rate of zinc leaching has been found to depend on percentage of zinc in the rubber (Pysklo *et al.*, 2006). Leaching of Zn increased with lower ambient pH, while higher pH inhibited zinc leaching but increased the leaching rate of organic compounds (Selbes *et al.*, 2015). Increase of salinity leads to lower rates of leaching because of ion saturation. No decrease in leaching rate had been observed for particles with a diameter >500µm after 4 days of leaching in quiescent water (Rhodes, Ren and Mays, 2012).

Area of rubber particles of identical size can vary depending on shape, and a significantly higher surface area and leaching rate had been observed in rubber obtained from ambient grinding in comparison to cryogenic grinding (Pysklo *et al.*, 2006). Road generated rubber particles have been found to display an elongated shape, while cryogenic grinding produced a more jagged shape. Particles created this way have shown to be an internal mixture of rubber material with minerals and tar from the road. Heat and friction from abrasion may also alter the chemical composition of rubber during road wear. (Dall'Osto *et al.*, 2014). Pysklo *et al.*, 2006 found truck tire granulate leached more zinc than car tire granulate. Rhodes, Ren and Mays, 2012 found a linear correlation of Zn leaching rate with specific surface area of granulate.

1.2 Leaching from antifouling paints

Marine fouling is caused by growth of flora on surfaces submerged in water, leading to speed reduction and maintenance cost in vessels, and may compromise stability and conceal structural defects in static structures (Karlsson, Ytreberg and Eklund, 2010). Antifouling paints containing biocidal substances are applied in boat hulls, marine equipment and submerged structures. In recent years, substances used have been mostly based on copper or zinc, such as cuprous oxide, copper thiocyanate or zinc oxide. Cu content can be as high as 35%, and Zn at 50% by mass. Cu and Zn are frequently used together because of their synergistic toxic effects (Holmes and Turner, 2009; Singh and Turner, 2009b; Turner, 2010). Tributyl tin, amongst others, had been used extensively in the past, but its use was banned in 1988. (Showalter, 2005).

Extensive use of antifouling paint had led to high concentrations of biocides to be found in marinas worldwide (Amara *et al.*, 2018)(Ytreberg, Karlsson and Eklund, 2010). Paint microparticles are principally generated through hull erosion or during the maintenance and repair of ships, and are found in abundance at the sediment in vicinity of boat repair facilities, abandoned structures and grounded ships. Depending on the cause of erosion, particle size can range from very fine to several cm in diameter. (Takahashi *et al.*, 2012).

Leaching of metals from discarded paint particles is well documented. Studies have been done of zinc and copper leaching from individual antifouling paint coatings (Ytreberg, Karlsson and Eklund, 2010), and collected discarded paint particles (Jessop and Turner, 2011)(Singh and Turner, 2009a)(Holmes and Turner, 2009). Studies have been done which show adverse effects of these compounds on non-target organisms in the marine environment such as invertebrates, crustaceans and fish (Amara *et al.*, 2018)(Guardiola *et al.*, 2012)(Katranitsas, Castritsi-Catharios and Persoone, 2003)

Leaching of Cu has been found to increase with higher salinity, decreasing temperature and addition of humic substances, while Zn leaching has been found to decrease with higher salinity and decreasing temperature. Particle size has been found to not influence metal leaching greatly, despite a difference in measured specific surface area (Turner, 2010). Singh and Turner, 2009a found evidence of microporosity in ground paint particles using nitrogen adsorption which gave results for specific surface area of the material an order of magnitude higher compared to its estimated geometric surface area. They also found Cu reached a much higher concentration when leaching in seawater than in river water.

1.3 Leaching mechanism

There are 2 mechanisms suspected to govern the metal release in the leaching process. One is the mass transfer from the surface of the particle into the medium, which correlates with the surface area of the particle, and is caused by the concentration difference between the particle surface and the medium (Rhodes, Ren and Mays, 2012). Second mechanism is polymer diffusion within the material, which is expected to be much slower than the surface transfer. According to this assumption, a two-phase leaching dynamic can be expected from particles. In the first phase, leaching would be limited by the mass transfer rate from the surface depending on the surface area of the particle, and after the metals on the surface will have leached out, the leaching will be limited by polymer diffusion, a much slower process. Polymer diffusion would be expected to continue to facilitate leaching at a decreasing rate until most of the material would have leached out.

1.4 Objective

The aim of this study was to collect data about metal leaching in laboratory conditions so that they could be related to environmental conditions. In this study leaching experiments were performed in very low concentrations of material relative to the medium (0.52 mg/mL), in an attempt make the influence of concentration in the medium on the mass transfer insignificantly small. These conditions are thought to be similar to conditions in the environment where an infinitesimally small ratio of particles to water can be assumed in most cases.

Regarding rubber, no studies have been found looking at leaching rates of metals from particles smaller than 0.2 mm, or linking leaching rate to the Zn pool depletion in particles. This study aimed to correlate the amount of metals leached and total metal content of rubber to determine how long it would take for the particles to deplete their metal reserve for both paint and rubber. No present studies conducted leaching in concentration of particles to medium under 50 mg/mL, or looked at the influence of concentration on leaching rate. This study included leaching from particles $\phi < 100 \,\mu$ m, which are thought to be more representative of the particles in environmental conditions made from ambient grinding. Regarding paint leaching, this study compared leaching freshly ground paint coatings from individual paints of varying metal content which hasn't been done so far.

2 Materials and methods

2.1 Sample preparation

Tires that were used for rubber samples were a winter tire "Fulda Kristall Gravito", summer tire "Sava Exact", truck tire "Ecomatic 28X9-15", and car tire granulate provided by Re-Match A/S. **S**oft edges of tires without strands or wires were cut and ground supercooled with liquid nitrogen using an electronic grinder. Ground material was then wet sieved through a series of sieves with flowing Sodium dodecyl sulfate containing water. Sieves used had opening sizes 5 mm, 2 mm, 1mm, 500µm, 200µm, 80µm and 40 µm. Contact of material with water lasted approximately 2 hours. Sieved material was rinsed with miliQ water and left to dry in an oven at 55 degrees until no further reduction in mass was measured.

For paint samples, 3 antifouling paints were used: Hempel Hard Racing Xtra Red (Xtra), Hempel Alusafe Black (Alusafe), Nautix A4 T.speed White (T.speed) and a building paint Jotun Premium Murmaling White. 3 layers of the paint were painted on a non-metallic surface (Baking paper). After drying the paint was ground in a mortar supercooled with liquid nitrogen, and sieved through the same series of sieves as rubber particles, although without the presence of water.

2.2 Particle size validation and estimation of specific surface area

Particle size validation using microscopy and particle counting software was performed to obtain more precise data about particle size distribution in each size fraction and for estimation of specific surface area (SSA). Zeiss SteREO Discovery.V8 microscope was used with ZEN 2 core SP1 camera software for acquiring and stitching images. Zen imaging software was used to collect data from the photos. Fractions above 200 μ m range were segmented manually, and watersheds automatic segmentation at count 2 was used for smaller ones. Particle area and perimeter were collected for each particle in a representative sample of each size fraction used. Density of material was measured using a density measuring kit on a Mettler Toledo XSE205 for estimation of SSA.

2.3 Sample analysis

Metal concentrations were analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) on an iCAP 6000. RF power was set to 1.15 kW, and auxiliary gas flow was 0.5 L/min, view was axial. Samples were introduced through a K-type concentric nebulizer and a quartz spray chamber. Metals sought and their respective resonance lines used in nm are: Al 167.1, As 189.0, Ba 233.5, Cd 214.4, Cr 267.7, Cu 324.8, Fe 238.2, Hg 184.9, Mg 279.6, Mn 259.4, Ni 221.6, P 177.5, Pb 220.4, S 180.7 and Zn 202.5. Calibration for leaching and paint digestion was done with mixed standards in 6.8% HNO3 of concentrations of 1 ppm, 0.1 ppm and 0.01 ppm, and a blank. Yttrium was used for internal standardization. Analysis of rubber digestion used standards with 8.2% HNO3 and 0.6% H2O2, which equaled composition of samples after dilution.

2.4 Digestion

Digestion experiments were conducted to determine the total metal content of paints and rubber samples.

Digestion of paints was conducted in triplicates using 20mg of material in 5ml of aqua regia (Mixture of PlasmaPure[®] concentrated HNO3 and Suprapur[®] 30% HCL in a ratio 1:3), in a water bath at 75° C for 2 hours, after which it was diluted to 50ml and filtered through a 0.45µm filter. Filtrate was used diluted to 1%, 10%, and undiluted for ICP readings.

Digestion of rubber was conducted in a Multiwave 3000 microwave oven, in triplicates, using 300mg of material in a mixture of 6mg PlasmaPure[®] concentrated HNO3 and 2mg of Suprapur[®] 30% H2O2. Program for the microwave oven was intended to run at 1200 W and 1500 W, but had to be tapered down before reaching 1200 W because maximum pressure had been reached in the tubes (20 bar). The program ran for 55 minutes. Digested material was diluted to 50 ml, filtered through a 0.45 μ m filter and used diluted to 1% and 10 % and undiluted for ICP readings.

2.5 Leaching experiments

Leaching was conducted triplicates, individually in 11.5 ml plastic vials with caps, in 11.5 ml of miliQ purified water. Tests were done with 1-2 mm, 200-500µm and 40-80µm size fractions of rubbers and antifouling paints to determine the influence of particle size and surface area on leaching rate. About 6mg of material was used per sample, which amounts to a concentration of 0.52 g/l. This approach was taken to investigate leaching of metals at lower concentrations more representative of environmental conditions, which had not yet been done for rubber in current studies. Truck tire and Xtra paint were additionally performed with 10x of material, amounting to 5.22 g/l of sample, to investigate how a change in concentration would influence the leaching rate of metals.

Samples were left to leach for 1, 6, 24, 48 and 72h hours on an orbital shaker at 110 rpm, before being filtered through a 0.45µm filter. Truck tire and Xtra paint had additional samples that leached for 216 hours (9 days) before being filtered. A blank triplicate was left shaking for 72 hours on each experiment. 1 ml of PlasmaPure[®] concentrated HNO3 was added to 9 ml of filtrate and analyzed on ICP. Setup for the leaching can be seen on Figure 2.1



Figure 2.1 Leaching of samples in progress on an orbital shaker.

3 Results

3.1 Particle size and SSA

Particle size distributions of the size fractions were made from the particle validation data. It was found that particle size distributions of size fractions after sieving varied between rubbers and paints, and varied between individual paints and rubbers as well. Morphology of paint and rubber particles was also very different; large paint particles had a distinctly flat shape.

Particle size validation provided data about the area and perimeter of each particle in a sample. A mean diameter was calculated for each particle from the area. Diameter was then used to estimate geometric surface area of particles, assuming their shape to be monodisperse spheres. Volume for particles was estimated from the diameter using the same assumption. Mass was obtained by multiplying volume with density of material. Densities of paints were measured as follows: Xtra – 2.43 kg/L, T.speed – 1.87 kg/L, Alusafe – 1.90 kg/L. Density of rubber was taken as 1.13 kg/L (Rhodes, Ren and Mays, 2012).

A sum of surface area and mass of particles was done to get a total surface area and mass of the sample. Specific surface area (SSA) of a sample was then calculated by dividing geometric surface area of the sample with the mass of the sample. Mathematic expression for SSA can be represented as:

$$SSA = \frac{A_g}{\rho_s * V}$$

Where SSA is the specific surface area of the sample $[mm^2/mg]$, A_g is the sum of geometric surface area of observed particles $[mm^2]$, ρ_s is the estimated density of material [g/mL], and V is the sum of geometric volumes of particles[mL]. List of SSAs of different size ranges of materials used can be seen in Table 1. Full particle size data sheets can be found in Electronic appendix 2.

Paint/rubber	Xtra	Alusafe	T.speed	Granulate	Truck	Winter	Summer
Unit	mm²/mg	mm²/mg	mm²/mg	mm²/mg	mm²/mg	mm²/mg	mm²/mg
ø 1-2 mm	4.97	6.58	6.60	3.65	2.39	3.34	3.78
ø 200-500 μm	8.41	11.17	10.02	11.90	13.34	13.36	15.19
ø 40-80 μm	60.12	43.00	51.83	36.98	67.13	89.60	69.38

Table 1 Specific surface area of each material's size fractions used in leaching

SSA for paint particles larger than 200µm was calculated using a different assumption because the shape of these particles better resembled an irregular prism than a sphere, with a measured thickness around 200µm. Thickness was measured by placing particles vertically on a microscope slide, and measuring the width of a visible edge. Geometric area for paint particles was estimated by multiplying measured perimeter with thickness and adding the measured area x2. Volume was estimated by multiplying area with thickness.

To relate to the data shown in Table 1 Specific surface area of each material's size fractions used in leaching Xtra paint in the 40-80 μ m fraction contained smaller particles than other materials, which is assumed to be the reason for its higher SSA regardless of higher density. The 1-2 mm fraction of truck tire had visibly larger particles than other rubbers, resulting in a lower SSA.

Reality is that the shape of particles from grinding doesn't resemble the shape of a sphere, as assumed in calculating SSA. Larger rubber particles had visibly irregular shapes and sharp edges which are bound to increase the surface area. There is also evidence for microporosity of paint particles (Singh and Turner, 2009a) SSA estimated here is in all cases certainly lower than the real SSA of particles, and may differ greatly between rubber and paint particles, therefore it is not meant as a realistic estimate but rather as a tool for comparison in between size ranges of paints and rubber separately.

3.2 Digestion experiments

3.2.1 Rubber digestion

Passenger car tires were found to contain over 1% Zn and S, and higher than 10 ppm quantities of Al, P, Mg and Fe. Truck tire was found to additionally contain Pb above 1mg/g, and As, Cu and Ba above 10 ppm. Truck tire and tire granulate were found to contain about 50% more zinc than passenger tires. Concentrations of metals detected in different tire rubbers in mg/g can be seen on Table 2.

Tire type	Zn	S	Mg	Fe	Al	Р	Pb	As	Ba	Cu
Granulate	14.11	15.43	0.22	0.11	0.31	0.14	0.02	<0.01	<0.01	0.02
Truck	14.51	18.20	1.15	0.37	0.33	0.25	1.47	0.14	0.11	0.04
Winter	11.29	14.00	0.10	0.09	0.19	0.18	<0.01	<0.01	<0.01	<0.01
Summer	9.38	14.25	0.07	0.05	0.16	0.07	<0.01	<0.01	<0.01	<0.01

Table 2 Metal concentration found in different rubber types (in mg/g)

Even though the granulate used was made from car tires, its zinc content is much higher than in the two car tires tested. This might suggest that tires used in this study might have a significantly lower Zn content than of an average passenger tire.

Considering that during digestion, the microwave oven didn't reach the power intended, it is not possible to know the efficiency of the test, however, it can be assumed that measured concentrations were relative to real concentrations in the rubber. Bocca *et al.*, 2009 lists several sources which detected between 6-17 mg/g of Zn in rubber granulate from turfs, therefore these results are within the expected range.

3.2.2 Paint digestion

Results from digestion of paints can be seen on Figure 3.1. Concentrations of metals detected were 70-90% of the concentration from the data for metal contents according to product sheets of the paints used, and almost 100% for sulfur. Percentage by mass for dry paint in metal containing compounds was used, and the mass of individual elements was calculated from the molar mass of the compound.



Figure 3.1 Metal concentration found in paints (In %)

In addition to Cu, Zn and S containing compound concentrations listed on the data sheets, small amounts of Al and Fe have been detected in some paints. None of the other metals measured on the ICP gave detectible concentrations. It should also be noted that T.speed paint contains 6-15% of Ti, a metal the ICP machine couldn't measure. Murmaling wall paint was found to not contain a significant concentration of any metal, which is why it was not tested for leaching.

3.3 Leaching experiments

Nearly all metals found in rubber were detected in the rubber leachate. Most prominent was leaching of Zn, followed by Mg, S, Pb and Al. Amount of material leached correlated with metal concentration in the rubber. Elements found to leach from paints were almost exclusively Zn, Cu, and S, depending on whether the paint contained the element or not. Sulfur leached readily from paints, Zn to a lesser extent, and Cu barely leached at all. Percentage of metals leached out of the smallest fraction of rubber after 72 hours into the medium can be observed on Table 3, and the same for paint in Table 4. Ratio of material to miliQ for these results was 0.52 mg/L.

Table 3 Percentage of metals leached after 72 hours from ø 40-80 μm rubber particles. ND = Not detected

	Zn (%)	Mg (%)	Ba (%)	P (%)	S (%)	As (%)	Pb (%)
Granulate	4.04	10.60	107.81	4.80	2.36	ND	ND
Truck tire	2.84	10.52	39.79	7.48	0.94	2.30	0.77
Winter t.	8.35	3.65	45.04	2.02	0.34	ND	ND
Summer t.	4.21	23.88	45.16	19.14	0.57	ND	ND

Table 4 Percentage of metals leached after 72 hours from ø 40-80 µm paint particles. ND = Not detected

	Zn (%)	Cu (%)	S (%)
Xtra	1.341	0.083	ND
Alusafe	0.706	ND	14.406
T.speed	6.538	0.013	2.911

It can be noted that certain metals have a much higher tendency to leach than others, with Zn leaching not as readily as Mg or Ba in rubber, and Cu leaching much slower than Zn in paints. Considering leaching rate of Cu increases with salinity while rate of Zn decreases, a higher leaching of Cu can be expected in salt water. Holmes and Turner, 2009 leached about 10% of total Cu and 5% of Zn from a mixed paint sample after 75h in seawater in a similar ratio of sample to medium, which is more than 100-fold faster than the leaching in ultrapure water in this study.

A higher than 100% detected concentration of Ba leached from granulate can either be attributed to metal content of granulate not being uniform, or a source of barium in the experimental setup for leaching.

3.3.1 Leaching dynamics of Zn

Some difference in leaching rates of Zn was noticed between rubbers; winter tire leached most rapidly, summer tires and granulate leached approx. half as fast and truck tire rubber leached the slowest. Out of paints, T.speed leached up to 2% of its Zn content, Xtra and Alusafe paints leached 1%. It was noted that Zn leached at the same rate from different paints regardless of their difference in Zn content. Graphs showing leaching of Zn from the Ø 0.2-0.5 mm fraction of rubber and paint can be seen on Figure 3.2



Figure 3.2 Percentage of total Zn content leached from rubbers (left) and paints (right) at 0.52 mg/mL

For rubber, a general dynamic of a high release within the first 6 hours, followed by a somewhat steady release of metals could be detected for almost all size fractions. This could be observed in the leaching of Zn, Mg and Ba although Zn provided the most stable results, as seen on Figure 3.2. For paint, a similar dynamic was present for leaching of both Zn and Cu.

Ratio of material to water was found to influence leaching. A comparison between 0.52 and 5.22 mg/L concentration with truck tire found that leaching of Zn was approximately 2 times faster in the lower concentration. Xtra paint was found to leach 4 times more Zn in the lower concentration, and 5 times more Cu. Comparisons between their leaching of Zn in time can be seen on Figure 3.3.



Figure 3.3 Comparison of Zn leaching from 5.22 and 0.52 mg/L ø of 40-80 μm fraction of a rubber (left) and a paint (right)

In the graphs, at 216 h Zn reached a concentration of 2.04 mg/L at 5.22 and 0.35 mg/L at 0.52 mg/mL of truck rubber, and for Xtra paint Zn reached 4.69 mg/L at 5.22 and 1,80 mg/L at 0.52 mg/mL of material. Similar patterns of leaching were also observed in the 1-2 and 200-500µm fractions, although at lower concentrations.

The difference in Zn leaching between 5.22 and 0.52 mg/mL concentrations indicates that the concentration gradient between the particle and the medium significantly influences leaching, even when very low concentration of Zn is present in the water. Because of this, when considering the mass transfer rate and the concentration gradient, it most likely isn't accurate to assume the influence of concentration in water is insignificant in these experiments. It should be possible to run leaching at even lower concentrations, where the scenario of concentration in water having negligible influence on leaching rate might be approached.

In the case of Cu leaching from Xtra and T.speed paints, a reduction in Cu concentration was be detected in some cases after the initial period of release. This was especially prominent in samples incubated for 216 h. Holmes and Turner, 2009 detected a reduction of Cu conc. in water spiked with Cu ions, and presumed the reason behind the losses is adsorption of metal ions to the container walls. It could be possible the same mechanism influenced leaching in this study.

Considering an even lower concentration of particles than what was experimented on can be assumed to exist in the environment, leaching rate based on the concentration gradient in those conditions might be even faster. However, it should be noted that environmental conditions possess many more variables that affect leaching such as pH, salinity, temperature etc. that are likely of larger influence than the concentration gradient.

3.3.2 Depletion of metals

An estimation of time needed for 50% of Zn in particles to leach out was calculated based on the assumption that leaching rate would continue to remain relatively steady after the period measured in the experiments. Leaching rate between 24 and 72 hours was used for this calculation. Time for Cu was calculated assuming Cu leaches at an identical rate to Zn in salt water. The results can be seen in Table 5.

Table 5 Estimation of time in years needed for 50% of Zn to leach out assuming a steady leaching rate.

	Granulate	Truck	Winter	Summer	Xtra	Xtra (Cu)	Alusafe	T.speed
1-2mm	1.3	17.9	1.3	7.7	3.1	6.5	3.9	1.1
0.2-0.5mm	1.1	3.0	0.5	1.7	1.8	3.8	1.8	0.6
40-80µm	0.4	0.5	0.1	0.3	1.8	3.7	1.4	0.8

In the environment, one could expect a wide of particle size distribution that would possibly include all of these fractions. Larger particles can be seen as longer-term pollutants as they would continue to leach for a longer time than smaller particles, although at slower rates. Large rubber particles specifically can be associated with rubber granulate used in synthetic turfs.

It should be noted that this is unrealistic as the diffusion driven process would continue to slow down overtime as less and less Zn remain in the polymer. These numbers can be taken as a lower limit to the time it would take for the metals would leach out, and the realistic values would certainly be higher than these, possibly manifold.

It would be interesting to see experiments leaching for a longer time to better understand the dynamic of leaching with the depletion of the metal pool content. It would also be interesting to know whether the metals in the polymer can leach out nearly completely which would render them harmless in terms of metal pollution, or if the leaching would remain slow enough for the particles to leach consistently for a very long time.

3.3.3 Relation to particle size

To relate leaching rate to particle size, the 3 size fractions of rubber and paint were looked at. Leaching rate was generally found to be higher with smaller particle size of material. Two exceptions are leaching of Zn in Alusafe paint, and leaching of Cu in T.speed paint, both of which leached the same amount regardless of particle size.

Amount of metal leached after 72 hours was used to determine the mass transfer rate coefficient α , unit min⁻¹. This value was then plotted against the SSA of the fraction estimated in section 3.1. The resulting chart can be seen on Figure 3.4 for rubber samples and Figure 3.5 for paint samples.



Figure 3.4 Mass transfer rate coefficient of Zn found in experiments plotted against the SSA of size fractions of different rubber types.

From the results on Figure 3.1, it can be seen that leaching coefficient for Zn is linearly correlated to the surface area of the material within the same type of rubber, which makes sense as the surface is where the mass transfer occurs. The correlation is linear very consistently, which indicates that surface transfer was the dominant governing mechanism for leaching, and that there is no evidence of metal depletion from the surface within 72 hours. It can also be noticed that the different types of rubber have slightly different relations of transfer coefficient to the surface area, which indicates different properties of the material. The steepness of the trendline did not correlate with the percentage of Zn found in the rubber. Consistent linear correlation of α with SSA was also found for Mg and Ba in rubber, although the trendlines didn't match those of Zn depicted here.



Figure 3.5 Mass transfer rate coefficients from experiments plotted against the SSA of size fractions of 3 paint types.

Mass transfer rate of metals from paints did not correlate with the SSA as precisely in paints, although there is still a definite correlation to be observed in leaching of Zn and Cu from Xtra paint, and Zn from T.speed. Leaching of Zn from Alusafe and Cu from T.speed was not related to particle size at all and was much lower related to the total content of the metal in paint, which could indicate the mechanism behind leaching was different in those cases.

Rubber particles in the environment are mostly created from ambient grinding in traffic, a mechanism that was shown to produce particles with a higher SSA than of particles produced by cryogenic grinding of the same particle size. Considering a correlation of SSA and mass transfer rate, a proportionally higher mass transfer could be expected to the SSA of environmental particles.

The correlation of mass transfer rate and SSA may find use in estimating leaching rate of rubber and paint particles found in the environment by undergoing the process of measuring the SSA of particles found at specific locations. This process would be more accurate for rubber particles than for paint particles, considering trendlines on Figure 3.4 for rubber are of similar slope. It would also be useful for determining leaching rate of samples with wide range of particle sizes. Additionally, the same process could be used to determine leaching rates from other types of microplastics.

4 Conclusion

Rubber and paint were found to leach metals they contained, most notably Zn. Size fraction ϕ 40-80 μ m of rubber leached between 3-8 % of total Zn after 72 hours in ultrapure water, while the same size fraction of paint leached between 0.7-7% of total Zn. Zinc leaching rate in paints was similar and largely independent of the paint's Zn content. Cu from paint was found to leach over 100 times slower in pure water than in saltwater in a different study.

Surface transfer rate for Zn, Mg and Ba in rubber scaled linearly with specific surface area (SSA) of material in size fractions ϕ 1-2 mm, 200-500 μ m and 40-80 μ m, which is consistent with findings so far. SSA could therefore be used as a tool for determining mass transfer rate of environmental rubber samples. Mass transfer also correlated with SSA for Zn leaching in Xtra and T.speed paint, and Cu leaching in Xtra, but Zn from Alusafe and Cu from T.speed leached the same rate from all size fractions.

Leaching of metals from winter tire was the fastest while truck tire leached the slowest, but related to their SSA, granulate had the fastest mass transfer rate while summer tire rubber had the lowest. Ratio of rubber and paint material to water of 0.52 mg/mL was found to likely not be sufficient to eliminate the influence of metal concentration in water on leaching rate. Experiments with lower concentrations may be attempted to more closely simulate leaching in environmental conditions.

It would take around 100 days for the ϕ 40-80 µm fraction and around 5 years for the ϕ 1-2 mm fraction of rubber on average to deplete their zinc reserves down to 50% should they continue to leach at the same rate as betwee 24 and 72 hours of incubation. Paint would reach this milestone at around 1.5 years from ϕ 40-80 and 3 years from ϕ 1-2 mm fraction. This is an overestimation and experiments testing leaching for longer periods of time would provide better insight into Zn depletion from polymers.

5 References

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