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Abstract

Risk assessment of leaching of substances from synthetic polymeric matrices

The leaching of substances from plastics is fundamentally different from leaching of substances from, for example, stony materials. However, the current environmental risk assessment of building materials has been derived for stony materials and does not account for ageing and wheathering of the material. These processes have higher rates in plastics and have an high impact on the leaching of substances. To obtain more knowledge about ageing and wheathering it is necessary to develop a specific testing strategy for plastics. This follows from a literature study of the RIVM, commissioned by the Ministry of Housing, Spatial Planning and the Environment.

Plastics, or synthetic polymeric matrices, contain unknown by-products and many additives, for example pigments, softeners, flame retardants and antioxidants, which are distributed in the environment when exposed to water. Bioassays are recommended as additional test to account for the environmental risk of exposure to cocktails of known and unknown substances. Bioassays are tests with living aquatic organisms and provide information about the effects of unknown substances or combinations of substances.

The use of plastics or recycled plastics for outdoor purposes is increasing. Yet, the knowledge about the identity and quantity of leached substances stays behind. The European Committee for Standardization (CEN) aims at harmonization of test and risk assessment methods for different building materials, such as stone, wood, metal and plastics. This aim is based on the assumed similarity of leaching mechanisms.

Key words: leaching, rubbers, plastics, risk assessment, building materials



Rapport in het kort

Risicobeoordeling voor de uitloging van stoffen uit synthetische polymere matrices

De uitloging van stoffen uit kunststof in het milieu verloopt fundamenteel anders dan de uitloging van stoffen uit bijvoorbeeld steenachtig materiaal. De gangbare milieurisicobeoordeling van bouwstoffen is evenwel voor steenachtig materiaal ontwikkeld en houdt geen rekening met de uiteenlopende wijzen waarop materialen verweren en verouderen. Dergelijke processen vinden in kunststoffen sneller plaats en bepalen daardoor in grote mate de uitloging van stoffen uit het materiaal naar het milieu. Om meer zicht op deze processen te krijgen is het noodzakelijk een specifieke teststrategie te ontwikkelen voor kunststoffen. Dit blijkt uit literatuuronderzoek van het RIVM, in opdracht van het ministerie van VROM.

Kunststoffen, oftewel synthetische polymere matrices, bevatten onbekende bijproducten en veel additieven. Het gaat bijvoorbeeld om kleurstoffen, weekmakers, brandwerende middelen en anti-oxidanten die zich in het milieu kunnen verspreiden als ze in contact komen met water (uitlogen). Vanwege de cocktail aan bekende en onbekende stoffen in kunststoffen wordt ook aangeraden om eventuele schade voor het milieu aanvullend te toetsen met behulp van bioassays. Bioassays, oftewel een test met levende waterorganismen die in contact worden gebracht met stoffen, leveren informatie op over effecten van onbekende stoffen of van combinaties van stoffen.

Het gebruik van kunststoffen en gerecyclede kunststoffen in het buitenmilieu neemt toe. De kennis van de aard en hoeveelheid stoffen die uitlogen blijft evenwel achter. Het Europese Normalisatiecomité (CEN) streeft naar gelijke test- en beoordelingsmethoden voor verschillende bouwstoffen, zoals steen, metaal, hout, kunststof. Dit streven is gebaseerd op een veronderstelde overeenkomst in de mechanismen waarmee deze bouwstoffen uitlogen.

Trefwoorden: leaching, rubbers, plastics, risicobeoordeling, bouwstoffen

Contents

Summary		9	
1	Introduction	11	
2	Relevant organic building materials	15	
2.1	Tyres / Styrene Butadiene Rubber (SBR)	15	
2.1.1	Shreds	16	
2.1.2	Chips	16	
2.1.3	Crumbs	16	
2.1.4	Dust/powder	17	
2.1.5	Toxicity of tyre-leachate	18	
2.1.6	Physical aspects of leaching	19	
2.1.7	Product improvement by zinc reduction	20	
2.2	Plastics	20	
2.3	Organic constituents in cement / concrete / asphalt	22	
2.4	Overall conclusion	23	
3	Test methods	25	
4	Risk assessment and modelling	27	
4.1	Risk assessment: a stepwise approach	27	
4.2	Determination of compounds of concern	27	
4.3	Determination of the emission pattern of substances	28	
4.4	Determination of environmental impact	30	
5	The case of rubber infill	33	
5.1	SBR crumbs used on artificial turf soccer field	33	
5.1.1	Selection of substances	33	
5.1.2	Standard leaching test, analysing zinc	33	
5.1.3	Indoor lysimeter study to ageing and leaching	34	
6	Conclusions and recommendations	39	
6.1	Conclusions	39	
6.2	Recommendations	39	
References		41	
Appendix 1	Research proposal 'Emissions from ageing rubber matrices'	45	
Annendix 2 Substance lists			

Summary

Buildings and public works in contact with rainwater will leach compounds from the construction products to the environment. Current regulations of the permissible emissions of polluting compounds to soil and water in the Dutch Soil Quality Decree (SQD) are in force for stony construction products only. Emissions of other materials are not regulated except that the precautionary principle applies. A common feature of stony construction products is that the leaching pattern of compounds shows an (exponential) decay with time. In the case of (organic) polymeric construction products the leached amount will not always decrease with time. The interactions of compounds with a polymeric organic matrix are fundamentally different from those in a stony matrix. For example, in the case of synthetic rubber granulate, used as infill in artificial turf, it has been shown that as a result of ageing of rubber, the leached amount of zinc, may temporarily increase with time, as the rubber matrix will breakdown due to oxidation processes, heat and UV-radiation. For polymeric matrices, ageing and weathering are often characteristic features influencing the mode of leaching. Besides (chemical) ageing as a major difference between stony and polymeric material, more differences will exist such as the usually nonionic backbone of mineral oil based polymers, and temperature dependency of dimensions of the diffusion routes in polymeric cross-linked networks. Depending of the matrix properties other leaching mechanisms will dominate, resulting in different leaching kinetics. The current permissible emission values in the SQD may not be applicable for construction products with a polymeric matrix.

Within the framework of the European Construction Products Decree (CPD), there is also a need for regulations for the leaching of toxic compounds from polymeric materials that become increasingly applied as or in construction products. A suite of polymeric products may end up as construction product. Also products for daily use, for example plastic bags end up in material for fences, (shredded) car tyres are used as landfill cover material and added in concrete.

The mechanism of leaching of substances from polymeric matrices is still to be elucidated. In this report, information is collected to support the need of a study that elucidates the proper leaching mechanism(s) from polymeric matrices. Recent literature on leaching from polymeric matrices is covered, existing test methods for leaching of compounds from (potential) building materials are described and the current model that describes the leaching process is given. An experimental setup is proposed that could provide results to enable the construction of a proper model describing leaching of substances from polymeric matrices.

The aim of the proposed study is to describe and model the leaching and ageing mechanisms for rubbers and plastics to ensure a correct interpretation of standard column tests (albeit possible slightly modified) for these products and to enable a feasible incorporation in existing legislation.

1 Introduction

According to the European Construction Products Directive (89/106/EC) (CPD), construction products must satisfy specified essential requirements (ER). To comply with ER 3, on hygiene, health and the environment, the construction works must be designed and built in such a way that they will not be a threat to the hygiene and health of the occupants and neighbours, nor to the environment. Standardised test methods for the determinations of the release of substances that are hazardous to health and the environment need to be developed at the European level.

Also, according to the European Landfill Directive (1999/31/EG) and Landfill Decision (2003/33/EG) (LD), procedures for basic characterisation of waste to be landfilled and compliance testing have to guarantee the compliance with limit values for the amount of leached substances or the total content of substances.

A 'horizontal' approach is considered the best route for such development of tests (within the framework of both CPD and LD), and consists of the development of test methods applicable for different products used in a certain scenarios. In this report we focus on leaching of substances under outdoor conditions and the impact on soil and groundwater.

Several testing purposes can be distinguished:

- Basic characterisation (and: Initial Type Testing in CPD): this includes tests to establish the
 properties of the material and the release of substances in order to identify the relevant release
 mechanisms. This information can be used for the derivation of compliance values
- Compliance testing (and: Further Testing in CPD): this includes routine tests, usually to determine a limited set of parameters that can be compared with compliance values

A straightforward way to set environmental criteria for polymer building materials would be based on total content of substances. However this is a very worst case approach and many building materials would not fulfill the criteria. For example, rubber infill contains 8-25 g Zn/l. This exceeds even the current action values for remediation (intervention values) of soil. As substances are gradually released from the matrix, total content is not a sound criterion for risk assessment. A constant relation between total content and emission does not exist; the release is dependent on matrix properties like particle size and resistance against oxidation. Therefore the release of substances needs to be measured and rules for extrapolation of emission over time have to be derived. This information forms the starting point for a proper risk assessment according to the SOURCE-PATHWAY-TARGET approach.

The release of substances from building materials is determined by physico-chemical properties of the material, properties of the substance and external conditions. The release of substances can be predicted based on a limited set of mechanisms, which is the background of the development of horizontal leaching tests (Van der Sloot and Dijkstra, 2004).

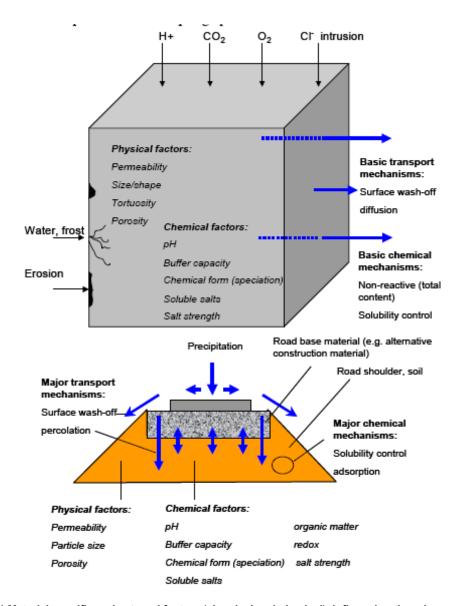


Figure 1.1 Material specific and external factors (chemical and physical), influencing the release of contaminants – schematic (taken from Van der Sloot and Dijkstra, 2004).

The methods developed so far, have focussed mainly on stony secondary building materials and waste. Current regulations of the permissible release of compounds to soil and water in the Dutch Soil Quality Decree (SQD) are in force for stony¹ construction products (including soil) only (Ministry of Housing, Spatial Planning and the Environment, 2007). The permissible releases are based on time-dependent modelling of the leachable amounts in stony materials. Standard leaching tests have been developed for compliance, which are applicable as long as the leaching mechanism is similar to the leaching in stony materials. The interactions of cations and anions with the (usual) silicate matrix and the diffusion mechanisms that make up the leaching process are well understood and the modelling for leaching of inorganic compounds from stony construction products is well developed. A common feature of stony construction products is that the leaching of potential

¹ Stony material is defined as material of which the total amount of Al, Si and Ca is larger than 10% (w/w), irrespective of the content of organic material.

pollutants shows an (exponential) decay with time. Changes in matrix porosity (due to physical ageing) are not taken into account, because this is considered a relatively slow process compared to the leaching processes.

In the case of the rubber infills (produced by granulating end-of-life car tyres) on artificial turf, it appeared that the amount of leached zinc was expected to violate existing regulations for the environmental protection of soil (Verschoor, 2007).

Unlike stony materials, the substances leached from polymeric construction products such as plastics, will not always decrease with time, indicating that the interactions of compounds with the organic matrix could be fundamentally different than interactions in a stony matrix. Physical and chemical properties of the organic matrix itself appear to be changing in time, thus affecting the release of compounds contained within the matrix. For example, in the case of synthetic rubber granulate, used as infill in artificial turf, it has been shown that as a result of ageing of rubber, the leached amount of zinc, may temporarily increase with time, as the rubber matrix will breakdown due to oxidation processes, heat and UV-radiation. Thus, the model of the leaching process for stony matrices is not applicable to polymeric matrices. To model the leaching of substances from polymeric matrices, for which ageing is very often a characteristic feature, the mechanism is still to be elucidated. Besides ageing as a major difference between stony and polymeric material, more differences will exist such as the usually non-ionic backbone of mineral oil based polymers, and temperature dependency of dimensions of the diffusion routes in polymeric cross-linked networks. Depending of the matrix properties other leaching mechanisms will dominate, resulting in different leaching kinetics. As a consequence the current permissible emission values in the SQD are not applicable for construction products with a polymeric matrix.

In this report, information is collected to support the need of a characterisation study that elucidates the proper leaching mechanism(s) from polymeric matrices. A framework is proposed of experiments that could provide results that can be helpful in the construction of a proper model describing leaching of toxic substances from polymeric matrices in different applications.

Although a massive body of knowledge exists on rubber ageing, this knowledge has however not yet been related to long term emissions of compounds from rubber to the environment. Up to now, the relevant technological knowledge about rubber ageing has been directed to improvement of product performance and durability or cost-effective use of raw materials or ingredients. The environmental aspects of the applications of rubber in constructions in relation to ageing have not received much attention and ageing has not been related to environmental standard tests for leaching.

In this report, relevant recent literature on leaching from polymeric matrices will be covered (chapter 2), existing test methods for leaching of compounds from (potential) building materials will be described (chapter 3) and the main risk assessment models will be reviewed (chapter 4). Our experience with the testing and risk assessment of rubber infill is described in chapter 5. Finally recommendation for a follow-up study to leaching processes in polymeric matrices is described in chapter 6. A possible experimental set-up will be proposed.

The study presented in this report will primarily be restricted to products from mineral oil based synthetic polymers, such as rubbers, and plastics, thus excluding biopolymers such as natural cellulose or wood. In some cases stony building materials will contain polymeric parts (e.g. application of rubber crumbs in cement). It is noted that also (other) products and (waste) materials will potentially be or become construction products after recycling, such as plastic bottles and car tyres.

2 Relevant organic building materials

A suite of polymeric products may end up as construction product. Also products for daily use, for example plastic pouches end up in material for fences, (shredded) car tyres are used as landfill cover material and added to concrete. From many of these polymeric materials, a variety of substances may leach out during the different lifetimes of the products. Usually, the leached amounts are very small, not giving rise to immediate environmental concern. However, as the amount of polymeric materials used in or as a construction product is increasing, it is worthwhile to gather possible evidence on the future environmental risks and on the possible leaching mechanisms involved. In a short review of recent literature in this chapter, convincing evidence is presented that in the case of a number of rubber and plastic materials the leaching mechanism of environmentally dangerous substances is fundamentally different from that of mineral (construction) products. It appears that mechanistic information on the leaching processes involved is virtually absent.

2.1 Tyres / Styrene Butadiene Rubber (SBR)

SBR has a widespread use in car and truck tyres. Until 2000 end-of-life tyres used to be disposed of on landfills. Markets for scrap tyres have expanded since the early 1990s with the development of value-added applications such as tyre-derived fuel and crumb-rubber-amended asphalt. Granulated tyres have also displayed the ability to adsorb volatile organic compounds, indicating that the rubber material can be a useful filter media. Moreover, due to the Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end-of life vehicles, an increasing amount of tyres is being recycled.

Some of the applications for recycled SBR are listed below:

- rubber infill on artificial soccer field
- rubber surface on athletic tracs
- rubber tiles on playgrounds
- light weight particles to improve drainage along roads
- constituent in asphalt for noise reduction
- light weight foundation beneath roads
- light weight filling/foundation in noise barriers
- tyre embankments in harbours
- rubber granulate as daily cover or drainage improvement on landfills (instead of sand)
- foundation beneath buildings in earthquake zones
- as a screen in groundwater remediation sites

Besides leaching of substances to the environment as a result of the use of SBR-recycling products, there is also the unintentional exposure of roadsides caused by wear of tyres. An important parameter for the environmental impact seems to be the specific surface area of the recycling product. A large contact surface with air, light or water generally enhances the release of substances from the matrix. Therefore it is relevant to make a distinction between 1) rubber dust (<0.5 mm), 2) crumbs (approximately 0.5-2 mm), 3) chips (approximately 2 mm-5 cm) and 4) shreds (approximately 5-30 cm). This section summarizes the findings of studies to the environmental aspects of some of the applications mentioned above.

2.1.1 Shreds

A study by Moo-Young et al. (2003) to determine the physical and chemical properties of tyre shreds for use in engineering constructions, revealed that their physical properties make tyre shreds useful in construction applications. Chemical analysis of tyre shreds was conducted to illustrate how total organic carbon (TOC), pH, and turbidity in elution water change with tyre shred size. As tyre shred size increases, the results illustrated a decrease in TOC (from 22.7 to 3.1 ppm). Continuous flow column tests were conducted on tyre shreds and showed that TOC, turbidity and iron-concentration decrease with time. However, pause flow column tests showed reduced water quality, which implies that placement of a tyre embankment below the water table where ponding can occur, may reduce the water quality.

In the leachates from shredded tyres, elevated amounts of Zn, Cd, and Ba have been attributed to the tyre material. In a study of Brophy and Graney (2004) it was concluded that it is important to evaluate the **combined** long-term effects of tyre shreds and runoff from roadways on groundwater quality where tyre shreds are used in highway construction.

In a study of Liu et al. (2000) recent laboratory investigations conducted to quantify possible leachates from various recycled tyre shreds are summarized. Extension of these results to reported field tests detailing the impact of recycled rubber on air, soil and water quality is also considered, as well as biological and toxicity issues.

2.1.2 Chips

Park et al. (2003) conducted a series of tests to investigate the fate of heavy metals and gasoline compounds in a **simulated** landfill, consisting of a 30 cm thick clay liner and a leachate collection layer containing tanks with and without tyre chips. Arsenic, selenium, mercury, barium, and lead concentrations were lower while zinc concentration was higher in the tank containing tyre-chips than the tank without tyre-chips. When samples were filtered, however, dissolved concentrations of zinc as well as other inorganics were lower in the tank containing tyre-chips, indicating that metals in the leachate exposed to tyre-chips are mainly bound to suspended solids. Additionally, two test cells were installed in a **real** landfill. In a test cell study, arsenic, cobalt, lead and nickel concentrations were lower in the cell containing tyre-chips than in the cell without tyre-chips, except iron and zinc. Both tests (simulated as well as real landfill) indicate that some inorganic contaminants are sorbed to tyre-chips. In some areas where contamination levels are high, tyre chips have been used as a sorbent for environmental clean-up.

2.1.3 Crumbs

Several studies to leaching of substances of rubber crumbs have been performed and reported in the grey literature (amongst others Intron 2006, Intron 2007, Intron 2008). In Appendix 1 the findings from the Intron reports about rubber crumbs is summarized. The presence of results in scientifically reviewed public literature is limited.

In a study of Bocca et al. (2009) metals contained in and leached from different types of rubber granulates used in synthetic turf areas were quantified. To investigate the total content of metals, about 0.5 g of material was added with HNO₃, HF and HClO₄ and microwave digested with power increasing from 250 W to 600 W. Leachates were prepared by extraction of about 5.0 g of material at room temperature for 24 h in an acidic environment (pH 5). Leaching with deionized water was also performed for comparison. Al, As, Ba, Be, Cd, Co, Cr, Cu, Hg, Fe, Li, Mg, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Tl, V, W and Zn were quantified by high resolution inductively coupled plasma

mass spectrometry (HR-ICP-MS) and ICP optical emission spectrometry (ICP-OES). The results indicated that the developed method was accurate and precise for the multi-element characterization of rubber granulates and leachates. The total amount and the amount leached during the acidic test varied from metal to metal and from granulate to granulate. The highest median values were found for Zn (10229 mg/kg), Al (755 mg/kg), Mg (456 mg/kg), Fe (305 mg/kg), followed by Pb, Ba, Co, Cu and Sr. The other elements were present at few units of mg/kg. The highest leaching was observed for Zn (2300 μ g/l) and Mg (2500 μ g/l), followed by Fe, Sr, Al, Mn and Ba. Little As, Cd, Co, Cr, Cu, Li, Mo, Ni, Pb, Rb, Sb and V leached, and Be, Hg, Se, Sn, Tl and W were below quantification limits. Data obtained were compared with the maximum tolerable amounts reported for similar materials, and only the concentration of Zn (total and leached) exceeded the expected values.

Sand-based root zones, typically used for golf course putting green and athletic field construction, lack sufficient cation exchange capacity to restrict nitrogen and phosphorus migration through the root zone and into sub-surface drainage systems. Amendment with tyre rubber crumbs could improve the nutrient holding capacity of the sandy soils. The adsorptive properties of tyre rubber for retaining nitrogen and phosphorus were studied by Lisi et al. (2004) when applied as a distinct subsurface drainage or intermediate layer in golf course putting greens. A statistically significant reduction in the concentration of nitrate in leachate was achieved by replacing traditional pea gravel with equally sized granulated tyres for the drainage layer media, although the mechanism of nitrate mitigation remains unclear.

2.1.4 Dust/powder

Tyre debris contains significant quantities of zinc (Zn), and there is concern about the diffuse Zn contamination of soils from tyre wear. An experiment was set up, by Smolders and De Gryse (2002) to quantify the fate and effect of Zn from tyre wear in soil. Two different soils were mixed with the <100-micrometer fraction of car and truck tyre dust (25 g TD/kg soil) or zinc sulfate (ZnSO₄) as a reference. Soils were transferred to soil columns with free drainage and placed outdoors for 11 months. Leachates of the tyre dust amended soils did not contain significantly (P>0.05) more Zn than control soils except for a 3-fold increase in one soil amended with car tyre debris. The increase in Zn leaching due to tyre dust was 3% of the corresponding increase in the ZnSO₄ treatment at the same total Zn in soil, under these experimental conditions. Tyre dust application increased the soil nitrification potential, whereas ZnSO₄ application, at corresponding or smaller total Zn concentration, decreased nitrification potential. An increase in soil pH was observed in all soils treated with tyre dust and explains the increased nitrification potential. About 10-40% of the Zn from tyre dust was isotopically exchangeable in soil sampled after 1 year weathering. It is concluded that a significant fraction of Zn is released from the rubber matrix within 1 year, but the parallel increase in soil pH limits the mobilization of Zn in soil.

In a study of Gualtieri et al. (2005) tyre particles (10-80 μ m), produced in laboratory from new rubber, were used to study the leaching of zinc. Two sets of experiments were set up to obtain eluates. One set used 50 and 100 g rubber/l water to produce eluates at pH 3-7. It was demonstrated that factors such as pH, size and particles aggregation deeply influence the elution process and that the amount of Zn leached from particles is related to their aggregation size rather than their quantity.

Tyre and brake wear particles contain transition metals and contribute to near-road particulate matter. Respirable fractions that were analyzed for water and acid-leachable metals contained a variety of transition metals, including zinc (Zn), copper (Cu), aluminum, and iron. Zn and Cu were detected at high levels in water-soluble fractions (Gottipolu et al., 2008).

Leachates derived from used tyres have been characterized, by Sarasa et al. (2006) by means of the evaluation of their organic matter content. The leachate from tyre powder presented a Chemical Oxygen Demand of 508 mg O_2 /l and a TOC of 214 mg C/l The main identified organic substances were constituents of the rubber structure: benzothiazole derivatives, phthalates, phenolic derivatives, hydrocarbons and fatty acids.

2.1.5 Toxicity of tyre-leachate

Car tyres contain several water-soluble compounds that can leach into water and have toxic effects on aquatic organisms. Softener in rubber mix of car tyres is made up by extracts of aromatic hydrocarbons (referred to as highly aromatic oils, HA-oil), which include significant amounts of PAH. Leakage of PAH from tyre dust are identified as a source of PAH exposure in the environment. In a study of Parkkonen et al. (2002) juvenile rainbow trout were exposed to intact tyres immersed in the fish tanks. Two types of tyres were tested: one with HA-oil in the tread and one without HA-oil in the tread. The exposure of fish resulted in liver enlargement, elevated levels of hepatic CYP1A1 expression and total liver glutathione.

The toxicity to *Daphnia magna* from 12 randomly selected car tyres was tested by Wik et al. (2005). Rubber from the tread of the tyres was grated into small pieces, to simulate material from tyre wear, and the rubber was equilibrated with dilution water for 72 h before addition of test organisms. The 24-h EC50s of the rubber pieces ranged from 0.29 to 32 g/l, and the 48-h EC50s ranged from 0.0625 to 2.41 g/l. Summer tyres were more toxic than winter tyres. After the 48-h exposure, the daphnids were exposed to UV-light for 2 h, to determine if the tyres contained compounds that were phototoxic. After UV-activation the EC50s ranged from 0.0625 to 0.38 g/l. Four of the 12 tyres had a very distinct photoactivation, with a toxicity increase of >10 times. This study has shown that the method used for toxicity testing with *Daphnia magna* according to ISO 6341, could be used as a basis for environmental labeling of car tyres.

Toxicity testing, toxicity identification evaluation (TIE) and groundwater modelling, were used by Sheehan et al. (2006) to determine the circumstances under which tyre shreds could be used as roadbed fill with negligible risk to aquatic organisms in adjacent water bodies. Elevated levels of iron, manganese, and several other chemicals were found in tyre shred leachates. However, chronic toxicity tests with Ceriodaphnia dubia and fathead minnows (Pimephales promelas) showed no adverse effects caused by leachates collected from tyre shreds installed above the water table. Exposure to leachates collected from tyre shreds installed below the water table resulted in significant reductions to both survival and reproduction in C. dubia. The TIE results indicated that exposure to soluble metals (likely ferrous iron primarily) and the formation of iron hydroxide precipitates on this invertebrate species likely were the causes of the observed effects. The available chemistry data show that iron concentrations in the affected groundwater decreased substantially within a short distance (0.61 m) downgradient of tyre shred fill. Based on geochemical modelling, the use of tyre shreds in applications below the water table is appropriate in settings where dissolved oxygen is greater than 2.0 mg/l, pH is greater than 5.8, and a downgradient buffer of approximately 3.0 m exists between the fill and the surface water. For settings with lower dissolved oxygen concentrations or lower pH, results of groundwater modeling indicate that a greater buffer distance (-11 m) is needed to dilute the leachate to nontoxic levels under various soil and groundwater conditions solely through advection and dispersion processes.

Large amounts of tyre rubber are deposited along the roads due to tread wear. Several compounds may leach from the rubber and cause toxicity to aquatic organisms. To investigate the toxic effects of tyre wear material from different tyres, rubber was abraded from the treads of twenty-five tyres, in a study by Wik and Dave (2006). Leachates were prepared by allowing the rubber to equilibrate

with dilution water at 44 °C for 72 h. Then the rubber was filtered from the leachates, and test organisms (*Daphnia magna*) were added. EC50s (48 h) ranged from 0.5 to >10.0 g/l. The toxicity identification evaluation (TIE) indicated that non-polar organic compounds caused most of the toxicity. UV exposure of the filtered tyre leachates caused no significant increase in toxicity. However, when tested as unfiltered leachates (the rubber was not filtered from the leachates before addition of *D. magna*) photo-enhanced toxicity was considerable for some tyres, which means that test procedures are important when testing tyre leachates for aquatic (photo) toxicity. The acute toxicity of tyre wear for *Daphnia magna* was found to be 40 times smaller than the predicted environmental concentration based on reports on the concentration of a tyre compound found in environmental samples, which emphasizes the need for a more extensive risk assessment of tyre wear for the environment.

Camponelli et al. (2009) studied the potential contribution of tyre debris to Zn accumulation by *Rana sylvatica* larvae and possible lethal or sublethal impacts resulting from exposure to weathered tyre debris during development. Eggs and larvae were exposed to aged sediments (containing either ZnCl₂ or tyre particulate matter, both providing nominal concentrations of 1000 mg Zn/kg) through metamorphosis. Water column Zn was elevated in both the ZnCl₂ and tyre treatments relative to the control treatment, indicating that aging allowed Zn leaching from tyre debris to occur. Tissue Zn was also elevated for the ZnCl₂ and tyre treatments indicating that Zn in the treatments was available for uptake by the amphibians. Exposure to both ZnCl₂ and tyre treatments increased the time for larvae to complete metamorphosis in comparison with controls. It was also observed that the longer the organisms took to complete metamorphosis, the smaller their mass at metamorphosis. The results indicate that Zn leached from aged tyre debris is bioavailable to developing *R. sylvatica* larvae and that exposure to tyre debris amended sediments can result in measurable physiological outcomes to wood frogs that may influence population dynamics.

2.1.6 Physical aspects of leaching

The study of McIsaac and Rowe (2005) presents the results of an experimental investigation into the clogging potential of rubber tyre shreds used as part of a leachate collection system at the base of a landfill when permeated with leachate. Clogging is a problem because it negatively affects the drainage of landfills. In the experiment several columns, filled with two different rubber tyre shreds and a conventional gravel drainage material, were used to study the spatial and temporal variation of leachate characteristics and porosity changes within the drainage materials. It is shown that there are significant differences in the pore structures of the drainage materials and that these differences affect clog development. It is likely that clogging affects the diffusion rate (and as a consequence the leaching rate) of substances from the polymeric matrix. On the one hand, leaching might decrease because by clogging the permeability of the material diminishes. On the other hand, clogging could accelerate leaching because substances are released by destruction of the polymeric matrix. It needs additional investigation to find out the dominant processes.

The leaching mechanism of a highly-soluble salt (sodium nitrate) encapsulated in novel polymeric waste forms were investigated by Quach et al. (2004) and Rengifo et al. (2004). The waste forms are solid monoliths composed of cured blends of polystyrene-butadiene and an epoxy resin. Leaching of the salt was carried out by exposing sections of the waste forms to large volumes of well-stirred water. The measured time dependence of the leaching process is described quantitatively by a model based on the diffusion of the salt through the waste form. The results obtained suggest that diffusion occurs through limited but significant continuous porosity. Preliminary experiments indicate that this porosity may be reduced to improve leach resistance by the use of a heat treatment.

2.1.7 Product improvement by zinc reduction

The effect of reducing the zinc oxide level in primary rubber products on the amount of zinc leached from secondary products like rubber granulate and powder has been investigated by Pysklo et al. (2006). A commercial rubber compound used for retreading truck tyres was chosen to evaluate the influence of the zinc oxide level on the amount of zinc leaching, and two grades of zinc oxide were applied. The amount of zinc leaching from rubber granulates produced from end-of-life tyres was found to depend mainly on zinc oxide level in primary tyre rubber products, particle size distribution and surface area of rubber granulates. The amount of zinc leaching was found to increase proportionally to zinc oxide concentration in tyre compounds up to certain level.

Metal (zinc) content, particle size distribution and surface of the rubber granule are therefore indicated as significant parameters for the environmental risk assessment.

2.2 Plastics

Plastic is a non-specific name for a group of polymers. Some commonly used plastics are listed in Table 1

Table 1. Names and uses of common plastics

Common	Full name	Used as/ used in:
name		
PP	polypropylene	car bumper bars
LDPE	Low Density polyethylene:	sandwich bags, cling wrap, car covers, squeeze
		bottles, liners for tanks and ponds, moisture
		barriers in construction
HDPE	high density polyethylene	freezer bags, water pipes, wire and cable
		insulation, extrusion coating
PVC	polyvinylchloride	electric insulation, guttering
TEFLON	polytetrafluoroethylene	widely used as non-stick coatings or films in
		cookery and many other medical, industrial and
		technological applications.
Polystyrene		packaging and insulation
Nylon-6,6		textile fibre
Dacron	polyethylene terephthalate	textile fibre (polyester)

The demand for mechanical recycling of plastic waste results in an increasing amount of recycled polymeric materials available for development of new products. In order for recycled materials to find their way into the material market, high quality is demanded. The concept of high quality for recycled plastics implies that besides a pure fraction of e.g. polyethylene (PE) or polypropylene (PP), containing only minor trace amounts of foreign plastics, knowledge is required about the type and amount of low molecular weight (LMW) compounds, like phtalates. During long-term use (service-life), products made of polymeric materials will undergo an often very slow degradation where a series of degradation products are formed and in parallel, additives incorporated in the matrix may also degrade. These compounds migrate at various rates to the surrounding environment. The release rate of LMW products from plastics depends on the initiation time of degradation and the degradation mechanisms. For polymers the formation of degradation products may be initiated already during processing, and subsequent use will add products coming from the surrounding environment, e.g. fragrance and aroma compounds from packaging. During recycling

of plastics, emissions which contain a series of different LMW compounds may reach the environment leading to unwanted exposure to additives and their degradation residues as well as degradation products of polymers.

Several extraction techniques are available for sampling of LMW compounds in polymers before chromatographic analysis. A paper by Moller et al. (2008) reviews and compares a number of (extraction) methods and appropriate sampling methods for LMW compounds in recycled polymers. Based on the review of the methods, the most promising techniques were tested with industrially recycled samples of HDPE and PP and virgin HDPE and PP for method comparison.

In a study, by Ojha et al. (2005) attempts were made to estimate phthalates content in leachates from commonly used plastic (pouches) in simulating condition media, such as water and normal saline using high pressure liquid chromatography (HPLC). The phthalates measured were di-ethyl-hexyl phthalates (DEHP), di-butyl-phthalate (DBP) and di-methyl-phthalate (DMP). In order to assess the continuous leachability, if any, the procedure of extraction was repeated 3 times in identical conditions using same plastic and no significant leachability of any of the phthalate could be observed in 2nd, 3rd and 4th extractions revealing no leachability of phthalates on repeated extraction.

In another study on phthalates in plastic, by Jahed Khaniki et al. (2006), it turned out that phtalates are not chemically but only physically bound to the polymer chains, they may be leached from the packaging material. The study was determined for two phtalate types, and their release into water stored in plastic tumblers at different temperatures and times. It was concluded that released phtalate levels into water samples has increased at high temperatures and longer times.

In the plastics industry, various chemical additives are used to improve certain properties of plastics, such as PVC. Some of these chemicals, have been proven to leach from the plastic containers in amounts toxic to mice (Jahed Khanik et al., 2006)

In a study by Bjorn et al. (2007) to investigate whether organotin-stabilized polyvinyl chloride (PVC) products could contribute to the pool of organotins observed in landfill leachates, it turned out that the release of organotin stabilizers increases considerably at temperatures above the glass transition of the PVC products (80 °C).

Although food contact polymers do not normally contain lead, it is suspected that lead may leach from some microwavable plastic ware items with lead-containing pigments. The purpose of the study of Inthorn et al. (2002) was to examine relationships with regard to lead leached from microwaveble plastic ware. Four factors were studied: pH, heat level, extraction time, and number of repeated extractions. The amount of lead leaching increased with decreasing pH and also increased with increasing heat level and extraction time. For all factors, the amount of lead leaching was lower than the permissible level of 1 mg/L. In conclusion, a combination of high acid, prolonged heating, and extraction time accelerated the amount of lead leaching from microwavable plastic ware, but the incidence of lead leaching was negligible.

The leaching tests of construction products made from recycled mixed waste plastics showed, in a study by Tominaga et al. (2003) that in leachates only bisphenol A was detected at $0.08 \mu g/l$ level and di-butyl phthalate at the environmental water level.

To investigate the effect of leachant on the leachability of polybrominated diphenyl ethers (PBDEs), Kim et al. (2006) determined the leaching concentrations of PBDEs from flame-retardant plastic samples (TV housings and raw materials before molding processing) that are regarded as a source of PBDEs in landfill sites. The leaching concentrations of PBDEs increased with increased content, and were found to be remarkably enhanced when methanol and dihexylsulphide (DHS) were used instead of distilled water. The enhancement of leachability in the presence of the latter was attributed to the cosolvency effect, and complex formations between the PBDEs and dissolved humic matter (DHM). PBDE concentrations in the leachate obtained from the leaching test and an actual landfill site revealed a significant presence of congeners below heptabromodiphenyl ethers (H7BDEs), detected in the leachate of the actual landfill, while significant amounts of nonabromodiphenyl ethers (N9BDEs) and decabromodiphenyl ether (D10BDE) were detected in the leachate of the leaching test.

In a guideline for the assessment of release of constituents from synthetic drinking water pipes, there exists a Dutch method from the Watercycle Research Institute (KIWA, 1994). The test is based on the assumption that the release toward the water phase is a kinetically controlled diffusion process. No ageing conditions, and no granulation of the PVC-material is applied in this test.

2.3 Organic constituents in cement / concrete / asphalt

Semi-volatile organic compounds are found in leachates from **reclaimed asphalt pavement.** Car exhausts, rubber tyres and the asphalt material itself are all probable emission sources, determined from the organic contaminants released from the stockpiles. Norin and Stromvall (2004) measured these organic substances in field samples and in laboratory column tests, through a GC/MS screentest methodology . Sixteen PAH (polyaromatic hydrocarbons) were also analysed in leachates from the column study. The highest concentrations of semi-volatile compounds, 400 µg/l, were measured in field samples from the stockpile. Naphthalene, butylated hydroxytoluene (BHT) and dibutyl phthalate (DBP) were the most dominant of the identified semi-volatiles. The occurrence of these compounds in urban groundwater, also indicates high emission rates and persistent structures of the compounds, making them potentially hazardous. The major leaching mechanism indicated was dissolution of organic contaminants from the surface of the asphalt gravels. In the laboratory column test, the release of high-molecular weight and more toxic PAH was higher in the leachates after two years than at the commencement of storage. These findings confirm the hypothesis that ageing accelarates leaching.

From experiments, by Azizian et al. (2003), with use of ground tyre rubber (crumb rubber) in **bituminous** construction, it appeared that its leachates contain a mixture of organic and metallic contaminants, such as benzothiazole and the metals mercury and aluminum in potentially harmful concentrations.

Poly-acrylamide-acrylic acid impregnated with zirconium phosphate produced from the treatment process of radioactive liquid waste was incorporated in different types of **cement** to prevent widespreading of radionuclides into the human environment. The rates at which ⁶⁰Co, ⁶⁵Zn and ^{152.154}Eu are leached from several types of cement have been reported. The leaching coefficients varied in the order: distilled water > ground water > synthetic sea water and was found by Abou-Mesalam (2002) to be dependent on the addition of poly-acrylamide compounds to the concrete.

2.4 Overall conclusion

Concluding from this literature survey it appears that leachates of polymeric substances can be toxic for aquatic species. However, detailed information on the mechanism of leaching of metals (and also organic compounds) from (shredded) polymeric matrices is largely lacking. Effect of ageing or weathering of rubbers and plastics has not systematically been investigated, but is an important factor for long term release from the material into the environment. Only effects of variables like porosity, particle size, the amount of ZnO, and the composition (pH and temperature) of the leaching solution have been mentioned. It is noted that Zn (from rubbers) and phthalates (from plastics) are frequently observed in the leachates, in the studies covered.

3 Test methods

To quantify the amount of leaching of substances from construction products (or waste) a number of leaching tests can be applied. Depending on the purpose of the investigation and on the form of the product, the tests may differ in applied pH, time to be elapsed, and the conditions for contact with the elution fluid. For granular materials, an upflow percolation column test is standard, for monolithic products a bath or tank test may be appropriate.

Standard leaching tests

Standard test methods to investigate leaching from stony construction products are NEN 7347 - Compacted Granular Leach test (column test) and the tank test NEN 7345. In NEN 7347, leaching characteristics are determined through the cumulative leaching of inorganic components from granular materials at anearobic conditions in a column test, filled with solid earthy and stony materials.

In NEN 7345, leaching characteristics of solid earthy and stony building and waste materials are determined for inorganic compounds from buildings and monolitic waste materials in a diffusion test

Further, a series of leaching test in which the experimental conditions can be varied, comprises:

- CEN/TS 14429 pH dependence leaching test (initial acid/base addition)
- CEN/TS 14997 pH dependence leaching test (continuous pH control)
- CEN/TS 14405 percolation test published
- CEN/TC 292/WG6 NWIP Tank leach test (in preparation)
- EN 12457 1-4 Granular waste compliance leaching test validated
- ISO/TC 190/SC7/WG6: Batch tests (ISO/AWI 21268 1 and 2)
- ISO/AWI 21268-3: percolation test for soil materials
- ISO/AWI 21268-4: pH dependence leaching test

In all these test, changes in the material as a result of ageing are not considered. The time variation is simulated by changing the L/S ratio, which is a effective tool in the case an ion exchange mechanism only is active. A complete overview of leaching tests for initial type testing is given in CEN/TR 00351003 (draft) (CEN/TC351, 2008).

For the final instrumental determination of metal or organic species in the leachates, ICP-MS and CG-MS respectively, are usually applied, or comparable methods.

Further characterisation testing

To elucidate the mechanism of leaching of substances from (construction) products with polymeric matrices, the effects of variables of ageing has to be quantified in order to construct an appropriate model of the lang term leaching under real-life conditions. Degradation of rubber, by ageing, is primarily due to oxidation of the crosslinking bonds in the rubber matrix (Li and Koenig, 2005).

Methods to establish such investigations often consist of:

- Ageing tests using enforced 'weathering' techniques such as the application of ozone, UV light, extreme heat treatments (diurnal and seasonal cycles) in freezing/thawing cylces (Hofstra, 2008).
- Lysimeters with which, for example, parts of football pitches are rebuild, equipped with artificial raining devices and percolate control, enabling prolonged experiments, however without enforced ageing (Moretto, 2007; Müller, 2007).

4.1 Risk assessment: a stepwise approach

The risk assessment of substance leaching from materials during its life-time distinguishes three major steps:

- 1. determination of compounds of concern
- 2. determination of the emission pattern in time
- 3. determination of environmental impact/concentration

Within these steps again a tiered approach is sometimes possible, ranging from easy when possible to difficult/advanced when necessary. The first tier could be quick, conservative and cheap. The next tier(s) involves more research, thereby diminishing uncertainty and becoming more realistic. Especially for step 3: the environmental risk assessment (ERA) tiered approaches are common. This report does not focus on a life-cycle analysis, so assessments for the production phase and the waste stage are not elaborated here.

4.2 Determination of compounds of concern

The major question in the first stage of the assessment is how do determine the substances of concern. Organic building materials consist of complex, polymeric structures enriched with 'supplements' such as pigments, stabilizers, anti-oxidants, anti-ozonants, UV-absorbents, plasticizers and residues of catalysts, ingredients and reaction products. Until now the risk assessment focuses on individual substances; however an approach that takes combination toxicity into account acknowledges the fact that the leachate usually contains a cocktail of substances.

Several (additional) approaches can be considered in order to select potentially relevant substances in the leachate of materials:

- Screening of prior information, such as information of the manufacturer, REACH, scientific
 or gray literature could be used in order to find the relevant substances. However the
 information might be incomplete and ignores metabolic products formed during production
 or decay of the material. It is also possible that substances arise with no available European
 Environmental Quality Standards (EQS).
- 2. Screening of substances included in standard analytical packages or regulatory substance lists is a reasonable initial approach, but might oversee specific substances with potential harmful effects. The advantage is that for substances on these lists compliance values are available. In Appendix 2 an overview is given of substances included in one of the following lists:
 - a. Priority Substances under the Water Framework Directive. For substances included in this list, European Environmental Quality Standards (EQS) for surface water have been set, annual average concentrations as well as maximum allowable concentrations. Compliance with the EQS can only be established after an environmental risk assessment. For actual EQS the reader is referred to EC (2008) or the European Chemical Bureau (http://ecb.jrc.ec.europa.eu/legislation/).

- b. Inorganic substances with emission limit values for monolithic stony building materials in the Dutch Soil Quality Directive²
- c. Inorganic substances with emission limit values for granular building materials in the Dutch Soil Quality Directive.
- d. Organic substances with a maximum total content in monolytic and granular stony building materials in the Dutch Soil Quality Directive.
- 3. Analysis of Total Organic Carbon and identification of substances with mass spectrometry. Checking the mass balance of organic substances, can indicate the presence of unknown, potentially toxic substances. This approach is not suitable for anorganic substances.
- 4. Application of bioassays as a screening method. As an example of bioassays the Whole effluent toxicity (WET) test (EPA, 2001) is an option here. The WET-test indicates whether the leachate is toxic to freshwater and marine organisms. It takes into account the effect of the whole mixture of known and unknown substances including effects of the pH. If the test result indicates a toxic effect an additional identification evaluation can be conducted to determine what the relevant toxicants are.

From a policy point of view, simple enforceable regulations are preferred. A direct comparison of laboratory leaching test with the emission limit values is simple and straightforward. The Dutch emission limit values are derived, taking into account a specific release pattern and a certain environmental distribution underpinned by an advanced geochemical model (Verschoor et al., 2006). However, adoption of the emission limit values for stony materials (as tabulated in Appendix 2) can not be done without critical evaluation of the release pattern. The next section goes into detail about the determination of the release pattern.

4.3 Determination of the emission pattern of substances

In order to have a potential effect, substances contained within the organic matrix should be released in the rainwater that runs along its surface. Substance emissions are therefore more relevant in risk assessment than total substance content. Unfortunately there are no univocal relationships between total content and emission from the matrix.

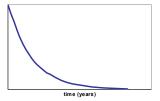
Test methods, as described in chapter 3, are applied to determine the emission within the period of the test, which is quite short as compared to the lifespan of the construction product. The test results should therefore be extrapolated to a time period which is relevant for the life span of the construction product.

The extrapolation method has a huge impact on the total (cumulative) emission. In Figure 4.1 three characteristic emission patterns are drawn.

1. The first one (left) is assumed to be characteristic for stony and earthy materials, where a diffusion-controlled exhaustion of substances in the material results in decreasing concentrations in time. Test methods (NEN 7343) have been set up to determine the k-factor, which is necessary for the extrapolation of test results over longer periods of time and describes the steepness of the curve. The mathematical expression for leaching from stony materials is described in Tekstbox 4.1.

² Stony building materials are defined as materials containing a total content of aluminium+calcium+silicium of more than 10% w/w. Compliance with these emission limit values is only required for stony building materials

- 2. The middle figure represents a solubility controlled constant emission and is assumed to be representative for the leaching of building metals, such as roof gutters, crash barriers etcetera. Of course at a certain moment, which could be within or beyond the time frame of interest, exhaustion of the emission will occur also.
- 3. The right figure shows an increasing or accelerating emission. Also this pattern will be followed by a decreasing release after a certain period of time. The hypothesis is that this pattern is characteristic for the leaching of substances incorporated in polymeric structures. Several processes, summarized under the name ageing, contribute to the phenomenon of progressive release. The consorted action of all process amplifies the sum of individual effects:
 - a. Oxidation of the polymer, accelerated by the influence of ozone and UV-radiation
 - b. Physical wear, abrasion
 - c. Leaching of anti-oxidants, anti-ozonants, UV-blockers and stabilizers
 - d. Loss of elasticity due to temperature fluctuations
 - e. Biodegradation
 - f. Dissolution of acidic compounds
 - g. Changing porosity by temperature effects





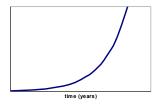
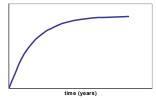
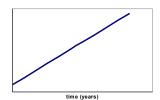


Figure 4.1 Three characteristic emission patterns: a decreasing emission, a constant emission and an increasing emission.

Often the emission pattern is expressed as a cumulative emission, which is the total emission over a certain period of time. In Figure 4.2 the cumulative emission patterns corresponding to the pictures in Figure 4.1 are shown.





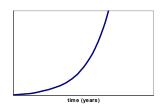


Figure 4.2 Cumulative emission patterns corresponding to the emission patterns in Figure 4.1.

For organic matrices there is no standard extrapolation method. The case of SBR rubber crumbs, described in section 5.1, is an example where the extrapolation method is still under debate. For polymeric matrices, the challenge is to develop a test method and matching extrapolation rules that are practical to perform and representative for outdoor situations. Existing methods, like the column leaching test may need amendment, because it shows a snap shot of the condition of the material, and does not inform about matrix ageing rates. The current extrapolation is valid for stony and earthy building materials but is clearly not valid for polymeric matrices.

Tekstbox 4.1 Mathematical description of the leaching pattern of inorganic substances from stony materials

For stony materials regulations for the environmental protection of soil, groundwater and surface waters exist; ecotoxicological limit values have been directly related to leaching test results for the (construction) material involved. Two models are involved in that relation:

- a model for the leaching mechanism of the construction product
- a model for the environmental distribution of the leached compounds

The mechanism within the construction products is, for stony materials, governed by ion exchange with the silicate based matrix. The resulting release pattern of compounds in the case of granulated stony materials in constructions is described by Aalbers et al. (1996):

$$I_{soil} = E_{construction} = \frac{E_{material} * d_b * h * (1 - e^{-K} * \frac{N_i * J}{d_b * h})}{(1 - e^{-K} * 10)}$$
(Eq.1)

where:

I_{soil}: source term (mg/m² per J years)

E_{construction}: emission from a construction (mg/m² per J years)

 E_{material} : emission from the construction product in the column test at L/S = 10 (mg/kg)

d_b: bulk density of a material (default 1550 kg/m³)
 h: height of material in a construction (m)

κ: a measure for the rate constant for release – element dependent

N_i: effective infiltration of rain (mm/year)

J: time (years)

A typical semi-mechanistic term is comprised in the factor $e^{-\kappa}$, an exponential decay function for the decrease of the diffusing amount with time. The constant κ has a specific value for each element and construction product and element. The model produces the input (source term) for the modelling of the environmental distribution of the leached substances. For polymeric matrices, equation 1 is not applicable, for reasons mentioned before. Moreover the equation is only used for the leaching of inorganic substances. Until the problems with extrapolating measuring leaching results of organic substances are solved, the Dutch regulation provides permissible total contents for organic substances in stony building materials.

4.4 Determination of environmental impact

The risk assessment of products is based on a comparison of properties of the product with compliance values (CV). In the EU Guidance document on inputs the concept of compliance values and compliances points is described (EC, 2006).

Examples of compliance values are:

- maximum content of certain chemicals in the product (mg chemical per kg, m³ or m² product)
- maximum concentrations dissolved in water in a standardized test (mg chemical per l water)
- maximum flux (mg chemical/m² soil/year)
- maximum load (kg/year)

Compliances values are connected to compliance points. Compliance values as well as compliance points (targets) are set by policymakers, aiming at a certain level of protection of the human health and ecosystem functions. Environmental scientists are able to propose compliance values, based on model calculations that predict the environmental fate of substances. This chapter describes how product limit values can be derived and how product properties can be used in environmental risk assessments.

Product limit values are compliance values of the material (source) itself. There can also be compliance points at certain distances from the source, for example in the upper layer of the soil, the interface of soil and groundwater, at the end of a mixing zone from a discharge point, at the intake point of a vulnerable object (for example a nature reserve or a drinking water abstraction point) at an early warning point between the source and the vulnerable object.

For construction products limit values are set to prevent harmful effects on human beings and the environment. Therefore the compliance values are derived from criteria which offer a high level of protection. Compliance values derived from HC5-or ADI-values are criteria within a precautionary policy.

In Table 4.1 an overview is given of compliance values and targets as used in the Netherlands.

	Target/Compliance point	Compliance value	•
ent	Construction	Emission limit value	Inversed risk assessment Derivation of product limit values
	product	Total content	it v
mss	Environment		Inversed risk assessment vation of product limit va
assessment	Soil		duc
jsk l	Groundwater	Target values	risk f pro
Direct Risk	Surface water	Maximum Permissible Concentrations	rsed
	Sediment		nve
	Protection goals		Deriv
↓	Human health	Acceptable Daily Intake (ADI)	
	Ecosystem	HC5 – Hazard Concentration 5%	

Table 4.1 Overview of compliance values and targets

There are two assessment routes:

1. Assessment of environmental and human risks

The distribution of *a given product value* (emission limit value or maximum content) is used as input in a model that calculates PECs (Predicted Environmental Concentrations in soil, groundwater, surface water and sediment). The risk is usually expressed as a risk ratio (RR) RR=PEC/CV. When the risk ratio >1 a risk management policy should be set up. This may include a decision to implement product limit values (see step 2), to demand risk reduction measures or product improvements, or phasing out or an official ban of the product.

2. Derivation of product limit values

The *maximum permissible product value* is balanced with the compliance value, using the same model as is used under (1). For each compartment a balanced product limit value can be derived.

From environmental point of view the product limit value from the most vulnerable compartment (that is the lowest emission limit value) should be implemented in legislations or directives.

In chapter 5, an example of a direct risk assessment approach is described. The same points of interest and attention are valid for the derivation of product limit values (inversed procedure). Environmental concentrations can be predicted, once the source term is defined. The following items should be described:

- 1. Describe representative use scenario's. Dimensions of the construction, surface area and contact area with water or solid to liquid ratio.
- 2. Describe the weather conditions. What is the exposure of the construction to water and how is the drainage or discharge organized. Is the construction exposed to oxygen, sunlight and ozone?
- 3. Describe the relevant routes and environmental compartments or protection goals. Describe the dimensions of the compartments, their physico-chemical characteristics and the compliance points.

Consider the period of interest. In the Netherlands the lifetime of the intended works are considered. For (public) works, 100 years has been applied (Ministry of Housing, Spatial Planning and the Environment, 2007), for football pitches 10-15 years (SenterNovem, 2009).

5 The case of rubber infill

There is no systematic approach for the risk evaluation of building materials, except for stony construction products. The responsibility for the environmental safety rests primarily with the manufacturers or importers. A 'precautionary principle' is laid down in Dutch regulation.

To fill in the 'precautionary principle' a suitable risk assessment method for substance leaching should be applied, in order to check whether environmental quality criteria in soil and water are met.

The adoption of the emission limit values for stony materials for a polymeric material is incorrect, as will be demonstrated for the case of SBR-infill. It is demonstrated that ozone initiated an accelerated release of zinc. The case of SBR also showed that a systematic approach to select the substances of concern is not yet available.

5.1 SBR crumbs used on artificial turf soccer field

5.1.1 Selection of substances

A literature study has been performed on substances in SBR-rubber (see section 2.1). It appeared that analytical parameters were chosen in a pragmatic way. Those parameters have been measured that were known to be used in the production process (i.e. zinc) or are suspected to be there (PAHs, phthalatic acids, phenols) or can be analysed in the same run (metals). Zinc was the most relevant substance; it appeared to be present in 1-2% of the rubber mass, and the water concentration in batch tests exceeded environmental quality standards. Total contents of mineral oil in crumb rubber did not fulfill the requirements either, but a regulatory exemption was granted.

5.1.2 Standard leaching test, analysing zinc

In the literature a batch-test with a liquid to solid ratio of 10 is most common, sometimes with addition of acid or alkali. Results were taken irrespective of the conditions in the test, without any reference to field conditions. It is known that solubility of metals such as copper and zinc is very dependent upon pH. The environmental relevance of these tests has not been assessed.

There are some disadvantages in batch experiments, especially for polymeric materials

- 1. polymeric granules tend to float on top of the liquid phase, thereby limiting the release of substances from the polymeric matrix.
- 2. a batch experiment is a static experiment, a flow-through system would simulate field-conditions better
- 3. a batch experiment is performed in the dark at a constant temperature, while it is known that exposure to sunlight and temperature changes can affect the stability of the polymeric matrix

To overcome the disadvantages of a batch experiment, a laboratory column study to the release of zinc from rubber infill was started in the Netherlands (Hofstra, 2007). Fresh production samples of rubber crumbs as well as rubber infill collected from soccer fields of 1 to 3 years old have been tested in a column leaching test. Moreover, column leaching was also determined in samples exposed to artificial sunlight equivalent to 1 or 3 years sunlight exposure (ISO 4892-3).

The emission of zinc was measured by the NEN 7383 column leaching test (NEN, 2004). This short test has been developed for the assessment of the leaching of inorganic substances from building materials. In this test a vertical column is filled with rubber crumbs (<4 mm particles) and eluted by an upward flow of deionised water for approximately 3 weeks until a liquid to solid ratio (L/S-ratio) of 10 has been achieved. The pH is not controlled, but is determined by properties of the material (rubber). Measurement of the inorganic compounds, pH and conductivity is performed at a L/S-ratio of 10.

The emission of zinc from rubber infill is not in agreement with patterns found for stony granular materials. In stony materials, the emission would slowly decrease (the dotted line), whereas in rubber the release is increasing. The emission patterns are illustrated in Figure 5.1.

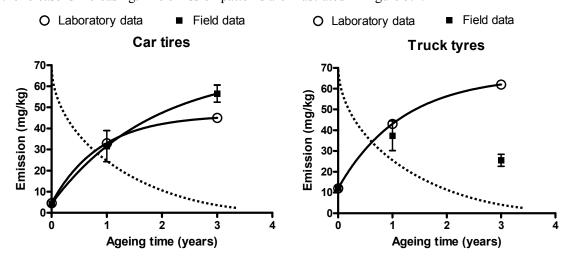


Figure 5.1 Measured emission (not cumulative!) of zinc from rubber crumbs of car tyres and truck in laboratory and field ageing experiments. Solid lines show the statistical trend along measured data, the dotted line is a typical shape of emission from stony materials (Verschoor, 2007).

We launched the hypothesis that degradation of the rubber matrix is responsible for an increasing emission of zinc (1). As extrapolation of these data suggested potential exceedances of soil, groundwater and surface water standards. A more advanced study was started, to verify the hypothesis (see section 5.1.3).

5.1.3 Indoor lysimeter study to ageing and leaching

An experiment was set-up which exposed small pieces of artificial turf (0.25 m²), filled with SBR-rubber crumbs to artificial rainfall, sunlight, ozone and a temperature cycle. The purpose is to accelerate natural ageing processes in the polymeric matrix and to measure the potential leaching over a period over several years.



Figure 5.2 Setup of the artificial turf test system. Artificial turf is exposed to UV-radiation, ozone, a temperature cycle from -5 to 40 °C and rainfall. Leachate is collected in the grey containers (taken from Hofstra, 2008).

Lysimeter 1 is filled with truck tyre crumbs, lysimeter 2 and 3 are replicates with car tyre crumbs. The lysimeters were exposed to the following regime: every 3 days 100 mm of rainfall was given in 1 hour, simulating a total rainfall of approximately 7 years; every 3 days the temperature changed from -5 to 40 °C; a constant UV exposure was given at 20-25 times the intensity of normal outdoor daylight, simulating a total UV exposure of approximately 7 years; an ozone generator was switched on starting day 39. Ozone ranged from a level of 30 ppb (normal outdoor concentration) to 300 ppb after starting a ozone generator. The cumulative ozone load simulates an expose of approximately 2.5 years.

The rainfall infiltrated through the artificial turf is collected in containers. Samples are taken after 35, 66, 95 and 120 days and zinc-concentrations are measured. More details are described in Hofstra (2008).

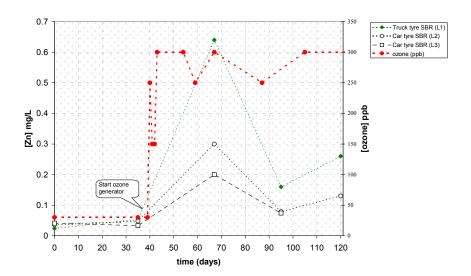


Figure 5.3 Zinc concentration (mg/l) in percolate of artificial turf with SBR-infill exposed to ozone (ppb) (data from Hofstra, 2008).

In Figure 5.3 the pattern of zinc emission from the artificial turf systems is shown. The figure shows that zinc-release increases when the ozone concentrations are elevated. The results confirm the hypothesis postulated in section 5.1.2. Unfortunately the interval between measurements is quite high and the response time between ozone exposure and elevated zinc-leaching can not be determined accurately. The sudden increase of the zinc concentration is followed by a decrease and subsequent apparent stabilisation.

The release pattern differs significantly from the characteristic release pattern of stony material. A pattern as presented in the middle graphs of Figure 4.1 or Figure 4.2 is more likely.

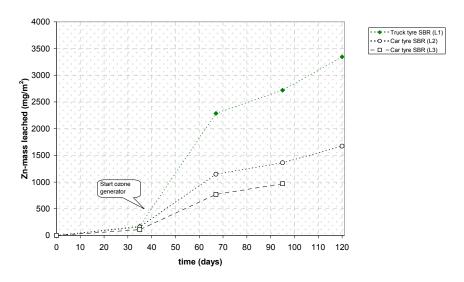


Figure 5.4 Total (cumulative) mass of zinc released (mg/m²) from artificial turf with SBR-infill exposed to ozone (ppb) (data from Hofstra, 2008). L3 was stopped after 95 days and the infill of L3 was tested further in a column leaching test.

There are some drawbacks on this study, that makes the result less reliable and not useful for a regulatory decision about permissible zinc-leaching.

For practical reasons the flow rate was set at 100 mm in one hour at an interval of three days. This flow rate is much higher than flow rates during natural rainfall and most probably has resulted in lower zinc concentrations because diffusion is the rate limiting step. At the end of the lysimeterstudy the infill of one lysimeter was collected and tested by the regular NEN 3783 column leaching test, which has a much lower flow rate (max. 10 mm/hour). It appeared that the infill material, after ageing and leaching in the lysimeter, was not exhausted but still released 51 mg Zn/kg infill. This was about 10 times the amount that was released in the lysimerstudy. It is concluded that the column study is able to release much more zinc than the lyimeterstudy.

The simulated ageing time should be considered as a rough, preliminary estimation. It is not clear if ageing rates can by extrapolated linearly, as is done in this study. Moreover, it is not clear how ageing reacts on a consorted action of UV, ozone, temperature changes and leaching of antioxidizers. Adittional research is required to find out how lysimeter leaching should be extrapolated over time.

6 Conclusions and recommendations

6.1 Conclusions

Polymeric construction products are increasingly being used under outdoor conditions. The number of applications for recycled synthetic polymeric products to be used as construction products is also growing. Knowledge of the environmental load of substances leaching from polymeric products is still limited.

A straightforward way to set environmental criteria for polymer building materials would be based on total content of substances. However this is a very worst case approach and many building materials would not fulfill the criteria. For example, rubber infill contains 8-25 g Zn/l. This exceeds even the current action values for remediation (intervention values) of soil. As substances are gradually released from the matrix, total content is not a sound criterion for risk assessment. A constant relation between total content and emission does not exist; the release is dependent on matrix properties like particle size and resistance against oxidation. Therefore the release of substances needs to be measured and rules for extrapolation of emission over time have to be derived.

It has been postulated by Van der Sloot and Dijkstra (2004) that for a number of widely different construction products the number of chemical and physical factors that control the release from those products is limited, and that the well-established release mechanisms of mineral construction products are the same as those in other products (synthetic, wood). This supposed similarity would allow the use of similar approaches and similar test methods for these construction products (CEN/TC 351 N0184, 2008). However, in several investigations mentioned in this report, convincing evidence is presented that in the case of a number of rubber and plastic materials the leaching mechanism of environmentally dangerous substances is fundamentally different from that of mineral (construction) products. Superimposed on a diffusional driven exponential decay in the release of those substances, an initial substantial increase in the release of substances may occur, of which the intensity and duration depend on a number of chemical and physical conditions, such as exposure to oxidizing agents and to elevated temperatures, and the characteristics if the matrix involved, such as degree of cross-linking. This increase is a result of what is commonly known as 'ageing' and 'weathering'.

6.2 Recommendations

The gap between the existing massive knowledge on characteristics of rubbers and plastics, in the technological world at one hand, and unprecedented environmental effects of applications of these polymeric materials on the other, that have been assessed in this report, results in recommendations for appropriate environmental investigations of these types of products. Such investigations should primarily be focussed on the understanding of the effect of a changing matrix, due to phenomena like ageing and weathering, generally consisting of a break-down with time of the degree of cross-linking. The release pattern of inorganic and organic substances from those matrices as a result of the conditions of the leaching processes occurring during outdoor use of the products involved, must be studied and related to matrix changes.

Secondly, also the identifications of leached organic substances, such a polymer weakeners, polymerisation initializers and still unknown break-down products can be included in the proposed investigations.

Additionally, we propose to develop or select bioassay methods as an additional screening tool, for the leachate of polymeric substances. With a bioassay, not only the combined effect of known substances is shown, but also the effect of unknown, forgotten or overseen substances becomes visible. A bioassay can serve as a safety-net to select potentially toxic materials for further risk assessment.

To start to fill the knowledge gap, it is recommended to start a research study of ageing and leaching from polymeric matrices with respect to expected inorganic substances. Requirements for a preliminary research proposal will be proposed in Appendix 1.

It is also recommended to refine the definition of stony material. For formally 'stony' materials with a significant organic matter content, extrapolation rules for emission of substances should be amended, because the leaching mechanism may be dominated by the properties of the polymeric matrix and not by the mineral/stony matrix. The existing leaching test methods as well as the extrapolation rules and risk assessment approach for stony materials should be amended, taking into account the matrix (in)-stability and its specific leaching mechanisms.

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Appendix 1 Research proposal 'Emissions from ageing rubber matrices'

Introduction

The mechanism of leaching of inorganic compounds form stony construction products (> 10% Al+Si+Ca) is well understood. Models for this leaching process have recently been updated for a suite of environmental systems in order to protect the environment (Verschoor et al., 2006). A number of standardized tests for these stony materials is available of which the results can be used, using these models, for estimations of emissions to be expected of toxic compounds, over periods up to a century.

For the leaching of potentially toxic compounds from *organic* materials (such as rubbers, plastics, et cetera) knowledge of the mechanisms involved is still very limited. From carbon-backbone based matrices, leaching processes of (in)organic compounds follow mechanisms that are not only inherently different from that for stony materials, also ageing effects are expected to strongly influence the leaching processes. In the case of rubber materials, it is known that due to oxidation processes, rubber structures will break down.

The different characteristics of the matrix, together with effects of ageing of organic materials complicate the issuing of legal regulations for the application of these materials as construction materials. Protection of the environment against toxic compounds leaching from stony materials is in the Netherlands warranted by the Dutch Soil Quality Decree (SQD).

The need for legal regulations for the leaching of toxic compounds from organic construction materials became urgent in recent years in cases where rubber infill on artificial turf (sports, mainly football, pitches) became increasingly applied. It appeared that from these rubber infills, produced by granulating tyres, the amount of leached zinc was expected to violate during the lifetime of the pitches, existing regulations for the environmental protection of soil.

To enable a sound modelling of emissions due to leaching processes from ageing rubbers and plastics, and consequently reformulating formulae for correct extrapolating results from standard leaching tests to real world situations, a research study is proposed. Because of the urgence for research on rubber infills, the proposal will initially be primarily focused on rubbers, with a possibility of widening the scope to plastics and to the identification of organic substances in later phases. From preliminary investigations and a quick review of relevant literature, it appeared that in such research study for rubber, three parameters are relevant in the ageing process of rubber: heat, UV-radiation and ozone. Although there exists a massive body of knowledge on rubber ageing, this knowledge has however not yet been related to long term emissions of compounds from rubber.

Overall goal

The main goal of the proposed research is to become able to correctly predict emissions of environmentally toxic compounds (such as zinc and cobalt) from rubbers and plastics after use of these type of materials over periods covering decenniums.

Proposed activities

A selection of the most frequently used rubbers and plastics in a 'second life'-form of these products (granulated or shredded forms) should be subjected to ageing experiments, and repeated column tests.

Based on the experimental results a hypothetisation on the leaching process from polymeric matrices should result in a feasible modelling of the leaching processes.

The first phase of the research proposal, dealing with different types of rubber from tyres, will be set up in a modular way, enabling a systematic building up of relevant data. The modulation comprises accelerated ageing of rubber from tyres through the application of heat (module 1), of (generated) ozone (module 2) and of UV-radiation (module 3). During the ageing experiments the rubber granules will be sprinkled with artificial rainwater, and will follow temperature cycles, both diurnal and seasonal. The sprinkled 'rainwater' will systematically be collected and analysed for zinc and cobalt.

Simultaneously, standard column experiments should be systematically performed during the test period to find out the effect of water flux on the leaching rate of metals from the organic matrix. Eventually a variable water fluxes could be applied as to mimic outdoor conditions such as drizzles, rainstorms and dry spells.

After sufficient data have been collected and the leaching and ageing mechanisms have been described, the data will be modelled according to hypothesis of the supposed physical ageing and leaching processes (module 4), and reckoning with the effects of adsorption of the supporting layers applied in pitches with artificial turf.

Preliminary scheme of the experiments in de simulated rubber ageing process:

1. Module 1

Ageing by heat treatment during one year

Keeping rubber granules at 60-80 °C

Application of a standard leaching test at regular intervals of the ageing

2. Module 2

Ageing by ozone treatment during one year

Ozone generators provide ozone concentrations at known and controlled levels

Application of a standard leaching test at regular intervals of the ageing

3. Module 3

Ageing by UV treatment during one year

Prolonged exposure to intense hard UV-radiation of rubber granules (sooted and non-soooted).

4. Module 4

Description of leaching and ageing mechanisms for rubbers and plastics and modelling of the data according to the hypothesis to be developed of the supposed processes should be aimed at input of results of standard column test (albeit possible slightly modified), to enable a feasible incorporation in existing legislation.

Implications for building material policy will depend on the results. The following policy options are foreseen:

- 1. Implementation of new or additional extrapolation equations using the current stand column leaching test. For example, a simplified equation based on organic matter content similar to the soil type correction for soil quality criteria in the Dutch Soil Quality Decree. In this case the additional research is incidental and not to be repeated for each test material.
- 2. The investigation can also result in a recommendation for a pretreatment of the test material, for example exposure to UV, ozone, heat. Optimal and representative test conditions should be defined. The intention is to maintain the current column leaching test and either (1) change the extrapolation equation or (2) to recommend a pretreatment, or a combination of (1) and (2).

Project coordination

For the co-ordination of the study, experts form the National Institute for Public Health and the Environment (RIVM) in Bilthoven are available. The experimental part of the study, with respect to rubber ageing technology, can be executed at or facilitated by the Department of Elastomer Technology and Engineering at the Faculty of Engineering Technology of the University of Twente. For the modelling part, RIVM will be in charge. Execution of the standard test can be outsourced to subcontractors (c/o ECN, VITO, INTRON and commercial analytical laboratories).



Appendix 2 Substance lists

Table A2.1. Overview of substances in Priority Substances List and Dutch Soil Quality Directive. x = priority substances, x = priority substances, x = priority substance.

	Element or CAS-number	Priority substance WFD	Emission limit value (mg/m²) Monolithic material	Emission limit value (mg/kg) Granular material	Total content (mg/kg d.s.)
Anorganic substances					
Antimony	Sb		8.7	0.16	-
Arsenic	As	х	260	0.9	-
Barium	Ва		1500	22	-
Cadmium	Cd	xx	3.8	0.04	-
Chromium	Cr		120	0.63	-
Cobalt	Со		60	0.54	-
Copper	Cu		98	0.9	-
Mercury	Hg	xx	1.4	0.02	-
Lead	Pb	XX	400	2.3	-
Molybdenum	Мо		144	1	-
Nikkel	Ni	х	81	0.44	-
Selenium	Se		4.8	0.15	-
Tin	Sn		50	0.4	-
Vanadium	V		320	1.8	-
Zink	Zn		800	4.5	-
Bromide	Br ⁻		670	20	-
Chloride	Cl ⁻		110000	616	-
Fluoride	F ⁻		2500	55	-
Sulphate	SO ₄ ²⁻		165000	1730	-
Organic substances					
Alachlor	15972-60-8	х			
Anthracene	120-12-7	XX			20
Atrazine	1912-24-9	XX			
Benzene	71-43-2	х			1
Brominated difenylethers		XX			
C10-13-chlooralkanen	85535-84-8	XX			
Chloorfenvinfos	470-90-6	Х			
Chloorpyrifos	2921-88-2	XX			
Chrysene	218-01-9				10
1,2-dichloorethaan	107-06-2	Х			
Dichloormethaan	75-09-2	х			
Bis(2-ethylhexyl)ftalaat (DEHP)	117-81-7	xx			

Diuron	330-54-1	XX	
Endosulfan	115-29-7	XX	
Alfa-endosulfan	959-98-8	Х	
Ethylbenzene	100-41-4		1.25
Fluorantheen	206-44-0	Х	35
Hexachloorbenzeen	118-74-1	XX	
Hexachloorbutadieen	87-68-3	XX	
Hexachloorcyclohexaan	608-73-1	XX	
Gamma-HCH (lindaan)	58-89-9	Χ	
Isoproturon	34123-59-6	XX	
Naftaleen	91-20-3	XX	5
Nonylfenolen	25154-52-3	XX	
4-(para)-nonylfenol	104-40-5	Χ	
Octylfenolen	1806-26-4	XX	
Para-tert-octylfenol	140-66-9	Х	
Pentachloorbenzeen	608-93-5	XX	
Pentachloorfenol	87-86-5	XX	
Phenol	108-95-2		1.25
Polycyclice aromatic hydrocarbons (PAH)		XX	50
Benzo(a)antracene	56-55-3		40
Benzo(a)pyrene	50-32-8	Х	10
Benzo(b)fluorantheen	205-99-2	Х	40
Benzo(g,h,i)peryleen	191-24-2	Х	40
Benzo(k)fluorantheen	207-08-9	Х	40
Indeno(1,2,3-cd)pyreen	193-39-5	Х	40
Simazine	122-34-9	XX	
Toluene	108-88-3		1.25
Tributyltin	688-73-3	XX	
Tributyltin (kation)	36643-28-4	Х	
Trichloorbenzenen	12002-48-1	XX	
1,2,4-trichloorbenzeen	120-82-1	х	
Trichloormethaan	67-66-3	х	
Trifluraline	1582-09-8	XX	
Xylenes (sum)			1.25

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