

Environmental and Health Hazards of Chemicals in Plastic Polymers and Products

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Abstract

Plastics are extremely diverse in terms of chemical composition, properties and possible applications, and are widely distributed in the society and the environment. In the last 15 years the global annual production has doubled, reaching 245 million tons in 2008. Several of the chemicals used to produce plastics are hazardous for human health and the environment. These, and their degradation products, may be released during the life cycle of a plastic product. The plastic polymers are not considered as toxic, but in plastic products there may be non-bound residual monomers, polymerisation chemicals, degradation products, and additives which have toxic properties.

The overall aim of this thesis, which is based on five papers [I-V], was to study the environmental and health hazards of chemicals in plastic polymers and products. Leaching tests, toxicity tests and Toxicity Identification Evaluations (TIEs) were made on plastic products [I, II], synthetic textiles [III], and discarded electronic products [IV]. A hazard ranking model was developed and used to rank plastic polymers based on monomer composition and environmental and health hazard classifications [V]. Also other hazardous substances needed to produce each polymer were identified [V].

Substances causing acute toxicity to *Daphnia magna* (water flea) leached from one third of all 83 plastic products/textiles even during short term (1-3 d) leaching in deionised water [I-III]. The toxic leachates came mainly from products that were soft to semi-soft, i.e. plasticised PVC (11/13) and polyurethane (3/4), and from epoxy products (5/5), and from synthetic textiles made of various plastic fibres [I-III]. The electronic product leachates that were acutely toxic came from mixed material and metal components, and not from plastics components. TIEs, performed on some leachates, indicated that the major toxicants were hydrophobic organics for the plastic product and synthetic textile leachates [I-III], and metals for the electronic product leachates [IV].

The polymers ranked as most hazardous are made of monomers classified as mutagenic and/or carcinogenic (category 1A or 1B). These belong to the polymer families of polyurethanes, polyacrylonitriles, PVC, epoxy resins, and styrenic copolymers (ABS, SAN and HIPS), and have a large global production (1-37 million tons/year). A considerable number of polymers, 31 out of 55, are made of monomers that belong to the two highest of the ranking model's five hazard levels [V]. Examples of such polymers, with a large global production (1-5 million tons/year), are phenol formaldehyde resins, unsaturated polyesters, polycarbonate, polymethyl methacrylate, and urea-formaldehyde resins [V].

The ranking model was useful for identifying and comparing hazardous substances, and the results from the hazard identification can be used for further hazard and risk assessment for decisions on the need for risk reduction measures, substitution or phase out.

In conclusion, considering the extensive dispersion in the society and the environment, the growing production, and the release and use of many hazardous chemicals, it is important to further assess the risks of chemicals associated with plastic polymers and products.

Key words: plastics, plastic products, plastic polymers, consumer products, environmental hazards, environment, health hazards, human health, hazard ranking, hazard assessment, chemical ranking, hazard identification, hazardous chemicals, emissions, toxic substances, toxicity, acute toxicity, aquatic toxicity, *Daphnia magna* Toxicity Identification Evaluation, TIE, leaching, leachates, product leachates

Sammanfattning (Summary in Swedish)

Plastmaterial uppvisar en stor mångfald i kemisk sammansättning, egenskaper och användningsområden, och har en stor spridning i samhället och i miljön. De senaste 15 åren har den globala årsproduktionen fördubblats, till 245 miljoner ton år 2008. Flera av kemikalierna som används för att tillverka plast är skadliga för människors hälsa och miljön. Dessa, eller deras nedbrytningsprodukter, kan avges under en plastprodukts livscykel. Plastpolymererna är inte betraktade som toxiska, men i plastprodukterna kan det finnas icke-bundna restmonomerer, polymerisationskemikalier, nedbrytningsprodukter och additiv som har toxiska egenskaper.

Det övergripande syftet med denna avhandling, som baseras på fem artiklar [I-V], var att studera miljö- och hälsofarorna av kemikalier i plastpolymerer och produkter. Lakteter, toxicitetstester och toxicitetsidentifiering (TIE) utfördes på plastprodukter [I, II], syntetiska textilier [III] och uttjänta elektroniska produkter [IV]. En farorankningsmodell utvecklades och användes för att rangordna plastpolymerer med avseende på deras kemiska beståndsdelar (monomerer) och miljö- och hälsofaroklassificeringar [V]. Även andra miljö- och hälsofarliga kemikalier som behövs för att tillverka respektive polymer identifierades [V].

En tredjedel av alla 83 plastprodukter/textilier släppte ifrån sig ämnen som orsakade akut toxicitet för *Daphnia magna* (vattenloppa), trots att lakningen pågick under kort tid (1-3 dygn) i avjoniserat vatten. De toxiska lakvattnen kom huvudsakligen från produkter som var mjuka till halvmjuka, dvs mjukgjord PVC (11/13) och polyuretan (3/4), och från epoxiprodukter (5/5), och från textilier gjorda av olika plastfibrer [I-III]. Elektronikprodukternas toxiska lakvatten kom från metall- eller blandmaterialfraktionen, inte ifrån den rena plastfraktionen [V].

Toxicitetsidentifieringen, som utfördes på några av lakvattnen, indikerade att giftigheten huvudsakligen orsakades av hydrofoba organiska ämnen för plastprodukterna och de syntetiska textilierna [I-III], och av metaller för elektronikprodukterna [V].

De högst farorankade polymererna är gjorda av monomerer som är klassificerade som mutagena och/eller cancerogena (kategori 1A och 1B). Dessa tillhör polymerfamiljerna polyuretaner, polyakrylonitriler, PVC, epoxiplast och styrensampolymerer (ABS, SAN och HIPS), och har en hög global produktion (1-37 miljoner ton/år). Ett betydande antal polymerer (31 av 55) är gjorda av monomerer som tillhör de två högsta av farorankningsmodellens fem faronivåer [V]. Exempel på sådana polymerer, som dessutom har en hög global produktion (1-5 miljoner ton/år), är fenolformaldehyd, omättad polyester, polykarbonat, polymetylmetakrylat och ureaformaldehyd. Farorankningsmodellen var ett bra verktyg för identifiering och jämförelse av farliga kemikalier, och resultaten från faroidentifieringen kan användas för fortsatt riskbedömning inför beslut om behov av riskminskningsåtgärder, substitution eller utfasning.

Sammanfattningsvis är det viktigt att ytterligare bedöma riskerna av kemikalier som rör plastpolymerer och plastprodukter, inte minst på grund av den stora spridningen i samhället och miljön, den ökande produktionen, och användningen av många farliga kemikalier.

Sökord: plast, plastprodukter, plastpolymerer, konsumentprodukter, miljöfaror, miljö, hälsofaror, hälsa, farorankning, kemikalierankning, faroidentifiering, farobedömning, farliga kemikalier, utsläpp, giftiga ämnen, toxicitet, akut toxicitet, akvatisk toxicitet *Daphnia magna*, toxicitetsidentifiering, TIE, lakvatten, produktlakvatten

List of papers

This thesis is based on the following papers:

- I. Lithner, D., Damberg, J., Dave, G., Larsson, Å., 2009. Leachates from plastic consumer products – Screening for toxicity with *Daphnia magna*. *Chemosphere* 74, 1195-1200.
- II. Lithner, D., Nordensvan, I., Dave, G., 2011. Comparative acute toxicity of leachates from plastic products made of polypropylene, polyethylene, PVC, acrylonitrile-butadiene-styrene and epoxy to *Daphnia magna*. *Submitted*.
- III. Lithner, D., Ivåker, J., Dave, G., 2011. Comparative acute toxicity of leachates from synthetic textiles made of plastic fibres to *Daphnia magna*. *Manuscript*.
- IV. Lithner, D., Halling, M., Dave, G., 2011. Toxicity of electronic waste leachates to *Daphnia magna* - Screening and Toxicity Identification Evaluation of different products, components and materials. *Submitted*.
- V. Lithner, D., Larsson, Å., Dave, G., 2011. Environmental and health hazard ranking and assessment of plastic polymers based on chemical composition. *Submitted*.

The papers are referred to by their Roman numerals. These papers appear after the summarizing chapter of this compilation thesis. For paper V supplementary materials (Report S1 and Table S1) are provided at the end of the thesis.

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1. Introduction

Humans, animals, plants, and microorganisms are exposed to a very large number of chemicals that are released from many different sources and may enter the organisms by different routes. Many of these chemicals may not cause harm individually, if they occur in low concentrations, but the combination effects from exposure to all these chemicals, even at low concentrations, during a prolonged period of time, may lead to adverse effects for human health and the environment.

Chemical diversity, abundance and hazardousness are one of the major environmental challenges of today. On the contrary to biological diversity, chemical diversity can be problematic from an environmental point of view. There is not sufficient knowledge to provide protection for human health and the environment against all these chemicals, which according to the European Inventory of Existing Commercial Chemical Substances (EINECS) is slightly above 100.000 (Ex ECB, 2011).

Plastic polymers and products, which are the focus of this thesis, are extremely diverse, both in terms of chemical composition, properties and possible applications. Several hazardous substances may be released during the life cycle of a plastic product; and considering the large and growing global consumption of plastic products, and their omnipresence and persistence in the environment, there is a need for assessing the hazards and risks of this large material group.

The overall aim of this thesis was to study the environmental and health hazards of chemicals in plastic polymers and products from a toxicological perspective.

1.1. Plastics in the society

Production of plastic materials started on an industrial scale in the 1940s and 1950s. In the last 15 years the global annual production of plastics has doubled, reaching 245 million tons in 2008 (calculated from PlasticsEurope, 2009). The annual plastic material consumption per capita in Western Europe, Canada, USA and Mexico, was 100 kg in 2005, which was ten times as much as African countries and five times as much as Asian countries, excluding Japan (PlasticsEurope, 2009). This means that there is a large potential for further increased consumption.

The world plastic demand is dominated by the thermoplastic types polypropylene (21%), low- and linear low-density polyethylene (18%), polyvinyl chloride (17%), and high-density polyethylene (15%). Other plastic types with high demand are polystyrene and expandable polystyrene (8%), polyethylene terephthalate, PET (7%, excluding PET fibre), and the thermosetting plastic polyurethane (6%; figures for 2007; Plastics Europe MRG, 2008).

Plastic polymers are not only used to make plastic products but also to make synthetic fibres, foams, coatings, adhesives and sealants, which are used in numerous applications, both indoors and outdoors. The synthetic fibres account for an additional 40 million tons/year (figures for 2009; Engelhart, 2010). In Europe the use of plastics is dominated by packaging (38%), followed by building and construction (21%), automotive (7%), electrical and electronic (6%), and other sectors (28%) such as medical and leisure (PlasticsEurope, 2009). Plastic use is dominated by single use or short term use, and at the same time most plastics are extremely persistent in the environment.

Plastics are important in our society and offer many benefits for human health and the environment, for instance (PlasticsEurope, 2009; Andrady and Neal, 2009):

- Plastic packaging protects food and goods from getting wasted and/or contaminated and thereby saves resources.
- The light weight packaging material (due to high strength-to-weight ratio) saves fuel and decreases emissions during transportation.
- Plastic water supply systems and storage containers/tanks provide clean water.
- Light plastic materials (replacing metals) in cars and aircraft save fuel and decrease emissions.
- Efficient plastic insulation materials in buildings save energy and provide climate protection.
- Plastic protective clothing and safety equipment (e.g. fire proof materials, helmets, air bags) protects from injury.
- Plastic products for medical applications are very important and contribute to improved health (e.g. blood pouches, tubings, disposable syringes, prosthesis).
- Solar heaters and solar panels, in parts made of plastics, provide renewable energy.

1.2. Plastics in the environment

Consumption, of course, leads to waste, and in the case of plastics, large volumes of extremely persistent waste are created. The problems with plastic waste are many.

1.2.1. Plastic waste management

The largest plastic waste fraction goes to landfill. For Europe the average is around 50% (Plastics Europe, 2009). Landfill space is scarce in many countries which leads to emissions from transportation over long distance, and increasing the landfill area may require valuable land. Emissions from landfills may also contaminate ground and surface water. Alternatives to landfilling are mechanical recycling, energy recovery, or chemical recovery. The heterogeneity of plastic products and types obstructs recycling, or makes plastic recycling difficult in many cases (Hopewell, 2009). Recycling is possible for some fractions, but in order to get a similar, or not a too low grade product, a homogenous fraction is required, which requires labour intensive sorting. Plastic waste for recycling is often transported over

long distances, for instance exported from the industrial to the developing countries, particularly in Asia (PlasticsEurope, 2010). Energy recovery by incineration of plastic waste in Europe has a larger share (30 %), than recycling (20%) (PlasticsEurope, 2009). Combustion of plastics may cause emissions of hazardous substances and contributes to global warming (since most plastics are fossil based). Chemical recovery is under development and means that chemicals, e.g. raw materials such as monomers and gases, are recovered/converted from the plastic material. This can, for instance, be done by controlled thermal degradation such as thermolysis, which is a non-catalytic cracking process (Al-Salem, 2009).

Some solutions to plastic waste and recycling problems have resulted in new uses for plastic waste, and sometimes even more chemically complex products are created, and further dispersion in the environment may follow. For instance in Bangalore, India, plastic asphalt is used as an alternative road material. The asphalt is made from churned plastic waste (mainly composed of plastic bags, PET bottles and thin plastic film) which is blended with bitumen. (Khullar, 2009; Gulati, 2010). The roads are expected to last for 4-6 years, and the end of life management is not described.

1.2.2. Plastic waste in the marine and terrestrial environment

A very large fraction of plastic waste ends up as litter in the terrestrial and marine environment. The marine environment is especially exposed and has been most widely studied. Large and increasing amounts of plastic products, debris, fragments and even micro-particles are found in the open ocean, on the surface, in the deep ocean and ocean bed, in coast lines, in sediments, and in organisms (Barnes et al., 2009; Thompson et al., 2004). The sources are not solely from dumping at sea, but a large quantity is likely to come from land sources, e.g. littering on land (especially coastal areas), plastics blown from landfill sites, and sewage effluents, as well as spillage during transport and accidents (Barnes et al., 2009). This plastic waste can be transported far by currents, for instance the great oceanic gyres (Yamashita, 2007). It can also accumulate in the centre of the gyres, as shown by e.g. Moore (2001; 2008) and Lavender Law et al. (2010). The plastic products and debris are fragmented into smaller pieces, even to sizes below 5 mm, called microplastics (Barnes et al., 2009).

Plastic fragments in the marine environment have been reported in scientific reports since the late 1960s (reviewed by Barnes et al., 2009). However, the extent of this plastic pollution, especially by microplastics, is much more prevalent than previously thought, both in terms of greater quantities and smaller particles. For instance, in surface trawl studies (net mesh size 330 μm) plastics were found at 55 of 76 locations in the Kuroshio Current area (North Pacific), in quantities ranging 0–3.52x10⁶ pieces/km², with a mean abundance of 1.74x10⁵ pieces/km² (Yamashita, 2007); and near the central pressure cell of the North Pacific subtropical high a mean abundance of 3.34x10⁵ plastic pieces/km² were found (Moore et al.,

2001). The particle sizes 1-3 mm constituted 62% of all marine plastic pieces (Yamashita, 2007). Even smaller sizes of plastic pieces $\leq 20 \mu\text{m}$ in sediment have been reported by (Thompson et al., 2004; Ng and Obbard, 2006).

Effects from entanglement or ingestion of plastic waste, including suffocation or blocking of digestive tract causing death, have been well documented for birds, turtles, and marine mammals (reviewed by Gregory, 2009). The consequences of exposure to microplastic in filter feeding organisms and deposit feeders are not yet known. Studies of exposure to microplastics in amphipods, lugworms, barnacles, sea cucumbers, and mussels have shown that the organisms ingest the microplastics (Thompson et al., 2004; Graham and Thompson, 2009; Browne et al, 2008). Further studies on the mussels showed that the microplastics were translocated from the gut to the circulatory system and were found in the hemocytes (blood cells; Browne et al., 2008).

The ability of plastics to sorb persistent organic pollutants may cause additional problems. In marine polypropylene pieces Mato et al. (2001) found 100.000 to 1 million times higher concentrations of PCBs (polychlorinated biphenyls) and DDE (dichlorodiphenyl-dichloroethylene) than in the surrounding seawater. If these pollutants are released when ingested by an organism remains to be investigated. Marine plastics can also be vectors for transport of sessile alien invasive species (Barnes, 2005) and may cause damage to ecosystems.

1.2.3. Plastic degradation

The persistence of plastic waste is another problem. Most plastic polymer types are resistant to biodegradation, i.e. degradation by microorganisms, and the two most abundant ones, polyethylene and polypropylene, are extremely resistant to biodegradation (Nicholson, 2006). In a polyethylene polymer only 0.1% of the carbon will be transformed into CO_2 per year by biodegradation under optimal laboratory exposure conditions, according to Andrady (1998). There are a few biodegradable plastics which today only have a minor, but growing, share in the plastic market. Not all of them, however, are completely biodegradable in the natural environment (Rudnik, 2008; O'Brine and Thompson, 2010).

Non-biodegradable polymers can be degraded by heat, oxidation, light, ionic radiation, hydrolysis and mechanical shear, and by pollutants such as carbon monoxide, sulphur dioxide, nitrogen oxide and ozone (Ravve, 2000). This causes the polymer to get brittle, to fragment into small pieces and to release degradation products. Different degradation mechanisms exist and which of them that will dominate depends on the polymer type. Chain scission involves breaking the chemical bonds in the polymer molecule, and is often random, but for some polymers it proceeds at the polymer end chains and the initial monomers are broken off, a process called depolymerisation (Alger, 1997; Braun, 2005). Another

degradation mechanism is chain stripping in which the side atoms/groups attached to polymer main chain are released; usually these are volatile molecules (Wilkes, 2005). Crosslinking can also occur for some polymers and bonds are then created between the polymer chains (Wilkes, 2005). Complete conversion of the plastic product and its breakdown products, into carbon dioxide, water and inorganic molecules by photo- and biodegradation (Gregory and Andrady, 2003), is for most plastic types extremely slow (Innocenti, 2003). In the marine environment degradation is especially slow, since degradation mainly is likely to occur by solar radiation and slow thermal oxidation (Gregory and Andrady, 2003). This means that the time frame for complete degradation is very long and could, in some situations, be several hundred years.

1.3. Regulations for hazardous chemicals in articles/plastic products

The European chemicals legislation, REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) aims to improve the protection of human health and the environment through an earlier and improved identification of the intrinsic properties of chemical substances (European Commission, 2011a). Provisions are laid down for substances and preparations and shall also apply to the use of these chemicals in articles (European Parliament and Council, 2006) and, thereby, to some extent cover chemicals in articles. For the finished article the requirements are not as far reaching as for single substances and preparations. Monomers and polymers are less strictly regulated than other chemicals, since there are some exemptions from the general requirements in REACH (ECHA, 2008).

However, in the European Union there are restrictions for use and even bans for some substances in certain product groups. The ones applicable to plastics and plastic products are for instance:

- The phthalate plasticisers DEHP (di(2-ethylhexyl) phthalate), DBP (dibutyl phthalate) and BBP (benzyl butyl phthalate) in toys and child care articles, at concentrations >0.1% by mass (European Parliament and Council, 2006).
- The phthalate plasticisers DINP (diisononyl phthalate), DIDP (diisodecyl phthalate) and DNOP (di-n-octylphthalate) in toys and child care articles which can be placed in the mouth (concentrations >0.1% by mass; European Parliament and Council, 2006).
- Cadmium for giving colour to plastics, or used as stabilisers in PVC (European Parliament and Council, 2006).
- The flame retardants polybrominated biphenyls (PBB) or polybrominated diphenyl ethers (PBDE) in electronic products (RoHS-directive; European Parliament and Council, 2003).
- Bisphenol A in baby bottles (from 1st March 2011; European Commission, 2011b).

Recently (17 February 2011), the European Commission announced a ban on use of six substances which is to be effective within three to five years, unless an authorisation has been granted to individual companies for their use (European Commission, 2011c). Four of them are used in plastics, i.e. the phthalate plasticisers DEHP, BBP and DBP, mainly used in PVC, and 4,4'-methylenedianiline (MDA) used as a curing agent for epoxy resins.

Also by international conventions there are regulations of use for certain substances. The Stockholm Convention on Persistent Organic Pollutants (POPs) requires the parties of the convention to eliminate or reduce the use of the listed POPs. Of the chemicals used in plastics some of the brominated flame retardants are listed. These include the polybrominated diphenyl ethers tetra-, penta-, hexa-, hepta-, and octaBDE and the polybrominated biphenyl hexaPBB (Secretary-general UN, 2009; UNEP, 2001).

The European Stabilizer Producers Association has made a voluntary commitment to replace lead stabilisers in PVC in the EU member countries by 2015 (Vinyl 2010, 2011).

There are no general requirements on release of hazardous chemicals from plastic products or for testing release, but there are some requirements for certain product groups. For instance, for plastic food contact materials there are EU directives which e.g. regulate migration levels and lists permitted additives (European Commission, 2011d). There is also a directive laying down the basic rules necessary for testing migration (release) from plastic materials and articles intended to come into contact with foodstuffs (European Council, 1982).

1.4. Plastic composition and hazardous chemicals

Plastic products are made from plastic polymers to which additives are added to enable processing and/or to give certain desired properties for a specific application (OECD, 2004). The polymers are made by polymerising monomers into macromolecular chains. These monomers are almost exclusively derived from non-renewable crude oil. Approximately 4% of world oil demand is used as raw materials for plastic production (British Plastic Federation, 2011).

Other substances (besides monomers) are often needed for polymerisation to occur, for instance initiators, catalysts, and depending on manufacturing process, solvents may also be used. The resulting plastic polymer can be blended with different additives, for instance plasticisers, flame retardants, heat stabilisers, antioxidants, light stabilisers, lubricants, acid scavengers, antimicrobial agents, anti-static agents, pigments, blowing agents and fillers, and is finally processed into a plastic product. There are many different plastic polymers and several thousand different additives, which results in an extremely large variation in chemical composition of plastic products (Rosato, 1998).

Plastic polymers are not particularly reactive and their large size limit transport across biological membranes (Anastas et al, 2000). They are, therefore, not considered as toxic. In the polymeric material, however, non-polymeric components such as residual monomers, oligomers, low molecular weight fragments, catalyst remnants, polymerisation solvents and a wide range of additives can be present (Crompton, 2007). Several of these are hazardous to human health and the environment, for instance carcinogenic, mutagenic, toxic for reproduction, sensitising and hazardous to the aquatic environment with long lasting effects. Since the non-polymeric compounds usually are of low molecular weight and are either weakly bound or not bound at all to the polymeric macro-molecules, they, or their degradation products, can be emitted from the plastic product (Crompton, 2007; OECD, 2004) to air, water or other contact media (e.g. food).

The content of non-polymeric substances varies between different plastic polymers and products. The residual monomer content depends on polymer type, polymerisation technique and techniques for reducing residual monomer content (Araújo, 2002). The contents presented for various polymers, in a review by Araújo (2002), was shown to vary from no or very low levels (100 ppm) to up to 40.000 ppm (i.e. 0.0001-4%). Also the amount of additives used is highly variable. PVC is the plastic type that requires by far the most additives. Of the world production of additives PVC alone accounts for 73% by volume, polypropylene and polyethylene account for 10 %, and styrenics account for 5% (Murphy, 2001).

Many additives are hazardous for human health and the environment. Some are especially hazardous, for instance brominated flame retardants used to retard ignition and prevent fire from spreading; some phthalate plasticizers mainly used to make PVC flexible; and lead heat stabilizers used to prevent degradation of PVC during processing (Murphy, 2001). Several polybrominated flame retardants are very persistent, very bioaccumulating and toxic, and are listed in the Stockholm Convention on Persistent Organic Pollutants (POPs) (Secretary-general UN, 2009). Among the phthalate plasticisers the most hazardous ones, i.e. BBP, DEHP and DBP, are classified as toxic for reproduction (category 1B). BBP is also very toxic to aquatic organisms with long lasting effects (European Parliament and Council, 2008; European Commission, 2009). In addition, these phthalates, as well as DEP (diethyl phthalate) and DCHP (dicyclohexyl phthalate), are being evaluated for endocrine disrupting properties (Groshart and Okkerman, 2000; Okkerman and van der Putte, 2002). The lead compounds used in heat stabilizers are classified as toxic for reproduction (category 1A), very toxic to the aquatic environment with long lasting effects (both acute and chronic), and may cause damage to organs (European Parliament and Council, 2008).

1.5. Release and fate

Release of chemicals associated with plastic products may occur in all phases of the life cycle, i.e. during production, use, and end-of-life (Figure 1). The environmental fate of the polymer and of the substances released during the life cycle, including the degradation products, as well as the bioaccumulation potential, will affect the exposure for humans and the environment. The physical chemical properties of these substances, e.g. boiling point, vapour pressure, water solubility, and octanol-water partition coefficient, can be used to predict the environmental fate and bioaccumulation potential of these substances. Since plastic products are composed of many different chemicals, and the main part of these broken down into something completely different, this complicates the predictions.

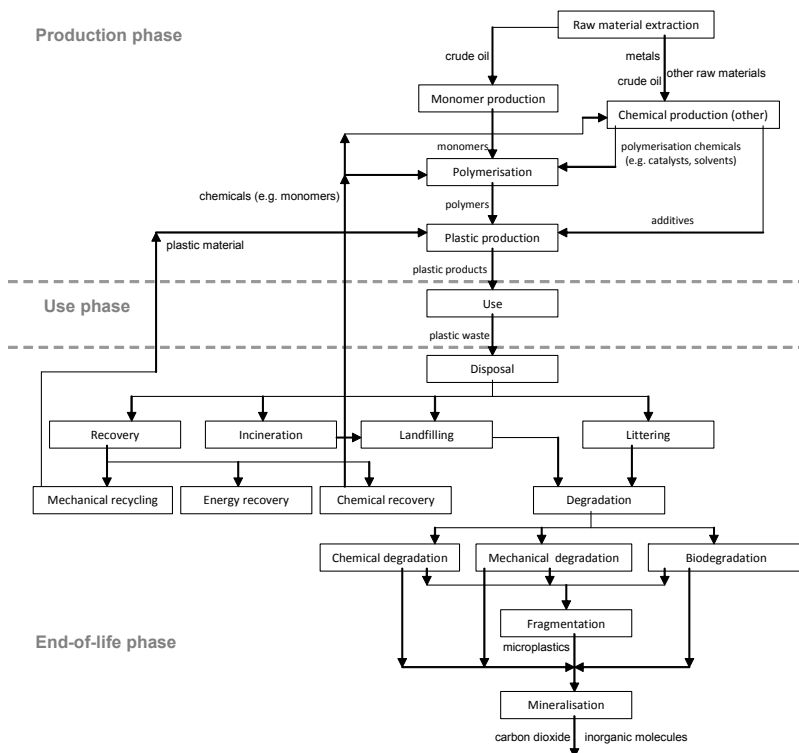


Figure 1. The life cycle of a plastic product (excluding energy input and emissions).

1.5.1. Release and release potential

The data of emissions to air and water from production of monomers, polymers and plastic products are very scarce. In EU risk assessment reports available for some of the monomers, there are a few emission data from polymer production. These data show varying emissions

between different production sites and different polymers (European Commission (JRC), e.g. 2002a; 2002b; 2004; 2010).

Release of hazardous substances from plastic products to air, extraction fluids, water, food, food simulants, saliva and sweat have been shown by chemical analysis. Examples of substances studied and released from various plastic products include phthalates (Rijk and Ehlert, 2001; Tønning et al., 2010), brominated flame retardants (Kim et al., 2006), bisphenol A (Brede et al., 2003; Geens et al., 2010; Sajiki et al., 2007; Olea, 1996), bisphenol-A dimethacrylate (Olea, 1996), lead, tin and cadmium (Al-Malack, 2001), formaldehyde and acetaldehyde (Mutsuga et al., 2006; Özlem, 2008), 4-nonylphenol (Fernandes et al., 2008; Loyo-Rosales et al., 2004), MTBE (methyl tert-butyl ether), benzene (Skjevraak, 2003) and many other volatile organic carbons (Henneuse-Boxus and Pacary, 2003; Lundgren et al., 1999). In several of the mentioned studies the released concentrations are low (e.g. compared to guideline values), but in others they are considerably higher.

The size and type of emissions from plastic products are controlled by many factors. The content of non-polymeric substances controls what can be released, while other factors control the potential of release into a surrounding medium, i.e. the migration potential. Migration is generally favoured if the polymer matrix is permeable; if the size of gaps between polymer molecules is larger than the size of migrant; if the migrant is small, has a similar solubility parameter as the polymer and is volatile; if the temperature is high; and if the surrounding medium is water for water soluble migrants, fat containing for hydrophobic migrant and acidic for metals (Brydson, 1999; Sheftel, 2000).

1.5.2. Degradation products

The degradation products formed during degradation (described in 1.2.3.) will vary depending on polymer type (Ravve, 2000). The type and quantity of degradation products formed may also be influenced by degradation mechanisms, presence of polymerisation impurities, and surrounding factors, e.g. temperature and oxygen (La Mantia, 2002; Ravve, 2000). During thermal degradation nitrogen-containing plastics (e.g. nylons, polyacrylonitrile, and polyurethanes) release hydrogen cyanide; chlorine-containing materials (e.g. PVC) release hydrogen chloride; and fluorine-containing polymers (e.g. polyvinylidene fluoride and PTFE) release hydrogen fluoride by a chain stripping mechanism (Fardell, 1998; Lokensgard and Richardson, 2003; Ravve, 2000). Polymers capable of depolymerisation by chain scission include polymethyl methacrylate, polytetrafluoroethylene, and polyoxymethylene, which can depolymerise completely into their initial monomers. Also polystyrene, polyesters (e.g. PET and polycarbonate), nylons and polyurethanes can depolymerise to some extent into their monomers (Alger, 1997; Ravve, 2000; Allen and Edge, 1992; La Mantia, 2002). All plastic types emit carbon monoxide and carbon dioxide upon burning (Fardell, 1998).

1.6. Exposure

For workers in the plastics industry the main route of exposure to toxic substances is by inhalation and absorption through the lungs, which according to Lokensgard and Richardson (2004) accounts for nearly 90 percent of the toxic symptoms observed in the plastics industry. This is quite expected since many of the hazardous chemicals used in plastic production are volatile organic compounds (VOCs). The VOCs are mainly emitted during the production phase, but also during the use and the end of life phase. This causes indoor air pollution which may be harmful for human health. VOCs also contribute to elevated ground-level ozone levels which may damage vegetation, can irritate the respiratory system, aggravate asthma and lung diseases, cause permanent lung damage, and affect the immune system (US EPA, 2011).

For consumers exposure to chemicals released from a plastic material during the use phase may vary greatly between different products. The exposure may for instance come from indoor air, food, water, and skin contact, but in most cases this is not likely to be so large that it will result in adverse effects. However, the actual exposure does not come from only one product but from a whole array of different plastic products, and exposure to a mixture of chemicals will often be continuous. Chemicals used in plastics have been detected in humans. Mainly presence of phthalates and bisphenol A, (reviewed by Koch and Calafat, 2009) and brominated flame retardants (Thomsen et al., 2010) have been studied. The main part of available research on chemicals associated with plastics is focusing on these substances.

Some consumer categories are particularly sensitive to hazardous chemicals, for instance infants, and larger margins of safety are, therefore, required. In Canada (2008) and the EU (2011), baby bottles made of polycarbonate have been banned because of the risk of bisphenol A leaching from the bottle. Bisphenol A has, within the EU strategy on endocrine disruption, preliminary been assigned category 1 based on evidence on human effects and high level of concern due to the risk of exposure, and is subject for evaluation for endocrine disrupting properties (Groshart and Okkerman, 2000).

At the same time, epoxy lining is promoted, and also used in some countries, as a very cost efficient alternative to re-piping in drinking water supply systems (Selvakumar et al., 2002). Epoxy lining means that the epoxy resin is injected and blown through to the piping system to prevent leaks and increase service life (Selvakumar et al., 2002). The most important epoxy resin (>80% of the market) is made from bisphenol A and epichlorohydrin (Gnanou and Fontanille, 2008). Both substances are classified as skin sensitizing, and epichlorohydrin is, in addition, classified as carcinogenic (category 1B). Migration of bisphenol A into food from epoxy lined cans have been shown (e.g. Sajiki et al., 2007; Geens et al., 2010).

Few data on measured environmental concentrations of plastic chemicals exist. In the EU drinking water directive the only parametric (limit) values related to plastic are for vinyl chloride, epichlorohydrin and metals (European Council, 1998). In the Swedish environmental monitoring program some of the plastic chemicals are included or have been screened, e.g. brominated flame retardants, phthalates, bisphenol A, and organotin compounds (Swedish EPA, 2007). Predictions of environmental concentrations (PEC) can be done for selected hazardous chemicals used in plastics.

1.7. Effects

Effects from chemical exposure can be studied from a human toxicological perspective and an ecotoxicological perspective. For the laboratory studies in this thesis aquatic ecotoxicological tests have been used to study effects.

In the field of ecotoxicology there are many ways to study effects of chemicals by using biological assays. This can be done by using:

- laboratory tests or field studies,
- *in vivo* (within a living organism) tests, which is most common, or *in vitro* (isolated organ, tissue, cell or biochemical system) tests,
- acute or chronic tests on a variety of test organisms (aquatic or terrestrial),
- species representing one or several trophic levels,
- single species or communities,
- various toxic endpoints to study different effects,
- standardised test procedures or test procedures adapted to a specific exposure scenario or ecosystem.

As all approaches have their pros and cons and none of them, of course, cover all aspects, it is important to be aware of the limitations with the chosen method when making assessments and predictions.

The simplest and least time consuming tests are usually aquatic acute toxicity tests in laboratory on bacteria, algae or small invertebrates. These show the effect of short term exposure, in terms of e.g. inhibition of growth, immobility or death, and require presence of toxicant(s) in relatively high concentrations. These tests can be advantageous for screening purposes, especially when the chemical composition of the test medium is not known, and thereby not either the anticipated toxic response. Chronic tests are usually more sensitive and ecologically relevant, since exposure to toxicants in the environment usually occurs in lower concentrations during a longer time period. Examples of other toxic effects include carcinogenicity, reproductive toxicity, mutagenicity, and various effects caused by endocrine disruption.

Many of the chemicals that are used to make plastic polymers and plastic products have been tested for toxicity to a varying extent, and the assembled data have provided the basis for harmonised environmental and/or health classifications for these substances. In paper V these hazard classifications are used to identify the potential environmental and health hazards associated with each plastic polymer type. The knowledge of effects from exposure to the mixture of substances that may be released from complexly composed plastic products is very limited. There are some toxicity studies made on different plastic materials. Most of them have been made on rodents exposed, by oral route, to either plastic powder or extracts from the plastic material. These studies, which mainly are in Russian, have been summarized and translated by Sheftel (2000) and they show toxic effects for some of the materials and no effects for others.

Few studies combining leaching tests with toxicity tests have been performed on plastic products. In this thesis acute toxicity of plastic product leachates are shown [I-III]. In another study, mudsnails cultivated in PET mineral bottles doubled their reproductive output, due to endocrine disruption, compared to those cultivated in Borosilicate Erlenmeyer flasks (Wagner and Oehlmann, 2009). In a study by Olea (1996), saliva samples collected after treatment with restorative dental filling composites (which are made from thermosetting acrylic composite bis-GMA) contained bisphenol-A and bisphenol-A dimethacrylate. The saliva samples were estrogenic in cell proliferation tests, compared to no estrogenicity in the saliva collected prior to filling.

1.8. Hazard and risk assessment

Hazard and risk assessments are used to assess the environmental and/or health hazards and risks of chemicals. Below hazard and risk assessment terminology is presented according to the harmonised definitions made by International Programme on Chemical Safety (IPCS, 2004). The definitions are very slightly paraphrased, and “agent or situation” is replaced with “chemical”.

A **hazard** is the inherent property of a chemical having the **potential to cause adverse effects** when an organism, (sub)population, or ecosystem is exposed to that chemical.

A **risk** is the **probability of an adverse effect** in an organism, (sub)population, or ecosystem caused under specified circumstances by exposure to a chemical.

Hazard assessment is a process designed to **determine the possible adverse effects** of a chemical to which an organism, (sub)population, or ecosystem could be exposed. It includes two steps:

1. **Hazard identification** is the identification of the type and nature of adverse effects that a chemical has an inherent capacity to cause in organism, (sub)population, or ecosystem.
2. **Hazard characterization** is the qualitative and, if possible, quantitative description of the inherent property of a chemical having the potential to cause adverse effects. If a quantitative description is possible it should include a dose–response assessment and its strengths and weaknesses.

Risk assessment is a process intended to calculate or **estimate the risk** to a given target organism, (sub)population, or ecosystem **following the exposure** to a chemical. A risk assessment includes four steps, of which the first two are from the hazard assessment:

1. Hazard identification
2. Hazard characterization (related term: Dose–response assessment),
3. **Exposure assessment** is the evaluation of the exposure of an organism, (sub)population, or ecosystem to a chemical (and its derivatives).
4. **Risk characterisation** is the qualitative and, if possible, quantitative determination of the probability of known and potential adverse effects of a chemical to occur in a given organism, (sub)population, or ecosystem, under defined exposure conditions.

Hazard and risk assessment methods, e.g. the European Union Technical Guidance Document (European Commission, 2003), are very comprehensive and have been developed for assessing single chemicals. Risk assessments are only available for a few of the chemicals used to make plastics. This thesis mainly comprises the hazard identification step and parts of the hazard characterisation step.

1.9. Aim of the thesis

The overall aim of this thesis was to study the environmental and health hazards of chemicals in plastic polymers and products from a toxicological perspective. This was achieved by evaluations of toxicity by standardised ecotoxicity tests and by identifying the hazards of chemicals used to produce different plastic polymers.

The specific objectives were to:

- determine the acute toxicity of substances leaching from a variety of plastic products [I-II], synthetic textiles [III], and discarded electronic products [IV],
- compare toxicity for different plastic polymer types, product types and components [I-IV],
- identify which class of toxicants that was causing the toxicity [I-IV],

- compile and identify the environmental and health hazards of chemicals used in plastic polymer production [V],
- make a hazard ranking of the polymers based on monomer classifications [V],
- make initial hazard assessments of the polymers [V],
- identify hazardous substances used in polymer production for which evaluation of risks are needed [V].

2. Methods and approach

The methods used are described in detail in the different papers, but are summarized and discussed here.

2.1. Determination of plastic product leachate toxicity

Since there is such a diversity in the chemical composition of plastic products and basically no knowledge on toxicity of leachates from plastic products, a screening approach with leaching tests, bioassays and toxicity characterisations was chosen. In total 83 plastic products and synthetic textiles were tested. In addition, 68 metal, mixed material or plastic components from discarded electronic products were tested.

2.1.1. Product leaching tests

In order to screen many different products, short term leaching tests were chosen. All products were leached in deionised water during a short term period (1 or 3 days). By using deionised water the comparability is increased and the leachate can be used directly for toxicity testing on any aquatic test species, after the addition of the specific stock solutions required by the test organism. Distilled water is also the required test medium in the EU for testing migration from plastic materials into aqueous food (European Council, 1982). The pH of the deionised water was 7.0, which could represent the pH of a lake or river (neither acidic, nor alkaline).

There is no general standardised method for testing leaching of plastic products for subsequent toxicity testing. The available methods have been developed for measuring migration levels of chemicals from plastic material and articles that are in contact with food into food simulants (e.g. EN 1186-14:2002), or for measuring migration into artificial sweat or saliva.

Two main methods for leaching were used, one batch leaching method based on CEN (2002) for the characterization of wastes, and one diffusion leaching method. One drawback with the batch leaching method, which involves shaking, is that most VOCs are probably not included in the leachate (Bjerre Hansen and Andersen, 2006). This probable VOC loss may be less with the diffusion leaching method, but can still be considerable (e.g. during preparation of concentration series). Both methods show the test-specific release of contaminants and not the potentially leachable fraction or total amount (Bjerre Hansen and Andersen, 2006) as extraction tests do.

The leaching temperature was either room temperature ($\approx 20^{\circ}\text{C}$) [I, IV] or 50°C [II, III]. A higher temperature was used in two of the studies because it was assumed that it could increase leaching, which had been shown in several leaching studies, and because it is a realistic temperature that the surface of a plastic material may reach when exposed to sunlight outdoors. A dark plastic material may be as much as 60°C warmer than the surrounding air, and a comparison between black and white PVC foils showed a $15\text{-}23^{\circ}\text{C}$ higher surface temperature for the black foils (Wypych, 1999). A higher temperature may, however, increase the release of dissolved gases (Tölgyessy et al., 1993), for instance volatile organic compounds. The reasons for increasing the leaching period from 24 h [I, IV] to 3 days [II, III] was partly because it was convenient; leaching can be initiated on Friday, and toxicity testing (screening, EC50 determination and TIE) can be performed Monday to Friday; and partly to compensate for the possible slower leaching when switching from shaking to leaching by diffusion.

Most products were cut into smaller pieces to enable testing of products with irregular shape and to increase the exposed surface area, which may enhance leaching. Glass laboratory materials were used during leaching and toxicity testing to avoid absorption of hydrophobic substances onto plastic laboratory ware (Figure 2).



Figure 2. Plastic product (bib for babies) [I] (left), and synthetic textiles (sporting sweater, stretch pants, and knitted muffler) [III] (right), prior to leaching.

The highest leaching concentrations for the plastic materials were either 100 or 250 g plastic/L (corresponding to a liquid to solid (L/S) ratio of 10 and 4, respectively), and were lower for the mixed material fraction (50 g/L) and metal fraction (25 g/L) of the electronic products. All products were removed prior to toxicity tests.

2.1.2. Toxicity tests with *Daphnia magna*

The test species used was the cladoceran *Daphnia magna* (water flea), a small zooplanktonic crustacean, which is pelagic, filter feeding, and a primary consumer in small freshwater habitats (Figure 3). *Daphnia magna* has been extensively used since the mid 1970s in regulatory testing and ecotoxicological research (Koivisto, 1995). For instance, in REACH *Daphnia* is specified as the preferred invertebrate for short-term toxicity testing, which is a standard information requirement for substances manufactured or imported in quantities >1 ton (European Parliament and Council, 2006). The relatively small size, short life span, high fecundity, ability of asexual reproduction, and ease to culture in the laboratory, makes it suitable for toxicity testing (Koivisto, 1995). *Daphnia magna* is also considered to be a sensitive organism, in general more sensitive to metals and other contaminants than fish (Jonczyk and Gilron, 2005). Some, e.g. Koivisto (1995), argue that *Daphnia magna* is not ecologically representative because it differs too much from other freshwater zooplankton, in terms of its larger size, different habitat, life history (more and smaller neonates that mature later), and poor ability to withstand fish predation.

Daphnia magna was chosen because it was considered to be a suitable test organism for screening studies; standardised reliable test methods were available; it is a sensitive species; the use of larger test organisms and vertebrates could be avoided; and there was a steady culture available at the laboratory. Acute toxicity tests (with immobility as toxic endpoint) were chosen partly to be able to screen many products, and partly because the variety in products, as well as the largely unknown chemical composition, made it difficult to know which chemicals that could be released and which toxic effect(s) to anticipate. However, acute toxicity is not the most probable toxic response to anticipate from plastic product water leachates (further discussed under 3.1.3).

Standardised toxicity tests according to ISO (1996) were chosen to increase comparability. The standard requires that stock solutions are added to give a hardness of 250 mg CaCO₃/L and a pH of 8. This is considered as a very hard water (>150 mg CaCO₃/L), but is well within the wide range of hardness of world ground waters (0->1000 mg CaCO₃/L), which primarily depends on the type of underlying bedrock (Hiscock, 2005). The pH of the leachate during the toxicity test could represent the pH in sea water, which has an average around pH 8 (Garrison, 2007). Both hardness of the water and pH can have a great influence on toxicity and are important to take into account when assessing the risks in a certain ecosystem. For instance for many metals, metal toxicity is decreased by increasing hardness (because of

complexation, and competition of binding sites on the organism, e.g. the gill surface), and metal release is increased by a lower pH (Manson, 2002).



Figure 3. Test organism *Daphnia magna* (size: 0.8 mm newborn, 5-6 mm adult), and Petri dishes during toxicity tests.

2.1.3. Toxicity Identification Evaluations (TIEs)

The chemical composition of a leachate from a plastic product, textile, or electronic product is to a great extent not known. In a screening approach when many different products and possible substances are involved, it is very difficult to choose the right chemical analyses. It is comparably easy to analyse for metals, but when organic substances are involved it is necessary to know which substances to analyse for. Even then, these analyses are time consuming and expensive without being extensive. By using Toxicity Identification Evaluations, phase I, based on US EPA methods (1991) to characterise classes of toxicants the number of possible toxicants is narrowed down, and information on which classes of toxicants (e.g. metals or hydrophobic organics) that are causing the toxicity can be obtained. Complete TIEs also include identification (phase II) and confirmation (phase III), in which also chemical analysis are included (Norberg-King et al., 2005). These can give information of which chemical substance that is causing the toxicity.

In this study only initial phase I TIEs were used. The number of different manipulations of the toxic leachate was usually limited to two or three. C18 solid phase extraction was used to remove hydrophobic organics, CM solid phase extraction was used to remove cations, and EDTA and sodium thiosulfate addition were used to complex cationic metals. Subsequent toxicity tests were performed to compare toxicity in manipulated and non-manipulated leachates.

2.2. Hazard ranking and assessment of plastic polymers

Also in the hazard ranking of plastic polymers a wide approach was chosen, with the intention to cover a large number of both thermoplastic and thermosetting polymers. A hazard ranking of plastic polymers was made based on monomer composition and environmental and health hazard classifications.

2.2.1. Chemicals in plastic polymer production and hazard classifications

Data on which chemical substances that were needed to produce the different plastic polymers were collected from the polymer literature (compiled in Report S1: supplementary material to paper V). For all substances which were identified as used in the production of each polymer type, hazard classification data were collected, mainly from the EU classification, labelling and packaging (CLP) regulation (European Parliament and Council, 2008) including the 1st Adaptation to Technical Progress (European Commission, 2009). All these substances and classifications are presented in Table S1 (supplementary material to paper V) in the very back of this thesis.

2.2.2. Hazard ranking model

There are several ranking and scoring systems for chemicals (evaluated by Davis et al., 1994), but there is no consensus on which of the methods that is the most effective. A new hazard ranking method based on hazard classifications was developed for this study. The EU classification, labelling and packaging (CLP) regulation was chosen because it contains harmonised classifications, and is based on the UN Globally Harmonized System (GHS) (European Parliament and Council, 2008; UN, 2009). Therefore, the model and the data in the model can be regarded as having an almost global validation. No previous ranking method was available for the GHS or CLP.

In the ranking model the CLP hazard classes for environment and health hazards, with accompanying categories, were sorted into five levels of hazards (*I-V*). The hazard classes and categories sorted as level *V* were: carcinogenicity, mutagenicity and reproductive toxicity (categories 1A & B), and hazardous for the ozone layer. Those sorted as level *IV* were: mutagenicity (cat. 2), acute toxicity (cat. 1 & 2), respiratory/skin sensitisation, specific target organ toxicity – single/repeated exposure, and hazardous to the aquatic environment (chronic cat. 1 & 4). Each level was assigned a rough hazard grade, increasing with a factor of 10 for each level of hazard (*I-V*). The hazard grades for each classification that a substance has were summarised to create a hazard score for the substance.

In the ranking of the polymers only the basic building blocks that define the polymer, i.e. the monomers (with a few exceptions), were included. These can not be changed without changing the polymer. Other chemicals needed for polymerisation to occur, such as catalysts, solvents, etc., were not included because they would add to much variability to the ranking. These substances have, however, been presented and discussed separately. Additives that are compounded with the polymer to make different plastic products were excluded because of the extreme diversity and variability.

The hazard score for the substance (in this case the monomer) was multiplied with the weight fraction of the monomer in the polymer. Finally the sum of the hazard scores for all monomers included in the polymer type was calculated and a hazard ranking of the different plastic polymers was made.

The hazard ranking model works well for separating the different levels of hazards, but is rough both in terms of hazard levels and hazard grades, and could need some refinement. The hazard scores should, therefore, not be regarded as absolutely true figures but rather as a way to enable an approximate relative ranking, and to identify presence of hazardous substances. A valuable contribution to the Globally Harmonised System would be the development of a harmonised grade for each hazard classification. These grades could be used to facilitate comparisons between different substances and could be used in hazard and risk assessments when many substances are involved.

2.2.3. Initial assessments

The assessments made for the different polymers do not cover the strict definition of hazard assessments (described in 1.8) and are, therefore, called initial assessments. These mainly comprise assessments of non-classified substances based on 1) available information from OECD SIDS Initial Assessment Reports of substances, 2) assessments of other hazardous substances used than monomers, and 3) comparisons between hazard rank and global annual production. Global annual production was used as a rough measure for quantifying the hazard in order to identify which polymers should be prioritised for further risk assessments.

Exposure and effect assessment have been discussed but were not possible to include in this study. Even when dealing with single chemicals, such assessments can be a hard challenge, although easy compared to assessing complex products such as plastic products.

3. Results and discussion

In this chapter the results from papers [I-V] are summarized and discussed.

3.1. Acute toxicity from product leachates

Acute toxicity was seen in all toxicity studies [I-IV] in approximately 30% of the samples.

3.1.1 Toxicity of plastic products and synthetic textiles

Twenty-eight of the leachates from the 83 studied plastic products and synthetic textiles [I-III] showed acute toxicity to *Daphnia magna* (Table 1). This represents 33.7% of the tested

products. Since the highest test concentration was lower (100 g/L) for the products in paper I, the results can also be expressed as 22 of the 83 tested (i.e. 26.5%) had 48-h EC50 ranging between 1 and \approx 100 g/L. The toxic products from paper I are shown in Figure 4.

Table 1. The 28 toxic plastic product [I, II] and synthetic textile [III] leachates and their 48-h EC50s for *Daphnia magna* (modified from papers I-III).

Product	Plastic type	48 h EC50s g plastic/L		TIE indication of toxicant	Leaching test
		Repl 1	Repl 2		
Plastic products					
I. Artificial leather, brand S	Plasticised PVC	8	8	organics (& metals)	24 h shaking 22°C
I. Artificial leather, brand,G	Polyurethane	38	31		24 h shaking 22°C
I. Artificial leather, brand M	Plasticised PVC	26	22	organics (& metals)	24 h shaking 22°C
I. Floor	Plasticised PVC with polyurethane surface	54	50		24 h shaking 22°C
I. Children's handbag	Polyurethane	44	54		24 h shaking 22°C
I. Bath tub squirt toys	Plasticised PVC	\approx 100	59		24 h shaking 22°C
I. Inflatable bathing ring	Plasticised PVC	71	75		24 h shaking 22°C
I. Table cloth	Plasticised PVC	62	76		24 h shaking 22°C
II. Watering can	High-density-polyethylene	17	24		3 d diffusion 50°C
II. Laboratory gloves	Plasticised PVC	2	4	metals	3 d diffusion 50°C
II. Boat fender	Plasticised PVC	21	11	organics	3 d diffusion 50°C
II. Arm pads for floating	Plasticised PVC	79	70	organics	3 d diffusion 50°C
II. Rain poncho	Plasticised PVC	172	160	organics (& metals?)	3 d diffusion 50°C
II. Wet room wall carpet	Plasticised PVC	235	219		3 d diffusion 50°C
II. Super epoxy (filler) ^a	Epoxy (cured)	10	2	organics	3 d diffusion 50°C
II. Marine epoxy (filler) ^a	Epoxy (cured)	9	6	organics	3 d diffusion 50°C
II. Quick epoxy glue ^a	Epoxy (cured)	44	39		3 d diffusion 50°C
II. Laminating epoxy ^a	Epoxy (cured)	>80	27		3 d diffusion 50°C
II. Epoxy putty (sealant) ^a	Epoxy (cured)	114	99		3 d diffusion 50°C
Synthetic textiles					
III. Awning cloth ^b	Polyacrylonitrile (acrylic) impregnated with polytetrafluoroethylene (PTFE; Teflon®)	1	1	organics	3 d diffusion 50°C
III. Furniture fabric	Polypropylene	4	3		3 d diffusion 50°C
III. Mesh fabric ^b	Plasticised PVC coated polyester (PET)	7	8	organics	3 d diffusion 50°C
III. Baby diaper outer material ^c	Polypropylene and polyethylene	75	68		24 h shaking 22°C
III. Knitted muffler	Polyacrylonitrile (acrylic)	108	131		3 d diffusion 50°C
III. Furniture fabric	Polyacrylonitrile (acrylic; 73%), polyester (27%)	176	185		3 d diffusion 50°C
III. Curtain	Polyamide (nylon)	172	145		3 d diffusion 50°C
III. Wool imitation fabric	Polyacrylonitrile (acrylic)	124	180		3 d diffusion 50°C
III. Stretch pants (golden)	Polyester (92%), thermoplastic polyurethane (elastane; 8%)	210	201		3 d diffusion 50°C

^a Cured epoxy resin

^b Technical fabric

^c The non-woven material was tested, excluding the absorbing core and covering top sheet. Some unspecified elastic material was also present.

The applications for the products varied, and no specific product category was tested. Examples of product categories include drinking water and ground pipes, floors, fillers, mattress, household articles (e.g. food and water containers, table cloths, plates), articles

intended for small children (toys, floating aid and diapers), garbage bag, rain and skin protection, and synthetic textiles (e.g. clothes and furniture and technical fabrics). The sample size for the different product categories is not large enough to draw general conclusions for respective product category. However, a few patterns have been noted. Considerably many leachates from products intended for children (5/13) were toxic. These include a floating ring, arm pads for floating, children's handbag, a bath tub squirt toy, and a diaper (excluding the absorbing core and top sheet). None of the 12 leachates from articles for food or drinking water contact were acutely toxic, an outcome which was expected since there are regulations for food contact materials (mentioned in 1.3). Among the synthetic textiles technical fabrics and furniture fabrics were among the most toxic ones, and the fabrics in the clothes category were less toxic.

Figure 4. Plastic products (from paper I) which caused toxic leachates, i.e.: artificial leathers (brand S, G and M), children's handbag, bath tub squirt toys, floor material, table cloth (transparent), and inflatable bathing ring. The CD was only toxic when cut into pieces and the silver layer was exposed [1].



Also the distribution of polymer types is uneven among the products, and the sample sizes are too small draw conclusions valid for the polymer type. However, a few patterns can be seen, most evident for PVC and epoxy. The number of toxic samples per polymer type is presented in Table 2. Leachates causing acute toxicity were produced by all epoxy products (5/5), almost all (11/13) plasticised PVC products, three out of four soft polyurethane products (including those mixed), four out of six polyacrylonitrile fabrics (including those mixed), and only one each of the 13 polyethylene, 10 polyester and 9 polypropylene products. The two rigid PVC products were not toxic. The toxic products were either soft to semi-soft plastic products (mainly made of plasticised PVC, and a few made of polyurethane), or epoxy products, or textile products. One exception was a high-density polyethylene watering can (Table 1).

Table 2. Distribution of tested polymers types and toxic product leachates.

Plastic polymer	Toxic leachates/ tested leachates
Polyethylene (HDPE 1/8; LDPE 0/1; MDPE 0/4)	1/13
Polyethylene and/or polypropylene	1/4
Polypropylene	1/9
Rigid PVC	0/2
Plasticised PVC	11/13
Polyurethane/plasticised PVC mix	1/1
Polyurethane	2/3
Polyester/thermoplastic polyurethane	1/2
Polyester	0/8
Polyacrylonitrile/polyester mix	1/1
Polyacrylonitrile (acrylics)	2/4
Polytetrafluoroethylene (PTFE; Teflon)/ polyacrylonitrile mix	1/1
Polytetrafluoroethylene (PTFE; Teflon)	0/1
Nylon	1/3
Nylon/polyurethane mix	0/1
Nylon/polyester mix	0/1
Epoxy	5/5
Acrylonitrile-butadiene-styrene	0/6
Polystyrene	0/2
Polycarbonate	0/1
Polymethyl methacrylate	0/1
Melamine-formaldehyde	0/1

In bold: polymer types with toxic leachates.

Release of non-polymeric substances is expected to be larger for more rubbery (soft) polymers, e.g. the plasticised PVC and soft polyurethane products, because they have larger gaps between the polymer molecules, compared to crystalline polymers which have a greater degree of molecular packing (Brydson, 1999; Godwin and Krauskopf, 2008). Plasticised PVC also contains larger amounts of additives which may be available for leaching. For instance plasticisers can be used in amounts up to 60 percentages by weight, but most commonly 35-40 weight percent is used (Navarro et al., 2010). For the epoxy products uncured residuals from resin and/or hardener are likely to have caused the observed toxicity. Polyacrylonitrile and polyacrylonitrile mix fabrics were overrepresented among the toxic textile leachates. However, a valid comparison between plastic fibre types could not be made because the sample size was too small, the distribution between fibre types was uneven, mixed fabrics were involved, and the toxicants were not identified and could, therefore, have been any textile processing chemical.

The initial Toxicity Identification Evaluations (TIE) made on the most toxic leachates indicated that hydrophobic (non-polar) organics were the major cause of toxicity for nine of the ten tested leachates, and that cationic metals may have been responsible for some of the toxicity in several of the samples (Table 1). For the laboratory gloves the TIE indicated that cationic metals were the major cause of toxicity, and metal release was also confirmed by chemical analysis [II].

3.1.2. Toxicity of discarded electronic products

Among the discarded electronic products 18 of the 68 leachates showed acute toxicity to *Daphnia magna* [IV]. This represents 26.5%, which is less than for the plastic products and synthetic textiles [I-III]. These results are, however, not comparable because the highest test concentrations for the tested electronic product were much lower for metal parts (25 g/L) and the mixed material parts (50 g/L), than for the plastic product and synthetic textiles (100-250 g/L). If instead only the 48-h EC50 values ≤ 25 g/L are considered, a higher share of low EC50s (i.e. more toxic) were found among electronic products, than among the plastic and textile products. However, the test set-up was slightly different, and besides, studies like these should primarily be used for comparing a more similar category of products.

The eight most toxic leachates had 48-h EC50s ranging from 0.4 to 20 g/L and belonged to the metal or the mixed material category (Table 3). All five tested electronic products contained components that generated at least one toxic leachate. The TIE indicated that cationic metals were the major cause of toxicity for the majority of the leachates, and that hydrophobic organics may have been involved to a lesser extent in a couple of the leachates.

Table 3 The eight most toxic leachates from discarded electronic product components made of metals and mixed materials respectively and *Daphnia magna* 48-h EC50s (modified from paper IV).

Sample	Component(s)	Type of electronic product	48 h EC50 g/L		TIE indication of toxicant
			Repl 1	Repl 2	
30 metal	IDE cable clips	Computer	5.4	5.7	metals
31 metal	Metal studs	Computer	4.4	7.9	metals
4 mixed mat.	Circuit sheet	Keyboard	0.9	0.4	-
37 mixed mat.	Circuit sheet	Keyboard	2.3	2.7	cations
14 mixed mat.	Circuit board	Computer mouse	6.6	7.8	metals, (organics?)
10 mixed mat.	Cord	Phone modem	18	13	
18 mixed mat.	Mixed parts (screen frame, microphone, speaker, antenna)	Cell phone	15	18	metals
1 mixed mat.	Circuit board	Keyboard	13	20	metals

Leaching was performed by diffusion for 3 d at 23°C.

None of the tested 13 plastic components showed any toxicity at the highest test concentration (100 g/L). Possible explanations for lack of toxicity could be that hard plastics are not particularly acutely toxic under the existing test conditions [I-II]; that possible content of readily available non-polymeric substances, which are the most likely to leach under the specific test conditions, had already been released during the use phase or were not released in high enough concentrations; and that most plastic pieces were covers and casings which had to be cleaned with a damp cloth to remove dirt prior to leaching, and this may also have removed some possible surface contaminants. In other studies plastic fractions from electronic products have been shown to release brominated flame retardants mainly to methanol (20%), and to a lesser extent to distilled water (Kim et al., 2006). The plastic fraction can also be contaminated with heavy metals. For instance, Morf et al. (2007) found average concentrations >1000 mg/kg for Cu, Sb, Sn, Zn, Pb, and Ni in the plastic fraction of various electronic products.

3.1.3. Acute toxicity and other toxic effects

The laboratory studies in papers I-IV show the acute toxicity of product leachates. This type of toxicity requires exposure to high concentrations of toxicants, or exposure to very acutely toxic toxicants, in order for the adverse effect (e.g. immobility, death) to occur. This means that large amounts of toxicants or very toxic chemicals had to leach from the materials under the short leaching period (1-3 days) in deionised water. For many plastic products leaching of chemical substances from the plastic materials is more likely to occur at low concentrations under a prolonged time period, and in many cases also under the influence of degradation. This statement is based on: a) the available data of chemical release from plastic products (examples given under 1.5) which are usually measured in the lower concentrations ranges, and b) on the physical structure of the polymer in which the gaps between polymer molecules are often quite small and, thereby, decreases the migration potential. Many other toxic effects such as carcinogenicity, mutagenicity, reproductive toxicity, sensitisation and chronic aquatic toxicity, as well as endocrine disruption, are not detected in the acute toxicity tests, but are common for many of the chemicals used for producing plastic polymers, as shown in paper V. However, acute toxicity tests can be used for screening purposes to identify toxic products, but should not be used alone to conclude that a certain plastic product is non-toxic.

3.2. Hazard ranking and initial assessments

In this section only some of the results from paper V are presented and the reader is referred to this paper for further information. The plastic polymers that ranked as the most hazardous ones are made of monomers that are classified as mutagenic and/or carcinogenic (category 1A or 1B). These polymers belong to the polymer families of polyurethanes, polyacrylonitriles, PVC, epoxy resins, and styrenic copolymers (ABS, SAN and HIPS). All have a large global annual production, ranging between 1 and 37 million tons. PVC has the largest production of them, accounting for 17% (by weight) of the world plastic demand (PlasticsEurope MRG, 2008). All these highly ranked polymers should be prioritised for assessments of risks.

A considerable number of polymers (31 out of 55) are made of monomers that have hazard classifications belonging to the two highest (i.e. levels *IV-V*) of the five hazard levels in the ranking model. These polymers are presented in Table 4. The polymers which are made of level *IV* monomers and, in addition, have a large global annual production (1-5 million tons) are phenol formaldehyde resins, unsaturated polyesters, polycarbonate, polymethyl methacrylate, and urea-formaldehyde resins.

Table 4. Hazard ranked plastic polymers that are composed of monomers with hazard classifications that belong to hazard levels *II* or *V* (modified from paper V).

Rank	Hazard score	Polymer	Monomers (weight%)
1	13844	Polyurethane (PUR) ^a , polyether based flexible foam, example	Propylene oxide (58); Toluene-diisocyanate (29); Ethylene oxide (7); HCF-134a (6)*
2	12379	Polyacrylonitrile (PAN) with comonomer, example acrylamide	Acrylonitrile (92); Acrylamide (8)
3	11521	Polyacrylonitrile (PAN)	Acrylonitrile (100)
4	10599	Polyacrylonitrile (PAN) with comonomer, example vinyl acetate	Acrylonitrile (92); Vinyl acetate (8)
5	10551	Polyvinyl chloride (PVC), plasticized, example with most toxic plasticiser	Vinyl chloride (50); Plasticiser: Benzyl butyl phthalate (BBP) (50)
6	10001	Polyvinyl chloride (PVC), rigid	Vinyl chloride (100)
7*	7384*	Polyurethane (PUR) ^a , polyether based rigid foam, example	Propylene oxide (31); 4,4'-methylenediphenyl diisocyanate (MDI) (52); Sorbitol (13)*; Cyclopentane (4)
8	7139	Epoxy resin DGEBA ^a , low mw (450), example with most toxic curing agent	Bisphenol A (45); Epichlorohydrin (37); 4,4'-methylenedianiline (MDA) (18)
9	6957	Modacrylic, example with vinylidene chloride	Acrylonitrile (60); Vinylidene chloride (40)
10	6552	Acrylonitrile-butadiene-styrene (ABS) terpolymer	Styrene (58); Acrylonitrile (22); 1,3-butadiene (20)
11*	5001*	Polyvinyl chloride (PVC), 50% non-classified plasticiser	Vinyl chloride (50); Diisodecyl phthalate DIDP (50)*
12	4515	Epoxy resin DGEBA ^a , low mw (450), example with least toxic curing agent	Bisphenol A (43); Epichlorohydrin (35); 4,4'-diamino diphenyl sulfone (DDS) (22)
13	4226	Epoxy resin DGEBA ^a , high mw (3750), example with non-classified curing agent	Bisphenol A (67); Epichlorohydrin (30); Dicyandiamide (3)
14	2788	Styrene-acrylonitrile (SAN) copolymer	Styrene (76); Acrylonitrile (24)
15	1628	High-impact polystyrene (HIPS)	Styrene (92); 1,3-butadiene (8)
16	1500	Polyoxymethylene (POM), homopolymer	Formaldehyde (100)
16	1500	Phenol formaldehyde resins (PF) ^a , example resol	Phenol (61); Formaldehyde (39)
17	1450	Phenol formaldehyde resins (PF) ^a , example novolacs	Phenol (72); Formaldehyde (18); Hexamethylenetetramine (10)
18*	1414*	Unsaturated polyester ^a (UP), example with methyl methacrylate	Phthalic anhydride (31); Methyl methacrylate (30?); Propylene glycol (18)*; Maleic anhydride (21)
19**	1187**	Poly(m-phenyleneisophthalamide) (MPD-I) (Nomex®)	Isophthaloyl chloride (65)**; m-phenylenediamine (35)
19	1177	Polycarbonate (PC), example with phosgene	Bisphenol A (70?); Phosgene (30?)
20*	1117*	Unsaturated polyester ^a (UP), example with styrene	Phthalic anhydride (31); Styrene (30); Maleic anhydride (21); Propylene glycol (18)*
21**	1094**	Thermoplastic polyurethanes (TPU) polyester based rigid example	Adipic acid, Ethylene glycol & 1,4-Butanediol** (35); 4,4'-methylenediphenyl diisocyanate (MDI) (49); 1,4-Butanediol (16)*
22	1021	Polymethyl methacrylate (PMMA)	Methyl methacrylate (100)
23	897	Polyphenylene sulfide (PPS)	1,4-dichlorobenzene (65); Sodium sulphide (35)
24*	882*	Melamine-formaldehyde resin (MF) ^a	Formaldehyde (59); Melamine (41)*
25	871	Polyoxymethylene (POM) copolymer, example with ethylene oxide	Trioxymethylene (96); Ethylene oxide (4)
26**	829**	Poly(p-phenyleneterephthalamide) (PPD-T) (Kevlar®)	Terephthaloyl chloride (66)**; p-phenylenediamine (34)
27*	750*	Urea-formaldehyde resin (UF) ^a	Formaldehyde (50); Urea (50)*
28**	610**	Polycarbonate (PC), example with diphenyl carbonate	Bisphenol A (50); Diphenyl carbonate (50)**
29**	556**	Thermoplastic polyurethanes (TPU) polyester based glycol soft example	Adipic acid, Ethylene glycol & 1,4-Butanediol (70); 4,4'-methylenediphenyl diisocyanate (MDI) (24); 1,4-Butanediol (6)**

^a Thermosetting plastics

In bold: monomers with level *II* and/or level *V* hazard classifications. These are presented in Table 5.

*Contains ≥10 wt% non-classified substance, but with indication of low level of hazard according to SIDS initial assessment reports.

**Contains ≥10 wt% non-classified substance, for which ranking may be underestimated, due to elevated concern according to SIDS initial assessment reports, or lack of data.

The most frequent hazard classifications among the monomers in the 55 polymers were: skin sensitization 1, respiratory irritation 1, acute toxicity 3 (inhaled; skin; oral, respectively), serious eye irritation 2, carcinogenic 1A & 1B, and skin corrosion 1A & 1B. Environmental hazard classifications were less frequent for the monomers than health hazard classifications. The monomers which have hazard classifications that at least belong to hazard level *IV* are presented in Table 5.

Table 5. Monomers from Table 4 that have hazard classifications, which at least belong to hazard level *IV*. Classifications belonging to hazard levels *I-III* are not shown (modified from paper V).

Level IV and V monomers	Hazard classifications and category code (hazard levels III-V)	Hazard score
1,3-butadiene	Carcinogenicity 1A (V), Mutagenicity 1B (V)	20001
1,4-dichlorobenzene	Aquatic chronic 1 (IV) , Carcinogenicity 2 (III), Aquatic acute 1 (III)	1210
4,4'-methylenedianiline (MDA)	Carcinogenicity 1B (V), Mutagenicity 2 (IV), Skin sensitization 1 (IV), Specific target organ toxicity -single exposure 1 (IV) , Specific target organ toxicity - repeated exposure 2 (III), Aquatic chronic 2 (III)	13200
4,4'-methylenediphenyl diisocyanate (MDI)	Respiratory sensitization 1 (IV), Skin sensitization 1 (IV) , Carcinogenicity. 2 (III), Specific target organ toxicity - repeated exposure 2 (III)	2240
Acrylamide	Carcinogenicity 1B (V), Mutagenicity 1B (V) , Specific target organ toxicity - repeated exposure 1 (IV), Reproductive toxicity 2 ^f (III), Acute toxicity 3 ^o (III)	22240
Acrylonitrile	Carcinogenicity 1B (V), Skin Sensitization 1 (IV) , Acute toxicity 3 ^{o,d,i} (III), Serious eye damage 1 (III), Aquatic chronic 2 (III)	11521
Benzyl butyl phthalate (BBP) (Note: plasticiser)	Reproductive toxicity 1B^{FD} (V), Aquatic chronic 1 (IV) , Aquatic acute 1 (III)	11100
Bisphenol A	Skin sensitization 1 (IV) , Reproductive toxicity 2 ^f (III), Serious eye damage 1 (III)	1210
Epichlorohydrin	Carcinogenicity 1B (V), Skin sensitization 1 (IV) , Skin corrosion 1B (III), Acute toxicity 3 ^{o,d,i} (III)	11400
Ethylene oxide	Carcinogenicity 1B (V), Mutagenicity 1B (V) , Acute toxicity 3 ⁱ (III)	20131
Formaldehyde	Skin sensitization 1 (IV) , Carcinogenicity 2 (III), Acute toxicity 3 ^{o,d,i} (III), Skin corrosion 1B (III)	1500
Hexamethylenetetramine	Skin sensitization 1 (IV)	1000
Maleic anhydride	Respiratory sensitization 1 (IV), Skin sensitization 1 (IV) , Skin corrosion 1B (III)	2110
Methyl methacrylate	Skin sensitization 1 (IV)	1021
m-phenylenediamine	Mutagenicity 2 (IV), Skin sensitization 1 (IV), Aquatic chronic 1 (IV) , Aquatic acute 1 (III), Acute toxicity 3 ^{o,d,i} (III)	3410
Phenol	Mutagenicity 2 (IV) , Acute toxicity 3 ^{o,d,i} (III), Specific target organ toxicity - repeated exposure 2 (III), Skin corrosion 1B (III)	1500
Phosgene	Acute toxicity 2ⁱ (IV) , Skin corrosion 1B (III)	1100
p-phenylenediamine	Aquatic chronic 1 (IV), Skin sensitization 1 (IV) , Aquatic acute 1 (III), Acute toxicity 3 ^{o,d,i} (III)	2410
Propylene oxide	Carcinogenicity 1B (V), Mutagenicity 1B (V)	20061
Toluene-diisocyanate (TDI)	Acute toxicity 2ⁱ (IV), Respiratory sensitization 1 (IV) , Carcinogenicity 2 (III)	3140
Vinyl chloride	Carcinogenicity 1A (V)	10001

^{o,d,i}toxic by oral, dermal and inhalation route

^{FD}may damage fertility and the unborn child (development)

^fsuspected of damaging fertility

In bold: level *IV* and *V* classifications

Several solvents used during polymerisation are classified as carcinogenic and mutagenic, or toxic for reproduction (category 1A & 1B), or very toxic to aquatic life with long lasting effects (aquatic chronic 1), and the most hazardous catalysts are classified as aquatic chronic 1 (see paper V).

Polyethylenes and polypropylene, which alone account for 54% of the world production of plastics (PlasticsEurope MRG, 2008), ranked as least hazardous, as did polyvinyl acetate and ethylene vinyl acetate. Also polyethylene terephthalate (PET), which also have a considerable global annual production, ranked as not particularly hazardous. The monomers used to produce PET were not classified so there is some uncertainty, however, the SIDS Initial assessment reports indicated low level of concern.

Since there is neither a hazard class in the GHS, nor hazard classifications in the CLP for endocrine disrupters, they could not be included in the ranking model. A few of the monomers used in plastics are under evaluation for endocrine disrupting properties within the European Union strategy for endocrine disrupters (European Commission, 2008). These include bisphenol A (used in polycarbonate and the main epoxy resin DGEBA; diglycidylether of bisphenol A), styrene (used in polystyrene and polystyrene copolymers), epichlorohydrin (used in the main epoxy resin DGEBA) and some phthalates (used in PVC) (Groshart and Okkerman, 2000; Okkerman and van der Putte, 2002). They have preliminary been assigned category 1 based on evidence of human effects, and assigned high level of concern due to risk of high exposure (Groshart and Okkerman, 2000; Okkerman and van der Putte, 2002). The polymers containing these monomers could be ranked as more hazardous if endocrine disruption is identified.

Another factor that can affect the ranking is a subsequent assessment of the environmental fate of the monomers in the hazardous ranked polymers. For instance, if the monomer is very volatile and/or very rapidly photo-degrading, readily biodegradable, and not bioaccumulating, the hazards may mainly be confined to the production phase with worker exposure through air. This is because many of the monomers and solvents used are volatile.

In paper V hazardous substances used in the production of different plastic polymers were identified. From a general point of view all level *V* substances ought to be considered as candidates for phase out. However, if no alternatives exist, the risks should be evaluated for decisions on either need for risk reduction measures or phase out. For level *IV* substances it is advisable with substitution when less hazardous alternatives exist, and evaluation of the need for risk reduction measures if there are no alternatives.

The hazard ranking model was found to be a useful tool for identify hazardous substances in polymer production and for ranking the polymers, and could be used in other hazard or risk assessments for comparing substances, mixtures or articles. The results from paper V and its

supplementary material can be used for further hazard and risk assessment of those plastic polymers identified as hazardous.

3.3. Most hazardous ranked polymers versus toxic products

When comparing the polymers types which were ranked as most hazardous with the leachates from plastic products that were toxic to *Daphnia magna*, there is a correlation. The most hazardously ranked polymers polyurethane, polyacrylonitrile, polyvinyl chloride, and epoxy, were also the polymers used in the products that had the most toxic leachates, with a few exceptions.

Since the ranking is based on monomer composition this would, if this correlation is valid also for a greater number of plastics, mean that residual monomers were leached in such high quantities from these products to cause acute toxicity. For the epoxy products, this correlation is likely to be valid. Uncured resin DGEBA or its monomers (bisphenol A and epichlorohydrin) and some of the curing agents are the most likely cause of toxicity seen for the epoxy products. For the other polymer types there are several other possible explanations for toxicity. The PVC and polyurethane products were soft to semi-soft, which facilitates migration of chemicals. In the plasticised PVC also the quantities of plasticisers and other non-bound additives, which may be available for leaching, are larger than for other plastic types. The polyacrylonitrile products were synthetic textiles. Any residual monomers in the fibres are according to Smith (2003) likely to be released during textile manufacturing processes, and, besides, there are many other possible chemical residues emanating from the processing of the textile fabric that could cause toxicity. Other reasons that argue against monomers being responsible for most of the toxicity seen in the leachates are that:

- a) the residual monomer content is generally quite low in a plastic product and, therefore, possible effects are more likely to be seen in chronic studies,
- b) many of the hazardous monomers are volatile and may have been lost during the leaching and preparation of solutions for toxicity testing, and
- c) none of the monomers which the tested plastic products were composed of are classified as very acute toxic to aquatic organisms, i.e. aquatic acute (category 1) (Table 2, paper V).

4. Conclusions

- Substances causing acute toxicity to *Daphnia magna* leached from one third of all 83 tested plastic products and synthetic textiles even during the short term (1-3 d) leaching period in deionised water [I-III].
- The toxic leachates came mainly from products that were soft to semi-soft, i.e. plasticised PVC (11/13) and polyurethane (3/4), and from epoxy products (5/5), and from synthetic textiles made from various plastic fibres [I-III].
- Only one each of the 13 polyethylene, 10 polyester and 9 polypropylene leachates were acutely toxic [I-III].
- A considerable number of leachates from products intended for children (5/13) were toxic [I-III].
- None of the 12 leachates from articles for food or drinking water contact were acutely toxic [I, II].
- The toxic leachates from discarded electronic products came from the mixed material or the metal fraction, but none came from the pure plastic fraction [IV].
- Toxicity Identification Evaluation, performed on some leachates, indicated that the major toxicants were hydrophobic organics for the plastic product [I, II] and synthetic textile [III] leachates, and metals for the electronic product leachates [IV].
- Many other toxic responses than acute toxicity are highly relevant in plastic leachates [V], and leaching is suspected to be more likely to occur at low concentrations during a long period of time.
- The plastic polymers ranked as most hazardous are made of monomers classified as either carcinogenic or both carcinogenic and mutagenic (category 1A or 1B) [V].
- These belong to the polymer families of polyurethanes, polyacrylonitriles, PVC, epoxy resins, and styrenic copolymers (ABS, SAN and HIPS), and have a large global production (1-37 million tons/year). PVC accounts for 17% of the global production of plastics [V].
- The polymers that ranked as least hazardous, i.e. polypropylene and polyethylene, account for 54% of the global production of plastics [V].

- A considerable number of polymers (31 out of 55) are made of monomers that belong to the two highest of the ranking model's hazard levels, i.e. levels *IV* and *V* [V].
- Polymers which are composed of level *IV* monomers, and also have a large global production (1-5 million tons/year), are phenol formaldehyde resins, unsaturated polyesters, polycarbonate, polymethyl methacrylate, and urea-formaldehyde resins [V].
- The most toxic plastic product leachates [I, II, III] were dominated by the polymers which had been ranked as the most hazardous [V], however, in many cases additives were suspected to be a more likely cause of toxicity than monomers.
- For several of the identified hazardous substances used in polymer production the risks ought to be evaluated for decisions on need for risk reduction measures, substitution, or even phase out [V].
- The hazard ranking model is a useful tool for comparing substances, mixtures or articles which can be used in hazard and risk assessment.
- There is a need to assess the risks from exposure in a wider context, including plastic pollution in the environment, degradation products, hazardous additives and mixture toxicity.

5. A more sustainable use of plastics

Considering

- the large global production of plastics and their omnipresence in both society and the environment,
- the persistence and partial degradation of plastic products,
- the large amounts of plastic waste and microplastic pollution in the world oceans,
- plastic diversity by means of types and applications,
- littering, poor waste management and low recycling rates,
- recycling obstacles because of heterogeneity,

as well as

- the use of hazardous chemicals in production, and the potential emissions of hazardous chemicals during the entire lifecycle,

there is a great need to assess the risks associated with plastics.

Exposure and effect assessments are important in order to assess the risks. This can be done by complementing the work in paper V, with predictions of environmental fate for level *V* and level *IV* monomers, and with data on degradation and degradation products of plastic materials under environmental conditions. Long term leaching, which reflects specific exposure scenarios during the use phase and the end of life phase under the influence of degradation, would be valuable, and bioassays studying chronic effects would be desirable. Research on occurrence of plastics in the oceans and the effects of microplastics is ongoing (Bowmer and Kershaw, 2010), and important considering the extensive microplastic pollution. In conclusion, there is too little knowledge of the release of chemicals from plastic products and potential effects.

“In today's world, life without plastics is incomprehensible”(quotation from American Chemistry Council, 2011). That is very true, plastics are extremely necessary in our modern society, but some of the current use and misuse is not sustainable. A more sustainable use of plastics can be achieved by many measures. There is a large potential for reducing the per capita use in the industrialized world, for instance by eliminating excessive packaging material and practicing material reduction when ever possible. By developing more plastics based on bio-based raw materials, the great dependence on non-renewable crude oil and the environmental consequences of crude oil extraction and refining, as well as the contribution to global warming during the end of life phase, can be decreased. Persistence is desired in many applications for long term use, but for short term and single use applications, especially in the packaging sector, the use and further development of biodegradable plastic materials that are fully degradable in the natural environment, are important. Recycling of plastics involve problems since a homogeneous fraction is needed for a similar grade end-product, but the recycling could be facilitated by practicing ecodesign for recyclability and systems for collecting recyclable fractions. Increased recovery (mechanical, chemical or energy recovery) when possible, saves resources and decreases the area needed for landfill. Global action and strong measures to reduce littering are essential to protect our oceans, coastlines, fresh water ecosystems and also our terrestrial environment.

Finally, the diffuse release of chemicals from consumer products (articles), needs to receive more attention. To decrease the hazards and risks from chemicals associated with plastic production and plastic products, reduction measures, substitution, or phase out of the most hazardous chemicals, and maybe even of some polymers (if risk assessments conclude high risk), are important.

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