Technical University of Denmark

# Life cycle assessment (LCA) of printed matter: Potential “additives” in recycled paper

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**Workshop proceedings**

# Environmental and health risks of chemical additives and recycling materials

## Report on the 3rd workshop of the RISKCYCLE Coordination Action

Rio de Janeiro, Brazil, 2nd – 6th Mai 2011

**Bilitewski, B.; Barceló, D.; Darbra, R.M.; Larsen, H.F.; Rydberg, T.; Benfenati, E.; Ginebreda, A.; Grundmann, V.;**

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# 1 RISKCYCLE workshop presentations

## 1.1 RISKCYCLE – A new paradigm in waste assessment and management

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### 1.1.1 Introduction

The global trade of chemicals and products containing chemical additives such as paint, cosmetics, household cleaners, paper and cardboard, plastic toys, textiles, electronic appliances, petrol, lubricants etc. has resulted in a substantial release of harmful substances to the environment with risk to man and nature on a worldwide scale.

The discussion of the assessment and management of chemicals and products at the 1992 Earth Summit in Rio de Janeiro led to the creation of the OECD programme Globally Harmonised System of Classification and Labelling of Chemicals (GHS). The World Summit on Sustainable Development in Johannesburg 2002 encouraged countries to implement the GHS, adopted by UN ECOSOC in July 2003, as soon as possible, with a view of having the system operating by 2008.

### 1.1.2 Assessment and Management of Additives in Products

In spite of some common efforts to harmonize the safety assessment of chemicals and products a new problem with recovered material additionally appeared by the material flow in a circular economy at global scale with its risks for health and the environment in consequence of the worldwide trade of chemicals and products. Circular Economy is a concept that is transforming traditional patterns of economic growth and production. The conventional perception of economic systems is that they are linear. The linear system is converted to a circular system when the relationship between resource use and waste residuals is taken into consideration.

In 1996 the German parliament passed worldwide first the law on Kreislauf-wirtschaft (Circular Economy) and since then a number of comments demand a revision of the law. The law on Circular Economy should be changed to a law on "Material Flow". But so far this approach seemed to be too complex to follow and describe every substance and material and their flow throw the economy and the consuming society.

Therefore the German government was guided by the following points:

- The waste and pollution prevention are the foremost aim of the development of a circular economy. The prevention could be reached by a change of technology of production to cleaner production.
- The better reuse and recycling of waste. Better and more recycling friendly construction of goods are demanded to fulfil higher recycling rates.
- Step by step a new economic pattern of production, reuse and recycling have to be established. Economic tools like producer responsibility, tax and fee polices, tax deduction etc. are established.
- Mobilization of the whole society to establish a new pattern of consumption, reuse, recycling and avoidance of waste.
- Development of legal system to promote circular economy.

Extended producer responsibility, as an example, is fixed in Article 22 of the German legislation by the following provision:

<u>§ 22 Producer responsibility</u>

*(1) In accomplishing the goals of a closed loop economy producer responsibility is carried by those who produce, process and distribute goods. To fulfil the requirements associated to this responsibility, product design has to take care of that waste is avoided in the manufacture and use, and that an environmentally sound recycling and disposal of the obtained waste is ensured after the use of this product.*

The main applicable instruments stated in paragraph 2 of the same article can be summarised as follows:

| | | |
|---|---|---|
| Ensuring the functionality, long-life and safety of products | Ensuring repair and the secondary use or utilisation of products after their original use | Using of secondary materials during production |
| Take-back and subsequent utilisation or recycling of the product and the waste arising from it | **Extended Producer Responsibility** | Avoiding and minimising the generation of production-specific wastes |
| Indicating the possibility for return, re-use and utilisation at the product and set up deposit-refund schemes | Giving products which contain components with a hazardous potential a clear specification and marking | Avoiding and utilising components with a hazardous potential |

**Figure 1:** Elements for the realisation of producer responsibility according to the Recycling Management and Waste Act

Subordinate legal documents containing specific regulations for the realisation of the producer responsibility in Germany are especially found in the

- Ordinance on packaging (VerpackV)
- Ordinance on batteries (BattV)
- Ordinance on end-of-life vehicles and
- Law on used vehicles (AltfahrzeugG)
- Ordinance on electric and electronic goods

On June 12, 1991, the Ordinance on the avoidance and utilisation of packaging waste in Germany, abbreviated as Packaging Ordinance came into force. The ordinance obligates the industry and traders of its products to take back or collect separately the packaging used for the packing, transportation and sale of goods, and to forward it to recycling and/or reuse. This ordinance set the first example for the transposition of extended producer responsibility in a legal document.

An integrated part of the Packaging Ordinance is important to note for the RISKCYCLE project are stipulations towards the limitation of heavy metal concentrations (lead, cadmium, mercury and chromium VI) in packaging items. As the limiting values were fixed:

- 600 ppm after 30 June 1998,
- 250 ppm after 30 June1999 and
- 100 ppm after 30 June 2001.

Although there are good examples on the national level the new threat is coming from closing the loop in a global scale with products of unknown specification. Unsafe consumer and industrial products get onto the global market. One is of compound with estrogenic activity that has been studied extensively as an intermediate in the production of polycarbonate and epoxy resin is Bisphenol A (BPA).

Toxic substances present in e-waste among them we can list heavy metals like lead, mercury and cadmium and persistent organ halogen compounds like polychlorinated biphenyl's (PCBs) and brominated flame retardants (BFRs). It is estimated that up to 80% of e-waste from industrialized countries is exported to Asian and African developing countries for recycling and exploiting the inexpensive labour costs and weak enforcement of environmental laws.A deeper analysis of the successful recycling of paper and cardboard show, as it is done in Europe, especially graphical paper undergo a recycling process and make their ways into recovered material with unpredictable and not foreseen health and safety problems. BPA is introduced into the paper cycle through the recovery of used thermal paper. BPA is found in the wastewater and detected in the next paper product. Toilet paper has a high concentration of BPA, which can be found in the wastewater after use. Printing ink used in newspaper is contaminating the cardboard for packaging and entering the packed food exceeding the threshold values for Polycyclic Aromatics in the food by up to more than 10 times (A.Kersten, U.Hamm, H.-J.Putz, S.Schnabel Wochenblatt für Papierfabrikation 1/2011 p.14-21)

All these examples show that in a circular economy the trade in a global dimension is not acceptable without a globally agreed risk assessment for existing and newly developed chemicals and products without using additional test animals.

Against this background, the overall objective of the introduced coordination action RISKCYCLE aims to establish and co-ordinate a global network of European and international experts and stakeholders from different programmes and countries of the EU, USA, Japan, China, India, Brazil, Vietnam etc. to explore the synergies of the research carried out within different programmes and countries, and to facilitate the communication with researchers, institutions and industries and make the information about the risks of hazardous chemicals and additives in products and the risk reduction measures for substances widely available. As a result of this we have to define together future needs of R+D contributions for innovations in the field of risk-based management of chemicals and products of a circular economy in a global perspective making use of alternative strategies to animals test. In addressing how this objective will be achieved it is relevant to consider what information on present activities in this area are available and what is still unknown.

The specific objectives of RISKCYCLE are:

- To exploit complementary elements needed with regard to the research objectives, methodologies and data of on-going as well as recently completed EU and international projects.
- To specify demands for tools for ecological design of consumer products, production, use and reuse of products and waste recycled to secondary material and products. Methods such as LCA, risk assessment and risk reduction strategies, environmental impact analysis, material flow analysis and economics related tools are considered to achieve socio-eco-efficient solutions.
- To create a powerful platform enabling discussion among all stakeholders on usage, risks, chemical properties of consumer products, labelling and the fate of certain chemicals in products traded, used and recycled in a global scale, identify problems and solutions.
- To contribute to the UN Globally Harmonized System (GHS) for chemical substances and mixtures.
- To start with a conceptual development of a global strategy for a risk-based management of chemicals and additives in recycling and trade products.

- To identify alternative testing strategies and methods to avoid the enlargement and the outsource of animal tests to East and Southeast Asia
- To identify knowledge and research gaps for future research activities
- To consider the most effective way of ensuring continuing progress in this field involving EU and other partners at global scale including also international organisations.

The RISKCYCLE network closely collaborates with related projects, EU and international bodies and authorities to communicate and agree on standards and to avoid duplication and redundant work.

The RISKCYCLE project will influence policy issues at a global scale, not only in developing countries but also in developed ones and will create awareness and enhance state of the art on risk-based management of chemicals and products among stakeholders.

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## 1.2 Additives in WEEE: A Challenge for Recycling

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Since the 1950s flame retardants such as polibrominated (penta- octa- and deca-) diphenyl ethers (PBDEs), tetrabromobisphenyl-A (TBBA) and hexabromocyclododeane (HBCD) have been used in circuit boards (computers, textiles, furnitures, televisions, building materials, automotive parts) to prevent or retard the spread of fires. These compounds may be incorporated by chemical reaction or simple addition. The burst of personal computers in the 1980s greatly increased the demand of fire retardants. Brominated fire retardants (BFRs) are very useful since under heating bromine radicals are generated (Br.), which act as a chain terminator thus stopping or slowing the combustion process. Total PBDEs production was 67,000 metric tons in 2003.

The rapid development of the technologies of electrical and electronic devices the production of waste electrical and electronic equipment (WEEE or e-waste) has been raising worldwide (according to United Nations, the production of e-waste in 2010 reached 150 million tons). Many e-wastes are being exported to some east and south Asia countries (China, India, Pakistan etc.). This procedure has been creating an increasingly large environmental problem in these countries because the technologies used to recycle e-wastes (manual treatment, open incineration etc.) are inadequate under both environmental and health viewpoints. Polychlorinated byphenyls (PCBs), PBDEs and polychlorinated dibenzo-p-dioxins/furans (PCDDs/Fs) may be emitted or generated during the recycling procedures. All these compounds have led to high pollution levels in the ambient environment and further to threaten the local ecosystem and peoples' health. For instance, 10 folds higher levels of airbone PBDEs have been monitored compared to the controls and much higher levels of PBDEs in serum of workers in e-waste recycling plants in China have been reported. High levels of persistent organic pollutants (POPs) such as PCDD/Fs, PBDEs and PCBs, have been reported in sediments (even very far from the recycling plant), ash, water, vegetable life, wild animals, food chain, soils and even human body (hair, blood, breast milk, adipose tissue). PCDD/Fs, PBDEs and PCBs are recognized as anthropogenic environmental pollutants with high toxicity. They are hydrophobic and persistent in the environment. They bioaccumulate in biota and thus may present a potential threat to human health. Their estimated half-lives in the human organism are very high (2-9 years). Penta-, octa- and deca-BDEs have been restricted in the European Union (Directive 2003/11/EC) and in some states of the United States from 2004. Also, such compounds cannot be used in textiles or articles that come into contact with the skin.

BFRs are a challenge for recycling strategies since such compounds may be present in considerable quantities in WEEE. Plastics make up a considerable amount (by weight) of WEEE (~30 wt%). Mechanical processing of WEEE may release BRFs in the dust (g/kg). The dismantling areas are the most contaminated sites in a recycling plant. Pyrometallurgical (and pyrolysis) processes may release brominated and/or chlorinated dibenzofurans/dioxins. Basically, according to some studies, hydrogen bromide (HBr) and elemental bromine (Br2) are the main bromine compounds formed under pyrolysis conditions. Bromine favors formation of PBDDs/Fs. However, addition of elemental sulfur or calcium oxide greatly reduces Br2 formation (more HBr is formed). Bromine can be reduced to bromide ions by passing the gaseous pyrolysis products in aqueous sodium thiosulfate. Recovery of bromine (via oxidation of bromide ions followed by stripping with air) is possible. Disposal of WEEE in the environment may release BFRs in the landfill leachate and in the neighboring air. Biological treatment (aerobic/anaerobic) of BFRs is usually ineffective (such compounds are POPs), although temperature may have some positive effect. Chemical reduction (for instance, with Zn metal in NaOH + sodium formate in methanol) generates considerable amounts of final wastes.

Since the technology of e-waste recycling is critical parameter for emission/production of POPs, the physico-chemical procedures adopted for treating E-wastes must ensure a safe recycling process. Flame retardants are among the most difficult additives in e-waste to be treated since they are widely dispersed along the circuit board. This aspect deals with the past (old technologies of manufacturing EEE). In the future, bromine-free flame retardants must fully replace the present brominated ones. At present, phosphorous compounds (such as triphenyl phosphate (TPPO4) have been used for many polymer products such as adhesives, thermoplastic resins and coatings. Even these compounds may release very toxic compounds in inadequate incineration processes. Also, alternative non-PBDE BFRs such as hexabromocyclododeane, pentabromotoluene and hexabromobenzene may bioaccumulate in the environment and food chain.

There are many techniques for removal of flame retardants from WEEE. Solventbased recycling technology is the most commercial viable and environmentally beneficial treatment option for removal of PBFRs. On the other hand, supercritical fluid extraction may extract flame retardants very rapidly (< 2 h) under appropriate conditions. CO2 is by far the most widely supercritical fluid employed. Board grinding is helpful to achieve a fast extraction: the smaller is the particle size the fastest is the flame retardant extraction. The use of methanol as a supercritical fluid leads to decomposition of BFRs (Br2 and HBr are formed). For analytical purposes, microwave assisted extraction and pressurized liquid extraction display high yields with low solvent consumption in short time. These new techniques are promising for removing BFRs from WEEE.

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## 1.3 WEEE in Brazil – local impacts of a pervasive product

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*Purpose:* The environmental impact of waste of electrical and electronic equipment (WEEE) is a growing concern due to the presence of hazardous substances. This paper presents the flow of a mobile phone equipment in Brazil. It focuses on the manufacture of parts and components, use and end of life treatment of mobile phones, selected to show the overall life cycle dispersion of the impacts of EEE in general.

### 1.3.1 Introduction

In order to analyze the flows of electrical and electronic waste products and substances in Brazil, and their importation and exportation to other countries, we perform material flow analysis for mobile phones as a tracer device.

This choice has several justifications. First of all, there are only a few original equipment manufacturers (OEM) with facilities in the country, most of them multinational companies. The grey market for mobile phones is small (Silva, 2011). Therefore, tracking of devices and components can be done with reasonable certainty. Second, mobile communication is widespread in the country. Indeed, there are now (2010) in Brazil more mobile lines than inhabitants (Teleco, 2011).

According to the International Telecommunication Union (ITU) it is the most popular and widespread personal technology on the planet, with an estimated 4.6 billion subscriptions globally by the end of 2009, and has been the most rapidly adopted technology in history (ITU, 2009). This changing technology has led to a short lifetime of mobile phones, usually bellow two years (Silva, 2011)

Mobile phone operation started in 1990 in Brazil. With the break-up and privatization of the Telebras, the national telephonic company, in 1998, the market began to expand hugely as several private fixed and mobile operators started to compete. In the last decade, a spate of mergers and acquisitions has led to market concentration in a few players. Under pressure from the impending reverse logistics requirements and growing public environmental awareness, both operators and equipment makers are starting to take actions related to the end of life of mobile devices.

### 1.3.2 The mobile market in Brazil

Revenues in the electrical and electronic equipment sector reached more than 4.2% of Brazil's gross domestic product in 2008, a total of US$ 67 billion (ABINEE, 2009). Revenues from telecommunication equipment accounted for a substantial portion of this - US$ 12 billion in 2008 (ABINEE, 2009). Brazil is the fifth biggest market in the world for mobiles lines, according to UIT, cited by Teleco (2011).

There is also a high market share concentration of mobile operators in Brazil. The biggest one, Vivo, has around 31% of the total market, followed by TIM with 25.9%, Claro with 25% and Oi with 17.9% (Teleco, 2011).

According to IDC, Nokia is the biggest mobile manufacturer in the world, with a 33.4% market share in 2010, followed by Samsung (21%) and LG (9%). This rank is similar in Brazil. OEM manufacturing in Brazil is concentrated in two industrial regions (Teleco, 2011):

Amazon – The Manaus Free Trade Zone (Zona Franca de Manaus): Nokia, Samsung, Siemens (BenQ), Gradiente, Vitelcom and Evadin. São Paulo State – Motorola, Sony Ericsson, LG, Samsung, Telemática (Venko), Kyocera and Huawei.
Table 1 presents the production and trade balance of mobile phones in Brazil. It can be seen the huge increased of production and trade up to 2006. After this year exportation decreased and internal sales continued to grow. Since 2007 estimates are of a internal sales of mobiles over 50 million unit per year.

**Table 1:** Production and sale of mobile devices in Brazil. Sources: (1) IBGE PIA; (2) MDIC; (3) Teleco, cited by Teleco (2011).

| Mobile Phones (million units) | 2003 | 2004 | 2005 | 2006 | 2007 | 2008 |
|---|---|---|---|---|---|---|
| Production (1) | 29.3 | 42.9 | 64.3 | 61.7 | 68.4 | 68.3 |
| Overall Sales(1) | 27.3 | 41.7 | 63.4 | 58.6 | 66.2 | 69.8 |
| Exportation (2) | 11.3 | 8.9 | 32.9 | 32.0 | 22.0 | 23.9 |
| Importation (2) | 1.4 | 1.3 | 4.5 | 3.0 | 3.9 | 6.2 |
| Brazil Sales (3) | 17.4 | 34.1 | 35.0 | 29.6 | 48.2 | 52.1 |

Abinee (2010) states that more than half (53%) of imports by value in the electrical and electronic goods sector is of components, and 25% of telecommunication equipment. According to Silva (2011), low-end mobile devices are almost entirely manufactured with local components while high-end ones have a higher percentage of imported components.

### 1.3.3 Hazardous substantes contained in mobile phones

Materials and substances do not diverge that much to others electronic equipments. But there are some particularities, since the weight of the device is a constrain. Mobile devices contain a large number of hazardous substances according to Fishbein (2002). Among them, those of special concern are:

Lead – 50 grams per square meter (mainly solder); and several types of Bromines such as Hexabromocyclododecane (HBCD), Polybrominated biphenyls (PBBs), Polybrominated diphenyl ethers (PBDEs), Decabromodiphenyl ether (Deca-BDE), Octabromodiphenyl ether (Octa-BDE), Pentabromodiphenyl ether (Penta-BDE) and Tetrabromobiphenol (TBBP-A). The author also cites other hazardous substances, among them: Beryllium in connectors; Gallium arsenic in semiconductors; Tantalum in capacitors; Liquid polymers and mercury in LCDs; and Cadmium in batteries.

These hazardous substances demand special treatment to avoid human health and ecological impacts. Nonetheless, current recycling activities are prompted mainly by the value of the precious metals recovered, mostly from circuit boards, like gold, silver and paladium.

Casper Boks et al. (2000, apud by Fishbein, 2002), found that the environmental impact of a mobile device is mainly due to the circuit board (59%), followed by the liquid-crystal display (39%). Another life cycle analysis, performed by MOCIE (2002, apudby Park, et.al, 2006), indicated that the weighted environmental impacts of the raw material acquisition stage were 58.7% of the total environmental impact of mobile phones, followed by the use stage (37.5%), manufacturing stage (2.4%), disposal stage (1.1%) and distribution stage (0.3%). It should be noticed that these studies do not fully consider completelly toxicity impacts of hazardous substances used as additives in WEEE, since even today there is no available data on impacts.

Although the recent design for environment (DfE) actions imposed or not by compliance to legislation (CEC, 2003a WEEE, CEC 2003b RoHS) has probably banned the use of many of those hazardous substances reducing environmental impacts, waste generation of a mix that contains old devices should not represent this new pattern.

### 1.3.4 Before the National Solid Waste Policy - PNRS

The Brazilian National Solid Waste Management Policy (PNRS) was enacted at the end of 2010 imposing reverse logistics and treatment of electrical and electronic waste, among others streams (PNRS, 2010). Follow-on regulations of this policy are still being discussed by stakeholders of each sector. Flows of hazardous substances in the country are regulated by Resolution 1-A of January 1986 from the National Environmental Council (CONAMA), which provides rules on the transport of hazardous substances based on the Basel Convention.

Araújo et al. (2011) estimate that the waste generation of mobile phones in Brazil for the year 2009 was 26.5 million units, with 4,522 tonnes. In 2010, selective waste collection in Brazil reached only 12% of the country’s population (Cempre CicloSoft, 2011), of which electrical and electronic equipment represented 1.9% of the total collected by weight.

Some companies have proactively created take-back schemes in advance of when the mandatory rules will be imposed. Vivo, the biggest mobile operator, started a program in 2006 called “Recycle Your Mobile”. According to Limonta (2010), from 2007 to 2009 588,842 mobile devices were collected at 3,400 points by Vivo. The action is organized by Vivo but the logistic operations are managed by Belmont Trading (http://www.belmont-trading.com/). A small portion (10%) of the collected devices are reconditioned for reuse.

The mobile devices collected in Brazil are dismantled in Guadalajara, Mexico, where the plastics are recycled. Batteries are sent to Inmetco (http://www.inmetco.com/index.html), near Pittsburgh, USA. Circuit boards are sent to Sims Recycling Solutions (http://simsrecycling.com/) a smelter located in Chicago, USA for precious metals recovery. The remaining material is sent to some industries for use as secondary raw material, or disposed of at industrial landfills, according to Limonta (2010).

Nokia also has a global collection program, called "WeRecycle". The company collected 4.6 million mobiles devices in the world in 2009 (www.nokia.com). In Brazil, Nokia started with collection points at its technical assistance stores and later expanded it to supermarkets and government buildings (Silva, 2011). Nokia also sends the CBs to Sims Recycling in Chicago, while batteries are sent to the recycler Suzaquim in Sáo Paulo, Brazil. This operation has no net cost for Nokia in Brazil because recovery of precious metals from circuit boards is sufficient to cover all the treatment costs.

### 1.3.5 Flow of devices, components and substances.

According to the official trade statistics for Brazil (MDIC – http://aliceweb.gov.br/), in 2008, 68% of the circuit boards used to manufacture mobile devices were imported from Asian countries, with an average FOB (freight on board) value of US $13 per board. Also, LCDs were mostly imported from Asia (96%), with an average FOB value of US $14 per unit. High-end mobile devices have a higher share of imported components and parts than do low-end ones.

According to statistics for 2008 (MDIC), the mobile devices manufactured by OEMs in Brazil had an average FOB price of US$ 90 per unit, while mobile sets exported to other countries (85% to Latin America) had an average FOB value of US$ 85 per unit and imported mobile devices (10% of total domestic sales) had an average FOB value of US$ 101 per unit.

The Vivo program has accounted for only 0.2% of the number of mobile units sold (301 million) since the beginning of mobile operation in Brazil. The remaining devices are assumed to be in use (174 million - ABINNE, 2009), disposed of in landfills or stored in homes and offices (127 million), or even in a very small proportion recycled by other take back scheme.

The take-back scheme of Vivo from 2007 to 2009 sent 530,000 mobile devices for recycling to Belmont Trading in Mexico, while 58,000 were reused in Brazil. Assuming an average device weight of 100 grams (incl. battery), this means 53 tonnes (metric tons) sent to Mexico. Assuming that a mobile CB weights 35% of total device (Huismann, 2004) grams, 18.5 tonnes were sent to Chicago for precious metals recovery and hazardous substances treatment.

### 1.3.6 Conclusions

Due to the large and still rapidly expanding global market for mobile devices, the disposal of these devices is a big concern in every country. As pervasive personal products, they are virtually everywhere. Consequently, their waste needs special attention from all stakeholders to in order to establish sound and fair policy measures for the end of life of these devices.

Substance, materials and components are extracted and manufactured in several different countries and then assembled on a mobile device. Predominant end of life scenarios are household storage or landfilling. A mobile operator established a collection scheme exporting the circuit boards of the discarded mobiles for precious metals recovery, revenue that finances the operational cost of the scheme. Nonetheless, the decreasing use of precious metals in new mobiles will make recycling for precious metal recovery less attractive.

The technology trend indicates growing convergence of the personal computer and communication industries, as new types of devices appear, such as Ipads, Iphones and so on, as well as the rapidly expanding use of with light-weight “smart” appliances that are equipped with many of the same parts and components (LCDs, CBs). Analysis of the strategies of the sector and government regulations is fundamental for an understanding of the generation and flows of WEEE.

No matter what governmental policies are actually put in place, it is of key importance to raise awareness of consumers of the impacts and risks generated by the waste created by mobile phones and other electrical and electronic devices. Then they will be more likely to take actions, such as avoiding over-consumption of equipment and participating in reverse logistics and recycling schemes set up by companies and governmental entities.

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## 1.4 Prioritisation of chemicals in the environment: analytical, modelling and risk issues

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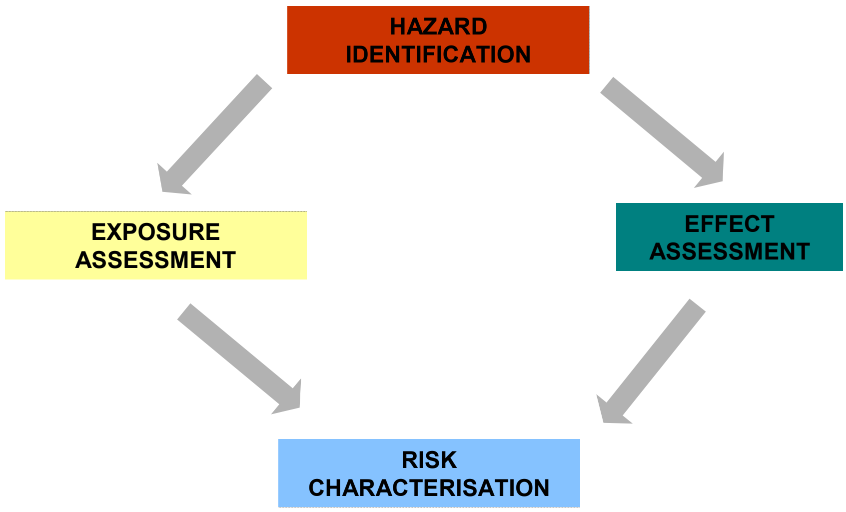
Our technological society makes extensive and intensive use of chemicals (most of them organics) and this number is continuously growing. Thus, for instance the European Inventory of Commercial Chemical Substances (EINECS) reports up today 100,204 commercially available substances and similar figures hold for the U.S.A.

Hence, depending on their properties, mode and extent (volume) of use this large amount of different chemicals can potentially reach the environment, being their environmental and health effects unpredictable in long term. This has become a matter of major concern and constitutes the reason for new regulations related to the safety of chemicals are being promoted. Thus, for instance, the existing European Union regulation REACH (EC 1907/2006) foresees to regulate chemicals used in commerce and consumer products, including a list of c.a. 30,000 compounds. About 10,000 have been already registered 2,782 of which are considered of high production (> 1,000 tons/year).

On the other hand, a simultaneous and huge progress on the analytical methods and techniques has taken place, mostly associated to the development of multiresidue analytical methods based on chromatographic techniques (GC and LC) coupled to mass spectrometry (MS), capable to identify and quantify compounds at environmental trace levels of ng or pg/l. Such progress has substantially enlarged the possibilities of environmental monitoring and control. However, since not all measurable compounds are worth to be measured some kind of prioritisation or ranking is required in order to allocate analytical control efforts towards some target compounds, otherwise the task would be unbearable.

The underlying rationale in the majority of the prioritisation lists of chemicals is based on the notion of their associated risk. Risk is broadly defined as the combination (i.e., product) of a probability of occurrence of some event by its hazard effects:




$$\textit{Risk} = \textit{Occurrence probability} \times \textit{Adverse Effects}$$

Occurrence probability is associated to environmental exposure and it is usually expressed in terms of environmental concentration. Environmental concentrations can be obtained by analytical measurements ("Measured Environmental Concentration", MEC) or predicted through modelling ("Predicted Environmental Concentration", PEC). Both methods offer pros and cons.

Factors influencing environmental concentration of chemicals are summarized below:

- **Intrinsic to the compound**
  Physico-chemical properties: Solubility, Vapor Pressure, Partition Behavior (Kow , Henry, Adsorption Isotherms), Reactivity etc.
- **Environmental conditions**
  Temperature, flow, wind velocity, humidity, rainfall, solar radiation etc.
- **Anthropogenic**
  Amount produced, mode of use, emission factors, recycling and recovery practices.

Adverse effects usually take into account compounds *persistence*, *bioaccumulation* and *toxicity*. Furthermore, *mutagenic*, *carcinogenic* and *reproduction effects* are also considered.

Different risk assessment approaches have been developed in order to identify and rank compounds of environmental concern for both *regulatory* and *monitoring* purposes. Whereas most of all the existing ranking and prioritization schemes share the basic underlying risk assessment paradigm, they differ on how both factors, i.e., occurrence and effects, are defined and hence quantified.

The aim of the presentation is to provide a general overview of the question.

## 1.5 Environmental risk assessment of brominated flame retardants using fuzzy logic

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In this study, a model for the evaluation of the environmental risk of polybrominateddiphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) for the aquatic organisms has been developed. These compounds are brominated flame retardants (BRFs) used in plastics, electronic devices, textiles and others to prevent fire. The model designed is based on a technical application of the Fuzzy Theory (Zadeh, 1965). In particular, three interconnected Fuzzy Inference Systems (FIS) have been created through the use of the Fuzzy Toolbox in Matlab (MATHWORKS, 2010). In order to improve and make the model scientifically robust, several international experts have been questioned about different information needed to build the fuzzy system. Information from 38 questionnaires have been collected and statistically treated. The model has been tested in two case studies, using the data provided by four samples campaigns in two Ebro tributaries in north east of the Spain, the Cinca River (2002 and 2004) (Eljarrat et al. 2005) and the Vero River (2004 and 2005) (Eljarrat et al. 2007). Concentrations in biota and sediments obtained in the sample campaigns have been used directly as input for the model. Missing data for HBCD and PBDEs, as BMF factor and toxicity data have been obtained through scientific literature. In both rivers, there exists an industrial park with a widespread use and consequently discharge of flame retardants into the water body. The proposed model evaluates the risk in different points according to the industrial parkposition. In the Vero River, only PBDEs have

been found. The risk of these compounds for the aquatic organisms before the source of pollution has been categorized as LOW (both in 2004 and 2005), with a value of 0.352 (in a range [0-1]). After the industrial park, the risk (0.62) has been considered to be mainly MODERATE in 2004, and mainly HIGH (0.78) in 2005. In CincaRiver, four different samples points have been analysed, finding a HIGH risk (0.78) for HBCD in the most contaminated site (near the industrial city of Monzón). Values for PBDEs are much lower in this case study, representing LOW risk in all the analysed points. Concerning the model design, the classic procedure of the FIS has been modified with the aim to give weights or relative importance to the several environmental variables involved in the model. This new insight has been compared with the classic FIS system and has proved to be more conservative and sensitive for all the case studies. The results obtained with the proposed methodology prove that the qualitative environmental risk assessment of PBDEs and HBCD is possible through fuzzy logic. Numerical values and bibliographic data can be translated into fuzzy sets, dealing with the uncertainty and providing a final output easy to understand by the human mind (e.g. LOW, MEDIUM, HIGH risk). This information can be very useful for the decision making processes

**References:**

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[2] ELJARRAT, E.; LABANDEIRA, A.; MARSH, G.; RALDÚA, D.; AND BARCELÓ, D. - Decabrominateddiphenyl ether in river fish and sediment samples collected downstream an industrial park. *Chemosphere Volume 69, Issue 8, October 2007, Pages 1278-1286*.

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## 1.6 Additives and Life Cycle Assessment – introduction and overview

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### 1.6.1 Introduction

#### 1.6.1.1 Life cycle assessment

Environmental life cycle assessment (LCA) is the calculation and evaluation of the environmentally relevant inputs and outputs and the potential environmental impacts of the life cycle of a product, material or service (ISO 14040:2006). Environmental inputs and outputs refer to demand for natural resources and to emissions and solid waste. The life cycle consists of the technical system of processes and transports used at/needed for raw materials extraction, production, use and after use (waste management or recycling) (Figure 1).

All stages in a product's life cycle result in the generation of wastes, in emissions, and in the consumption of resources. These environmental exchanges contribute to regional and global impacts such as climate change, stratospheric ozone depletion, photooxidant formation (smog), eutrophication, acidification, toxicological stress on human health and ecosystems, the depletion of resources, and noise, among others. The need exists therefore to assess the contributions to these impacts that are associated with the provision of a product in an integrated manner. This life cycle assessment provides complimentary insights to those of many regulatory and more site or process orientated risk and impact assessments.

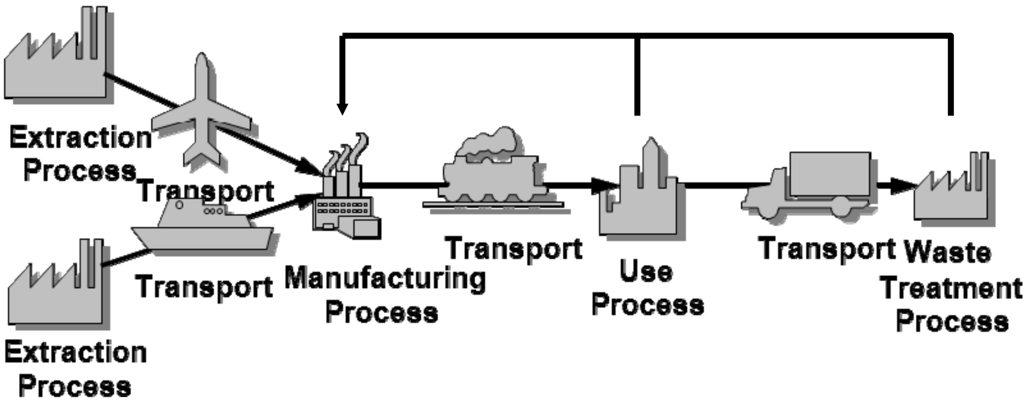


**Figure 1:** A schematic life cycle including recycling

### 1.6.2 The LCA procedure

In the *goal and scope definition* of an LCA the practitioner defines the product system in terms of the system boundaries of the study and a functional unit.

*Life cycle inventory (LCI)* is the methodology for estimating the consumption of resources, the quantities of wastes, the emissions, etc. that are associated with each stage in a product's life cycle. The processes within a life cycle and the material and energy flows are modelled. The overall models provide mass and energy balances for the product system, its total inputs and outputs, on a per functional unit basis.

*Life Cycle Impact Assessment (LCIA)* provides indicators for analysing the resource extractions, the wastes, the emissions, and other data in the inventory in terms of contributions to different impact categories.

*Interpretation* occurs at every stage in an LCA. If two product alternatives are compared and one alternative has a higher consumption of each resource, for example, an interpretation purely based on the LCI can be conclusive. In many other studies, drawing conclusions will require at least an LCIA, a sensitivity analysis, and consideration of the statistical significance of differences in each impact category.

### 1.6.3 Impacts of concern

In theory, all potential environmental impacts relating to the inputs and outputs should be studied, but limitations of the scope of an LCA study is necessary (ISO 14044:2006).

*Global warming:* The most relevant emissions in this category are carbon dioxide ($CO_2$), for which a distinction is made between $CO_2$ from fossil and biomass sources; methane ($CH_4$), dinitrogen oxide ($N_2O$). In addition, it is now common to take also nitrogen oxides ($NO_x$) and non-methane volatile organic compounds (VOC) into consideration. The GWP100 characterisation factors (global warming potential) are used, in which the potential contribution to climate change is modelled for a 100- year time span.

*Acidification:* The emissions in this category are sulphur dioxide ($SO_2$, $SO_x$), nitrogen oxides ($NO_x$); and hydrochloric acid (HCl). Other emissions are normally insignificant in this category. The emissions are characterised according to the maximum possible contribution to acidification (Acidification potential)

*Eutrophication:* The emissions contributing to overfertilisation of soils and surface waters (eutrophication) are nitrogen- and phosphorous-containing compounds. In addition, organic matter released to waters are covered in this category as they ultimately give the same effect, i.e. oxygen consumption and deficiency in water environments. The basis for the characterisation (Eutrophication potential) is the ratio of C : N : P in water organisms.

*Tropospheric ozone creation:* Emissions contributing to this problem are hydrocarbons, other volatile organic compounds, and nitrogen oxides (NO, $NO_2$). The characterisation basis is the chemical's ability to contribute to photochemical ozone (photochemical ozone creation potential).

*Resource depletion:* The resource category is predominantly interesting in the present study for assessing energy-containing materials. Therefore the chosen method is to evaluate the energy balance in the different scenarios.

For a number of other important environmental problems, methods are still relatively in their infancy. For e.g. *biodiversity loss*, the mechanisms are not really clear, and also, the effects is rather far down the cause-effect chain. For *water consumption* and *land use effects*, methods to account for these are under discussion, and inventory data (i.e. sources of information for inputs and outputs) often do not cover appropriately these aspects. Basically the same statements can be made for *toxicity and eco-toxicity aspects*, i.e. there has been a lack of agreed methods, but many attempts have been made until now. In fact many different methods are available, but there has been relatively little common understanding and harmonisation of the methods. In reality, this also has contributed to a lack of data about occurrence in products and about emissions of pollutants relevant to assess toxicity and eco-toxicity stress, in the context of LCA studies.

### 1.6.4 "Footprinting" methods

To put it simply, the carbon footprint, and by analogy water footprint, and chemical footprints (also toxic or ecotoxic footprint) are detailed methods and descriptions on how to assess specific impact categories. Typically the "footprints" are developed to be a form of Life cycle based assessment. For carbon footprint and water footprint, ISO standardisation is under way (ISO 2011 a, 2011 b). For chemical/toxic footprint, SEAC Europe LCA Steering committee has initiated a process to tentatively arrive at a scientifically founded and agreed method. An inaugural meeting for the setup of some form of working group is scheduled within the frame of SETAC Europe Annual Meeting 2011 in Milan, Italy (SETAC 2011)

### 1.6.5 Methods to balance effects against each other

In LCA it may become desired or he analysis and evaluation to balance across impact categories, particularly when there are trade-offs in terms of impact categories between product alternatives or if it is desirable to prioritise within a product's life cycle. This is often termed Valuation or Weighting. See figure 2. For example, emissions of $CO_2$ equivalents in one life cycle may result in a higher climate change indicator than in another, but the alternative involves the use of more pesticides and therefore has a higher potential contribution to regional toxicological risks. A stakeholder may therefore want more information to help guide which difference is of a higher priority. Resolving such issues draws not only on natural sciences but often relies on social science and economics. In some applications, particularly for policy support, this results in the monetisation of externalities (impact indicators) to provide results for different impact categories in terms of Euros, Yen, etc.

The methods are typically sorted into the following three categories:

- Expert judgement
- Relation to environmental standards
- Estimate the economic value of damages

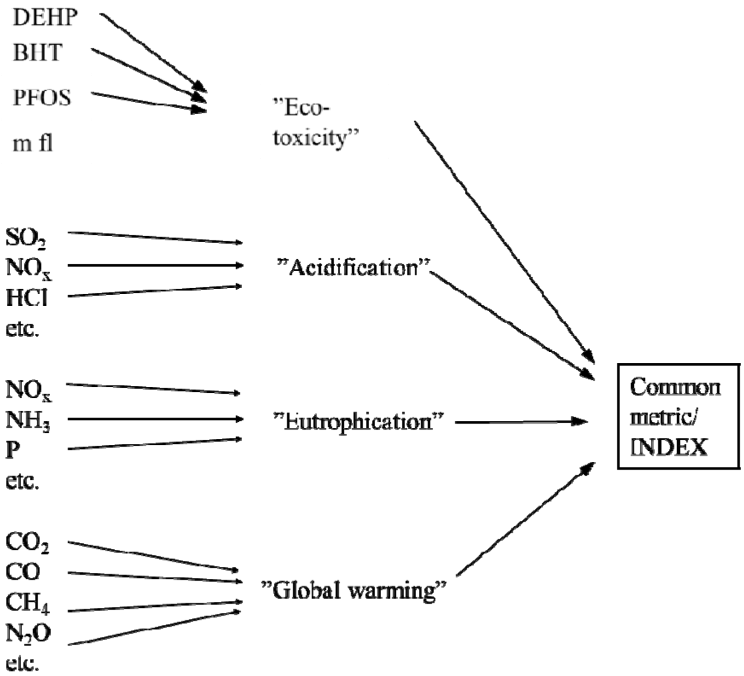


**Figure 2:** Structure for aggregating and balancing environmental impact categories in LCA

### 1.6.6 Monetary valuation

The monetary valuation of different effects is not a straightforward procedure since many of the effects have no market value. The total value is often composed of both use values and non-use values. The use value is the value derived from actual use of a good or service. This use value includes direct, non-direct and option values. The direct use value is the value attributed to direct utilization of ecosystem services. Non-direct-use values or "functional" values relate to the ecological functions performed e.g. by forests, such as the protection of soils and the regulation of watersheds. Option value is the value that people place on having the option to enjoy something in the future, although they may not currently use it. The non-use values, also referred to as passive use values, are values that are not associated with actual use, or even the option to use a good or service. The non-use values include both bequest and existence value. Bequest value is the value that people place on knowing that future generations will have the option to enjoy something. Existence value is the value that people place on simply knowing that something exists, even if they will never see it or use it. In order to assess these values, environental economics uses several methods. These methods may be based on stated preferences or revealed preference. Stated preference methods, involving studies, including questionnaires, asking respondents for their willingness to pay (WTP), such as in the case of contingent valuation and choice experiment methods, as well as asking the respondents for their willingness to accept (WTA). Other methods are based on revealed preferences that are often based on consumers´ or producers' behaviour or actions such as: The hedonic price method is used to estimate the value of environmental effects on properties such as the effect of noise or air pollution on house prices; The production function method is used to estimate the value of the environmental effects on production such as the effect of ground-level ozone on the production of wheat or timber. WTP:s studies is used to determine market price for a non-market good. The current preferences of the survey population state the current price, given their awareness of the subject and the information available. The values mirror the current attitude and preferences, rather than the importance of the environmental impact. The result can be compared to the values of marketed goods.

#### 1.6.6.1 Example Hazardous substances in WEEE

Some of the substances of potential concern in WEEE flows are: Mercury, used in the light source of flat panel displays; Lead, used among others for solders in electronics components; polybrominated diphenyl ethers (PBDE), used as flame retardants in plastic housing of electric products; Triphenyl phosphate (TPP), used as flame retardant and plasticiser, sometimes as substitute for brominated flame retardants.

#### 1.6.6.2 Mercury

A literature review related to damage cost of Hg based on IQ decrement in the USA was performed by Spadaro and Rabl (2008) in which they concluded on the basis of their review that it is proper to use US$ 18,000 per IQ point. Reviewed studies indicated values ranging from US$ 4500 up to US$ 22,300 per IQ point. The value taken corresponds to a marginal cost for emissions of mercury to be 1,500 $/kg or 3,400 $/kg, depending on the method to calculate the dose-response function.

#### 1.6.6.3 Lead

Lead is perhaps the most studied toxic metal in the environment. The main reason is its effects on the central nerve system and its extensive use as additive in gasoline. Steen (1999) estimated the global average impact of lead emissions on human health to be 2910 ELU/kg emission.

### 1.6.7 Additives in products and waste, and their concern in LCA

Concerns about possible effects on human health and the environment from additives/impurities accumulated in globally recycled waste/resources like paper and plastics was one of the main reasons for starting up the EU FP7 Coordination Action project RiskCycle (www.wadef.com/projects/riskcycle). A key aim of the project is to identify research needs within this area focusing on both risk assessment (RA) and life cycle assessment (LCA). Work package 6 of RiskCycle “Life cycle assessment (LCA) of additives” addresses the issue on how to include additives (including accumulation of additives/impurities in globally recycled waste/resources) in life cycle assessment. Case studies on plastics and paper are going to be performed including the provision of relevant inventory data (process-related resource consumptions and emissions) and life cycle impact assessment (LCIA) characterisation factors for specific additives/impurities. Until now reviews on the state of knowledge regarding additives and LCA have been performed on plastics and printed matter/paper. Furthermore, the degree to which LCIA characterisation factors already exists for the proposed additives have been investigated.

For example, within the Swedish research project ChEmiTecs emissions of about 200 organic chemicals from consumer products containing plastic materials have been estimated and reports also in RISKCYCLE publications (Rydberg *et al.* 2011). These plastic additives have a wide range of physical-chemical and (eco) toxicological properties which is why it is of interest not only to assess the emission loads but also the potential risks. Therefore also Impact assessment characterisation factors have been derived for the additives (Andersson et al, 2011). The findings in these studies may provide added value to LCA studies from now on, as they contribute to better inclusion of considerations of content and emission mechanisms of additives and thus the related potential health and environmental risks.

## References

[1] ISO 14040

[2] ISO 14044

[3] ISO 2011 a

[4] ISO 2011 b

[5] SETAC 2011

## Acknowledgement:

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## 1.7 Life cycle assessment (LCA) of printed matter: Potential "additives" in recycled paper

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### 1.7.1 Introduction

Concerns about possible effects on human health and the environment from additives/impurities accumulated in globally recycled waste/resources like paper was one of the main reasons for starting up the EU FP7 Coordination Action project RiskCycle (www.wadef.com/projects/riskcycle). A key aim of the project is to identify research needs within this area focusing on both risk assessment (RA) and life cycle assessment (LCA). Besides the sector on paper (being in focus here) also plastics, lubricants, textiles, electronics and leather are included in RiskCycle. In Figure 1 the life cycle of printed matter (paper) is illustrated showing the recycling step which is in special focus in RiskCycle.

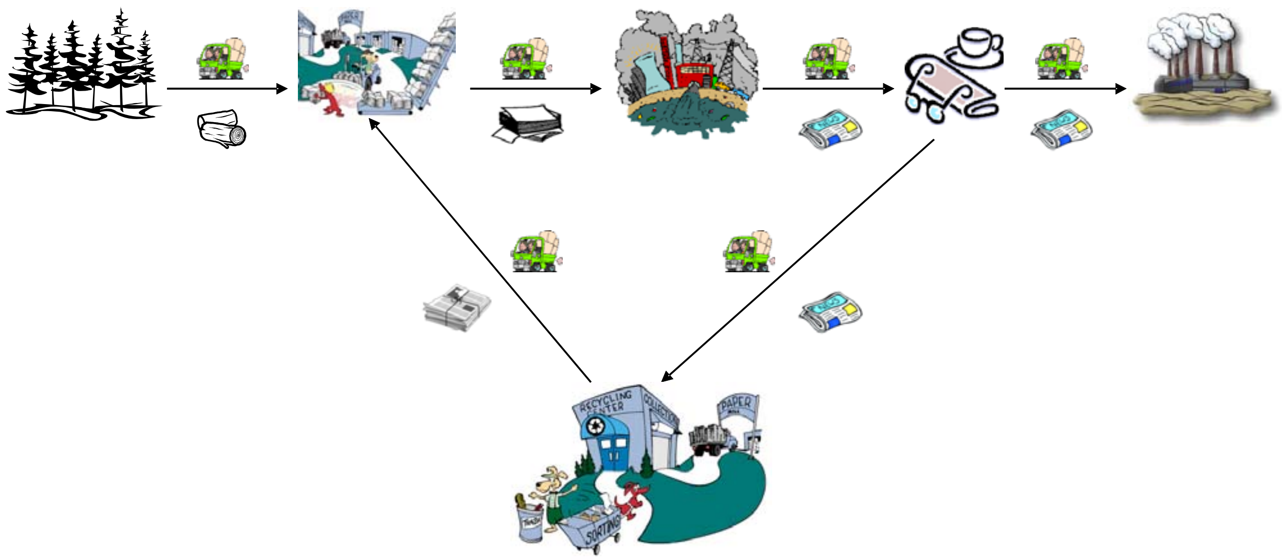

**Figure 1**: Life cycle of printed matter including recycling [1]

Work package 6 of RiskCycle "Life cycle assessment (LCA) of additives" addresses the issue on how to include additives (including accumulation of additives/impurities in globally recycled waste/resources) in life cycle assessment. Case studies on paper and plastics are going to be performed including the provision of relevant inventory data (process-related resource consumptions and emissions) and life cycle impact assessment (LCIA) characterisation factors for specific additives/impurities. This document deals with the importance of additives/chemicals, used in the printing industry, for the LCA impact profile on printed matter. Furthermore, highly problematic additives/chemicals that might stay/accumulate in the paper when recycled are also addressed. The research reported here is based on an LCA on printed matter [1] and a Danish substitution project [2] – both performed by the author.

### 1.7.2 Life cycle assessment of printed matter

Only a few LCA studies have been done on printed matter (including paper) – mostly focusing on the energy part [1;3]. However, one of the most recent and comprehensive studies [1;3] actually include toxic impacts from chemical emissions – mostly printing chemicals like printing ink of which some components may accumulate in recycled paper. Even though recycling is included in that study there is no special focus on the additives/impurities in the recycled paper. However, the study shows that potential toxic impacts from the production and use of chemicals like pigments, solvents, metals, AOX and biocides may play a very significant role in the impact profile of printed matter as shown below (in brackets: percentage of total normalized and weighted impact potential, EDIP97 methodology):

- Emissions of ink residues (tetradecane) and cleaning agents (hexane, tetradecane) during the printing process and cleaning (35%)
- Emissions (dichlorobenzidine, chloroaniline, cuprous chloride) during pigment production (17-20%)
- Emissions of heavy metals and AOX (as dichloro benzene) during paper production (>3%)
- Emissions of fountain chemicals (i.e. isopropyl alcohol, IPA) during the printing process (6%)

- Emissions of biocides and hydroquinone from the repro- and plate making process (3%)

Anyway, the study only considered a few generic chemical recipes (one printing ink, few cleaning agents etc.) and at least the following shortcomings in need of further research may be identified:

- Ink components (and their precursors) production: siccatives, antioxidants, pigments, dyes etc.
- Water emissions from paper production: softeners (BPA), other phenolic compounds (NPE, APE), other surfactants (LAS), biocides (benzothiazoler, dibromo-compounds), wood extractions (terpenoids, resin acids) and more
- Recycling of paper: Fate of paper chemicals, ink chemicals, glue chemicals etc.
- Treatment of chemical waste: Fate of (hazardous) waste from printing (ink waste, used cleaning agents, used rinsing water etc.) and from recycling of paper (sludge from repulping)

### 1.7.3 Chemicals of high concern in the printing industry

The implementation of the EU REACH regulation will most probably promote substitution within sectors handling a lot of different chemicals like the printing industry. With the aim of being at the cutting edge of this development the Danish printing industry started up a substitution project in 2006. A major part of the work has been mapping the presence of chemicals which are potential candidates for substitution (e.g. PBT, CMR, vPvB, EDS). The mapping comprises a combination of a literature study and an investigation of the actual (2007) presence of candidate substances at 15 Danish printing houses including the examination of almost 900 MSDS's (i.e. products). Furthermore, a focused search in the Danish Product Register has been included.

**Table 1.** Substances of very high concern (SVHC) appearing on the recently updated EU REACH Annex XIV candidate list and found in the Danish printing industry

| Name | CAS No. | Annex XIV criteria | Use |
|---|---|---|---|
| Chromtrioxide | 1333-82-0 | Carc 1, mut 2 | Chrome plating (gravure) |
| Trichloroethylene | 79-01-6 | Carc 2 | Inks |
| Cobalt-siccatives * | (10124-43-3) | (Carc 2) | Inks (off-set, screen printing) |
| Acrylamide | 79-06-1 | Carc 2, mut 2 | Unknown (impurity?) |
| Pigment Yellow 34 (lead-chromate) | 1344-37-2 | Rep 1 | Inks (screen printing) |
| Pigment Red 104 (lead-chromate) | 12656-85-8 | Rep 1 | Inks (screen printing) |
| 2-Methoxy ethanol | 109-86-4 | Rep 2 | Photochemistry |
| Di(2-ethylhexyl)phthalate, DEHP | 117-81-7 | Rep 2, EDS-list | Inks |
| Dibutylphthalate, DBT | 84-74-2 | Rep 2, EDS-list | Inks (screen printing, flexo) |
| Benzylbutylphthalate, BBT | 85-68-7 | Rep 2, EDS-list | Inks |
| Boric acid and borax | 10043-35-3 and 1301-96-4 | Rep 2 | Photochemistry |

* Possible content of soluble cobalt(II)salts. Cobalt(II)sulphate, cobalt dichloride, cobalt(II)rbonate, cobalt(II)dinitrate and cobalt(II)diacetate all appears on the recently updated REACH Annex XIV candidate list [25]. IARC classify all soluble cobalt(II)salts as possible carcinogenic, i.e. group 2B (http://monographs.iarc.fr/ENG/Monographs/vol86/mono86.pdf)

More than 200 of the mapped substances are candidates for substitution according to Danish legislation (List of Undesirable Substances) and a total of about 60 of these substances fulfil one or more of the criteria (e.g. CMR, EDS) for the REACH Annex XIV candidate list (Authorisation List).

**Table 2.** Substances meeting Annex XIV candidate list criteria and found in the Danish printing industry (not listed on the REACH Annex XIV candidate list but potential candidates that may be listed in the future

| Name | CAS No. | Annex XIV criteria | Use |
|---|---|---|---|
| Benzene | 71-43-2 | Carc 1, mut 2 | Inks, cleaning agents |
| Epichlorohydrin | 106-89-8 | Carc 2 | Unknown (impurity?) |
| 2-Methylaziridine | 75-55-8 | Carc 2 | Inks (flexo) |
| Aziridine | 151-56-4 | Carc 2, mut 2 | Inks (flexo, screen printing) |
| Propylenoxide | 75-56-9 | Carc 2, mut 2 | Inks, cleaning agents |
| 2-Methoxy propylacetate | 70657-70-4 | Rep 2 | Inks (screen printing) |
| Triethylene glycol dimethylether | 112-49-2 | Rep 2 | Brake fluid |
| 2-Methoxypropan-1-ol | 1589-47-5 | Rep 2 | Unknown |
| Alkylphenolethoxylates | (25154-52-3) | EDS-list | Inks, cleaning agents |
| Chloroalkanes, C14-17 | 85535-85-9 | Possible PBT/vPvB-substance | Chain oil |
| Octamethylcyclotetrasiloxane (polydimethylsiloxane) | 556-67-2 (9016-00-6) | Possible PBT/vPvB-substance | Inks |
| Bisphenol A | 80-05-7 | EDS-list | Inks, thermal paper |
| Resorcinol | 108-46-3 | EDS-list | Glue |
| Styrene | 100-42-5 | EDS-list | Inks, glue |
| Decamethyl-cyclopentasiloxane | 541-02-6 | Possible PBT/vPvB-substance | Inks |
| Stoddard solvent | 8052-41-3 | Carc 2 | Unknown |
| Solventnaphtha (crude oil), hydrogen treated light naphthen-(benzene >= 0.1%) | 92062-15-2 | Carc 2 | Cleaning agent |

In Table 1 and 2 the about 30 substances actually found in the Danish printing industry in 2006 and 2007 (i.e. the novel printing industry inventory and the searches in the Product Register) which meet one or more of the REACH Annex XVI criteria are shown. Eleven of these substances are now (December 2010) part of the Annex XIV candidate list [4], see Table 1. Regarding five out of these eleven substances, i.e. the lead-chromate pigments Pigment Yellow 34 and Pigment Red 104, and the phthalates DEHP, DBT and BBT, inclusion in Annex XIV (Authorization List) is recommended by ECHA and adopted by the Member State Committee [5;6].

Regarding the three phthalates in Table 1, i.e. DEHP; dibutylphthalate, and benzylbutylphthalate, a total yearly consumption above 1 ton, an appearance in about 40 products and a concentration range of 0.1% – 75% in the products are observed in the Danish printing industry. These substances are of interest as they are components of printing inks and remain in the ink after drying and therefore follow the substrate, i.e. paper, plastic or textile, when recycled. They may therefore appear in the recycled material. Actually, according to a German investigation [7] dibutylphthalate have been found in recycled paper used for food packaging. Also other substances in Table 1 and 2 may be of interest as being components of printing inks like the lead chromate pigments, the siloxanes and bisphenol A. Furthermore, 26 hydrocarbon mixtures, most probably containing hazardous single substances (e.g. hexane, heptane, naphthalene) are found in the Danish printing industry. Many of these are used as components in printing inks (and cleaning agents) and therefore may follow the printed substrate when recycled. Some of the hydrocarbon mixtures are used in relatively high amounts in the Danish printing sector like "naphtha (petroleum), hydrodesulfurized (benzene < 0.1%)" used at a total level of 1 500 ton/year, in 35 products with a content of 0.1% – 100%. Finally, it should be noted that highly toxic substances only found in the literature study, like potassium dichromate and hydrocarbon mixtures with high benzene content (>> 0.1%), are probably still in use at places on the world market with less strict environment and health regulation (e.g. Asia), even though phased out on the Danish market. These substances may therefore be relevant when looking at globally recycled printing substrates like paper, plastics and textiles.

### 1.7.4 Conclusions and discussion

Based on the results obtained until now within RiskCycle it may be concluded that in order to perform LCAs on waste/resources recycled globally both new inventory data and new characterisation factors have to be provided. A preliminary solution to the lack of inventory data may be to use Material Flow Analysis and emission factors. One of the main reasons for this lack of useable data on additives for LCA is probably the general focus on energy which has dominated LCA until recently and the lack of consensus on how to include toxicity. Impact categories related to toxicity (and chemicals) are more difficult to handle than e.g. acidification and global warming for which a much higher degree of consensus have existed among method developers for several years. Anyway, consensus on how to deal with human toxicity and ecotoxicity in LCIA is approaching and the USEtox model is probably the best candidate.

The survey of chemicals which are potential candidates for substitution within the Danish printing industry resulted in about 200 substances/substance groups. In total about 60 of these substances fulfil one or more of the criteria for the EU REACH Annex XIV candidate list. Some of these, like the phthalates and the lead chromate pigments, may be relevant when looking at the potential hazard of globally recycled paper based on printed matter.

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## 1.8 Research relationships in Waste Management between Brazil and Germany

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### 1.8.1 Introduction

The research relationship between Brazil and Germany has a very long history of more than 40 years. Germany and Brazil joined already in 1969 an intergovernmental agreement on scientific and technological cooperation. Amon other agreements, in 1997 the framework agreement on scientific research and technological development between Germany and Brazil has been updated. It then included the integration of industry partners in collaborative projects.

The focus of research relationships lies predominantly on the areas of environment, climate and sustainable development, aerospace, agriculture, health, and higher education and training. Since 2007 the cooperation in the areas advanced materials, biotechnology, production technology, nanotechnology and information and communication technologies have been intensified.

The results of a IP-UNILINK PROJECT Macro-Analysis from 2009 [1] highlighted among others, existing Science, Technology and Innovation cooperation initiatives between Brazil and the European Community. The data of the study have been collected from various sources, including the CORDIS databases. According to CORDIS, the following countries are the most active when it comes to research cooperation with Brazil:

| COUNTRY | NUMBER OF PROJECTS |
|---|---|
| France | 61 |
| United Kingdom | 60 |
| Germany | 45 |
| Spain | 36 |
| Italy | 28 |
| Belgium | 20 |
| Netherlands | 14 |
| Portugal | 10 |

**Figure 1:** EU financed projects with Brazilian participation [1]

The most active Brazilian ministries and government research and funding institutions in science and technology agreements with the EU are shown in figure 2.

| INSTITUTION |
|---|
| **MRE** - Ministry of External Relations (broader agreements) |
| **CAPES** - Brazilian Federal Agency for Support and Evaluation of Graduate Education |
| **INPE** - National Institute For Space Research |
| **CNPq** - National Counsel of Technological and Scientific Development |
| **FAPESP** - São Paulo State Foundation for the Promotion of Research |
| **MCT** – Ministry of Science and Technology |
| **MMA** – Ministry of the Environment |

**Figure 2:** Most active Brazilian ministries and government research and funding institutions in science and technology agreements with the EU [1]

The most active funding institutions in Brazil are: MCT (Ministry of Science and Technology), CNPq (National counsel of Technological and Scientific development) and CAPES (Brazilian Federal Agency for Support and Evaluation of Graduate Educaion). In Germany it is amongst others: the DAAD (German Academic Exchange Service), Alexander von Humbold Foundation and DFG (German Research Foundaion). On a EU level the majority oft he research fundings are based on the Framework Programmes FP6, FP7 and the Erasmus Mundus funding.

### 1.8.2 Cooperations with German Academic Exchange Service DAAD [2]

On the field of International Co-operation programs and consultancy projects the DAAD can look back on many years of experience in higher education cooperation projects with its partner countries. It has large expertise in international technical assistance projects and contribution to shape education policy in the project region. DAAD is successful in International project predominantly because of the experience made in its own range of programs and because of long-term cooperation with decision makers in university and at government level. Further on its global network of regional offices and information centres worldwide, a large pool of experts, its representation on decision-making bodies and national committees responsible for questions of education policy and a wide variety of programs that are offered from student to scientist are the key reasons for successful partnership in research colacorations.

#### 1.8.2.1 DAAD – CAPES partnerships

Brazil is a major beneficiary of DAAD scientific cooperation and has for decades been one of the most important partner countries in higher education cooperation. In 2006 184 partnerships between German and Brazilian universities were recorded in the Higher Education Compass of the Rectors' Conference. The efficient and continuous activity with CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superio) is one of the cornerstones of many years of cooperation with Brazil. CAPES is partner and co-financer for individual scholarships for Brazilians as well as in the program for individual-related project funding “PROBRAL”. CNPq (Brazilian Research Council) is also a strong partner for the DAAD. In 2006 820 Brazilian students, graduates and scientists have been in the promotion of DAAD and 548 new scholarships have been awarded. A total of 1503 German and Brazilian students, graduates and scientists have been promoted. The Average over the last few years is ca. 1/3 of the DAAD with all Latin American countries sponsored exchanges, were in cooperation with Brazil.

In cooperation with DAAD and CAPES the following programs for Brazilians have been offered: 1 year scholarships, short research fellowships and Surplace scholarships. 1 year scholarships have been promoted 104 Brazilian scholarship holders, predominantly doctoral studies and another 125 Brazilian government scholarship in 2006 were mentored by the DAAD. 26 Brazilian students have had a scholarship for a 2 up to 6 month research stay, funded as part of their doctoral dissertation.

The Programs for Germans can be divided in programs for students, graduates, lecturers and others. In 2006 20 German students received a scholarship for one-or two-semester to study abroad at Brazilian universities, 26 graduates were able to perform their graduate work in Brazil with DAAD support and a total of 135 German students completed an internship with the support of the DAAD in Brazilian companies and Universities. Further on 16 German graduate students (6 short-term grants, 10 annual grants) were encouraged for research and study in Brazil.

In 2006 17 German and 28 Brazilian scientists travelled at the invitation of the respective cooperation partner to a one up to three-month research visit to Brazil and Germany within the Academic Exchange Programs.

Within the program of project-related exchange (PROBRAL/CAPES) 75 bilateral research projects under involvement of young scientists were promoted with 159 German participants in the projects and a similar number of Brazilian scientists and students. PROBRAL thus represents a cornerstone in the exchange of scientists with Brazil.

Integrated projects of cooperation in higher education (UNIBRAL), is a exchange of students for a fully recognized part of their studies at a partner university. The exchange of students will be supplemented with High school teachers travelling for evaluation purposes and teaching projects. In 2006 25 projects with 118 German academics were in the promotion.

#### 1.8.2.2 Exemplary projects with Brazilian-German cooperation

The project “Pollutants into the residual waste and landfill sites due to electrical and electronic equipment (**WEEEBRAL**)” started in 2008 and was done by TUD (Technische Universität Dresden – IAA) and USP (University of Sao Paulo - School of Public Health. It was funded by DAAD and PROBRAL/ CAPES.

The intension was that due to worldwide shortage of primary resources an extensive collection of small electronic Equipment (WEEE) and the recovery of recyclable materials (raw material) is urgently needed. The release of significantly high freight-specific contributions of toxic and polluting heavy metals and halogens and their discharge into groundwater is caused by disposing WEEE in unsecured landfills (sink material). That`s why an analysis of potentials and distribution channels for pollutants from WEEE in Brazil and Germany was done. With the help of a material flow analysis of WEEE from private households of Brazilian mega-cities, the WEEE amounts, which are deposited in landfills were determined and with regard to the heavy metals the risks were assessed.

As a result of the project it wsas found out that the the percentage of electrical and electronic equipment in the residual waste in Brazil is much lower than in Germany. The per capita revenue of residual waste from households is also lower than in Germany. Based on this, a relatively small load of heavy metals from WEEE is expected to be in landfill leachate. A detailed risk assessment is possible only after having access to MFA and more accurate data regarding the specific amounts of waste as well as the technical equipment (leachate collection and treatment) of the Landfill Gramacho. Figure 3 shows a part of the separated WEEE, which were found during the analysis.

**Figure 3:** Parts of the separated WEEE

In 2011 another 2 year project **EMOWIB** (Envorinmental management of waste in Brazil) started, which is a cooperation between Technische Universität Dresden and Federal University of Rio de Janeiro. The main goal of this project is the development of new methodologies for the determination of the best scenario for the management of municipal solid waste and recuperation of contaminated areas. The project aims to address mechanisms for environmental management of municipal solid waste, in its various phases, from recommendations and limitations at the design of the products to the final destination in landfills, passing through recycling, incineration, energy recovery and composting. Tools and methodological approaches such as life-cycle analysis, flow of materials, flow of materials, environmental risk analysis, multicriteria analysis, among others, will be used. Therefore, it is expected to help minimize risks to human health and ecosystems associated with the possible decisions for waste management

Also, research regarding waste recycling is going to be an important issue of this project.

### 1.8.3 Exemplary projects funded by GIZ – German society for international collaboration

One of the projects, done by GIZ is called "Integration of the Informal Recycling Sector in Solid Waste Management in Brazil" [3]. It aims at listing up key factors, unexpected events and circumstances, leading to an increased involvement of the informal sector in solid waste management in Brazil and to have an outlook on further necessary steps and requirements for consolidation of this trend.

As final considerations it was found out that there is an importance of a complimentary approach to strengthen the synergy amongst waste pickers´ organizations, governments, Non governmental organizations and the private sector. Without a feasible economic strategy in municipal recycling programs, waste pickers are either condemned to poverty or to charity. There is a need to strengthen their ability to "compete" in the SWM sector as reliable service providers. Without a social strategy monetary gains derived from the transformation of recycling market will not alter the state of social exclusion they are submitted to.

### 1.8.4 Exemplary projects funded by BMBF

The S & T cooperation with Brazil, which are funded by BMBF, are focused on the areas environment, climate and sustainable development, aerospace, agriculture, health, and to working in higher education and training. Since 2007 they intensified the cooperation in the areas advanced materials, biotechnology, production technology, nanotechnology and information and communication technologies.

For 2010 66 projects are listed in 10 topics, including 18 projects related to the topic „Health and medicine", 14 projects related to the topics „Environment and sustainability" and 4 projects related to the topic „Energy".

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## 1.9 Health risk assessment for Lead released by e-waste recycling processes, using a multimedia exposure model (2-FUN model) – Preliminary calculations based on a case study designed for a region located in South of China.

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E-waste is the generic term used for technological waste. At present, e-waste has increases rapidly in the world. The developed countries export E-wastes to Asia by different ways, which inevitably cause severe pollution of the environment in the victim countries. The unregulated processing of E-waste usually recovers gold and other valuable metals by applying some simple techniques such as burning, melting, using acid chemical bath, and so on. These activities can cause severe pollution by highly toxic heavy metals (such as Pb, Cu, Ni and Hg) in aquatic and terrestrial ecosystems, and even to the atmosphere. In this study a review of the existing data on the lead concentrations in water bodies and the surrounding environment of Guiyu town (Guangdong Province, China) has been conducted. Successively, these data have been used on the development of scenarios for the health risk assessment of general population in Guiyu town and the simulation undertaken using a multimedia model, the 2FUN Tool. The multimedia models are succesfully used as tools for environmental and health risk assessment and management, especially for the possibility of taking into consideration different environmental compartments.

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