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Chapter 14 Emissions of additives from plastics in the societal material stock – A case study for Sweden

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Abstract

Estimating the size of the problems related to release, fate, exposure and effects from the human use of chemical substances in materials and consumer products is daunting. More than 100,000 chemical substances are in commercial use and a reasonable description of their existence in, and release from, plastic polymers, glues, paints, fibres, lubricants etc. comprise a big challenge. Here we report the initial results from a generic emission model that has been developed and applied to estimate emissions of a set of organic chemicals from products. The scope of the study was to estimate emissions from products containing plastic materials during their average lifetime within the geographical boundaries of Sweden. The results show that approximately 2% of the plastic additives are emitted annually. Plasticisers, flame retardants, organic pigments and stabilisers are the use categories of additives that are emitted in the largest quantities. Until now, the method has only been used to estimate emissions of additives from plastic materials, but it is believed to also be applicable to other materials.

1 Introduction

This chapter will present a methodology for estimating emissions of organic substances from the societal stock of products. It will also present the resulting estimated emissions of plastic additives from the Swedish stock of products. The data presented here are interim results from ongoing research in the Swedish research programme ChEmiTecs – Organic Chemicals Emitted from Technosphere Articles, which has been funded by the Swedish Environmental Protection Agency (EPA). The goal of the ChEmiTecs research programme has been aiming at an improvement of the understanding of emissions of organic substances from articles and to clarify and determine the magnitude of them.

In the society, a vast number of different products and materials are accumulated. When calculating emissions from the entire stock of products and materials in the society, the sheer number of products and materials does not make it feasible to describe the exact chemical composition of specific materials and products in detail and estimate the emissions based on that (Molander *et al*., 2011). The methodology presented here is instead aimed at a simplified initial approximation of emissions of a set of organic chemicals from products containing plastic materials.

The emissions from the considered plastic articles during the year 2006 within the geographical boundaries of Sweden are the scope of the emissions approximation. This includes products manufactured in Sweden as well as imported. Even though emissions from processes outside Sweden occur, no emissions outside Sweden are covered here.

2 Method

The methodology used comprises four steps. First the accumulated stock of selected product categories was estimated using trade statistics. Secondly, material composition data were compiled for the product categories with the largest stock. Information on additive compositions for a number of plastic materials contained in the selected product categories was gathered and mapped to the product categories. Lastly, the emissions from the stock of products were estimated using a simple emissions model. In the following sections, this methodology will be described in more detail.

2.1 Quantification of accumulated stock of goods

In order to quantify the emissions of organic chemicals from technosphere articles, the accumulated stock of articles in society need to be estimated. A previous study by the Swedish EPA and the Swedish Chemicals Bureau (1999) described that the accumulated stock of articles in society could be estimated based on the annual net supply of articles to the society in combination with the average lifetime of the articles according to the following relation:

$$\text{Accumulated stock} = \text{Net supply} \times \text{Average lifetime} \tag{1}$$

This relation is only valid if the net supply has reached steady state (that is the net supply does not change over time). In this study, the net supply was estimated based on national trade statistics covering manufacturing of goods in Sweden, together with import to and export from Sweden. The net supply can be obtained by:

$$\text{Net supply} = \text{Domestic manufacturing} + \text{Import} - \text{Export} \tag{2}$$

Trade statistics are compiled by the Statistics Sweden and are reported according to the customs Combined Nomenclature. The Combined Nomenclature is comprised of the so called Harmonised System (HS) nomenclature with further Community subdivisions (European Commission, 2010). In the Combined Nomenclature, statistics are reported for different groups of articles, called CN-product categories. All these 99product categories are hierarchically divided into different sub-categories, called CN2, CN4, CN6 and CN8, where the ingoing articles are divided into smaller sub groups with increasing tier. To give an example, product category 39 (CN2-level) is described as Plastics and articles thereof. Within this category, there are 26 subcategories of articles at CN4-level, for example “3901 Polymers of ethylene in primary forms”. Within each CN4 category, there are additional subgroups, CN6-categories, and so on.

The net supply of articles was compiled for the year of 2006, reported as tonnes/year for all CN4 product categories (Westerdahl *et al.,* 2011). A portion of all products are also transferred over the national boundary, but not exported in the statistical meaning, and therefore not accounted for in national customs statistics. This includes private import and export, and illegal smuggling. These product flows are therefore not included.

Here, the average lifetime regard all episodes of how products are handled, actively or passively. The lifetime is defined as the period, from the point in time when products are either domestically manufactured or when they enter Sweden as imported goods, until all points in time when the products are incorporated as components of other products, or they are discarded and then enter the waste stream. The average lifetime of the different product categories was obtained from the Swedish EPA and the Swedish Chemicals Bureau (1999). There, the average lifetime was assigned as 1, 5, 25 or 50 years for the different CN4 categories. For all CN4 categories, the accumulated stock was calculated according to Equation 1. Since the ChEmiTecs research programme focuses on emissions of organic chemicals from technosphere articles, product categories that were assumed to not contain any organic chemicals were excluded. This means that for example sand and other inorganic ore-based products were excluded. The product categories with an accumulated stock larger than 100 000 tonnes were selected for further investigation, for which material compositions were to be described.

2.2 Specifications of materials in product categories

For the selected CN4 product categories, the contents of materials were specified aiming at a description of type of material and amount in each product category. In Table 1 below, the main plastic materials that were identified in the studied product categories are listed.

Table 1 Plastic materials included in this study

Plastic materials	Abbreviation
Acetals	
Acrylics	
Acrylonitrile butadiene styrene	ABS
Epoxy resin	
Phenolic resin	
Polyamide	PA
Polycarbonate	PC
Polyester	
Polyethylene	PE
Polypropylene	PP
Polystyrene	PS
Polyurethane	PUR
Polyvinyl chloride	PVC

The specifications of what product categories that contained certain amounts of the plastic materials were based on information of articles included in the different product categories, in combination with information from life cycle assessments and building product declarations, covering the material content of specific articles. The specifications resulted in mass percentages of the materials contained in a product category. Furthermore, the average thickness of the ingoing materials was estimated in order to calculate the exposed surface area of the ingoing materials, which in turn was needed for the emission calculation of additives. Surface areas were estimated based on the shape of the products. The areas were modelled as being constant over the entire product lifetime. The surface areas were calculated according to Equation 3.

$$\text{Area} = \text{Mass}/(\text{Thickness} \times \text{Density}) \quad (3)$$

The thickness of a specific material in a product category can vary, depending on specific application, producer etc. To cover the likely thicknesses of a material used in a product category, a thickness interval was assigned for each material in a specific product category. When estimating the thickness, product specific information was preferred, but such information was not available for all product categories. For those product categories where no such information was known, a list of different materials and their typical thicknesses was developed and used instead, see Table 2. If it was known that a product category contained a material with very different thicknesses, two or more intervals were assigned to cover the range of thicknesses of that specific material. In order to calculate the area from known masses the density of all the plastic materials was set to 1000 kg/m^3.

Table 2 Typical thicknesses of different materials

Example of materials	Thickness
Varnish and paint layers, thin plastic films	0,00001-0,0001 m
Textiles, foils and paper	0,0001-0,001 m
Plastic components, carpets	0,001-0,01 m
Wood, tyres, soles	0,01-0,1 m
Concrete, building materials	0,1-1 m

2.3 Specification of chemicals in materials

For the identified plastic materials in the selected product categories, more detailed chemical specifications were made. Lists of additives commonly used in different plastic materials were compiled, based on a thesis by Jansson (2008) and information from Zweifel et al. (2009). Out of all the identified chemicals, the high production volume chemicals (HPVC) and the low production volume chemicals (LPVC) were selected for further study at this stage.

All additives were divided into use categories, for example antioxidants, flame retardants, fillers etc. For each additive category and each plastic material, a minimum and maximum percentage of content was defined. Within each use category, there can be several different specific additive compounds possible to use to obtain a certain function in the plastic. Often only one or a few of these additives is used in a single product. Since no information was available regarding what specific additive that was used in a certain article, it was instead assumed that a mixture of all listed additives in a use category was used in all the materials To avoid overestimation the minimum and maximum amounts of each additive were divided by the number of additives within each use category before summation.

All products do not contain all use categories of additives, and to account for this fact, an estimation of how commonly the different categories of additives are used in products were developed, see Table 3. These correction factors were applied to additives in plastic products to avoid overestimation of the stock of additives.

Table 3 Assumed use of different plastic additives in plastic products

Additive	Amount of plastics containing a specific additive
Antifogging additive	10%
Antioxidant	100%
Antistatic additive	10%
Flame retardant	10%
Lubricant	10%
Pigment	50%
Plasticiser	50%
Slip additive	10%
Stabiliser	100%
UV stabiliser	10%
Whitening agent	10%

2.4 Estimation of emissions of organic chemicals from plastic materials

The emissions of organic chemicals were estimated based on mass, area and additive composition of all plastic materials in the selected CN4 product categories. The method used is based on Fick's Second Law of diffusion (OECD, 2009) and the emissions can be calculated according to Equations 4 and 5.

$$N_{add} = 0.02 \times A_{polymer} \times F_{add,polymer} \times \rho_{polymer} \times \left(\frac{D_{add} \times t}{\pi} \right)^{0,5} \quad (4)$$

$$D_{add} = \frac{10^{(-7,83-0,0062 \times Mw)}}{10000} \quad (5)$$

N_{add} is the emitted amount of an additive (kg), $A_{polymer}$ is the area of a certain polymer (m^2), $F_{add, polymer}$ is the mass percentage of additive in the polymer and $\rho_{polymer}$ is the density of the polymer which here is assumed to be 1000 kg/m^3 for all plastics and t is the time period for the calculation (s). D_{add} is the diffusion coefficient (m^2/s) of the specific plastic additive, which is estimated based on its molecular weight (M_w) at 40 ˚C according to Equation 5. By using this equation, the emission of plastic additives from the polymer surface as a result of passive diffusion in the polymer is obtained. In the model, it is assumed that the additives are uniformly distributed within the polymer and that the additives are not chemically bound to the polymer. It is also assumed that the polymer is not subject to physical or biological degradation (OECD, 2009). Finally, the model does not consider how the properties (like e.g. temperature) of the surrounding media could affect the diffusion.

The time period of interest in this study is one year. When using the above Equations (4 & 5), it is predicted that the rate of diffusion will slow over time. When calculating the emissions during one year for the accumulated stock, it is not appropriate to calculate this based on the first year of a products lifetime, since the products in the stock are of varying age and doing so would overestimate the emission. Here, the emission from the stock during one year was instead calculated as the average emission during the entire lifetime. That is

$$\frac{Emission}{Year} = \frac{N_{add}(t = average\ lifetime)}{Average\ lifetime} \quad (6)$$

This assumption is valid if the accumulated stock has reached steady state.

These calculations were performed for all additives in all materials and product categories, resulting in emissions that can be traced back to the different product categories.

3 Results

In the following sections, the obtained results from the different calculation steps will be presented, i.e. information regarding the accumulated stock of plastic materials and additives in the Swedish societal stock of products as well as estimated emissions of plastic additives from these products for the year of 2006.

3.1 Accumulated stock of plastic materials and additives in the Swedish society

In total, the stock calculations showed that approximately 100 CN4 categories had a stock larger than 100 000 tonnes. These CN4 categories constitute approximately 99% of the total stock of articles in the Swedish society. In this study, the focus was on plastic containing products excluding e.g. wood or concrete from this study.

Many of the product categories with a stock larger than 100 000 tonnes have a relatively long average lifetime, 25 years or longer. If the average lifetime is short, the products do not have the ability to accumulate in the society to the same extent as products with long average lifetime, thereby obtaining a smaller accumulated stock in society.

In total, 61 CN4 product categories were identified as containing organic chemicals and were studied in more detail. The Swedish accumulated material stock of these product categories was estimated to be 130 million tonnes in the year of 2006, out of which approximately one third, or 43 million tonnes, was assumed to be plastic materials. Figure 1 shows the relative distribution of different polymers in the accumulated stock. In van Oers *et al.* (2011), statistics on the demand of different plastics materials per polymer in the EU were presented. Compared to these statistics, the fractions of PE and PET are lower in this study. Here, packaging materials covering finished products are not included since the trade statistics used in this study covers data on products excluding their packaging. Since two major packaging materials are PE and PET, the fraction of these materials therefore becomes lower in this study. However, the accumulated stock of packaging materials sold as packaging materials is included in this study. The fractions of the stock that is constituted by PP, PVC and PS correspond well with the sales data presented in van Oers *et al*. (2011), while for PUR and PC, this study suggests higher fractions.

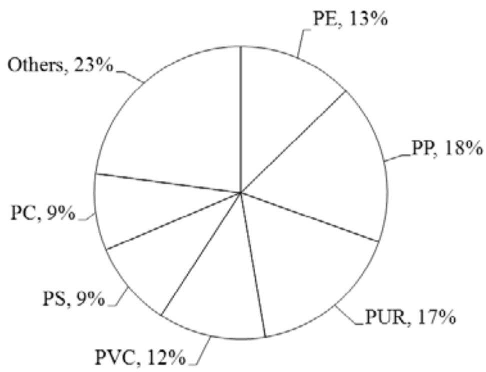

Figure 1 Distribution of plastic materials in the Swedish stock of products.

The plastic materials in the stock contain a number of additives. The results from this study show that the amount of additives in the plastic material stock studied here corresponds to approximately 6 % (w/w) or 2.7 million tonnes of additives.

In Table 4, the net inflow and stock of additives in the Swedish society is presented for different additives use categories. Plasticisers is the type of additives that has the largest stock in the Swedish society, for which the main application is softened PVC. Flame retardants, organic pigments and stabilisers are other categories of additives with large stocks.

Comparing the net inflow obtained here with the sales data for plastic additives presented in van Oers *et al.* (2011), it can be concluded that the Swedish net inflow of additives represents approximately 1-4% of the global annual sales of additives. This estimated net inflow seems reasonable as the Swedish economy constitutes approximately 0.5% of the world economy (CIA, 2010).

Table 4 Estimated net inflow of additives and amount of additives in the accumulated stock of plastic products in the Swedish society in 2006.

Additive	Net inflow (1000 tonnes/year)	Stock (1000 tonnes)
Antifogging additives	0.98	10
Antioxidants	8.2	140
Antistatic additives	1.4	17
Flame retardants	36	450
Bromine based compounds	*31*	*350*
Phosphorous based compounds	*4*	*80*
Other flame retardants	*1*	*20*
Lubricants	6.1	80
Organic pigments	38	480
Plasticisers	66	1100

Phthalate plasticisers	*33*	*550*
Other plasticisers	*33*	*550*
Slip additives	0.13	1.3
Stabilisers	25	370
UV stabilisers	1.2	18
Whitening agents	1.1	20
Total	180	2700

3.2 Emissions of plastic additives

The estimated emissions of different types of additives are presented in Table 5. In total, approximately 2% of the additives in the stock are estimated to be emitted through molecular emissions during one year.

The surface areas of the materials as well as the molecular weight of the additives are the two main parameters that influence the calculated emissions. Large emissions correspond to large areas of plastic materials and low molecular weights of the additives. The emissions are also influenced by the stock of additives in the products, where higher concentrations also yield higher emissions.

Table 5 Emissions of plastic additives from the accumulated stock of plastic products in the Swedish society in the year of 2006.

Additive	**Emission (1000 tonnes/year)**
Antifogging additives	0.26
Antioxidants	0.66
Antistatic additives	0.078
Flame retardants	5.6
Bromine based compounds	*3.7*
Phosphorous based compounds	*1.6*
Other flame retardants	*0.3*
Lubricants	1.4
Organic pigments	6.9
Plasticisers	24
Phthalate plasticisers	*13*
Other plasticisers	*11*
Slip additives	0.042
Stabilisers	8.0
UV stabilisers	0.360
Whitening agents	0.026
Total	47

Since the emitting area is one of the major parameters that influence the emission of additives, the product categories with the largest areas will give rise to the largest emissions. Of the product categories included in this study, the CN2-category with the largest stock and emitting area is CN39; Plastics and articles thereof. Other product categories that give rise to large emissions of plastic additives are CN85 which consist of electrical machinery and equipment and parts thereof such as engines and televisions, CN87 which consist of vehicles and vehicle parts and CN 94 which partly consist of prefabricated buildings. It should be noted that all subcategories within these CN2-categories have not been included, e.g. for CN94, "CN9406 Prefabricated buildings" is the only CN4 category included.

4 Uncertainties and improvements

Within these calculations, there are different uncertainties which affect the results. Some of them are linked to the model, some to the object of study and others to the data quality. As well as for the net inflow of additives, it is believed that the emissions of additives are overestimated. The origin of these uncertainties as well as their effect on the end results is discussed below.

The emissions of plastic additives are based on the accumulated stock of additives found in plastic products in the Swedish society. When calculating the accumulated stock of products, net inflow of the selected product categories for the year of 2006 in combination with the average lifetime of the product categories were used. The net inflow of a product category can vary from year to year. By using trade statistics from a single year, as in this study, thus yields uncertainties. If trade statistics covering more than one year are used instead, the uncertainty within the stock estimations can be reduced.

The area of the stock which was obtained by using Equation 3 also has a large impact on the emissions of additives. In Equation 3, one uncertainty lies within the estimation of the thickness of the material. A product category can be quite diverse and it can therefore be difficult to estimate the thickness of the material, which causes uncertainties in the obtained emissions.

Additionally, the emission model itself also cause uncertainties in the estimated emissions. The emission model used here estimates emissions of additives from plastic materials to air through molecular diffusion in the plastic material, where it is assumed that the additives are not chemically bound to the matrix. Since chemical interactions between the additives and the polymer do occur, this assumption causes an overestimation of the emissions. Another factor that causes uncertainties is the temperature of the material and the surroundings. In this model the diffusion coefficients were, due to the empirical equation, calculated at 40 ˚C. As the average temperature in Sweden is lower than 40 ˚C and the diffusion in plastic materials is affected by the temperature, this assumption will give rise to an overestimation. More information regarding important assumptions and uncertainties within the emission model can be found in the Emission Scenario Document on Plastic Additives by OECD (2009). To improve the quality of the obtained emissions and to reduce the uncertainties connected to the emission model, a new emission model is being developed (Holmgren et al, 2010).

As a result of these uncertainties, the final emissions are judged as being overestimated.

5 Conclusions

By using information from national trade statistics and a rough emission model, it is possible to estimate emissions of additives from the accumulated stock of products in society during one year of the product's average lifetime. This far, the method has only been used to estimate emissions of additives from plastic materials, but it is believed to also be applicable to other materials.

The obtained results shows that the accumulated stock of products containing plastic materials is approximately 130 million tonnes and that out of the stock approximately 43 million tonnes consist of plastics. These plastic materials contain almost 3 million tonnes of additives, of which plasticisers, flame retardants, organic pigments and stabilisers constitute the largest fraction. According to model calculations almost 2% of these additives are emitted to the environment yearly. The additive categories that are emitted in the largest amount correspond well to the categories with the largest stock, i.e. plasticisers, flame retardants, organic pigments and stabilisers.

The results contain uncertainties, which are caused by both model uncertainties and uncertainties in the input data. The most influential factors are believed to be the net inflow, the average life, the thickness of the material and the emission model used. By using trade statistics covering more than one year and by using a more detailed emission model, a large fraction of the uncertainties can be reduced.

The methodology and models presented here will be further improved to minimise the identified uncertainties and thereby improve the emission estimates.

6 Acknowledgements

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