SUBSTANCE FLOW ANALYSIS OF NONYLPHENOL AND NONYLPHENOL ETHOXYLATES IN TURKEY

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

SUBSTANCE FLOW ANALYSIS OF NONYLPHENOL AND NONYLPHENOL ETHOXYLATES IN TURKEY

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Nonylphenols (NP) are among the chemicals presenting a substantial risk to the aquatic environment and therefore listed as “Priority Hazardous Substances”. Nonylphenol ethoxylates (NPEs) that are produced from NP, are nonionic surfactants, and used in a wide range of industrial activities and various consumer products. In the environment, NPEs degrade to NP. In this study, a substance flow analysis was performed to track the pathways of NP/NPEs in Turkey and to contribute to their appropriate management.

All possible sources of NP and NPEs were determined considering production, processing, private use, and disposal life cycle stages. The emissions were calculated for each source considering all the environmental compartments; i.e. emissions to water, air and soil, using production, import-export statistics and emission factors collected from the literature. The results showed that the primary emission flows of NP and NPEs in Turkey, include use of detergents; washing of textiles; and leather, textile and paper-and-paper products industries. A total of 7437 ton NP and 28,920 ton of NPEs are used annually and more than 10% ends up in the environment.

Surface waters appear as the main environmental compartment receiving NP/NPEs pollution via wastewater treatment plants. Annually, 456 tons of NP and 2694 tons NPE enter wastewater treatment plants and 88.2 % (340 ton/year) of NP releases and 86.9 % (946 ton/year) of NPE emissions are lost to surface waters. In addition to surface waters, land and air are other compartments receiving NP/NPEs. Major sources to soil and to air appeared as use of pesticides/veterinary medicines and volatilization from wastewater treatment plants, respectively.

Keywords: Nonylphenol, Nonylphenol ethoxylates, Priority pollutants, Substance flow analysis

ÖZ

TÜRKİYE'DE NONİLFENOL VE NONİLFENOL ETOKSİLATLAR İÇİN MADDE AKIŞ ANALİZİ

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Nonilfenoller, sucul yaşam için önemli ölçüde risk eşkil eden kimyasallardan biridir ve bu sebeple "Öncelikli Tehlikeli Madde" olarak belirlenmiştir. Nonilfenol etoksilatlar, nonilfenollerden üretilen noniyonik yüzey aktif maddelerdir ve çok çeşitli endüstiyel faaliyetlerde kullanılmakta ve birçok tüketici ürününde bulunmaktadır. Nonilfenol etoksilatlar, doğada bozunarak nonilfenole dönüşmektedir. Bu çalışmada, Türkiye'de nonilfenol ve nonilfenol etoksilatların akışlarının belirlenmesi ve yönetimlerine katkıda bulunmak amacıyla madde akış analizi yapılmıştır.

Nonilfenol ve etoksilatların olası tüm kaynakları, üretim, proses, özel kullanım ve bertaraf yaşam döngüsü aşamaları göz önüne alınarak sınıflandırılmıştır. Emisyonlar her kaynak için, tüm çevresel kompartmanlar; su, hava, toprak ele alınarak; üretim verileri, ithalat-ihracat istatistikleri ve literatürden derlenen emisyon faktörleri kullanılarak hesaplanmıştır. Sonuçlara göre, nonilfenol ve nonilfenol etoksilatların ana emisyon kaynakları deterjanların kullanımı; tekstil ürünlerinin yıkanması; deri, tekstil ve kağıt-ve-kağıt ürünleri sektörleridir. Yılda toplam 7437 ton nonilfenol ve 28,920 ton nonilfenol etoksilat kullanılmaktadır ve bunun %10'dan fazlası doğaya salınmaktadır. Yüzey suları, atısu arıtma tesisleri yoluyla en fazla nonilfenol ve etoksilat kirliliğine maruz kalan çevresel kompartmandır. Atıksu arıtma tesislerine yılda 456 ton nonilfenol ve 2694 ton nonilfenol etoksilat ulaşmaktadır ve nonilfenol emisyonlarının % 88.2'si (340 ton/yıl) ve etoksilatların % 86.9 'u (946 ton/yıl) yüzey sularına bırakılmaktadır. Yüzey sularına ek olarak, toprak ve hava nonilfenol/nonilfenol etoksilat emisyonlarını karşılayan diğer çevresel ortamlardır. Toprak ve hava için temel kaynaklar sırasıyla; pestisit/veteriner ilaçları ve atıksu arıtma tesislerinden kaynaklanan buharlaşmadır.

Anahtar Kelimeler: Madde Akış Analizi, Nonilfenol, Nonilfenol etoksilatlar, Öncelikli maddeler

To My Beloved Family

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ABBREVIATIONS

NP : Nonylphenol
NPE : Nonylphenol Ethoxylate
NP_{eq} : Nonylphenol Equivalents
SFA : Substance Flow Analysis
MFA : Materials Flow Analysis
APnEO: Alkylphenol polyethoxylates
NPnEO: Nonylphenol polyethoxylates
NP1EO: Nonylphenol monoethoxylate
NP2EO: Nonylphenol diethoxylate
NP1EC: Nonylphenol monoethoxy carboxylate (nonylphenoxy acetic acid)
NP2EC: Nonylphenol diethoxy carboxylate (nonylphenoxyethoxyacetic acid)
NPnEC: Carboxylated nonylphenol ethoxylates (Nonyl phenoxycarboxylic acids)
TNPP : tri- (4-nonlphenyl) phosphite
WFD : Water Framework Directive
EQS : Environmental Quality Standard
BCF : Bioconcentration factor
PBT : persistent, bioaccumulative, toxic
EU : European Union
ECHA : European Chemicals Agency
USEPA: United States Environmental Protection Agency
TOBB : The Union of Chambers and Commodity Exchanges of Turkey
TÜİK : Turkish Statistical Institute
WWTP: Wastewater Treatment Plant
REACH: Directive on Registration, Evaluation, Authorization and Restriction of Chemicals

CHAPTER 1

INTRODUCTION

1.1 General

Nonylphenol (NP) is an organic, toxic and endocrine disrupting compound which is a breakdown product of nonylphenol ethoxylates (NPEs). NP is used mainly in the production of NPEs and also as stabilizer in paints, rubber and plastics. NPEs are widely used surfactants in industrial and domestic detergents and cleaning agents. Also, they are used in various industrial activities such as textile, leather, pulp & paper and in wide range of consumer products such as personal care products, cosmetics and paints. The substance is being produced since 1940's in large volumes all over the world. The annual production of NP is known to have reached 154,200 tons in the USA, 16,500 tons in Japan and 16,000 tons in China. With a volume of 700,000 tons per year NPEs are being used for a wide variety of industrial and domestic applications.

Not surprisingly, for a substance with such hazardous effects and common usage, there are a number of applications to prevent adverse effects on environment and living organisms. NP is identified as one of the "Priority Hazardous Substances" in the European Water Framework Directive (WFD, 2000/60/EC). WFD requires achieving "good status" in surface and ground waters until 2015. The use of NP and NPEs has been restricted within the European Union (EU) since 2006 by the Directive on Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) (1907/2006/EC). In Turkey with the harmonization to the European Union some limitations are of concern. The uses of NP and its ethoxylates, releases of the substances to different environmental compartments, especially surface waters will gain importance.

In order to meet the good chemical status requirement in water bodies, water quality based Environmental Quality Standard (EQS) values are introduced with the Environmental Quality Standards Directive (2008/105/EC), for the priority pollutants identified in WFD. In order to comply with EQS, concentrations of priority pollutants in receiving waters should be controlled. For this purpose; the sources of priority pollutants, their usage amounts and releases to water bodies as well as concentrations in receiving surface waters are important and should be identified. Substance flow analysis (SFA) is a useful tool to gather all the above mentioned information of a pollutant.

SFA can be considered as an effective tool for environmental management. It is used to provide knowledge about the inflows and outflows of the selected substances by tracking them at all stages of their lifecycle, based on simple mass balance principle. This knowledge will assist in identifying the points where measures are required to diminish loads to environment. SFA results are useful for decision makers to generate strategies against pollution. SFA provides a flexible methodology such that, determination of the substance, system boundaries, processes and time frame depends on the context and extent of the analysis.

SFA is being conducted in EU countries for many substances including micro pollutants such as NP. Mostly, SFA of metals like mercury and cadmium and priority pollutants have been investigated. For Turkey, hazardous substances are hot topics of environmental management but, SFA concept is rather new.

In Turkey with the ongoing project called “KIYITEMA; Determination of Dangerous Substances in Coastal and Transitional Waters of our Country and Ecological Coastal Dynamics Project”, 3300 chemical substances have been investigated for the selection of the specific pollutants for Turkey. All European and Turkish legislation on water management and hazardous substances have been reviewed while creating this list. NP is one of the substances in the list as it is mentioned both in European and Turkish regulations. In addition to the prioritization, a large inventory about hazardous substances including production, import, export, usage areas, sectorial distribution, risk codes, PBT (persistent, bioaccumulative, toxic) properties, and toxicity data has been generated during the project.

The Priority Substances of the WFD are within the compass of water management of Turkey. EQS both for inland and coastal waters and discharge standards are being developed for these pollutants. However, there is not enough knowledge about the sources of these substances and amounts used. Huge production volumes, hazardous properties and endocrine disrupting effect of NP makes it one of the target species in the list. Due to their extensive use for a variety of purposes, it is important to know the inflows and outflows of NP in order to take account of different measures for minimizing their releases and to push decisions on their control in Turkey.

1.2 Objective and Scope of the Study

The objective of the thesis is to identify the sources and emissions of NP and its ethoxylates by conducting a substance flow analysis in Turkey.

For this purpose, sources of NP and its ethoxylates are identified and the emissions to environmental compartments are calculated for each source with the emission factors and production, import/export data. This way, the inflow of NP, the stocks within the products and the emissions to environmental media can be identified within the scope of substance flow analysis.

In this study, after introducing background information on NP, NPE with some detail on substance properties, production volumes and legislative framework, SFA concept is introduced (Chapter 2). Recent SFA studies conducted for various pollutants found in the literature are reviewed (Chapter 2). In Chapter 3, the methodology followed in conducting the SFA and the extent of the work is explained. After the representation of the results in Chapter 4, and discussion in Chapter 5, some recommendations for the present and future work are made in Chapter 6 and 7, respectively.

CHAPTER 2

BACKGROUND INFORMATION

2.1 Nonylphenol and Nonylphenol Ethoxylates

NPs are from the family of alkylphenols and its name applies to a number of isomer substances with a phenol ring and alkyl chain C_9H_9. The difference between its isomers depends on the position of substitution position of the nonyl group to the phenol molecule and the branching degree of the nonyl group. In Figure 2-1, the chemical structure of 4-nonylphenol; which is the most widely used commercial type of the substance is given.

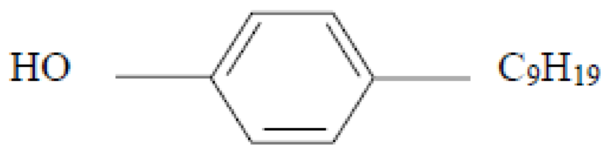

Figure 2-1 Chemical Structure of 4-nonylphenol

NPs are produced industrially by the alkylation of phenol with nonene by an acidic catalyst as shown in Figure 2-2. NPs are produced from intermediates in the refinement of petroleum and coal tar. Under ambient conditions NPs are viscous liquids with a pale yellow color and phenolic odor.

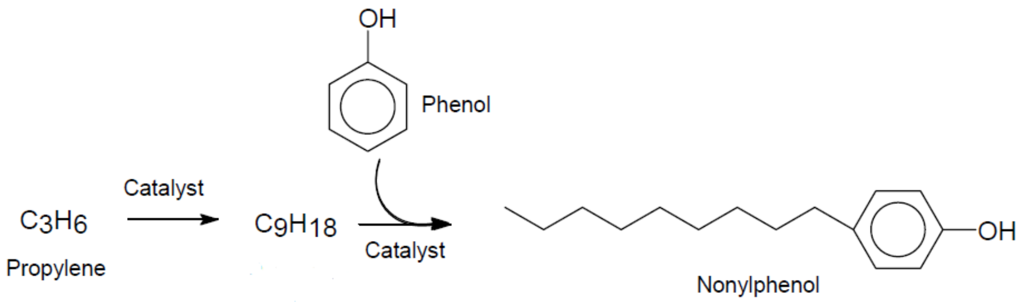

Figure 2-2 Manufacture process of nonylphenol [1]

There are different CAS numbers for different isomers of NP. The properties of the substance can vary according to the degree of branching in the nonyl group. Physical and chemical properties of NP are given in Table 2-1. In this study, data from any of the isomers are accepted to be representative for NP and NP is used as a generic name for all isomers.

Table 2-1 Physical and chemical properties of nonylphenol [2]

Property	**Nonylphenol**
Physical state (at NTP)	Colorless or pale yellow viscous liquid
Molecular weight	220.34 g/mole
Melting point	-8 °C
Boiling point	290-300 °C
Relative density	0.953 (at 20 °C)
Vapor pressure	0.3 Pa (at 20 °C)
Partition coefficient (log K_{ow})	3.28, 3.8-4.77, 4.48
pK_a	10.7
Water solubility	6 mg/L (at 20 °C)
Flash point	141-155 °C
Auto-flammability	370 °C
Viscosity	2,500 mPa (at 20 °C)

NPEs belong to the family of alkylphenol ethoxylates and they constitute about 90 % of all alkylphenol ethoxylates in tonnage. They are produced by the reaction of NP and ethylene oxide. NPEs are manufactured after etherification of NP by condensation with ethylene oxide in the presence of a basic catalyst. Most of the NP produced is used as an intermediate chemical to produce nonionic surfactants called NPE. These substances are liquids or waxy solids and their physical and chemical properties change with the degree of ethoxylation. They are generally colorless. Physical and chemical properties of NPEs with four and nine alkyl chain length are summarized in Table 2-2.

Table 2-2 Physical and chemical properties of nonylphenol ethoxylates [3]

Property	**NP4EO**	**NP9EO**
Physical state	White to light amber liquid	Almost colorless liquid
Molecular formula	$C_{15}H_{24}O[C_2H_4O]_4$	$C_{15}H_{24}O[C_2H_4O]_9$
Molecular weight (g/mole)	396.2	617.6
Melting point (°C)	-40	2.8
Relative density	1.020-1.030 (at 25 °C)	1.057 (at 20 °C)
Partition coefficient (log K_{ow})	4.24	3.59
Water solubility (mg/L)	7.65	Water soluble

Fate of NP and NPEs in the environment is an important aspect of environmental pollution. Chemical properties of the substances assist in explaining its environmental fate. The most important properties can be summarized as;

- Water solubility is lower for low molecular weight NPEs and NP, and higher for higher chained NPEs.
- Octanol water partitioning (log K_{ow}) is higher for lower chained NPEs and NP, and lower for high molecular weight NPEs.
- Vapor pressure is low for both NPEs and NP.

These properties indicate that NPs tend to adsorb on sediment or sludge and NPEs with higher chains tend to stay in water phase. Emission via volatilization of both substances is limited [4].

The environmental fate of nonylphenolic substances are rather complex. The main degradation pathway of NP and ethoxylates is biodegradation [4]. Biological degradation pathway of NPE is represented in Figure 2-3. Basically, NPE with long ethoxylate chains tend to degrade to carboxylated nonylphenol ethoxylates (NPnECs) and shorter chained ethoxylates under aerobic conditions. Degradation to NP takes place in anaerobic stages. The reason of the complexity is that these metabolites can be present together at different amounts in different stages of the degradation process.

The biodegradation of NPE's in water environments occur with the detachment of the ethoxylate chains, and consequently lower chained NPE's, NPnECs and NP are formed. These substances are more persistent than the parent higher chained NPE compounds. It is important to note that low NP concentrations detected in surface waters may be misleading without the analysis of the associated sediment.

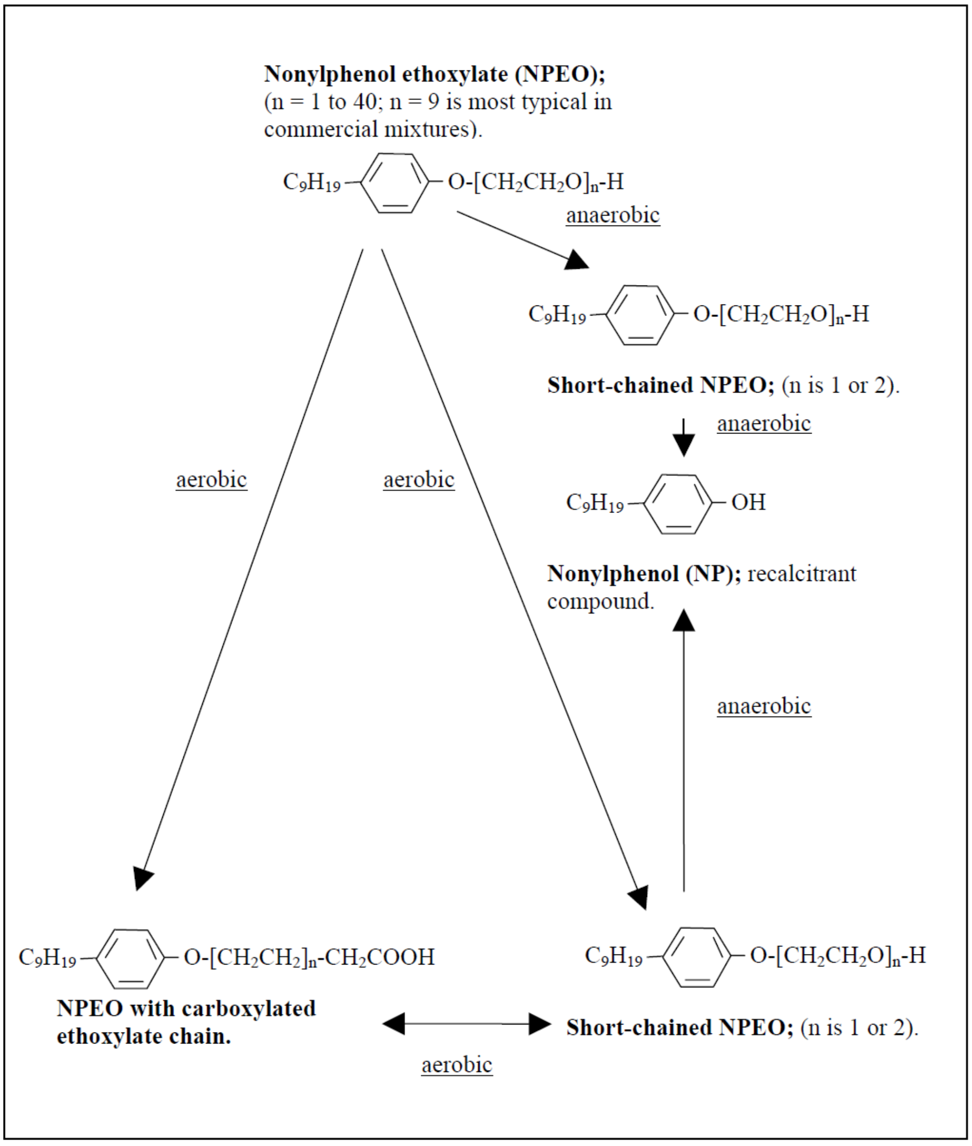

Figure 2-3 Biological degradation pathway for nonylphenol ethoxylates [5]

The entrance route of nonylphenol metabolites to environment is majorly by wastewater. So, in order to predict the amount and composition in effluent, the fate of substance in wastewater treatment plants is of primary importance. The degradation of the substance in wastewater treatment plants starts with the primary degradation of NPE's. This occurs faster than natural environments in wastewater treatment plants because of the high concentration of microorganisms [3]. NPE's entering wastewater treatment plants exit in effluents and sludge as more stable, persistent and toxic compounds which are short chain NPE's and NP. Primary degradation of NPE's with eight or more ethoxylate units to shorter chain metabolites with lower molecular weight can occur both under aerobic and anaerobic conditions. The ultimate biodegradation is more significant than primary degradation because of the formation of metabolites which are more persistent, liable to bioaccumulate and toxic than the parent APnEO. NP and NP1EO/NP2EO are known to be more lipophilic than NP's. This results in tendency of nonylphenol to adsorb on sludge in high concentrations. NPnEC's formed in activated sludge treatment, are more water soluble and released to environment in effluent at high levels. In addition to NPnEC's, NP and NP1EO/NP2EO are also observed in treatment plant effluents. The treatment processes applied in wastewater treatment plants determine the final effluent composition. For example, primary treated effluent is rich in NPnEO (n=3-20) and poor in NP, NP1EO/NP2EO and NP1EC/NP2EC. In contrast, in secondary effluents NP1EC/NP1EC are dominant and NPE with high chain numbers are relatively low [3].

The following lines summarize the review for fate of the substance.

- Primary biodegradation of NPE's result in the formation of lower chain NPE's and NPnEC's.
- Lower chain NPE's (NP1EO/NP2EO) and NP tend to adsorb on sludge and sediments and NPnEC along with NPEs appears mostly discharged with the effluent.
- Breakdown products of NPE's, especially NPs are more toxic, persistent, estrogenic and lipophilic.

2.1.1 Hazardous Properties of the Substance

European Chemicals Agency investigated the persistence, bioaccumulative and toxic (PBT) properties of NP in detail. It is concluded that the substance is neither persistent nor bioaccumulative according to the PBT (persistent, bioaccumulative, toxic) criteria of REACH Directive [6]. Biodegradation tests shows that the substance can be considered as readily biodegradable under aerobic conditions according to the criteria provided in REACH Annex XIII. This supports the fact that the primary removal process of NP in surface water and treatment plants is via biodegradation. According to the criteria a substance is not considered as "bioaccumulative" if the bioconcentration factor (BCF) is below 2000 or "very bioaccumulative" if below 5000 or log K_{ow} is below 4.5. The highest BCF reported is 1300 which is still below the criteria [6].

The toxic properties of the substance fulfill the criterion in Annex XIII of REACH which requires LC50 or EC50 <0.1 mg/L. Acute toxicity test results range from 135 to 950 µg/L. For aquatic invertebrates EC50 values are 85-150 µg/L. Acute and chronic toxicity data for aquatic organisms indicates that NP is highly toxic to fish, aquatic invertebrates, and aquatic plants [7].

NPs are known to influence the endocrine system but before discussing the endocrine disruptor properties of NP, providing the definition of the term "endocrine disruptor" will be appropriate.

"An endocrine disrupter is an exogenous substance or mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub) populations" [8].

NP is found to demonstrate endocrine disruptor effects on fish. It was found that male fish subject to NP produce vitellogenin which is a major constituent of blood protein in maturing female fish. Vitellogenin is normally not produced by male fish and when they are exposed to estrogens it can be produced in similar levels observed in maturing female fish. In fact, not only NP, but also NP1EO and NP2EO were found to show almost the same effect [3]. In addition to the change in level of vitellogenin, changes in sperm stages in males and secondary sex characteristics were observed. There are also some data showing that NP exerts endocrine disrupting effects in amphibians. In two frog species NP exerted sex reversal towards females at even very low concentrations [7]. When invertebrates are considered NP is found to exert endocrine disrupting activities in some species, however, there is no clear evidence for this taxonomic group because the endocrine mechanism in invertebrates is still not clearly known [7].

2.1.2 Production and Usage Patterns of the Substance

NPs are mainly used in the manufacture of NPE, resins, plastics and stabilizers. Use area of NPEs is wider than the parent compound. They are mainly used as surfactants for cleaning purposes. They are commonly used in industries such as paint, textile, leather, pulp and paper and agriculture. The wide use of the substance requires big production volumes around the world. The production data for 1997 is summarized in Table 2-3. The most comprehensive data belongs to 1997. However, accurate and more recent data is also summarized in the paragraphs below.

Table 2-3 Production data for nonylphenol and its ethoxylates [2; 9]

1997	Place	Production (tons)
Nonylphenol	EU	73,500 (use: 78,500)
	USA	145,000
	Japan	40,000
	Other	70,000
	World	335,000
Nonylphenol Ethoxylates	EU	118,000 (use: 77,600)
	USA	240,000
	Japan	65,000
	Other	105,000
	World	530,000

According to The Restriction Report for Nonylphenol and Nonylphenol Ethoxylates in Textiles [10], the total nonylphenol production in EU is around 10,000-50,000 tons in 2010. For NPEs, the data shows about 28,000 tons of production while

32,000 tons represent alkylphenols in total. It is clear that there has been a decreasing trend in EU from 1997 to 2010 in production volumes of NP and its derivatives.

According to US EPA's Nonylphenol and Nonylphenol Ethoxylates Action Plan, the US demand for NP was 380 million pounds which corresponds to 172,520 tons in 2010. NPE surfactants consumption in US corresponds to approximately 270-370 million pounds, which is 122,580 – 167,980 tons in 2002. Canadian NPE consumption in 2002 is 13,166 tons [11]. China produces 47,000 tons of NP and more than 50,000 tons of NPEs are being used annually.

2.1.3 Regulatory Framework for Nonylphenol

In 2000 with the WFD (2000/60/EC), the first list of priority substances were generated and placed in Annex X of the Directive [12]. WFD aims to reach good status in water bodies until 2015. According to the WFD, the goal for good chemical status in a water body can be reached when it complies with the environmental quality standards for all priority substances and other pollutants listed. So, Environmental Quality Standards Directive (2008/105/EC) replaces the first list (Annex X) of WFD with its Annex II and EQS values are generated for the listed pollutants [13]. To protect water sources in an effective way EQS values are preferred to be used in accordance with discharge standards. Priority pollutants constitute of substances such as pesticides and endocrine disruptors with persistent, bioaccumulative and toxic properties. These pollutants generally occur at low concentrations in waters and therefore called as "micropollutants". NP is identified as one of the priority hazardous substances in relation with the abovementioned legislation.

The REACH Directive (1907/2006/EC) puts restriction for 58 substances and substance groups which include NP and NPEs [14]. According to the regulation the substance is not to be placed on market or used, as itself or in mixtures in concentrations equal or greater than 0.1 % by weight for listed purposes. The restriction covers main uses of NP and its ethoxylates. In the authorization part of the regulation the aim is to control the risks of the Substances of Very High Concern, which are published in accordance with REACH Directive, by for example, proposing suitable alternatives to them. Substances of Very High Concern are determined by European Chemicals Agency (ECHA) and 4- Nonylphenol is one of the substances in the abovementioned list [15].

US Environmental Protection Agency (EPA) released an action plan addressing NP and NPEs in 2010 [11]. The action plan aims to develop rules for the restriction of products containing these substances and to support the voluntary phase-out of NPEs in industry. EPA found the way to manage with the widespread use of these substances by identifying eight safer alternatives. In addition to the action plan EPA has set aquatic life criteria for NP for freshwater and saltwater aquatic life which can be thought as EQS for US waters [16]. Finally, in context of the Toxics Release Inventory Program of EPA, NP is added as a category to the list of reportable chemicals and release data is required to be reported by industries.

Up to now, the actions that EU and US take in order to control NP and its ethoxylates are reviewed. EU legislation has effectively reduced the use of NP and NPE. There are also country specific measures and voluntary actions taken by industries to phase out the use of the substance and offer safer alternatives to it. Some effort has been devoted in Turkey to restrict the use of hazardous substances. Current policy for management of chemicals is targeting EU REACH (1907/2006/EC).

In Turkey, in context of the Regulation on Inventory and Control of Chemicals, the Ministry of Environment and Urbanization keeps track of the import, export, production data and properties of the substances of concern for every three years. Manufacturers and importers of these substances in Turkey are responsible of the notification. In scope of the Regulation on Inventory and Control of Chemicals, NPs are in the list of high volume chemicals, which are identified to be imported / produced over 1000 tons per year in Turkey. In addition, NP is identified as one of the priority chemicals in 2012 [17].

The regulation on Restriction of the Production, Placing on the Market, and Use of Certain Dangerous Substances, Preparations and Articles (26.12.2008, Official

Gazette No: 27092) works similar to REACH (1907/2006/EC) and it limits the use of the substance in some activities in Annex I [18]. According to the regulation, the substance is not to be placed on market or used, as itself or in mixtures in concentrations equal or greater than 0.1 % by weight for listed purposes. The regulation came into force in 2008 and NPs and its ethoxylates were added to the list in 2011.

In addition to these, the Regulation on the Control of Pollution Caused by Dangerous Substances in Water and Its Environment (26.11.2005, Official Gazette No: 26005) [19] introduces two lists which include hazardous substances and less hazardous substances. NP is in the second list which means that its discharge has to be controlled and EQS and discharge standard has to be identified. In addition, an inventory of dangerous substances is prepared according to this regulation.

2.2 Substance Flow Analysis

Before giving a definition of substance flow analysis, defining materials flow analysis will be appropriate. "Materials flow analysis" is defined as a systematic assessment of the flows and stocks of materials within a system in a particular space and time. So, the sources, pathways and sinks of the material are connected together. This connection is done through the application of the law of conservation of matter, in other words a mass balance. SFA is a type of materials flow analysis (MFA) which is used to determine the entrance pathways of substances to the environment, the processes related to these emissions, the stocks and flows in an industrial system, the chemical, physical and biological transformations and the resulting concentrations of substances in the environment [20]. The slight difference between the two tools is that MFA focuses on economic terms such as consumer or investment and deals with the analysis of flows and stocks of goods in an economic system.

In brief, SFA is a tool which deals with the flows and stocks of specific substances such as chemical compounds and elements to provide relevant information for an overall management strategy.

Three basic terms very commonly used in explaining SFA methodology are inflow, outflow and stocks. The relation between these three is shown in Figure 2-4.

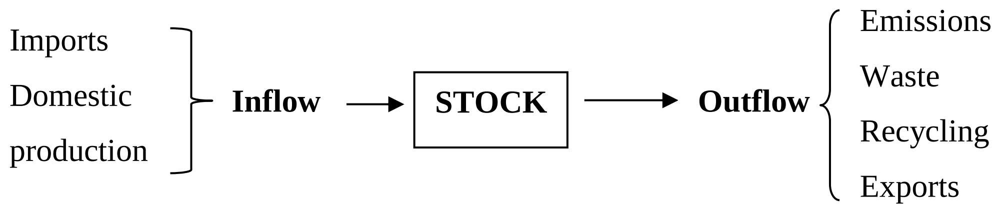

Figure 2-4 Schematic illustration of Substance Flow Analysis with inflow, stock and outflow [21]

The term inflow describes the entrance route of the substance to the system. The substance of concern may enter the system with raw materials for industries, with products for consumers etc. Stock is basically the accumulated amount of substance in the system Stock builds up in the system when the product containing the substance has a longer service life than the analysis period. There may be cases when there is no stock for very short service lives. In this case only inflows and outflows are considered. The outflow of the substance from the system can be via export of products, waste, and emission to soil, water or air during the different stages of the product's life cycle [22].

SFA methodology is based on the mass balance principle [23]. The basic substance balance below can be used to describe the flows through the system.

$$\text{Input} + \text{Formation} = \text{Output} + \text{Degradation} + \text{Accumulation}$$

There is no standard method that describes the procedure of the substance flow analysis but in general SFA methodology involves three steps; goal and system definition, inventory and modeling, and interpretation of the results [24]. In the following subsections, these steps are described in detail.

2.2.1 Goal and System Definition

Definition of the goal: SFA studies can serve for different purposes. One of them is that it can be used for data acquisition by checking inconsistencies in data and determining some missing flows. Another purpose of SFA studies can be the determination of major problem causing flows to the environment. In addition to these, SFA studies can be used to predict future scenarios and to identify points that can be further investigated by other tools such as life cycle assessment (LCA). Besides these, the most important purpose of SFA is that it serves as a supporting tool for environmental decision making. As the substance is traced in the environmental compartments, the possible adverse effects of it to the environment and the source that is causing it can be predicted. Finally, SFA can be considered as an important tool for resource management [25]. It can be used to predict the primary resources depleting or the new sources accumulating.

Definition of the system and subsystems: In this step, the substance and substance group, the system boundaries, possible subsystems, inputs and outputs of the system and the subsystem and the possible elements within the system and subsystem are defined.

In SFA, only one substance or a group of substances is studied. The selection of substance or substance group is directly related with the purpose of the study. The term "system" consists of all the processes related to the selected substance within a region. In order to define the system boundaries the goal of the study must be known. The boundaries can be a region with political boundaries, a watershed, coastal seas, agricultural units or an industrial firm etc. Generally the SFA's are conducted at regional scale. An administrative region such as a country or a group of countries has advantages in terms of data availability such as production and trade statistics [20].

The next step is to determine the inputs and outputs of both the system and the subsystems. In any substance flow analysis the flows should be expressed as mass units per time unit. Generally, the unit for time is one year. In cases when variations within a year are significant, a shorter period of time can be used. On the contrary if the process is slow a longer period is more appropriate.

Then, the elements i.e. the unit processes, stocks that are accumulating and flows between processes are defined. In the end, all of the information can be expressed with a substance flow diagram.

2.2.2 Inventory and Modeling

Three methods can be used in the inventory and modeling part for the quantification of the stocks and flows:

- Accounting or bookkeeping,
- Static (stationary) modeling and
- Dynamic modeling.

<u>Accounting or bookkeeping:</u> Accounting is basically keeping track of the flows and stocks by registering them. Data is collected for a specific period of time from trade, production, consumption, and waste management statistics. In addition, data about the amount of substance in products and materials may be required. The data is combined together with the mass balance principle and the inflows and outflows are balanced for each process.

The accounting procedure is useful for various purposes. For example, it can be used for error checking, to identify missing data and fill it by estimations done with mass balance. It can also be used as a monitoring tool in which changes over time can be registered periodically.

<u>Static (stationary) modeling:</u> In static modeling, the steady state relations between stocks and flows are used. This is done by expressing the process with a set of linear equations that describe the flows and accumulations that are dependent on one another. In other words, with the help of equations describing the system the outputs can be computed from the inputs and vice versa. Constants like emission factors and

partition coefficients can be required for this type of modeling. In addition, some data is needed for the calibration of the equations. Still, data requirement is not as much as the accounting procedure.

Dynamic Modeling: In dynamic modeling the process equations include a time variable. So, information with regard to time dimensions of the variables such as, half-life or retention time of compounds is required.

With dynamic modeling, predictions about future scenarios can be made if the data is available with adequate accuracy. In contrast to static modeling, the substances that are accumulating in materials, products or in the built environment are included in dynamic modeling. This is an advantage of dynamic modeling because one can estimate the dangerous effects of future emissions.

However, a disadvantage of dynamic modeling is that it requires lots of data; for example, all of the data of stocks and flows and the relations between them with respect to time variable. Consequently, the accuracy of dynamic modeling may be limited.

2.2.3 Interpretation of the Results

In SFA studies, the results are given in terms of flows and accumulations of the substance studied. For policy makers there may be a need to further elaborate the SFA results especially when a group of substances is studied [24]. In this case a solution can be to define the contributions of the individual substances to the environmental problem. This way, the results can be evaluated in detail based on each substance. When dealing with one substance the result of the SFA study in terms of the total overview of the flows and stocks may be too complicated to evaluate for policy makers. In this case, a flow or stock can be selected as an indicator for an environmental problem. Indicators help in the interpretation of environmental data for environmental policy making.

2.2.4 Limitations of SFA

There are a number of limitations of SFA studies. First, SFA deals with one substance only. For example, if a substance is replaced with a new one, the effects of the replacing substance are not considered. However, it is stated that this limitation can be solved by conducting LCA studies [24]. The second drawback of SFA is that it only deals with the physical economy and not the financial economy. So, the relationship between the substance data and the economic data cannot be seen because the economic data is generally about products, not the substances in products.

It is important to add that finding data for individual substances in SFA studies is very hard because knowledge about substances in products and in the environment can be insufficient. This can be considered as the main limitation of the SFA studies in countries lacking reliable data on substances and their release amounts to the environment.

2.3 Literature Review for Substance Flow Analysis

In this part, SFA studies that were previously done for NP are reviewed. The number of these studies in the literature is limited and generally they were conducted as workpackages of certain projects about hazardous substances.

Within the context of the European Source Control Options for Reducing Emissions of Priority Pollutants Project (ScorePP), SFA is conducted in two case cities for eight selected priority pollutants as given in Table 2-4 [22]. The pollutants that showed high concentrations in effluent and sludge in the monitoring campaign performed earlier were selected. This makes comparison of the measurement and SFA data possible, which is the main characteristic of the study.

Table 2-4 Substances selected in ScorePP Project [22]

Case City A	**Case City B**
Di(2-ethylhexyl)phthalate (DEPH)	Di(2-ethylhexyl)phthalate (DEPH)
Cadmium	Cadmium
Mercury	Mercury
Benzo(a)pyrene	Nickel
Pentabromodiphenyl ether (pentaBDE)	Lead
	Naphthalene

Data was collected from various sources and emissions were distributed to different environmental compartments. The distribution to stormwater and the fate of pollutants in wastewater treatment plants (WWTP) were also taken into consideration. When measured values and predicted values based on SFA are compared it was found that they were mainly in good correlation. Also it was noted that there were cases where good correlation was not achieved. This was explained with data uncertainty which can be accepted as the main disadvantage of substance flow analysis studies and limitations in measurement.

The objective in conducting SFA in the project for the selected priority pollutants was to develop source control strategies for authorities to reduce emissions and SFA was found to be an effective tool for this purpose.

The project named Source Control of Priority Substances in Europe Work Package 2, studied material flow analysis for selected priority substances in 2009. In this study the term material flow analysis refers to substance flow analysis. The selected priority substances were brominated diphenyl ethers (PBDE), tributyltin (TBT), di(2-ethylhexyl)phthalate (DEPH), nonylphenol, isoproturon, atrazine, mercury, cadmium, hexachlorobenzene (HCB) and polycyclic aromatic hydrocarbons (PAH’s). The MFA for NP in Europe was prepared with data of 2000. The environmental compartment receiving the highest emission was determined as land with emissions from application sewage sludge on agriculture soil. Following this, releases to water were significant and the main contributor was production of different materials using nonylphenol ethoxylates. The main limitation of this study is that it does not use up-to-date data. In addition, the sources of substances were not identified in detail and stocks in products were not considered [26].

Control of Hazardous Substances in the Baltic Sea Region (COHIBA) Project studied SFA in a very comprehensive manner [27]. In context of the project, SFA of substances and substance groups listed in Table 2-5 were conducted. The aim of the project was to identify the sources of the selected hazardous substances, quantify their inputs to the Baltic Sea, analyze their pathways from production to the environment, and to develop management options for decision makers.

Table 2-5 Substances of concern in COHIBA Project

Number	Substances or Substance Groups
1	Dioxins (PCDD), furans (PCDF), dioxin-like polychlorinated biphenyls (PCBs)
2	Tributyltin compounds (TBT), triphenyltin compounds (TPhT)
3	Pentabromodiphenyl ether (pentaBDE), octabromodiphenyl ether (octaBDE), decabromodiphenyl ether (decaBDE)
4	Perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA)
5	Hexabromocyclodecane (HBCDD)
6	Nonylphenols (NP), nonylphenol ethoxylates (NPE)
7	Octylphenols (OP), octylphenol ethoxylates (OPE)
8	Short-chain chlorinated paraffins (SCCP), medium-chain chlorinated paraffins (MCCP)
9	Endosulfan
10	Mercury
11	Cadmium

SFA for NP and its ethoxylates is prepared country specific by Baltic Sea countries, and also EU-wide (EU27). The time frame was one year but generally the analysis does not refer to a specific year and the most recent available data were used. The sources were classified according to their NACE codes and emissions were calculated for all environmental compartments. The main source categories and the receiving compartments are given in Figure 2-5.

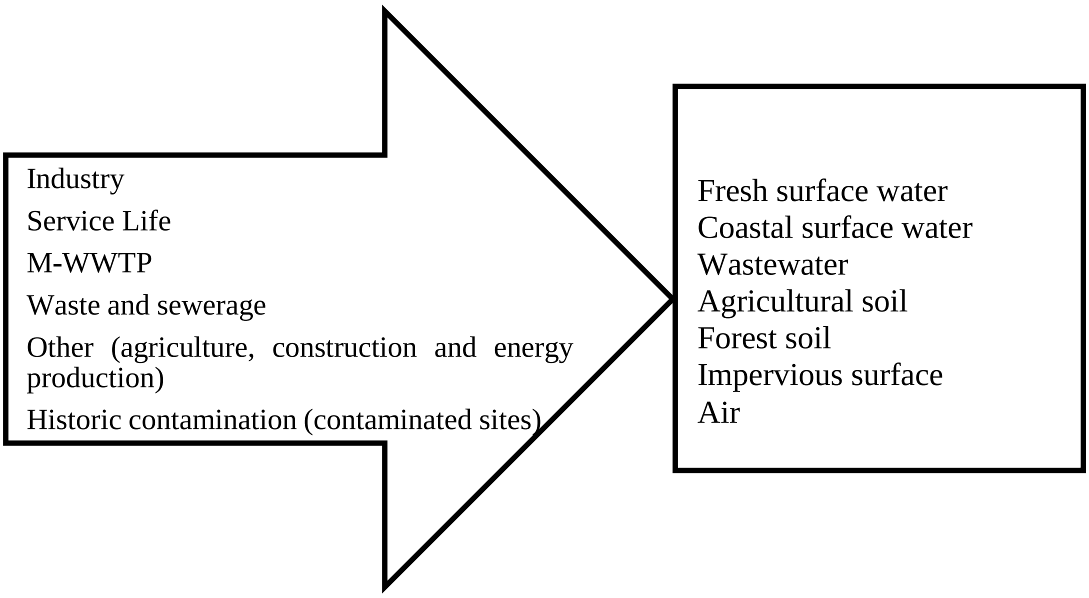

Figure 2-5 Source categories and receiving compartments

The main points in the substance flow analysis for NP and its ethoxylates conducted by Sweden, Finland, Poland, Estonia and Latvia are summarized in Table 2-6.

Table 2-6 Main findings of the COHIBA Project

Country	Findings of SFA for Nonylphenol and Nonylphenol Ethoxylates
Sweden [28]	• The major sources of nonylphenol to the environment were found as atmospheric deposition, washing of textiles and private cleaning with products from outside EU. • For nonylphenol ethoxylates, the use of products containing NPE is considered as major sources of emissions to wastewater. • Water is the environmental compartment that receives the highest emissions. • The emissions to soil are important because of the use of pesticides
Finland [29]	• The most important receiving compartment of nonylphenol emissions is soil and surface water. • The major emission sources to surface waters were identified as wastewater treatment plants and leaching of concrete. • The upstream sources to wastewater treatment plants are mainly car washing, washing of textiles, industrial cleaning, manufacture and application of paint.

Table 2-6 (continued)

Country	Findings of SFA for Nonylphenol and Nonylphenol Ethoxylates
Poland [30]	• Municipal wastewater treatment plants were found to result in low loads of NP and NPE, in contrast to Sweden. • Industrial use of the ethoxylates in cleaning is found to be the major source of emissions across the country
Estonia [31]	• Most of the emissions were not estimated due to missing data and reliable information. • Among the calculated ones use of private use of detergents from outer EU, textile washing and cosmetic products result in highest emissions. • The most important receiving compartment is wastewater and surface water accordingly.
Latvia [32]	• Most important sources were found as washing of textiles, cosmetic and hygienic products and industrial cleaning.

The EU wide SFA reveals that washing of imported textiles and atmospheric deposition were the major emission sources of NP. In case of ethoxylates the use of cleaning agents, textiles, cosmetics and paint; especially the products those are imported from outside EU, are the sources in wastewater and consequently surface waters.

When the overall results are considered, substance flow analysis in EU revealed that the highest emissions belong to short-chain chlorinated paraffins (SCCP) and medium-chain chlorinated paraffins (MCCP) and lowest emission belongs to endosulfan. For NP and its ethoxylates industrial point sources are significant. Next follows municipal wastewater treatment plants. Minor emissions of the substance are from service life stage, i.e. uses in products. About 80 % of the release of NP and its ethoxylates is distributed to surface waters and remaining to land.

In COHIBA project, SFA was used for identifying the most important sources for emissions of substances to the environment. This identification is supposed to serve for developing management measures for the selected hazardous substances in the Baltic Sea Region. By the use of SFA, the hotspot areas in countries were also identified. For example, for NP and its ethoxylates, it was found that there were major industrial sources in Lithuania and Poland. In Stockholm, the releases were high originating mainly from washing of textiles and concrete. With substance flow analysis a dataset of emission estimates for the listed substances in Baltic Sea Action Plan is generated and the awareness for these substances in the region has increased. Despite the uncertainties arising from the input data about the products, substances and emissions and the extrapolation of the data, the study was found to be useful for new SFA studies.

Mansson et al. [33] conducted substance flow analysis for alkylphenols and alkylphenol ethoxylates in Stockholm, Sweden. There was need for the identification of the sources of alkylphenol and alkylphenol ethoxylates due to the wide use of the substances, lack of information of their sources and the high loads in municipal wastewater treatment plants in Stockholm. In the study, emphasis was given to NPEs since it is the most widely used type of alkylphenol ethoxylate. The study was done on an urban scale so; products in which alkylphenol and alkylphenol ethoxylates are used had great importance. The product groups studied were: agricultural products, cleaning products, concrete, products such as lubricants and degreasers used in engineering work, glue, paint, paper, personal care products, photographic chemicals, plastics, textiles and leather.

The major use of alkylphenol and alkylphenol ethoxylates was in textile, leather products and paint. The sources of emissions to wastewater treatment plants were calculated and textile and leather products were estimated to result in 0.7-1.6 tons NP_{eq} while cleaning agents 0.1 tons NP_{eq}. This corresponds to 70-150 % of the total flows to WWTP. The study was found significant as it highlights the sources of NP in urban areas and links to the importance of global management actions rather than country specific ones.

Andersson and Sörme [34] studied SFA regarding alkylphenols and alkylphenol ethoxylates with focus on NP. Their purpose was to find the sources and release routes of the substances within Stockholm to minimize the emissions. Study revealed that the most important source for alkylphenol ethoxylates was cleaning agents and personal care products. Besides these, paint, concrete and plastics were identified as possible sources and paper, agriculture and textile were identified as not being as important. It is surprising that textiles were not found to be a major source in contrast to the study of Mansson et al. [33]. The reason can be that in this study textile products imported from outside of EU which are likely to contain NP, were not considered.

Jonsson et al. [35] summarizes the SFA studies conducted in Stockholm for organic pollutants such as diethylhexyl phthalate (DEPH), alkylphenol ethoxylates (APEO), polybrominated diphenylethers (PBDE) and chlorinated paraffins (CP).

The summary aims to serve as a support document for decision makers to reduce the load of pollutants in urban environment. It links to the importance of the stocks of substances as it can be an important source of environmental pollution load of hazardous substances for a long time period. In case of NPs it is stated that the use of the chemical can be phased out while still emissions can arise from imported products. With this perspective the study focuses on the alkylphenol ethoxylate contents of products. In conclusion it was found that the stock of alkylphenol ethoxylate accumulates majorly in concrete. Although textile products and detergents include higher concentrations, they are emitted almost totally in first use.

Björklund [36] studied SFA of phthalates and NPs in stormwater. The analysis was performed in an area of 5 ha in Gothenburg, Sweden [36]. The study is found significant as it investigates flows of substances in urban environment by focusing on stormwater systems. The sources of NP species in urban environments were identified as concrete, vehicles, tire wear, parking spaces, human activities, atmospheric deposition, roofing, PVC, other plastics and sealants. Emission factors were generated for all sources and emissions were calculated accordingly. It was found that 780 g of NP species are emitted per year within the system and 450 g of this reaches the stormwater. Of the 780 g 570 g is found to result from vehicles and 140 g from concrete [36]. So, among the identified sources, concrete and vehicles were estimated to be the most important ones. The data estimated with SFA were compared with observed loads in the study area and the numbers are found to be in good correlation. The study of SFA for NPs in stormwater it is found to be important as it shows the main emission sources of NP species to urban stormwater and the application of emission factors in calculating the flows of pollutants.

The studies discussed up to now have somehow different perspectives and slightly different results. While COHIBA, ScorePP and SOCOPSE projects focus on substances important within their scope, Mansson et al. [33] investigated the inflows and outflows through Stockholm city boundaries. Björklund [36] and Jonsson et al [35] focused on stormwater systems and stocks in products, respectively. Even though the number of studies is limited, they provide enough knowledge about the inflow, outflow and stocks of the selected pollutant in EU countries.

CHAPTER 3

METHODOLOGY

3.1 Goal and System Definition

Substances focused in this study are nonylphenol and nonylphenol ethoxylates. Although each substance has its own CAS and EC number, it is hard to predict which individual NP or NPE is used for different activities. For this reason, NPs are covered as a whole. In other words the name NP will refer to all isomers. The same approach is accepted for NPEs.

The goal of the SFA study is to determine the sources, emissions and accumulation of NP and NPEs in Turkey to provide information for the reduction of the emissions and usage of the substance across the country.

The system is defined as “Turkey” and the time frame for the study is “one year”. However, the analysis does not apply to a certain year. The most recent, available and reliable data is used in order to end up with the most accurate results. Within the system all possible sources of emissions are investigated and the receiving compartments are air, water and land.

3.2 Inventory and Modeling

Accounting and bookkeeping approach was used in the study. In order to identify the sources that are likely to cause NP and NPE emissions, different life cycle stages of the substances are considered. These are releases during production, formulation, processing, private use and disposal as illustrated in Figure 3-1.

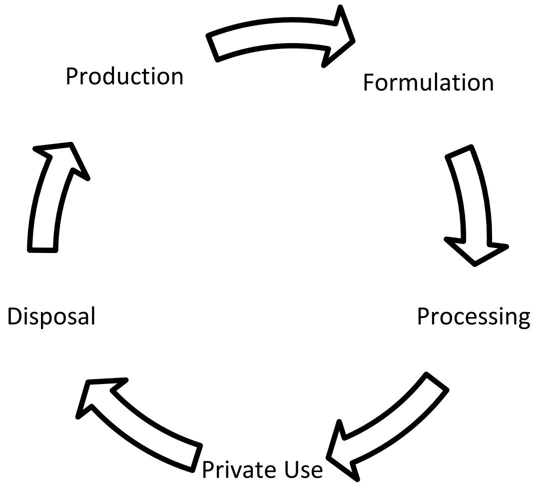

Figure 3-1 Life cycle stages of the substance

For NP and NPE production, processing (industrial use), private use (product use) and disposal stages are valid. Processing stage is the step where the substance is applied or used. In formulation step, the chemical is used to obtain a product or preparation. For NP there is no formulation step in between production and processing in the lifecycle stage. For NPEs the formulation stage is crucial. The substance is either used as itself or in mixtures for example in textile, leather auxiliaries or other preparations. In addition NPEs can be present as ingredients of surfactant mixtures. It is known that some companies dilute NPE before usage. In this study releases from formulation stage of NPEs are accepted to be minor and so, this stage is not considered in the release estimations. Processing and private use stages are significant for NPEs. Considering the lifecycle stages the sources studied for NP and NPEs are provided in Table 3-1 and Table 3-2, respectively.

Table 3-1 Sources of nonylphenol

Life Cycle Stage	Name of the Source
Production	Not valid for Turkey (no production of NP)
Processing	- Manufacture of nonylphenol ethoxylates - Manufacture of phenol and formaldehyde resins - Manufacture of epoxy resins - Manufacture of plastic stabilizers

Table 3-1 (continued)

Life Cycle Stage	Name of the Source
Private Use (Use in products)	Considered under nonylphenol ethoxylates
Disposal	Wastewater treatment plants

Table 3-2 Sources of nonylphenol ethoxylates

Life Cycle Stage	Name of the Source
Production	Manufacture of nonylphenol ethoxylates
Processing	- Manufacture of textiles - Manufacture of leather - Manufacture of paper and paper products - Manufacture of paint, lacquers and varnishes - Use in the photographical industry - Manufacture of furniture - Manufacture of motor vehicles - Manufacture of basic metals - Production of soap, detergent and cleaning preparations - Use in wood preservation - Application of paints lacquers and varnishes - Maintenance and repair of motor vehicles - Use of pesticides - Use of veterinary medicines
Private Use (Use in products)	- Concrete - Painted and coated surfaces - Textiles - Cosmetic and hygienic products - Hard plastic products - Detergents, cleaning agents and industrial and institutional cleaning - Vehicles - Parking lots - Use in car washes
Disposal	Wastewater treatment plants

As it is presented in Table 3-1 and Table 3-2 NP and NPE's have a variety of uses that are investigated within the scope of this study. NPs are used as monomers in manufacture of phenol formaldehyde resins, accelerator or curing agent in hardening agents used in manufacture of epoxy resins, and additives in plastic stabilizers. Its main use is accepted as manufacture of NPEs. NPEs are known to be used for various purposes. For instance, in textile manufacturing they serve as detergents, lubricants and emulsifiers in different processes of production. NPEs are used as surfactants in manufacture of leather and related products. NPEs are used as antifoaming agents, retention aids, deposit control, cleaning and maintenance agents in paper and board industry. They are used as additives in manufacture of paint resins. Generally, NPEs serve as surfactants. For example, they are consumed for manufacturing of soap and detergents both for private and industrial use. In photographic chemicals and agricultural products such as pesticides and veterinary medicines they are preferred as wetting agents owing to their surface active properties. As a result of their industrial use, it is possible to observe the substance in consumer products such as, textiles, leather, detergents and cleaning agents, plastics and cosmetics. The releases from use of these products are estimated in this study.

The uses and emission sources of NP and NPEs are not limited to the ones investigated in this study. For instance, NPs are known to be used in the manufacture of tri- (4-nonlphenyl) phosphite (TNPP). This substance is used widely in plastics industry as stabilizer for various plastics and rubber [37]. The most important use is in plastic food packaging. TNPP is known to contain up to 3 % NP which is gradually released in the stabilization process [2]. The releases of NP from TNPP are likely to be very small. There are some studies investigating the amount of substance adsorbed on food from contact with plastic packaging. According to inventory data of the Ministry of Environment and Urbanization, TNPP is neither produced in Turkey, nor imported. So, this source is not considered in the study.

In addition to TNPP, manufacture of phenolic oximes also consumes NP. Phenolic oximes are used in the extraction of copper from copper mines. Releases of NP with mine drainage can be a possible source of pollution. However, the production or usage amounts of this substance and the concentration in mine drainage are not available in order to quantify possible releases.

NPE is known to be used in anti-icing agents in aircrafts and as laboratory chemical in scientific research activities. The releases from these sources are not included in this study.

Releases by landfill leachate, atmospheric deposition and storm water could not be identified for Turkey. Concentration data of NPs are missing for landfill leachate. Emissions from this source probably will be minor. For atmospheric deposition, there are some measurements and emission factors in the literature. However, the fate of NP in atmosphere is not very significant as the substance does not volatilize. In addition there is no data in the literature about atmospheric deposition rates both for dry and wet deposition of NP in Turkey. Thus, atmospheric deposition is not considered under the scope of this thesis. Stormwater can be a receiving compartment of emissions where final destination will be surface waters via WWTPs. Load of NP and NPEs via storm water in Turkey is not possible to quantify as the concentration of substance in stormwater is not known. In fact for some of the sources emissions can pollute stormwater and directly reach surface waters and land. This situation can make stormwater an important source of pollution.

Data on production, usage, import, export, quantity of the substance used, wasted, recycled in industrial processes, quantity of substance in various products were gathered for the sources listed in Table 3-1 and Table 3-2. The next important point is the need of emission factors for the calculation of emissions to different environmental media. The methodology followed in the inventory and modelling step of the thesis involves two approaches.

Approach I: This approach is used for quantifying the amount of substance used and emitted in industrial processes in other words releases during processing lifecycle stage. In this approach, production data is required for the activity in which NP/NPE is used in the process. To be able to calculate the emissions, average content of the substance in the product and emission factor is necessary. The following equation describes the calculation logic.

$$E = P \times C \times EF$$

E = Emission,

P = Total production amount,

C = Concentration of NP/NPE in product,

EF = Emission factor.

The variables in the above equation can result in uncertainties. The production data is generally gathered from Turkish Statistical Institute and TOBB Industry Database. So, they are actual numbers representing Turkey. For the concentration of substance in product and emission factors, the data is given as exact numbers for some sources. For some emission sources these variables are found as a range. In order to make an uncertainty analysis of these variables more data would be required. Further discussion on uncertainty can be found in Part 5.2 of the thesis.

Approach II: This approach is used mainly in calculation of emissions from products in other words private use lifecycle stage of the substance. Instead of the production volume, the amount of substance used within the system is required. This amount can be estimated with manufacturing, import and export data as given in the equation below.

$$E = PU \times C \times EF$$

$$PU = Manufacture + Import - Export$$

E = Emission,

PU = Total amount of product used in the system,

C = Concentration of NP/NPE in product,

EF = Emission factor.

However, for some of the products, the emission factor provided in the literature generally involves the population criteria. This way, the amount of product used is not required and emissions are estimated with population data. The emission factors used in this study are provided in Table 3-3 and Table 3-4.

Table 3-3 Nonylphenol emission factors [2]

Life Cycle Stage	Name of the Source	Emission Factor	
		Wastewater	Air
Processing	Manufacture of nonylphenol ethoxylates	0.007	0.00001
	Manufacture of phenol and formaldehyde resins	0.00001	0.00001
	Manufacture of epoxy resins	0.0001	0.0001
	Manufacture of plastic stabilizers	0.0005	0

Table 3-4 Nonylphenol ethoxylate emission factors [2]

Life Cycle Stage	Name of the Source	Emission Factor	
		Wastewater	Air
Production	Manufacture of nonylphenol ethoxylates	0.003	0
Processing	Manufacture of textiles	0.85	0.05
	Manufacture of leather	0.9	0.001
	Manufacture of paper and paper products	1	0
	Manufacture of paint, lacquers and varnishes	0.003	0
	Use in the photographical industry	0.8	0.000035
	Manufacture of furniture	0.0005	0
	Manufacture of motor vehicles	0.0005	0
	Manufacture of basic metals	0.0005	0
	Production of soap, detergent and cleaning preparations, cosmetic and hygienic products	negligible	negligible
	Use in wood preservation	n.a	n.a.
	Application of paints lacquers and varnishes	0.0005	0
	Maintenance and repair of motor vehicles	0.0005	0
	Use of pesticides*	0.10	0.05
	Use of veterinary medicines*	0.10	0.05

Table 3-4 (continued)

Life Cycle Stage	Name of the Source	Emission Factor	
		Wastewater	Air
Private Use (Use in products)	Concrete	0.25	0
	Parking lots	0.002 mg NPe_q/m^2 parking space and year	0
	Painted and coated surfaces	2.6 mg NP_{eq} / inhabitant and year	0
	Textiles	1.5 g NP_{eq} / inhabitant and year	0
	Cosmetic and hygienic products	7.77×10^{-4} g per inhabitant and year	0
	Hard plastic products	2.78×10^{-12} kg NP_{eq} /$m^2$of plastic	0
	Detergents, cleaning agents and industrial and institutional cleaning	1	0
	Vehicles	0.14 µg NP_{eq} /driven km	0
	Use in car washes	0.1 mg NP_{eq} /car and washing activity	0

*0.85 to soil,
n.a. =not available

For some cases it is found that the distinction between NP and ethoxylates could not be made, such as for substances in products. Also, it is known that ethoxylates easily degrade to NP in WWTPs or in the environment. It is not easy to differentiate between the emissions of NP and its ethoxylates. To prevent this, sometimes emissions are reported in terms of nonylphenol equivalents (NP_{eq}). The conversion of NPE to NP_{eq} changes for different chain lengths, according to molecular weight (MW). General formula for NPE is R_n-C_6H_4-$(EO)_m$-OH. Here, m represents the ethylene oxide and n represents the ethoxylate chain length. The chain length is known to range from 2 to 80. In Table 3-5, three examples for the conversion are given.

Table 3-5 Conversion from NPE to NP_{eq} (Mansson et al., 2008) [33]

Number of Ethoxy Group	**Example Product**	**Conversion to NP_{eq}**
<10	Detergents	m=8 $MW_{NP:}$ MW_{NPE} ≈ 2:5 Conversion factor = 2.5
10-30	Cosmetics	m=20 $MW_{NP:}$ MW_{NPE} ≈ 1:5 Conversion factor = 5
>30	Paint, biocides	m=40 $MW_{NP:}$ MW_{NPE} ≈ 1:10 Conversion factor = 10

Inevitably, all substance flow analysis studies require assumptions. In this study, in order to deal with the uncertainty accompanied by the assumptions and to attain realistic results, two scenarios are created. In the first scenario, the maximum usage of the substance and the maximum emissions are considered. In other words, a worst case scenario for NP in Turkey is created. The second scenario, on the other hand, aims to take into account the restrictions currently in force for the substance. This can be considered as a better and ideal scenario in which all plants respect the requirements of the regulations.

The Regulation on Restriction of the Production, Placing on the Market, and Use of Certain Dangerous Substances, Preparations and Articles (26.12.2008, Official Gazette No: 27092) [18] introduces some restrictions for the use of NP and its ethoxylates. According to the regulation the restricted applications are as below:
Nonylphenol ($C_6H_4(OH)C_9H_{19}$, CAS No: 25154-52-3, EC No: 246-672-0) and nonylphenol ethoxylate ($(C_2H_4O)_nC_{15}H_{24}O$) are not allowed to be placed on the market as substance and preparation in concentrations 0.1 % or higher by mass, for the following applications:

1. Industrial and institutional cleaning, except;
    - Controlled closed dry cleaning systems where the washing liquid is recycled or incinerated,
    - Cleaning systems with special treatment where the washing liquid is recycled or incinerated,

2. Domestic cleaning,
3. Textile and leather processing, except;
   - Processing with no release into waste water,
   - Systems with special treatment where the process water is pre-treated to remove the organic fraction completely, prior to biological waste water treatment (degreasing of sheepskin),
4. Emulsifier in agricultural teat dips,
5. Metal working, except;
   - Uses in controlled closed systems where the washing liquid is recycled or incinerated,
6. Manufacture of pulp and paper,
7. Cosmetics
8. Other personal care products, except;
   - Spermicides
9. Coformulants in pesticides and biocides.

So, for the activities listed above, 0.1 % concentration restriction is assumed in the calculations for the second scenario.

3.3 Interpretation of the Results

The findings of the study were illustrated in substance flow analysis diagrams showing the inflows and outflows through the system. The inputs to the system, in other words, production and import of the substance are balanced with the outputs which are the releases to different environmental media. After the establishment of the mass balance, the suitable scenario is decided and major sources are identified. Two scenarios were established. In the first scenario, the maximum possible emissions are estimated. In the second scenario, the sources for which the abovementioned regulation forces restriction are calculated according to the limit (0.1 % concentration of the substance). For sources that the use of the substance is not restricted, the estimations are accepted to be same as in first scenario. The results of the scenarios were evaluated according to the production and import amounts of the substances. Finally, the suitable scenario that best fits the available data about the substance is selected and main activities consuming and emitting the substances are identified. This way the sources in which measures should be taken to reduce the emissions are identified.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter the usage amounts and emissions of NP and NPE are estimated according to the life cycle stages which are production, processing, product use and disposal. The sources investigated are provided in detail in Table 3-1 and Table 3-2. Each source is provided with its European industrial activity classification codes i.e. NACE codes in 4 digits. In subsections 4.1 and 4.2, uses of NPE and NP are calculated followed by corresponding releases.

4.1 Calculation of the Emissions for Nonylphenol Ethoxylates

4.1.1 Manufacture of Nonylphenol Ethoxylates

NACE Code 20.14 Manufacture of other organic basic chemicals

During manufacture of NPEs, some emissions to wastewater are likely to occur. The releases can be both NP and NPEs. Under this heading, the release of NPEs during the production stage is calculated by using the emission factors. The emission factor for NPE release into wastewater is given as 0.003 [2]. In other words, 3 kg NPE is emitted to wastewater when 1 ton of NPE is produced. The total production of NPEs in Turkey is 364.2 tons/year (from Table 6.5). Then the releases to wastewater from the manufacture of NPEs are quantified as 1092.6 kg/year.

4.1.2 Processing

Processing can be defined as the stage where NPEs are used in various industries, either in formulations or by itself for a variety of purposes such as surfactant, emulsifier, lubricant etc. The estimations were performed according to the first approach explained in the methodology part of the thesis.

4.1.2.1 Manufacture of textiles

NACE Code 13 Manufacture of textiles

It is known that NPEs with chain length 7 to 15 are generally used in textile manufacturing but, shorter and longer chained ones are also used. NPEs are used in manufacturing processes of textiles for the following functions:

- Washing and scouring of raw wool and cotton,
- Fiber lubrication,
- Dye leveling,
- Surface active agent for cleaning and rinsing textiles,
- Auxiliary agent in bleaching step,
- Wetting agent for textiles,
- Emulsifier for oils, fibers.

From this list it can be seen that NP can be used at almost any stage in the textile manufacturing process. So, NP and NPE are expected to be present in almost all types of textile products. NPEs are not used as pure chemicals. They are supplied in preparations such as detergents, wetting agents etc. in which they are used as surface active agents [38]. NP in discharges of textile industry can be attributed to breakdown of NPE.

Turkey's production capacities are provided in Table 4-1. The capacity utilization rate for the Turkish textile manufacturing industry is given as 77.3 % in 2010 [39]. Production volumes are multiplied with the capacity utilization rate for the year 2010 and NPE amount used, in order to find total usage of the substance. For wool production the capacity utilization rate is not used because the data represents the actual wool production amount. The results achieved are presented in Table 4-1.

Table 4-1 Data for NPE usage in textile manufacturing, first scenario

Product	Production capacity (tons/year)	Amount of NPE used in product	Amount of NPE used for different products (tons/year)
Wool	51,180 [40]	10 kg NPE/ton textile product [41]	511.8
Yarn	3,500,000 [42] (2,750,000 fiber)	10 kg NPE/ton textile substrate [43]	27,500.0
Knitted Fabric	2,250,000 [42]	20 kg NPE/ton textile product [44]	34,785.0
Woven Fabric	1,350,000 [42]	20 kg NPE/ton textile product [44]	20,871.0
TOTAL			83,667.8

As indicated in Table 4-1, the total NPE used in Turkey is calculated as 83,667.8 tons/year. The emission factors for NP and NPE in textile manufacturing are provided in the EU Risk Assessment Report as 0.05 to air and 0.85 to wastewater [2]. The total emissions of NP and NPE to wastewater and air are calculated and found as 71,117.6 and 4183.4 tons/year, respectively.

When the Regulation on Restriction of the Production, Placing on the Market, and Use of Certain Dangerous Substances, Preparations and Articles is considered, 0.1 % is the maximum allowed concentration of NP in textile manufacturing. The limit of 0.1 % concentration corresponds to 100 mg NP/NPE per kg textile [10]. It is assumed that all textile products contain NPE at the same amount (100 mg/kg textile). Based on this, in Table 4-2, the amount of NPE used in different textile products is estimated.

Table 4-2 NPE release estimation for manufacture of textiles, second scenario

Product	Production capacity (tons/year)	Amount of NPE used in product	Amount of NPE used for different products (tons/year)
Wool	51,180 [40]	100 mg NPE/kg textile product	5.1
Yarn	3,500,000 [42] (2 750 000 fiber)	100 mg NPE/kg textile product	270.6

Table 4-2 (continued)

Product	Production capacity (tons/year)	Amount of NPE used in product	Amount of NPE used for different products (tons/year)
Knitted Fabric	2,250,000 [42]	100 mg NPE/kg textile product	173.9
Woven Fabric	1,350,000 [42]	100 mg NPE/kg textile product	104.4
TOTAL			554.0

In the second scenario, the total NPE used in textile manufacturing is calculated as 554 tons/year. The emissions to wastewater and air are calculated with the same emission factors and found as 470.9 and 27.7 tons/year respectively. NP and ethoxylate concentration expected in untreated textile effluents are provided in

Table 4-3 [45]. Table 4.3 shows that textile manufacturing results in emissions of NP and its ethoxylates and support the calculations performed above.

Table 4-3 Representative wastewater concentrations for the textile industry [45]

Substance	Concentration of substance in raw wastewater (mg/L)
NP	0.15
NPE	4.1

4.1.2.2 Manufacture of leather

NACE Code 15 Manufacture of leather and related products

In the manufacture of leather and leather products NPEs are used as surfactants mainly in soaking, degreasing and fat-liquoring processes. Surfactants account for 1% of the total chemical consumption for a conventional tanning process. The input of chemicals to a conventional tanning process is about 500 kg/ton of raw hide treated [46]. So, 5 kg NPE is assumed to be used per 1 ton of raw hide.

There are about 500 tanneries in Turkey. Ovine hides provide the majority of hides (70-80 %) processed by the leather manufacturing industry in Turkey [47]. Turkey raw hide production data are provided by The Union of Chambers and Commodity Exchanges of Turkey (TOBB) Industry Database [48]. Production codes retrieved from the database are 10.11.42.00.00, 10.11.43.00.00, and 10.11.44.00.00. Some data are given as weight but some are in number. For an estimate of production amount, the following assumptions are made: one bovine hide weighs approximately 20 kg and one ovine hide weighs approximately 5 kg. Raw hide production of Turkey is not enough to meet the demand and production in this sector. Thus, imported raw hides constitute an important input in the leather production. In Turkey 75 % of the demand for raw ovine hide and 45 % of the demand for raw bovine hide are supplied by imports [47].

Information on the leather industry in Turkey and NPE usage in leather manufacturing are quantified in Table 4-4.

Table 4-4 Data for NPE usage in leather manufacturing, first scenario

Raw hide	**Production (tons/year)** [48]	**Import (tons/year)**	**Total raw hide (production + import) (tons/year)**	**Amount of NPE used (tons/year)**
Bovine	75,075.8	61,425.6	136,501.4	682.5
Ovine	72,873.3	218,619.9	291,493.2	1457.5
TOTAL	147,949.1	280,045.5	427,994.6	2140

The total NPE usage for leather manufacturing industry is found as 2140 tons/year. The emission factors are 0.9 to wastewater and 0.001 to air [2]. Then, the releases from the manufacture of leather and leather products to wastewater and air are calculated as 1926 tons/year and 2.14 tons/year, respectively.

The Regulation on Restriction of the Production, Placing on the Market, and Use of Certain Dangerous Substances, Preparations and Articles (26.12.2008, Official Gazette No: 27092) [18], requires 0.1 % NPE concentration in preparations used for leather manufacturing. For the second scenario, the limit value for NPEs in leather is given as 1000 mg NPE /kg leather [49]. The production data and the amount of NPE used for this scenario are represented in Table 4-5.

Table 4-5 Data for NPE usage in leather manufacturing, second scenario

Raw hide	Production (tons/year) [48]	Import (tons/year)	Total raw hide (production + import) (tons/year)	Amount of NPE used (tons/year)
Bovine	75,075.8	61,425.6	136,501.4	136.5
Ovine	72,873.3	218,619.9	291,493.2	291.5
TOTAL	147,949.1	280,045.5	427,994.6	428.0

The total NPE usage for leather manufacturing industry is found as 428 tons/year. The releases from manufacture of leather and leather products are calculated as 385.2 tons/year and 0.428 tons/year, respectively.

4.1.2.3 Manufacture of paper and paper products

NACE Code 17 Manufacture of paper and paper products

There are 48 paper and board production sites in Turkey with a total capacity of 2,847,326 tons of production in 2011 [50].

NPEs are used as antifoaming agents, retention aids, deposit control, cleaning and maintenance agents in paper and board industry. Antifoaming agents are used 0.03 % by weight within production. It is known that NPE amount in antifoaming agents is 1%. So, this gives 3 g NPE used per ton paper produced [2]. In addition, it is assumed that there is 0.95 % recycling of antifoaming agents through the system, so the releases are occurring as 5% of the agent used. Retention aids are used 0.5 % by weight within production and typical NPE content in retention aids is 1%, which means 0.05 kg of substance is used when 1 ton paper is produced [2]. Retention aids are used in the production of board and newsprint. Newsprint production in Turkey is assumed to be negligible so, board production data is used for calculation [50]. Production data are for 2011. NPEs are used for cleaning and maintenance purposes in paper industry [51]. Here approximately 0.56 kg NPE is assumed to be used per ton product. Retention aids and cleaning agents are assumed to be emitted 100%. Release estimation according to the above information is summarized in Table 4-6.

Table 4-6 Data for NPE usage in paper and paper products industry, first scenario

Usage of NPE	**Amount of NPE used**	**Production (ton/year)** [50]	**Amount of NPE used for products (ton/year)**	**Amount of NPE emitted (ton/year)**
Anti-foaming agent use	3 g NPE/ton paper [2]	2,847,326	8.5	0.4
Retention aid use	0.05 kg NPE/ton paper [2]	1,957,812	97.9	97.9
Deposit control, cleaning and maintenance agents	0.56 kg NPE/ton paper [51]	2,847,326	1594.5	1594.5
TOTAL			1700.9	1692.8

The amount of NPE used in this sector is found as 1700.9 tons/year. The total releases from paper and board manufacturing industries in Turkey adds up to 1692.8 tons/year. All releases are to wastewater, emissions to air and soil are assumed to be zero.

With the mentioned regulation, 0.1 % NPE concentration is allowed for paper manufacturing. Antifoaming agents are used 0.03 % by weight and this corresponds to 0.3 g NPE used per ton paper produced. With 0.95 % recycling, 5% of the substance used is released. Regularly, retention aids are used 0.5 % by weight within production. 0.1 % NPE means 5g of substance used when 1 ton paper is produced. For cleaning and maintenance purposes, approximately 0.56 kg NPE is assumed to be used per ton product. This amount is already lower than the required NPE limit. The data for the second scenario is provided in Table 4-7.

Table 4-7 Data for NPE usage in paper and paper products industry, second scenario

Usage of NPE	Amount of NPE used	Production data [50] (ton/year)	Amount of NPE used for products (ton/year)	Amount of NPE emitted (ton/year)
Anti-foaming agent use	0.3 g NPE/ton paper [2]	2,847,326	0.85	0.04
Retention aid use	5g NPE/ton paper [2]	1,957,812	9.8	9.8
Deposit control, cleaning and maintenance agents	0.56 kg NPE/ton paper [51]	2,847,326	1594.5	1594.5
TOTAL			1605.2	1604.3

The amount of NPE used in this sector is found as 1605.2 tons/year. The total releases from paper and board manufacturing industries in Turkey adds up to 1604.3 tons/year. All releases are to wastewater, emissions to air and soil are assumed to zero.

4.1.2.4 Manufacture of paint, lacquers and varnishes

NACE Code 20.3 Manufacture of paints, varnishes and similar coatings, printing ink and mastics

NPEs are used in preparation of paint resins, manufacture of water based paints, indoor varnishes, printer inks, concrete floor paint and they provide easier spreading, wetting and improved mixing. NPEs are used in paint manufacturing typically in concentrations of 0.6 – 3 % [52].

Paint production capacity of Turkey is 800,000 tons/year with a capacity utilization rate of 65 % in 2011. So, the average yearly production corresponds to 520,000 tons [53].

In EU 4000 tons of NPE is reported to be used in paint manufacturing and total yearly load to wastewater is given as 12.3 tons to wastewater [54]. From this information the emission factor to wastewater can be calculated as 0.3 %. The releases to air and soil from manufacture of paint are assumed to be zero.

The amount of NPE used in paint manufacturing in Turkey is estimated below with the following assumptions:

- All produced paint contains NPEs and the amount of substance is same in all products.
- Concentration of substance in product is assumed to be maximum in the given range.

Based on these assumptions the amount of NPE used in paint industry is 15,600 tons/year and the yearly load to wastewater is 46.8 tons.

4.1.2.5 Use in photographical industry

NACE Code 74.2 Photographic activities

NPEs are used in photographic industry as wetting agents in developing photographic films. They are both used in products for amateurs and professionals. The average concentration of the substance in products used in photographic industry is 3 -5 % [2].

Production data is provided in TOBB Industry Database for chemical preparations used in photography, ready to use and unmixed products as 3,438,288 kg. There are 6 producers registered to this database for production code 20.59.12.00.00 [55].

In addition to production data imports of these products are considered. Turkish Statistical Institute import data shows that 355,218 kg of chemical products for photography are imported in 2013 [56].

The production and import numbers add up to 3,793,506 kg/year. Assuming the maximum concentration, which is 5%; the amount of NPEs used in photographic industry chemicals in Turkey is calculated as 189.7 tons per year. The emission factors for this source are 0.8 to wastewater and 0.000035 to air [2]. Calculations of the yearly loads are provided in Table 4-8.

Table 4-8 Calculation of NPE emissions for photographic industry chemicals

<table>
<tr><th colspan="2"></th><th>Production + Import (kg/year)</th><th>Total NPE amount in products (tons)</th><th>Emissions to wastewater (tons/year)</th><th>Emissions to air (tons/year)</th></tr>
<tr><td>Production in Turkey (kg)</td><td>3,438,288 [55]</td><td rowspan="2">3,793,506</td><td rowspan="2">189.7</td><td rowspan="2">151.8</td><td rowspan="2">6.64×10^{-3}</td></tr>
<tr><td>Import to Turkey (kg)</td><td>355,218 [56]</td></tr>
</table>

Emissions to wastewater either reach municipal WWTP or discharged directly to surface waters. According to Turkish Statistical Institute [57] the amount of municipal wastewater discharged without any treatment is 20% of the total municipal wastewater discharges. So, with this information it can be said that from photographic industry 30.4 tons/year NPEs are directly discharged to surface waters and 121.4 tons/year reach WWTP.

4.1.2.6 Manufacture of Furniture

NACE Code 31 Manufacture of furniture

NPEs are used indirectly in manufacture of furniture as additives in paint. The average paint production of Turkey is 520,000 tons/year [53] . The export and import quantities for paint in 2010 are 376,067 tons and 456,218 tons, respectively [53]. The distribution of uses of paint types are provided with their percentages in Figure 4-1.

Total paint used in the country = Production + Import – Export

$$520{,}000 + 456{,}218 - 376{,}067 = 600{,}151\ tons/year$$

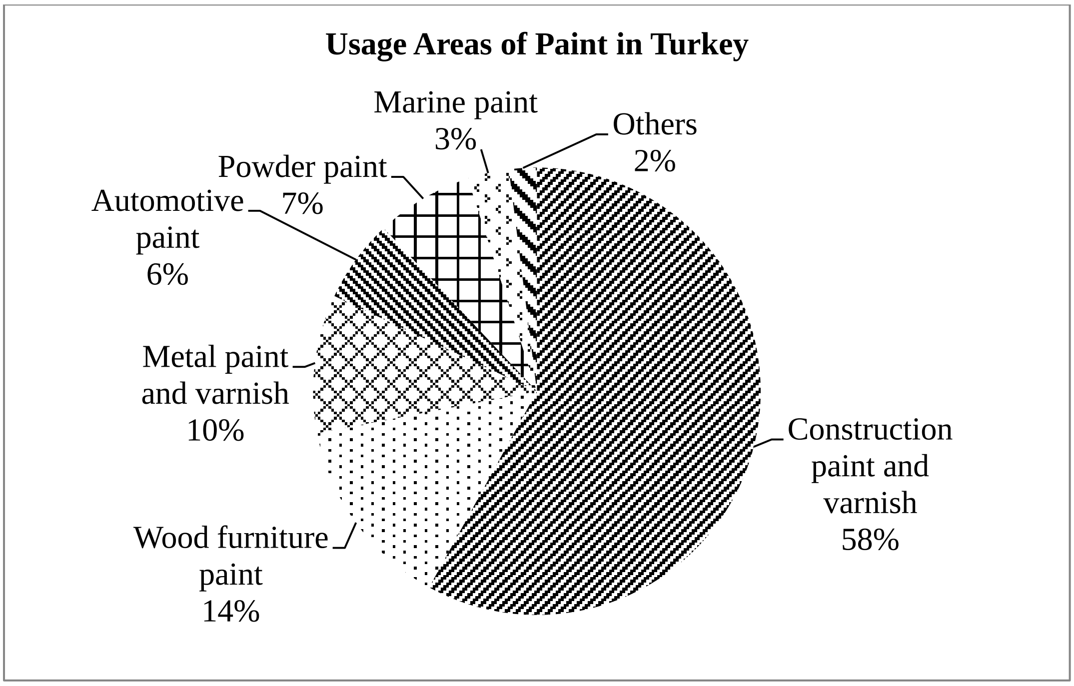

Figure 4-1 Distribution of paint usage areas in Turkey [53]

As one can depict from Figure 4-1 which presents the distribution of different paint types; furniture paint, constitutes 14 % of the total paint usage in Turkey. The usage of the substance in furniture paint and emissions of NPEs for this source can be estimated with the following assumptions.

- All of the paint used for this purpose contains NPEs (both manufactured in the country and imported),
- Paint contains NPEs at a concentration of 3% by weight [52].

Based on the above assumptions, the amount of the substance used in paints is estimated as 2520.6 tons per year. The emission factor is given as 5 kg NPE released to wastewater when 1 ton of paint is used [54]. So, the release of substance from manufacture of furniture as a result of usage of paint containing NPEs is estimated as 12.6 tons/year to wastewater.

TÜİK data [57] show that 20 % of municipal wastewaters discharges are untreated while 80 % of them are discharged after treatment. For manufacture of furniture NPE emissions are distributed as 10.1 tons/year to WWTP and 2.5 directly to surface waters.

4.1.2.7 Manufacture of motor vehicles

NACE Code 29 Manufacture of motor vehicles, trailers and semi-trailers

NPEs are used in manufacture of motor vehicles indirectly, in painting step. As a result of this, during manufacture of automotive, in coating step, paint containing NPE can result in emissions reaching wastewater. In Figure 4-1 it is observed that 6 % of paint production in Turkey consists of automotive paints. The usage amount of NPE and releases to wastewater are calculated in Table 4-9 with the following assumptions.

- All of the paint products used for automotive coating contains NPEs.
- The concentration of the substance in all products is 3 % [52].
- Automobile painting is known to be mostly done with electrostatic spraying which results in less effluent generation in comparison to other methods. Here, 50 % of the installations are assumed to use electrostatic spraying.

Table 4-9 Calculation of the releases from manufacture of motor vehicles

Total amount of paint used in Turkey (tons/year)	**Amount of paint used in this application (tons/year)**	**NPE content in paint** [52]	**Emission factor** [2] **(kg NPE/ton paint)**	**Emission to wastewater (tons/year)**
600,151	36,009.1	3 %	5	2.7

NPE used for this application is 1080.3 tons/year and the releases to wastewater are calculated as 2.7 tons/year.

4.1.2.8 Manufacture of basic metals

NPEs are used in metal extraction, refining and processing industries as lubricants in metalworking fluids such as cutting oils, drilling fluids, degreasing agents etc. NPEs are readily available and cost efficient so, they are widely preferred for this application.

In order to estimate the NPE amount used for this purpose, mineral oil consumption of Turkey should be investigated. In 2012, 408,000 tons of mineral oil was consumed in Turkey. The distribution of different usages is given in Figure 4-2.

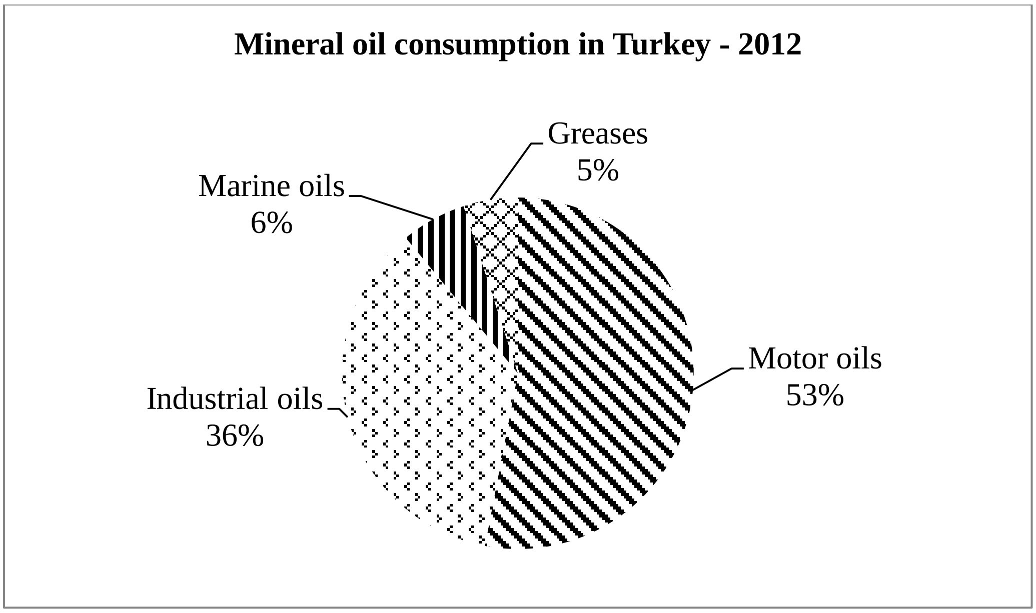

Figure 4-2 Mineral oil product groups and their distribution [58]

From the consumption data, it is understood that except for motor oils, approximately 192,000 tons of mineral oils were used in 2012 in Turkey. This corresponds to 47% of the total mineral oil amount. NPE concentration in mineral oils is given as 1% - 5% [59]. Three percent is selected as typical amount for release estimations. The emission factor is reported as 5 kg NPE / ton substance used in mineral oils [60]. The amount of NPE used for this application is calculated as 5760 tons/year. Based on these data, the release to wastewater from this source is estimated as 28.8 tons/year.

The restriction allows 0.1 % NPE content which is much lower than the typical values. In this case, the amount of substance used for this source is 192 tons and with the emission factor of 5 kg NPE / ton, the emission corresponds to 0.96 tons annually.

4.1.2.9 Production of soap, detergent and cleaning preparations, cosmetic and hygienic products

NACE Code 20.41 Manufacture of soap and detergents, cleaning and polishing preparations

The main usage area of NPEs in the world is known as production of soap and detergents. Especially cleaning agents for industrial and institutional use are potential sources of NPE. This can be attributed to their perfect surfactant property, cheap prices and being readily available. Generally, NPEs with chain length smaller than 10 are used for detergent manufacturing purposes.

The soap production capacity is 550,000 tons and detergent production capacity is 1 300 000 tons per year in Turkey [61]. For the year 2011, capacity utilization rate is given as 55 – 60 % [61]. This corresponds to about 1,110,000 tons of soap and detergent production. Typical concentration of NPE in soap and detergent is 1 - 10 % [59]. With the assumption that all products in this sector includes the substance at the same amount which is the average amount; 5%, quantity of NPE used can be estimated as 55,500 tons/year. Releases of substance from manufacturing stage of cleaning agents are accepted as negligible.

For the second scenario considering the restriction, the content must not be higher than 0.1 %. This concentration results in a total NPE usage of 1110 tons.

In addition to detergents and cleaning agents, NPEs are used as surfactants in products such as cosmetics, spermicides, shampoos, shower gels, shaving foams. NPEs with chain length between 10 and 30 are preferred for cosmetics. The amount of cosmetic and hygienic products consumed in Turkey in 2010 is 260,824 tons [62]. Consumption is assumed to represent the production amount. This is a valid assumption as the import and export values are found close to each other [62]. The typical concentration of NPEs in cosmetic products is given as 0.2 to 2 or 3 % [59].

2% NPE content is accepted in all cosmetic and hygienic products produced in Turkey. This corresponds to 5216.5 tons of NPE is used annually. The releases from manufacturing are assumed as negligible and the releases from private use of these products are dominant.

According to the Regulation on Restriction of the Production, Placing on the Market, and Use of Certain Dangerous Substances, Preparations and Articles (26.12.2008, Official Gazette No: 27092) [18], the allowed concentration is maximum 0.1 % which means that 260.8 tons of NPE is used in cosmetic and hygienic products in Turkey. Emissions from the production stage are considered as negligible because major releases to wastewater will occur with product usage lifecycle stage.

4.1.2.10 Use of nonylphenol ethoxylates in wood preservation applications

NACE Code 0.2 Forestry and logging

NPEs are used as additives in wood preservatives. For this NPE source, the amount of substance used for this application is estimated by making comparison with Swedish and Turkish sawnwood production data represented in Table 4-10.

Table 4-10 Sawnwood production of Sweden and Turkey in 2012 [63]

	Sawnwood Production in 2012 (m^3)
Sweden	15,900,000
Turkey	6,682,000

The amount of NPE used in Sweden for wood preservation purpose is 0.02-2 tons in 2008 and the sawnwood production is 17,601,000 m^3 for the same year [28; 63]. According to Table 4-10, the consumption for Turkey corresponds to 7.56×10^{-3} – 0.758 tons per year. Receiving compartment for emissions is estimated to be to forest soil and surface waters. However, emission factors for this source could not be found. Still, it is clear that releases will be minor as the used amount of substance is almost negligible. The usage amount and releases from wood preservation applications is estimated to be negligible compared to emissions from other sources.

4.1.2.11 Application of paints, lacquers and varnishes in construction activities

NACE Code 43.34 Painting and glazing

Application of paints in construction activities is likely to cause emissions to wastewater. Total paint used in Turkey in 2011 is 600,151 tons as calculated in part 4.1.2.6. From Figure 4-1, it is observed that, construction paint and varnishes constitute 58 % of the total paint used in Turkey in 2011. This corresponds to 348,087.6 tons/year. Sixty % of this amount is known to be water-based and contain NPEs [64]. The emissions are estimated as presented in Table 4-11 and the receiving compartment is determined as wastewater.

Table 4-11 Calculation of releases from paint application in construction activities

Total amount of paint used in Turkey (tons/year)	**Amount of paint used in this application (tons/year)**	**NPE content in paint** [52]	**Emission factor** [2] **(kg NPE/ton paint)**	**Emission to wastewater (tons/year)**
600,151	348,087.6	3 %	5	31.3

The emissions to wastewater from application of paints in construction activities are reaching directly to surface waters with untreated wastewater or to WWTP. 20% of municipal wastewaters in Turkey are discharged without treatment. So, emissions to WWTP and surface waters are 25 tons/year and 6.3 tons/year, respectively.

4.1.2.12 Maintenance and repair of motor vehicles

NACE Code 45.20 Maintenance and repair of motor vehicles

NPEs are used as dispersants in motor oil. Emissions can result from maintenance and repair of vehicles by spillage or leakages and also from manufacture and blending steps of motor oil. During use of motor oil, NPEs are known to be mostly burnt off. In Figure 4-2, it can be seen that 53 % of mineral oil consumption in Turkey corresponds to motor oils. It is known that, average NPE concentration in motor oil corresponds to 0.03 [59]. Emission factor for this source is 0.005. With the information given above, the possible releases to wastewater from maintenance and repair of motor vehicles are estimated in Table 4-12 [59].

Table 4-12 Estimation of emissions from maintenance and repair of vehicles

Total amount of motor oil used in Turkey (tons/year)	**Amount of motor oil used in this application (tons/year)**	**NPE content in motor oil** [59]	**Emission factor (kg NPE/ton)**	**Emission to wastewater (tons/year)**
408,000	216,240	3 %	5	32.4

Maintenance and repair of vehicles results in NPE emissions to wastewater. These releases majorly reach WWTPs. Still with untreated wastewaters some amount is directly discharged. So, 6.5 tons/year of NPE is assumed to directly released to surface waters while, 25.9 tons/year reach WWTP.

4.1.2.13 Pesticides

NACE Code 01 Crop and animal production, hunting and related service activities

NPEs are used as additives in pesticides in which they serve as wetting agents. They provide surface tension reduction of pesticide sprays so that target crops are better covered. NPEs are generally sold as part of pesticide formulation. The amount of NPEs applied to agricultural land is reported as 50-200 g/ha [2]. Emission factors for this source are provided in Table 4-13.

Table 4-13 Emission factors for agricultural use of nonylphenol ethoxylates [2]

Receiving Compartment	**Emission Factor**
Air	0.05
Surface Water	0.10
Agricultural Soil	0.85

It is accepted that 100 g/ha NPE is used in Turkey for pesticide applications. 2010 data show that 39.1 million ha of agricultural land that is cultivated is 16.5 million ha [65].

According to these numbers, amount of substance used for this purpose corresponds to 1650 tons/year. The emissions are distributed to the environmental compartments and illustrated in Figure 4-3.

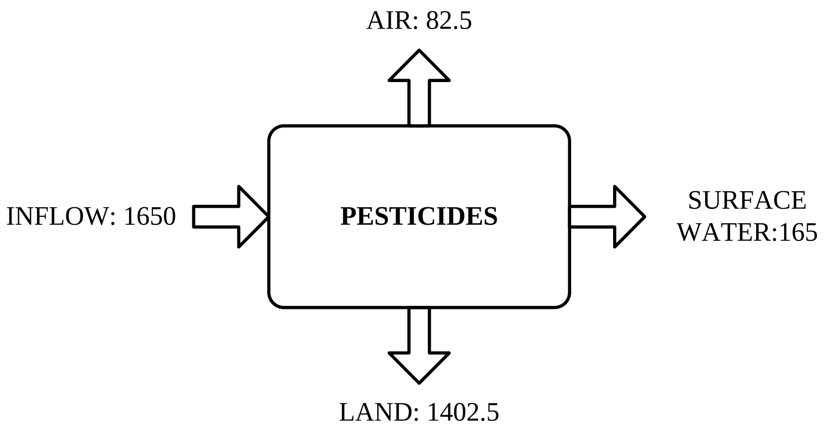

Figure 4-3 Distribution of NPE emissions resulting from pesticide use (tons/year)

The amount of pesticide used in Turkey in 2010 is 22,900 tons [66]. According to Regulation on Restriction of the Production, Placing on the Market, and Use of Certain Dangerous Substances, Preparations and Articles [18], maximum allowed concentration of NPEs in pesticides is 0.1 %. It can be estimated that 22.9 tons of NPE is used annually in pesticide formulations. The releases to soil, water and air compartments are estimated as 19.5, 2.3 and 1.1 tons/year, respectively.

4.1.2.14 Veterinary medicines

NACE Code 01.4 Animal production

NPEs are used in veterinary medicine products for both ovine and bovine animals. They are used as surfactants in teat dips for treatment of mastitis. Isodophores and chlorohexanes are likely to contain the substance. NPEs are also used in sheep dips to prevent sheep scab and similar impurities.

NPE content in 25 L formulation is 5%. 25 L of teat dip is used for an average herd of 100 cows in 2 weeks. This shows that approximately 0.09 kg of NPE is used per day for 100 cows [2]. The number of milked animals in Turkey is 5,431,405 [40].

The estimation of amount of substance used in teat dip formulations with data given above corresponds to 1784.2 tons/year.

Typical concentration of NPE in sheep dips is 800 mg/L and typical volume of sheep dips is 1000 L. With 1000 L sheep dip volume 500 sheep can be washed. The number of sheep in Turkey is 27,425,233 [40]. Amount of substance used in sheep dip applications is estimated as 43.9 tons/year.

In total, for veterinary medicines consisting of teat dips and sheep dips, 1828 tons/year of NPEs is used in Turkey. The emission factors in Table 4-13 are used for the estimation of the releases and the results are summarized in Figure 4-4.

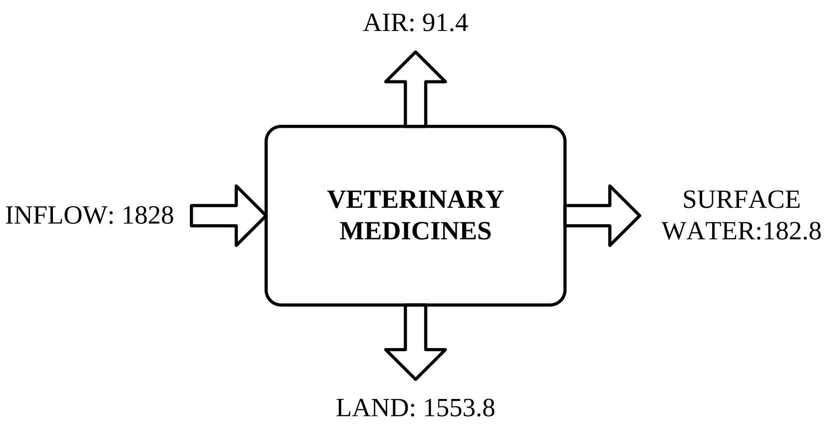

Figure 4-4 Distribution of emissions resulting from uses of veterinary medicines (tons/year)

According to the regulation NPE content can be maximum 0.1 %. With 25 L formulation used for 100 cows in 2 weeks, 1.78×10^{-3} kg/day NPE is used. The number of milked animals in 2012 in Turkey is 5,431,405 [40]. So, 35.3 tons of NPE is used annually for this purpose.

For sheep dips, the concentration was given as 800 mg/L with a typical dip volume of 1000 L. With 1000 L sheep dip volume 500 sheep can be washed. The number of sheep in 2012 in Turkey is 27,425,233 [40]. A NPE concentration of 0.1 % corresponds to 54.9 tons NPE used annually.

For the second scenario, total used amount of substance for veterinary medicines is 90.1 tons/year. The releases to soil, water and air compartments are estimated as 76.6, 9.013 and 4.5 tons/year, respectively.

The flow diagram, summarizing the calculations for processing life cycle stage of NPEs is presented in Figure 4-5. Total release estimations to wastewater, soil and air are represented and numbers in brackets represent the estimations of the second scenario. The total amount of substance used for industrial purposes was found by the addition of all inflows to the system. In order to prevent double counting, manufacture of furniture, manufacture of motor vehicles and application of paints, lacquers and varnishes in construction activities were not included. The inflow of NPE via these sources is included in manufacture of paint, lacquers and varnishes.

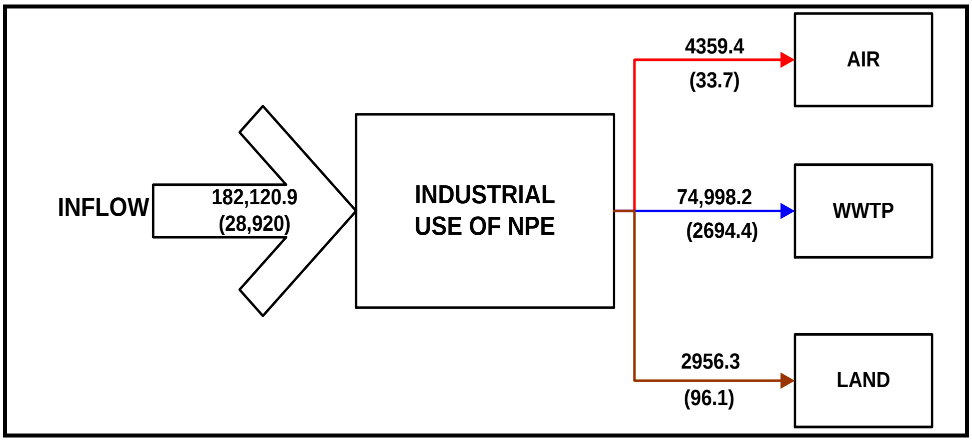

Figure 4-5 Flow diagram of total industrial usage of NPE (tons NPE/year)

4.1.3 Private Use (Uses in Products)

In this section the emissions of NPE from private consumption are covered. NPEs are likely to be emitted from goods, products, chemical preparations in which they are used in manufacturing processes. In this part, the releases are estimated according to the second approach explained in Chapter 3.

4.1.3.1 Concrete

NACE Code 41 Construction of buildings - NACE Code 42 Civil engineering

NPEs are used as additives in concrete. The additive in which NPE is used create air void in concrete provide improvement of freeze resistance and reduce water usage. Generally this type of concrete is used in outdoor constructions such as roads, bridges, parking lots and balconies.

This source is considered as building large stocks of the substance in concrete which is emitted over a large period of time up to 30–40 years. The estimation of the amount of NPEs in concrete is done by considering the concrete consumption data of the past years. Concrete production amounts from 2003 to 2012 and population statistics are provided in Table 4-14. With this information, concrete consumption per capita for the 10 year period is calculated.

Table 4-14 Concrete consumption per capita in Turkey

Years	Concrete Production of Turkey (m^3) [67]	Population of Turkey [68]	Concrete consumption per capita
2003	25,800,000	68,109,470	0.38
2004	31,600,000	68,893,920	0.46
2005	46,300,000	69,660,560	0.66
2006	70,730,000	70,413,960	1.00
2007	74,300,000	70,586,256	1.05
2008	69,600,000	71,517,100	0.97
2009	66,400,000	72,561,312	0.92
2010	79,700,000	73,722,988	1.08
2011	90,500,000	74,724,269	1.21
2012	93,000,000	75,627,384	1.23

According to data in Table 4-14, average concrete consumption for 10 year period is 0.89 m^3/capita and year. Current population is 76,667,864 [69]. The average concrete consumption in Turkey can be estimated as 68 million m^3 per year.

The calculation of leaching of NPE from concrete involves the following assumptions.

- 10 % of concrete contains NPE, which corresponds to the usage area identified as roads, bridges etc.
- 1 m^3 concrete is made with 350 kg cement and NPE is added to cement 0.1 % by weight. So 1 m^3 of concrete is assumed to contain 350 g NPE [34].
- 10 % of concrete is known to be available for leaching and it is accepted that 25 % of the added NPE leaches [34].

The calculation results show that in 10 years average, 2380 tons of NPEs are used in concrete in Turkey. 59.5 ton of the added amount is estimated to leach and reach wastewaters.

NPEs used for this source are known to have chain lengths longer than 30 so; according to in Table 3-5, the conversion factor for this source is 10. When the conversion is done, the emission can be expressed as 5.95 tons NP_{eq} /year.

The leaching of NPE from concrete reaches either wastewater treatment plants or directly surface waters. According to TÜİK data [57], 20% of municipal wastewaters are discharged to surface waters without treatment. This means that 4.8 tons /year of NP_{eq} releases end up in WWTP and 1.2 tons/year in surface waters.

4.1.3.2 Use of nonylphenol ethoxylates in car washing activities

NACE Code 52.2 Support activities for transportation

Emissions of NPEs from car washing activities result from usage of detergents and other car care products that contain NPEs. The emission factor for this application is given as 0.1 mg/car and washing activity [70]. In order to estimate the emissions using this factor, the car number in Turkey and the average number of washing activities should be known. It is assumed that a car is washed in average 12 times a year. The total number of cars in Turkey is 9,393,391 [71]. The receiving compartment for the NPE releases from this activity is evidently wastewater. A portion of this NPE emission may reach to impervious surfaces and stormwater. But, this portion is neglected and all releases are assumed to reach wastewater. With the provided information, the relevant NPE emission into wastewater can be estimated as 11.27 kg NP_{eq}/year.

Eighty percent of municipal wastewaters discharged in Turkey is treated [57]. With this information, NPE emission to wastewater from car washing can be distributed as 9.02 kg/year to WWTP and 2.25 kg/year directly to surface waters.

4.1.3.3 Parking lots

In parking lots; NPEs can be emitted by leakage or spillage of motor oil and from maintenance products. Especially rain can cause emissions from this source. Emission factor is provided as 0.002 mg NPe_q/m^2 parking space and year [70]. The receiving compartment for emissions is identified as impervious surfaces and stormwater.

According to Turkish Statistical Institute (TÜİK) data, there are 9,393,391 cars in Turkey [71]. It is assumed that on average 1 car uses 20 m^2 area when parking. With this information, 0.38 kg/year of NPEs is the estimated emission reaching stormwater from impervious surfaces. This amount is assumed to reach wastewater. From parking lots, annually 0.304 kg NP_{eq} reach municipal WWTP and 0.076 kg is discharged directly to surface waters.

4.1.3.4 Painted and coated surfaces

NPEs can leach from surfaces painted with NPE containing paints. This can occur as a result of washing activities and especially rain. In the literature, emission factor is given as 1.3 – 3.9 mg NP_{eq} / inhabitant and year [34].

The population of Turkey in 2014 is 76,667,864 [69] and with the average emission factor, the release is quantified as 199.3 kg/year. The receiving compartment is identified as stormwater and finally wastewater. The amount of NP_{eq} reaching WWTP from this source can be calculated as 159.4 kg/year and 39.9 kg/year is released to surface waters.

4.1.3.5 Textiles

NPEs used in manufacturing processes of textiles remain residues on products. When these products are washed, the substance is eventually released to wastewater. Big portion of substance is known to be released during first wash. Emission factor for release of NPEs from washing of textile products is 0.9 – 2 g/ inhabitant and year [33]. The estimation of releases from washing of textiles is calculated with the assumptions given below.

- All textile products contain NPEs.
- The average concentration of NPEs in textile products is 514 mg/kg (According to measurement results [33]).
- The substance is released every time the products are washed.

The average of the emission factor (0.9 – 2 g/ inhabitant and year) is equal to 1.5 g/ inhabitant and year. Current population is 76,667,864 [69]. As a result, the release from washing of textiles containing NPEs is calculated as 115 tons NP_{eq} /year and annually 92 tons NP_{eq} will be reaching WWTP and 23 ton/year will be discharged without any treatment.

4.1.3.6 Cosmetic and hygienic products

NPEs are used as surfactant in production of cosmetic and hygienic products. Products in which NPE can be included are shampoos, hair dyes, make up etc. Emission factor for Sweden is 0.00026 – 0.0078 g NP_{eq}/ inhabitant and year [33].

Consumption patterns of cosmetic and hygienic products may differ from one country to another. In order to overcome possible errors, emission factor provided for Sweden should be refined for Turkey. The correlation between consumption patterns are best made with gross national income per capita values as shown in Table 4-15.

Table 4-15 Gross National Income of Sweden and Turkey [72]

Country	Gross National Income per Capita ($)
Sweden	56.120
Turkey	10.830

As a result, the mean value of the emission factor range is selected and emission factor is determined for Turkey as 7.77×10^{-4} g per inhabitant and year. Based on the current population of Turkey, the emissions resulting from use of cosmetic and hygienic products correspond to 59.57 kg NP_{eq}/year to wastewater. This 59.57 kg NP_{eq}/year is distributed between WWTP and surface waters as 47.7 and 11.9 kg, respectively.

4.1.3.7 Hard plastic products

Plastics such as PVC, polystyrene and PET are likely to contain nonylphenol species. NPs and NPEs are known to be used in manufacture of plastics as additives and their migration from such products is of importance as it can result in direct human exposure. At this point, it becomes important to estimate the amount of substance likely to be released from plastic products.

Total plastic consumption in Turkey is 7.2 million tons. Out of this amount, 1.5 million ton is exported indirectly by automotive, packaging and construction industries. So, the remaining 5.7 million tons is consumed directly in the country. According to 2013 data, consumption per capita is 74 kg/year [73].

The emission factor is defined as 2.78×10^{-12} kg NP_{eq} /$m^2$of plastic [70]. The factor is for weight of PVC plastic assumed as 2 kg with 1m^2 of area and 1.5 mm thickness. From this information, the density of the plastic material is calculated as 1333.33 kg/m^3. The average density of plastic materials is accepted as 1000 kg/m^2 [74]. To use the emission factor, the area for plastic materials consumed in Turkey must be known. Area can be estimated basically with the following equation.

$$Area = Mass / (thickness \times density)$$

Area of plastic materials used is 2850 million m^2 and the release from plastic products is estimated as 7.9×10^{-3} kg NP_{eq} /year for Turkey.

When untreated municipal wastewater is taken into consideration (which is 20% of total [57]), the release of NP from this source can be distributed as 6.32×10^{-3} kg to WWTP and 1.58×10^{-3} kg to surface waters.

4.1.3.8 Detergents, cleaning agents and industrial and institutional cleaning

Detergents are considered as the major source of emissions of NPEs to wastewater. Especially industrial and institutional cleaning is expected to cause high emissions; because, the products are sold and used in high volumes.

For Turkey there exists no data to distinguish between industrial, institutional and domestic usage. The data which is found to be most accurate about consumption of cleaning agents considers the total numbers. The amount of NPE used in production of detergents, soaps and cleaning preparations was estimated 55,500 tons/year [62].

The releases from this source will be almost equal to the amount of substance included in the product. This is valid with the assumptions that the products are used within the year they are produced and that all products are washed away with water. Also, it is accepted that recycling or incineration of the washing liquid is not taking place in all industrial activities. Almost all cleaning products may end up to wastewater which means that 55,500 tons/year as NPE, dividing with 2.5 gives 22,200 tons NP_{eq}/year to wastewater. Knowing that 80% of municipal wastewater is treated in Turkey [57], it can be said that 17760 tons NP_{eq} reach WWTP and 4440 tons is discharged untreated.

NPE content in cleaning preparations was assumed as 5 % for industrial, institutional and domestic cleaning purposes. However, for the second scenario considering the restriction, the content must not be higher than 0.1 %. With the same assumptions above, this concentration gives 1110 tons of NPE used and 444 tons NP_{eq} emitted annually in Turkey. As a result, 355.2 tons NP_{eq} go to WWTP and 88.8 tons is directly discharged to surface waters.

Industries where washing liquid is incinerated or recycled, the emissions of NPE do not occur. However, it is hard to estimate the number of these plants. In addition, private use of cleaning products is considered together with industrial use so, the above assumptions are reasonable.

4.1.3.9 Vehicles

This source considers the emission of NPEs from plastic materials, paint, maintenance products used in vehicles. During driving such emissions can occur especially in case of rain events. The use of substance for this source is already determined separately for plastics, paint and motor oil. Here, the possible releases of NPE from these sources during vehicle driving are considered. The emission factor is provided as 0.14 µg NP_{eq} /driven km [70]. The emissions are assumed to be released to impervious surfaces such as roads and eventually reach to storm water, wastewater treatment plants and surface waters.

In order to use the emission factor, the yearly driven distance in Turkey should be known. This data is not readily available for Turkey. So, it is estimated in Table 4-16 from the average total driven distance in Finland, which is 53,350 million km.

Table 4-16 Fuel consumption data of Finland and Turkey [72]

Country	Gasoline fuel consumption (kton oil equivalent)	Diesel fuel consumption (kton oil equivalent)	Total fuel consumption (kton oil equivalent)	Total driven distance (million km)
Finland	1,493	2,373	3,866	53,350
Turkey	2,028	9,016	11,044	152,404

Release of NPEs from vehicle driving is estimated as 21 kg NP_{eq}/year. This is further distributed to WWTP and surface waters as 16.8 kg and 4.2 kg, respectively.

Emissions of NPE from product life cycle stage in terms of NPeq are summarized in Figure 4-6. Total releases from products to WWTP correspond to 17,857 tons NP_{eq} /year for the first and 452 tons NP_{eq}/year for the second scenario. The highest share belongs to detergents and cleaning agents.

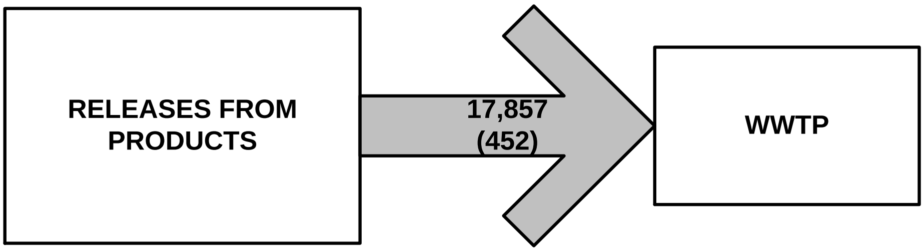

Figure 4-6 Summary of total releases from product use (tons NP_{eq}/year)

4.1.4 Disposal – Wastewater Treatment Plants

NACE Code 36 Water collection, treatment and supply - NACE Code 37 Sewerage

Disposal stage is where the substance reaches its final destination which is the wastewater treatment plant or landfills. Waste treatment and disposal is known to cause emissions via landfill leachate. Products such as textiles, leather, plastics, and paint residues can cause NP presence in leachate. However, data about the concentration of NP or NPEs in landfill leachate in Turkey is not available which makes the estimation of emissions from this source unfeasible. Still, it is known that landfills may be an important source of NP and other metabolites of the substance to soil and groundwater.

In this part, only disposal via WWTPs is considered since it can be accepted as the main route of NPEs to the environment. In order to quantify the releases from WWTP, the fraction of the substance degraded in treatment and released with sludge and treated water should be known. Degradation of NPEs is investigated in EU RAR [2] in detail. When all of the available data are considered, the fate of NPEs in wastewater treatment plants can be summarized as represented in Figure 4-7. Formation of NP during the biodegradation of NPEs is taken into consideration.

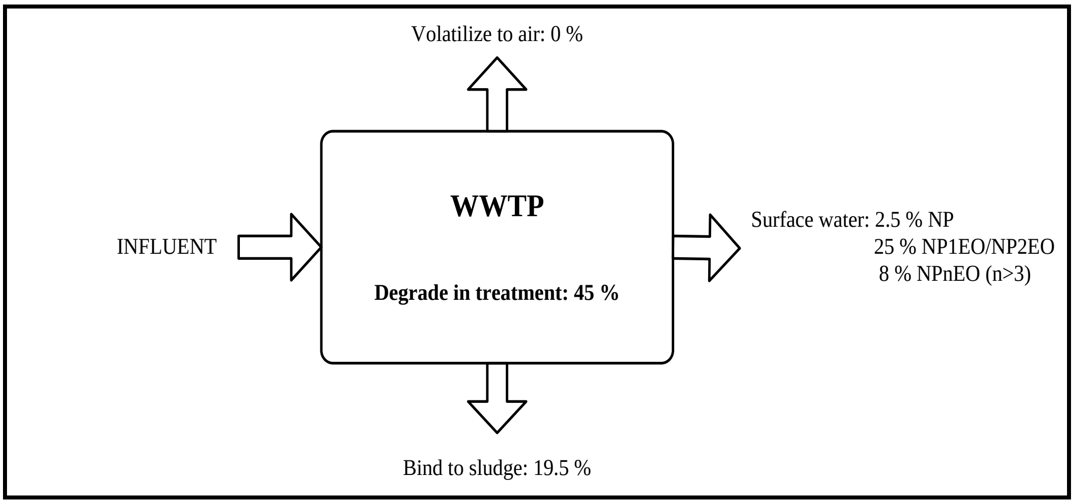

Figure 4-7 Fate of NPE in WWTP [2]

Based on the calculations for the high emission scenario, 74998 tons of NPE are emitted to wastewater treatment plants. The distribution in Figure 4-7 results in, 14,624.6 tons NPE bind to sludge, 24,749.3 tons NPE and 1874.9 tons NP released to surface water.

In the second scenario, total influent NPE load to wastewater treatment systems adds up to 2694.4 tons. According to the model results, 525.4 tons of NPE binds to sludge, 889.2 tons/year NPE and 67.4 tons NP are released to surface waters.

Municipal wastewater treatment plants

Oğuz and Kankaya [75] measured alkylphenol ethoxylates in influent and effluent of Van wastewater treatment plant and the results are summarized in Table 4-17.

Table 4-17 Concentration of APEs in Van WWTP [75]

	APE Concentration (ng/L)
Influent of WWTP	4.050 ± 0.799
Effluent of WWTP	3.551 ± 0.533

Wastewater statistics in Turkey reveal that total wastewater treated with three different systems i.e. physical, biological and advanced, is 3,248,184 thousand m^3 per year in 2012 [76]. Assuming that Van WWTP represents all municipal wastewater treatment plants across the county the APE load to surface waters is estimated as 11.5 kg/year. NPEs constitute about 80-90 % of all alkylphenol ethoxylates. So, this load can be accepted as NPE load.

Application of sewage sludge on land

According to Table 4.17 and total treated wastewater amount in Turkey, the influent alkylphenol ethoxylate load to municipal wastewater treatment plants in Turkey is 13.16 kg/year. According to the model results 19.5 % of the influent binds to sludge. This corresponds to 2.56 kg/year. Approximately 6 % of municipal/urban WWTP sludge is used in agricultural activities [77]. With the assumption that no treatment is applied to sludge, this application results in a load of 0.15 kg/year NPE to agricultural soil. Approximately 45% of sewage sludge is disposed in an uncontrolled manner [77]. This is also considered as a route to soil where, 1.15 kg of NPE is discharged. In total 1.3 kg NPE is estimated to pollute soil in Turkey.

4.2 Calculation of the Emissions for Nonylphenol

4.2.1 Manufacture of Nonylphenol

According to data obtained from the Ministry of Environment and Urbanization, NP is not being produced in Turkey. However, product registers to TOBB Industry Database reveals production code 20.14.24.10.00, monophenols which include octylphenols, nonylphenols, their isomers and salts. The production capacity is not provided but two plants are known to produce these substances. With the information provided by the database distinction between octylphenol and nonylphenol cannot be made and the calculations in this study it is assumed that there is no production of NP in Turkey.

4.2.2 Processing

Processing stage for NP considers the industrial activities in Turkey in which the substance is used for specific purposes and that are likely to cause emissions to the environment.

4.2.2.1 Manufacture of nonylphenol ethoxylates

NACE Code 20.14 Manufacture of other organic basic chemicals

During the production of NPEs, NP can be released with emission factors 0.007 tons/tons to water and 0.00001 tons/tons to air [2]. 364.2 tons/year ethoxylates are produced in Turkey (Table 5-5). The production data is multiplied with the emission factors and releases to water and air are 2.55 tons/year and 3.64×10^{-3} tons/year, respectively.

4.2.2.2 Manufacture of phenol and formaldehyde resins

NACE Code 20.14 Manufacture of other organic basic chemicals

NP is used in manufacturing of phenol and formaldehyde resins. It can be used alone or sometimes mixed with other phenols. For the calculation of the amount of NP used, it is assumed that about half of the manufacturers produce phenol and formaldehyde resins from NP. Since estimating how much NP is used is hard, this assumption has to be done. There are 11 installations producing phenolic resins registered to TOBB Industry Database with production code 20.16.56.50.00. The total capacity of them is 88,000 tons/year [78]. From EU Risk Assessment Report, it is understood that 25 sites use 22,500 tons of NP. For Turkey, assuming 5 sites use the substance, 4500 tons NP is consumed. The emission factors are given as 0.00001 to air and to water [2]. So the releases from this source are quantified as 0.045 tons.

4.2.2.3 Manufacture of epoxy resins

NACE Code 22.2 Manufacture of plastic products

NPs are used as hardeners in epoxy resins. It is used as an accelerator or curing agent in hardeners. Epoxy resins are produced at 11 sites registered to TOBB Industry

Database with production code 20.16.40.30.00 in Turkey with a yearly production of 6,386,035 kg [79]. The concentration of NP in epoxy resins is given as 0.5 – 3% [2]. With the high end of the range, it is calculated that 191.6 tons of NP is used in production of epoxy resins. The emission factors are given as 0.01 % to water and air [2]. The emissions are estimated as 19.2 kg to both water and air. It is important to note that this estimation is valid assuming that NP is used in production of all epoxy resins.

4.2.2.4 Manufacture of plastic stabilizers

NACE code: 22.2 Manufacture of plastics products

According to EU Risk Assessment Report [2], one site manufacturing plastic stabilizers uses 100 tons of NPEs per year. In Turkey, there are 26 sites producing plastic stabilizers registered with 20.59.56.50.00 production code and 146,276,535 kg of production capacity per year [80]. The emission factor is 0.0005 to water [2]. It is assumed that the 26 manufacturers use yearly 2600 tons of the substance and the releases to water are estimated as 1.3 ton/year.

In Table 4-9, inflow and outflow of NP from industrial usage is illustrated.

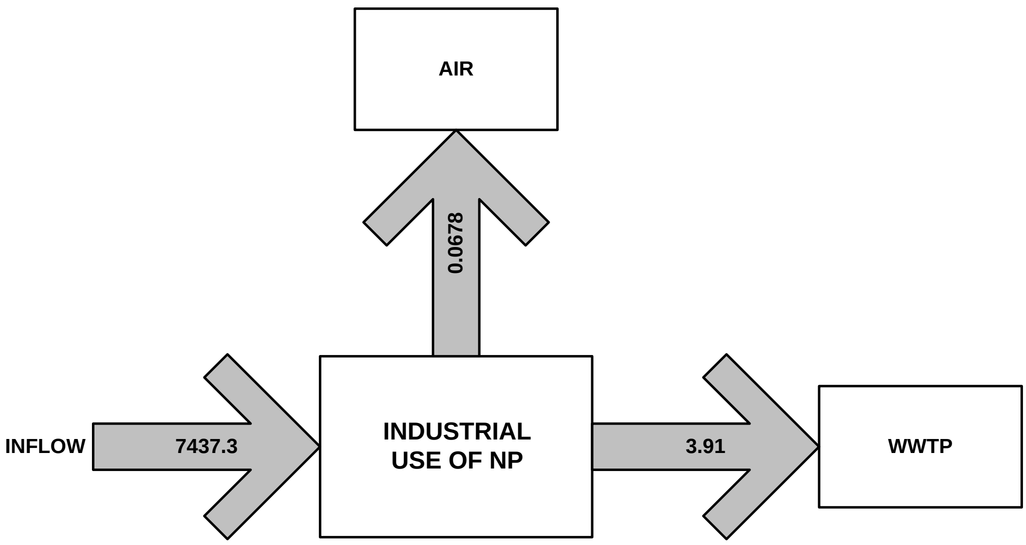

Figure 4-8 Flow chart for NP for industrial use (tons NP/year)

4.2.3 Private Use (Uses in Products)

NP emissions resulting from product use is considered under emissions from NPEs. Releases from products are estimated in terms of NP equivalents since it is difficult to distinguish between the emissions of NP and ethoxylates.

4.2.4 Disposal - Wastewater Treatment Plants

NACE Code 36 Water collection, treatment and supply - NACE Code 37 Sewerage

Disposal step is where the substance reaches its final destination. Here, the fate of substance in wastewater treatment plants is considered because the main disposal of NP occurs via wastewater in wastewater treatment plants. In order to quantify the releases from degradation of the substance, the behavior of the substance in WWTP should be analyzed.

The fate of NP in wastewater treatment plants is investigated by European Union System for the Evaluation of Substances (EUSES) [2] and Simple Treat Model [7]. The distribution of the substance in WWTP is summarized in Figure 4-9.

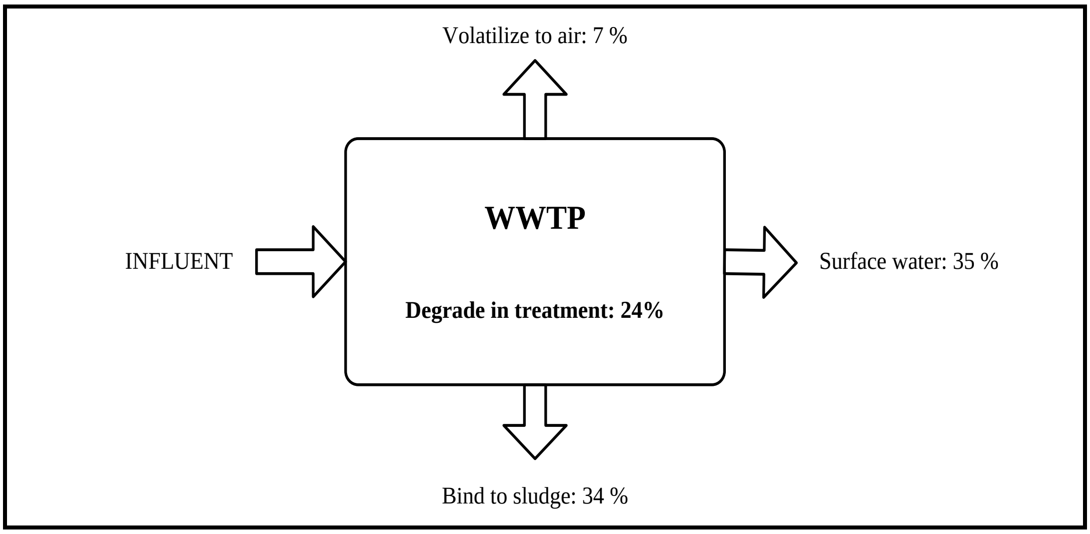

Figure 4-9 Fraction of releases of NP in WWTP

For the first scenario, 17,861 tons of NP is estimated to reach wastewater treatment plants annually. Based on the distribution in Figure 4-9, the releases are 6251.4 tons to surface water, 1250.3 tons to air and 6072.7 tons bind to sludge.

According to calculations performed above for the low emission scenario, annually 456.2 tons of nonylphenol influent reaches wastewater treatment plants in Turkey. Based on model results, 159.7 tons of substance is emitted to surface water, 155.1 tons bind to sludge and 31.9 tons volatilize to air.

Municipal wastewater treatment plants

NP that enter municipal wastewater treatment plants via various uses are sources of emissions to the environment. Can et al. [81] monitored NPs in three wastewater treatment plants in İstanbul. This is the only available data on concentration of NP in municipal WWTP in Turkey. The results for NP measurements are provided below in Table 4-18.

Table 4-18 Influent and effluent concentrations of NP [81]

	Paşaköy WWTP	Tuzla WWTP	Kadıköy WWTP
Influent (ng/L)	277 ± 384	378 ±575	264 ± 426
Effluent (ng/L)	32 ± 41	43 ±100	169 ±397
% Removal	76 ± 27	61 ± 27	49 ± 33

Paşaköy Wastewater Treatment Plant operates in advanced biological treatment process, Tuzla WWTP has conventional biological wastewater treatment plant and Kadıköy WWTP only has primary treatment. In this part, Paşaköy WWTP is assumed to represent all advanced biological treatment plants in the country. Similarly, Tuzla WWTP will represent conventional biological treatment plants and Kadıköy WWTP will represent WWTPs with physical treatment.

The amount of wastewater treated in wastewater treatment plants in Turkey in 2012, which is the latest data found, is given in Table 4-19.

Table 4-19 Wastewater treatment plant numbers and volume of water treated [76]

Type of WWTP	Number of wastewater treatment plants	Amount of wastewater treated by wastewater treatment plants (thousand m^3/year)
Physical	57	929,334
Biological	244	1,072,873
Advanced	70	1,245,977

It is accepted that the concentration of NP in three WWTPs represent all treatment plants in Turkey. The effluent concentrations from municipal WWTPs are multiplied with treated wastewater amounts to find NP load. In a year, 243.06 kg nonylphenol is found to be reaching surface waters from effluents of municipal WWTPs in Turkey. This amount is the total NP resulting from physical, biological and advanced WWTPs.

Application of sewage sludge on land

Calculations based on Table 5.18 and Table 5.19 show that the influent NP load to wastewater treatment plants in Turkey is 996.02 kg/year. According to the model results 34% of the influent is binds to sludge. This corresponds to 338.65 kg/year. Approximately 6 % of municipal/urban wastewater treatment plant sludge is used in agricultural activities [77]. With the assumption that no treatment is applied to sludge, this application results in a load of 20.3 kg/year NPE to agricultural soil. Approximately 45% of sewage sludge is disposed in an uncontrolled manner [77]. This is also considered as a route to soil where, 152.4 kg of NP is discharged. In total, the application of sewage sludge on land results in a load of 172.7 kg NP to soil compartment.

In a recent study, Ankara Central Wastewater Treatment Plant sludge was analyzed for nonylphenol. The sum of NP, NP1EO and NP2EO concentrations of sludge samples were found between 5.3 mg/kg and 25.5 mg/kg dry weight [82]. About 500 000 tons/year of sewage sludge is generated in municipal WWTPs in Turkey [83]. Assuming that substance concentration in Ankara WWTP sludge represents all municipal WWTP in Turkey, 2.65 – 12.75 tons/year nonylphenol (NP, NP1EO, NP2EO) is found in sludge. Approximately 6 % of municipal/urban WWTP sludge is used in agricultural activities [77]. With the assumption that no treatment is applied to sludge, this application results in a load of 0.16 – 0.77 tons/year NPE to agricultural soil. Approximately 45% of sewage sludge is disposed in an uncontrolled manner [77]. This is also considered as a route to soil where, 1.19 – 12.75 tons/year of NP is discharged. Total load of NP (NP, NP1EO, NP2EO) to soil compartment from application of sewage sludge is estimated as 1.4 – 13.5 tons/year. This estimation is found more valid than using model result that provides the information that 34 % of influent is bind to sludge since, the concentration of the substance is measured in sludge directly.

CHAPTER 5

DISCUSSION

The results are represented for the two scenarios for NP and NPEs separately. Sources were classified according to life cycle stages. The amounts of substance used and emitted to environmental media are represented in Table 5.1 - Table 5.4. Tables 5.1 and 5.2 represent results for the first scenario and Tables 5.3 and 5.4 show the second scenario. The releases from products use stage are quantified as NP_{eq} and included in the tables for NP. However, they are indicated as NPE use. For some sources the releases are not quantified and remained as question marks. For emissions from vehicles, painted and coated surfaces and parking lots, land is identified as receiving compartment via impervious surfaces and stormwater. However, the actual emission cannot be quantified due to data unavailability and assumed to be totally reaching WWTP. For wood preservatives emission factors are missing so the releases could not be quantified for this source.

Table 5-1 Summary of findings for NP (1st scenario)

Life Cycle Stage	Activity	NP Consumed (ton/year)	NP Emission to WWTP (ton/year)	NP Emission to Surface Waters (ton/year)	NP Emission to Air (ton/year)	NP Emission to Land (ton/year)
Production	Manufacture of NP	0	0	0	0	0
Processing	Manufacture of NPE	145.7	2.55	0	3.64×10^{-3}	0
	Manufacture of phenol and formaldehyde resins	4500	0.045	0	0.045	0
	Manufacture of epoxy resins	191.6	0.0192	0	0.0192	0
	Production of plastic stabilizers	2600	1.3	0	0	0
Private use (Uses in products)	Cosmetic and hygenic products	5216.5 (NPE)	0.048	0.012	0	0
	Washing of textiles		92	23	0	0
	Hard plastic products		6.3×10^{-3} kg/year	1.58×10^{-3} kg/year	0	0
	Private use of detergents, cleaning agents, stain removers, industrial and institutional cleaning	55500 (NPE)	17760	4440	0	0
	Vehicles (plastic materials, maintenance products etc.)		16.8 kg/year	4.2 kg/year	0	?
	Concrete	2380(NPE)	4.8	1.2	0	0
	Painted and coated surfaces		159.4 kg/year	39.9 kg/year	0	?
	Car washes		9.02 kg/year	2.25 kg/year	0	0
	Parking lots		0.304 kg/year	0.076 kg/year	0	?
Disposal	Wastewater treatment plant			6251.4	1250.3	0
	Sewage sludge		0	0	0	13.5

Table 5-2 Summary of findings for NPE (1st scenario)

Life Cycle Stage	Activity	NPE Consumed (ton/year)	NPE Emission to WWTP (ton/year)	NPE Emission to Surface Waters (ton/year)	NPE Emission to Air (ton/year)	NPE Emission to Land (ton/year)
Production	Manufacture of NPE		1.1	0	0	0
Processing	Manufacture of textiles	83667.8	71117.6	0	4183.4	0
	Manufacture of leather	2140	1926	0	2.14	0
	Manufacture of paper and paper products	1700.9	1692.8	0	0	0
	Manufacture of paints, lacquers and varnishes	15600	46.8	0	0	0
	Photographical industry	189.7	121.4	30.4	6.64×10^{-3}	0
	Manufacture of furniture	2520.6	10.1	2.5	0	0
	Manufacture of motor vehicles	1080.3	2.7	0	0	0
	Use of NPE in wood preservation	0.758	?	?	?	?
	Manufacture of basic metals	5760	28.8	0	0	0
	Maintenance and repair of motor vehicles	6487.2	25.9	6.5	0	0
	Production of soap, detergent and cleaning preparations	55500	0	0	0	0
	Production of cosmetic and hygenic products	5216.5	0	0	0	0
	Use of pesticides	1650	0	165	82.5	1402.5

Table 5-2 (continued)

Life Cycle Stage	Activity	NPE Consumed (ton/year)	NPE Emission to WWTP (ton/year)	NPE Emission to Surface Waters (ton/year)	NPE Emission to Air (ton/year)	NPE Emission to Land (ton/year)
	Use of veterinary medicines	1828		182.8	91.4	1553.8
	Application of paints, lacquers and varnishes in construction activities	6265.6	25	6.3	0	0
Private use (Uses in products)	Painted and coated surfaces		SEE NP	SEE NP	SEE NP	SEE NP
	Washing of textiles		SEE NP	SEE NP	SEE NP	SEE NP
	Cosmetic and hygenic products	5216.5 (NPE)	SEE NP	SEE NP	SEE NP	SEE NP
	Concrete	2380 (NPE)	SEE NP	SEE NP	SEE NP	SEE NP
	Hard plastic products		SEE NP	SEE NP	SEE NP	SEE NP
	Private use of detergents, cleaning agents, stain removers, industrial and institutional cleaning	55500 (NPE)	SEE NP	SEE NP	SEE NP	SEE NP
	Vehicles (plastic materials, maintenance products etc.)		SEE NP	SEE NP	SEE NP	SEE NP
	Car washes		SEE NP	SEE NP	SEE NP	SEE NP
	Parking lots		SEE NP	SEE NP	SEE NP	SEE NP
Disposal	Wastewater treatment plant			24,749.3	0	0
	Sewage sludge		0	0	0	13.5

Table 5-3 Summary of findings for NP (2nd scenario)

Life Cycle Stage	Activity	NP Consumed (ton/year)	NP Emission to WWTP (ton/year)	NP Emission to Surface Waters (ton/year)	NP Emission to Air (ton/year)	NP Emission to Land (ton/year)
Production	Manufacture of NP	0	0	0	0	0
Processing	Manufacture of NPE	145.7	2.55	0	3.64×10^{-3}	0
	Manufacture of phenol and formaldehyde resins	4500	0.045	0	0.045	0
	Manufacture of epoxy resins	191.6	0.0192	0	0.0192	0
	Production of plastic stabilizers	2600	1.3	0	0	0
Private use (Uses in products)	Cosmetic and hygenic products	260.8 (NPE)	0.048	0.012	0	0
	Washing of textiles		92	23	0	0
	Hard plastic products		6.3×10^{-3} kg/year	1.58×10^{-3} kg/year	0	0
	Private use of detergents, cleaning agents, stain removers, industrial and institutional cleaning	1110 (NPE)	355.2	88.8	0	0
	Vehicles (plastic materials, maintenance products etc.)		16.8 kg/year	4.2 kg/year	0	?
	Concrete	2380 (NPE)	4.8	1.2	0	0
	Painted and coated surfaces		159.4 kg/year	39.9 kg/year	0	?
	Car washes		9.02 kg/year	2.25 kg/year	0	0
	Parking lots		0.304 kg/year	0.076 kg/year	0	?
Disposal	Wastewater treatment plant			159.7	31.9	0
	Sewage sludge		0	0	0	13.5

Table 5-4 Summary of findings for NPE (2nd scenario)

Life Cycle Stage	Activity	NPE Consumed (ton/year)	NPE Emission to WWTP (ton/year)	NPE Emission to Surface Waters (ton/year)	NPE Emission to Air (ton/year)	NPE Emission to Land (ton/year)
Production	Manufacture of NPE		1.1	0	0	0
Processing	Manufacture of textiles	554	470.9	0	27.7	0
	Manufacture of leather	428	385.2	0	0.428	0
	Manufacture of paper and paper products	1605.2	1604.3	0	0	0
	Manufacture of paints, lacquers and varnishes	15600	46.8	0	0	0
	Photographical industry	189.7	121.4	30.4	6.64×10^{-3}	0
	Manufacture of furniture	2520.6	10.1	2.5	0	0
	Manufacture of motor vehicles	1080.3	2.7	0	0	0
	Use of NPE in wood preservation	0.758	?	?	?	?
	Manufacture of basic metals	192	0.96	0	0	0
	Maintenance and repair of motor vehicles	6487.2	25.9	6.5	0	0
	Production of cosmetic and hygenic products	260.8	0	0	0	0
	Production of soap, detergent and cleaning preparations	1110	0	0	0	0
	Use of pesticides	22.9	0	2.3	1.1	19.5

Table 5-4 (continued)

Life Cycle Stage	Activity	NPE Consumed (ton/year)	NPE Emission to WWTP (ton/year)	NPE Emission to Surface Water (ton/year)	NPE Emission to Air (ton/year)	NPE Emission to Land (ton/year)
	Use of veterinary medicines	90.1	0	9	4.5	76.6
	Application of paints, lacquers and varnishes in construction activities	6265.6	25	6.3	0	0
Private use (Uses in products)	Painted and coated surfaces		SEE NP	SEE NP	SEE NP	SEE NP
	Washing of textiles		SEE NP	SEE NP	SEE NP	SEE NP
	Cosmetic and hygenic products	260.8 (NPE)	SEE NP	SEE NP	SEE NP	SEE NP
	Concrete	2380 (NPE)	SEE NP	SEE NP	SEE NP	SEE NP
	Hard plastic products		SEE NP	SEE NP	SEE NP	SEE NP
	Private use of detergents, cleaning agents, stain removers, industrial and institutional cleaning	1110 (NPE)	SEE NP	SEE NP	SEE NP	SEE NP
	Vehicles (plastic materials, maintenance products etc.)		SEE NP	SEE NP	SEE NP	SEE NP
	Car washes		SEE NP	SEE NP	SEE NP	SEE NP
	Parking lots		SEE NP	SEE NP	SEE NP	SEE NP
Disposal	Wastewater treatment plant			889.2	0	0
	Sewage sludge		0		0	13.5

In order to discuss the estimated emissions, the production and import data of Turkey is required. Production and import data is vital for the study simply because it represents the inflows to the system which is the fundamental to the construction of the mass balance. This information is gathered by personal contact with the Ministry of Environment and Urbanization. Regulation on the Inventory and Control of Chemicals (2008) requires that importers or manufacturers of products more than 1000 tons per year until 2010 to report details about the substances and 3 year average numbers of import and production. The import and production values for different CAS numbers of NP and NPEs are represented in Table 5-5. It is clear that Turkey's production is minor and imports are prominent.

The total import and manufacture of NPE and NP are approximately 29,387 and 166,943 tons, respectively. Total NPE used in the first scenario is 182,121 tons. The total NP usage is 7437 tons. In the second scenario the total NPE and NP usage are estimated as 28,920 tons and 7437 tons, respectively.

To rationalize the estimations and decide on the scenario that fits Turkey better, NP and NPE consumption data of other counties are compared with manufacture and import of Turkey. As given in Section 2.1.2 of the thesis, the amount of NP production and consumption in different countries and in the world show that it is meaningless for Turkey to import 166,943 tons. This value corresponds almost to the world NPE demand, which is not plausible. In case of NPE, the import and production of Turkey which is 29,387 tons is an acceptable amount. However, NPE demand is 182,121 tons for the first scenario and 28,920 tons for the second scenario. The produced and imported NPE does not seem to supply the requirement in the first scenario. The explanation for this situation may be that manufacture of ethoxylates from the mother compound NP in Turkey is higher than reported.

Table 5-5 Production and import data of nonylphenol and its ethoxylates in Turkey (in tons/year)

EC NO	CAS NO	CAS Name	Synonym	Import	Production	Total
246-672-0	25154-52-3	Nonylphenol	Phenol, nonyl-	740,98	0	740,98
284-325-5	84852-15-3	Phenol, 4-nonyl-, branched	Phenol, 4-nonyl-, branched	166202,41	0	166202,41
500-024-6	9016-45-9	Poly(oxy-1,2-ethanediyl), α-nonylphenyl-ω-hydroxy-	Nonylphenol, ethoxylated	28526,39	363,15	28889,54
500-209-1	68412-54-4	Poly(oxy-1,2-ethanediyl), α-nonylphenyl-ω-hydroxy-, branched	Nonylphenol, branched, ethoxylated	67,51	0	67,51
500-315-8	127087-87-0	Poly(oxy-1,2-ethanediyl), α-nonylphenyl-ω-hydroxy-, branched	4-Nonylphenol, branched, ethoxylated	83,2	1,04	84,24
230-770-5	7311-27-5	Ethanol, 2-[2-[2-[2-(4-nonylphenoxy)ethoxy]ethoxy]-	2-[2-[2-[2-(4-Nonylphenoxy)ethoxy]ethoxy]-ethoxy]ethanol	345,71	0	345,71

With 1 ton of NP, 2.5 tons of NPE can be produced [2]. This is a very rough conversion however; this conversion factor will be used here to determine the actual amount of substance produced. NPE import, manufacture and estimated use amounts show that the substances are produced more than the reported amount. So, with the conversion factor, in the first scenario, the total NP demand of Turkey is estimated as 68,531 tons, which means that according to this study, 61,094 tons of NP is used in the production of NPE. The imported NP is still much higher than the estimated demand. For the low emission scenario, NPE demand is in good agreement with the imported and manufactured amount. However, NP requirement estimated in this study is still small.

Another explanation for the case that NPE demand in Turkey is exceeding the import and manufacture of the substances in the first scenario can be the unreported data of NPE manufacturers or importers. On the other hand, even for the high emission scenario, NP import is higher than the demand. This contradiction can be attributed to the errors in entries to the system of the Ministry of Environment and Urbanization in which manufacturers and importers provide data manually.

The first scenario fails when the NP demand is compared with the production and consumption patterns in other countries and world. NP requirement of 68,531 tons almost equals NP production in EU in 1997 where there were no restrictions on the use of the substance. It seems like the second scenario is meaningful and valid for Turkey as long as the regulation is satisfied in all emission sources. In this scenario, estimated NPE demand is in good agreement with Table 5.5.

5.1 Substance Flow Analysis Diagrams

In this section, the results presented in Tables 5.1 - 5.4 are demonstrated in substance flow analysis diagrams. These diagrams constitute the results of the study. SFA for NP and NPE are represented in separate flow charts. The values for the selected scenario are provided in brackets.

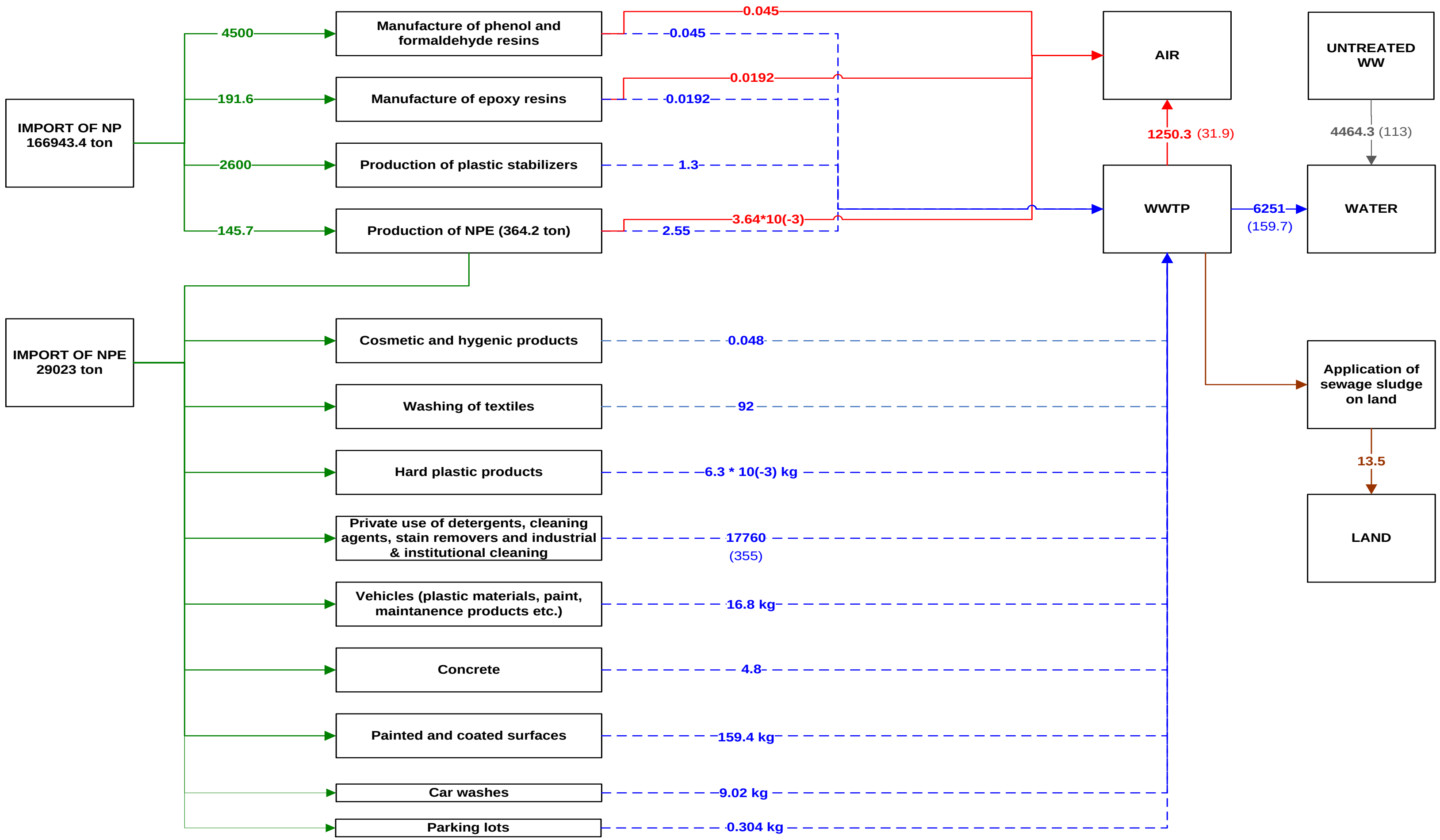

Figure 5-1 Substance flow analysis diagram for NP (tons/year), Numbers in parenthesis represent the second scenario

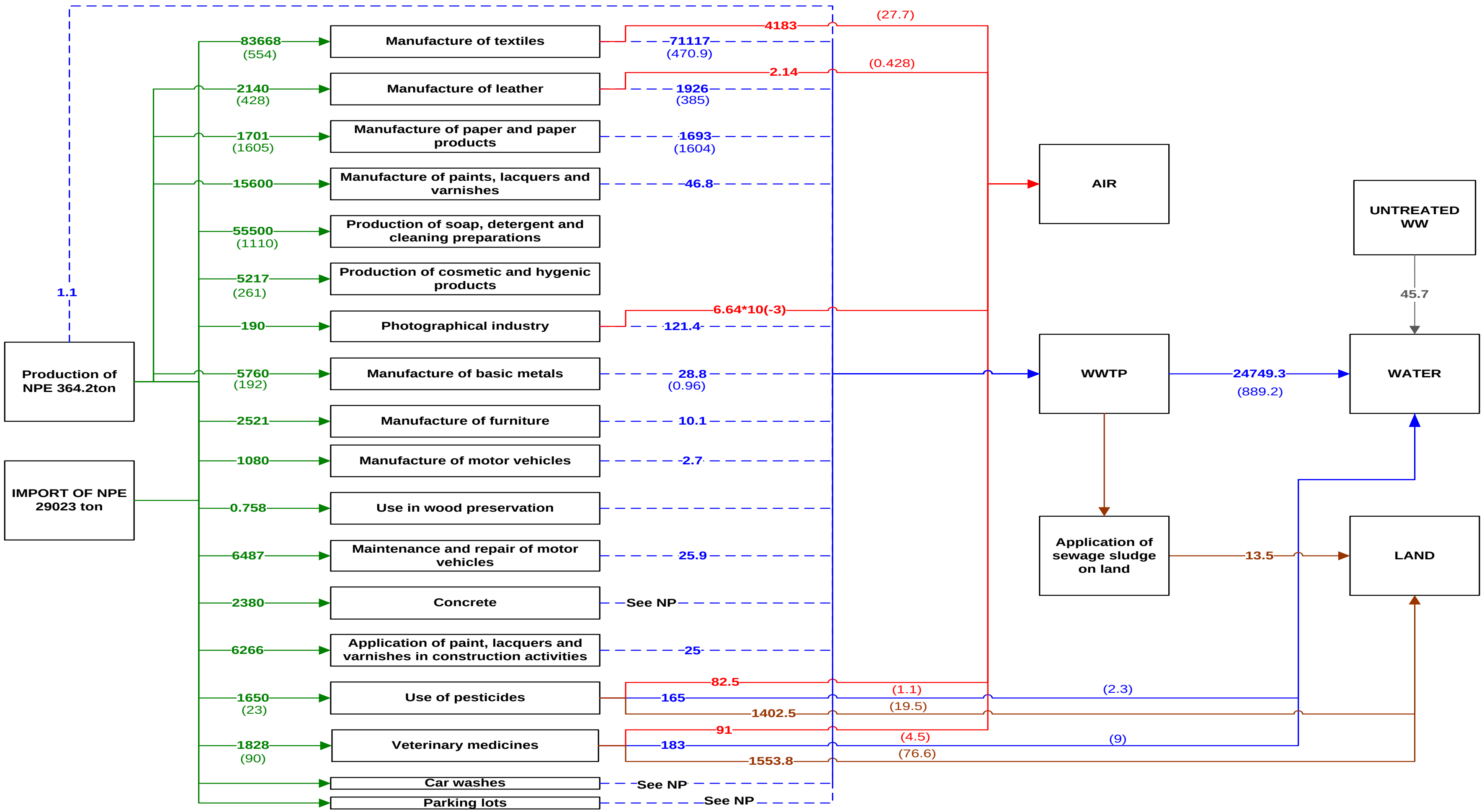

Figure 5-2 Substance flow analysis diagram for NPE (tons/year), Numbers in parenthesis represent the second scenario

5.1.1 Results of the first scenario

The results for the high emission scenario reveal that the main use of NPEs are manufacture of textiles, production of soap, detergent and cleaning preparations and manufacture of paint, lacquers and varnishes. These three sources constitute 80 % of total ethoxylate usage. For NP the primary use is manufacture of phenol and formaldehyde resins and plastic stabilizers.

In case of emissions of NPE to wastewater treatment plant, manufacture of textiles is significant. This is followed by manufacture of leather, paper and paper products. Based on the SFA diagram in Figure 5-1, private use of detergents and industrial and institutional cleaning result in a total release of 22,200 tons NP_{eq}/year and compared to this amount other emissions from other products are almost negligible. Releases to land compromise of use of pesticides and veterinary medicines which, result in total 2956 tons NPE /year. Manufacture of textiles is main cause of air emissions of NPEs followed by agricultural use. In case of NP, volatilization of substance from WWTPs is significant.

When Figure 5.2 is analyzed, total load of NPE to WWTPs is 74,998 tons. According to the results of the first scenario, emissions of NPE to the environment are distributed as 25,143 tons to surface water, 2970 tons to soil, and 4359 to air. NP entering wastewater treatment plants is quantified as 17,861 tons. From WWTPs, 8126 tons NP are released to surface waters. This value includes the NP formed from NPE degradation during treatment. NP load reaching surface waters directly with untreated municipal wastewater is estimated as 4464 tons. Total NP load to surface waters equals 12,590 tons. Other releases are 1250 tons to air and 13.5 tons to soil.

Percent distribution of emissions of substance to the environment is given in Figure 5-3. Majority of emissions reach surface waters. For NP releases to air, the most significant source is volatilization from WWTPs. So, the air emissions are also occurring as a result of loads to wastewater.

First scenario reveals high and unrealistic results for some sources like textile manufacturing where 83,668 tons of NPE is estimated to be used. As discussed in upper parts, this scenario does not seem to represent the real substance flows.

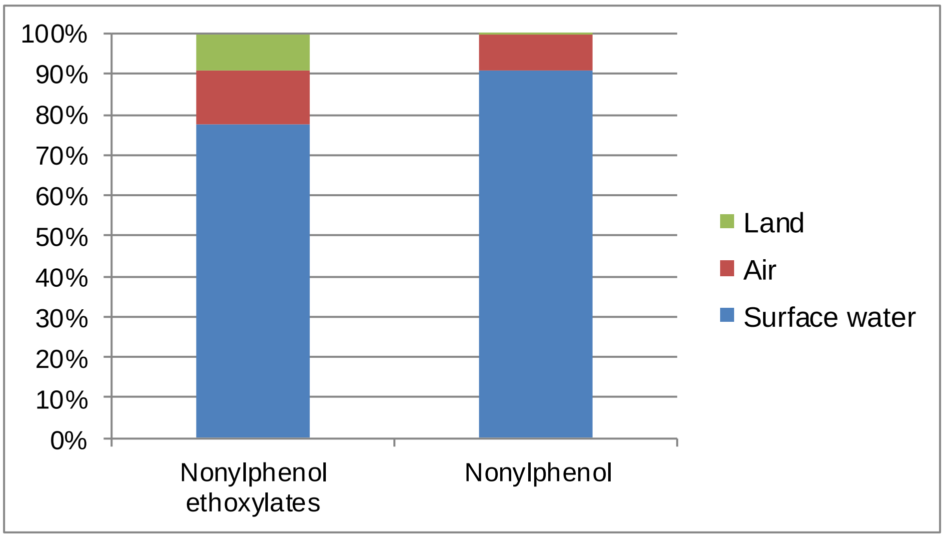

Figure 5-3 Distribution of emissions to environmental compartments (1st scenario)

5.1.2 Results of the second scenario

According to Figure 5-1, for the second scenario, the main use of NP in processing life cycle stage is manufacture of phenol formaldehyde resins and plastic stabilizers, same with the first scenario.

Based on the SFA of NPEs in Figure 5.2, the primary use of the substance in processing life cycle stage is manufacture and application of paint, lacquers and varnishes. This is followed by manufacture, maintenance and repair of motor vehicles, manufacture of paper and paper products, production of soap, detergent and cleaning preparations and concrete. The distribution is quite different from the first scenario. For example, use of ethoxylates in textile manufacturing is not as significant as in the first scenario.

Figure 5-1 shows that emissions of NP from uses in products are mainly from private use of detergents, cleaning agents, stain removers and industrial and intuitional cleaning and washing of textiles. The uses in products results in emissions of 469 NP_{eq} tons per year to wastewater treatment plants and surface waters. It is important to note that 355 tons corresponding to about 76 % of the releases belong to private use of detergents, cleaning agents, and industrial and institutional cleaning. Washing of textiles is another remarkable source. When compared with emissions from product life cycle stage, the releases from processing can be considered as minor. NP releases to air and land are governed by volatilization from WWTP and application of sewage sludge, respectively.

According to Figure 5.2, the main upstream sources of NPEs from processing lifecycle stage to WWTPs are manufacture of paper and paper products, textiles and leather. The releases of NPEs to soil compartment are from agricultural activities which are use of pesticides and veterinary medicines. In addition, application of sewage sludge on land causes NP pollution. The emissions to air are dominated by manufacture of textiles. Agricultural use also contributes to air emissions.

When the SFA diagram for NPE is analyzed, it can be seen at first glance that majority of emissions reach WWTP and consequently surface waters. The total load of ethoxylates to WWTPs in Turkey adds up to 2694.4 tons. The annual load to surface waters from wastewater treatment plants is 889.2 tons. Based on the results of this study, emissions of NPEs to environmental compartments are distributed as 946.2 tons to surface water, 109.6 tons to soil, and 34 tons to air.

Results for NP indicate that annually 456.2 tons of NP enters wastewater treatment plants. At this point, untreated municipal wastewaters are also important. Yearly, 113 tons NP is estimated to be discharged to surface waters directly, without any treatment. Based on the outcomes of the SFA study, total NP releases to environment are quantified as 340.2 tons to surface waters, 31.9 tons to air and 13.5 tons/year to soil. Here, releases to surface waters include NP formed from NPE degradation during treatment.

The percent distribution of emissions to environmental compartments is represented in Figure 5-4. It can be seen that 87 % of the emissions of NPEs are to surface water compartment via WWTPs. Releases to land and air are found relatively minor. For NP it is observed that almost 90 % of the emissions are to surface waters while releases to air are also prominent. It is important to note that these releases are estimated to occur majorly from volatilization from WWTPs.

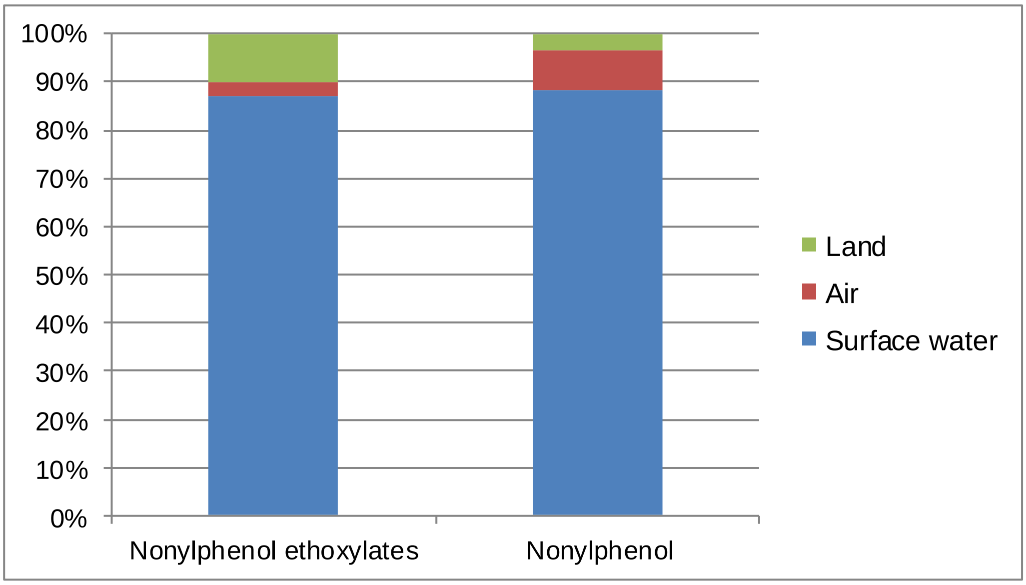

Figure 5-4 The distribution of emissions across environmetal compartments (2^{nd} scenario)

The results of the SFA point out that environmental compartment receiving highest loads of the substance is water. Then, the concentration of NP and its metabolites in surface waters in Turkey gains importance.

In context of the European Union project called EU Wide Monitoring Survey of Polar Persistent Pollutants in European River Waters measurement of NP and nonylphenol monoethoxy carboxylate (nonylphenoxy acetic acid) (NPE1C) was conducted in Sakarya River and Dilderesi Creek in Turkey [84]. The concentration of nonylphenol in Sakarya and Dilderesi was identified as 280 and 500 ng/L, respectively. For NPE1C, 1465 ng/L is measured in Sakarya River and 976 ng/L is the measured concentration in Dilderesi Creek. During the monitoring study, 35 selected compounds were analyzed in 122 water samples from 100 European rivers from 27 European Countries. NP concentrations higher than Dilderesi Creek are observed in Austria, Belgium and Spain in 6 samples. NPE1C concentrations higher than Sakarya River are observed in Belgium, Bulgaria and Cyprus in 7 samples. This study indicates that Sakarya River and Dilderesi Creek in Turkey are exposed to high loads of NP and other metabolites of the substance compared to most of the European Rivers. Both water bodies are located in highly industrialized areas of Turkey and especially Dilderesi Creek is known to be severely polluted. It is important to note that analyses were done in 2008 and restriction of NP was added to the Regulation on Restriction on Manufacturing, Supply and Use of Some Dangerous Substances, Preparations and Articles in 2011. Unfortunately there is no study in the literature to discuss and compare up to date concentrations of the substance in Turkish surface waters.

Alkylphenols were measured and quantified in water, sediment and fish tissues in Sakarya and Değirmendere Rivers, Turkey [85]. NP was not detected in water samples however, it was found in sediment of Değirmendere River as 4.46 µg/g sediment [85]. Fish sampled from both Degirmendere and Sakarya River showed NP presence in their tissues which shows that there is NP pollution in the river. The reason of NP not being detected in water can be the analysis method applied in the study, the substance being hydrophobic and accumulating in sediments and aquatic organisms. Even if the substance is not detected in water samples in this work, the sediment and fish analysis shows that both rivers are subject to NP loads.

5.1.3 Textile products and nonylphenol

The results of the SFA show that one of the prominent sources of releases from products is washing of textile products. Use of NPEs in textile manufacturing has drawn considerable interest in recent years. Greenpeace International has conducted a study investigating NPE concentrations in textile products from 13 different manufacturing countries [86]. Textile products from Turkey were also analyzed for NPE content and 5 samples out of 9 were identified to contain NPE. The concentration range was identified as <1-47 mg/kg and with a median of 1.6 mg/kg [86]. The samples analyzed are well known textile brands and the products are exported outside Turkey. NP ethoxylate investigation by Greenpeace is not limited to the above mentioned analysis. In three t-shirts manufactured in Turkey NPE was detected in concentrations of <1, 5.6 and 25 mg/kg. These products were mostly exported from Turkey however, there are products containing NPE, imported to Turkey.

UK Environment Agency investigated NPEs in textile products that are imported to UK. Four textile products were sampled from Turkey and one of them was found to contain NPE of 44.5 mg/kg which shows that NPEs are being used in Turkey in textile manufacturing [87].

Swedish Society of Nature Conservation tested 17 t-shirts for the presence of NPEs. The results of the analysis indicated that the highest concentrations originated from Turkey and China. Three t-shirt samples manufactured in Turkey showed concentrations of 22, 230, 270 mg/kg [88].

5.2 Discussion on the Method and Hypothesis

SFA approach has been used for different substances and systems around the world in recent years. Results of SFA studies are found useful for decision makers. Where and how SFA studies will be used is an important point from environmental management perspective. Another crucial subject is the approach followed in conducting the flow analysis. The strengths and weaknesses of the method and obstacles faced during the study will highlight possible questions that can come to mind.

The first thing that should be discussed is uncertainty. Uncertainty can arise from almost all steps in substance flow analysis studies and it is almost impossible to come up with exact numbers representing the flows throughout the system. This is basically a result of complexity of the system and validity of the data. For instance, in this study the system is selected as borders of Turkey and data is gathered considering production and consumption all over the country. So, the results of the calculations performed are not expected to be exact numbers.

In addition, NP and NPE content in products are accepted to be constant for all products. Another assumption that should be discussed is the estimation of no losses in the system. This means that all NP and NPE entering the system are consumed in the same year both for industrial and products usage. This hypothesis is valid even if it is known that all products may not contain the substance and goods have different service lives. The uncertainty resulting from data gathering and complexity of the system and the assumptions may seem to cause big errors in calculations. However, the study investigates the magnitude of the amount of substance entering the environment and the acceptable percentage of uncertainty is large for such a large and complex system.

Data availability and validity is another important issue. The emissions estimated for NP and NPE have to be compared with measurement results. In this study the predictions based on SFA and available measurement results in the literature are integrated. At this point, data availability seems to limit SFA studies both in performing the estimations and comparing the results i.e. validation.

Another important point is that SFA studies provide information on quality as well as quantity. The methodology applied in this study provides information about the paths of flows of the substance and the structure of the system. In addition to quantities of flows, sources and pathways of substances resulting in emissions to environment can be identified. This type of qualitative conclusions can even be more relevant than quantitative results for environmental policy making.

CHAPTER 6

SUMMARY AND CONCLUSION

This study is the first in Turkey concerning substance flow analysis of NP and NPEs. In fact, it is the first SFA conducted in Turkey. The possible sources of the substance are identified and emissions to environmental compartments are estimated. Two cases for Turkey are examined. One of them considers the releases from the high emission scenario estimations. Other scenario deals with releases, considering the Regulation on Restriction of the Production, Placing on the Market, and Use of Certain Dangerous Substances, Preparations and Articles (26.12.2008, Official Gazette No: 27092) [18]. The limitations for the use of NP and NPEs under the scope of this regulation are accepted to represent the second scenario.

The results are evaluated in accordance with the import and manufacture data of Turkey and production/consumption amounts of other countries. Second scenario is found to represent consumption and emission of Turkey better because the estimations of SFA approach the actual import and manufacture data. The main conclusions that can be driven from the results of the second scenario are summarized in Table 6-1 and Table 6-2.

In Table 6-1, the distribution of releases to different environmental compartments is provided. It can be concluded that surface water is the main environmental compartment receiving NP and ethoxylates pollution via WWTP and untreated municipal wastewaters. Annually, 456 tons of NP and 2694 tons NPE enter wastewater treatment plants. After degradation in WWTP, the amount of substance discharged with the effluent is summed with the releases that are estimated to reach surface waters directly and the total annual load to surface waters is found.

NP/NPE load to surface waters due to untreated municipal wastewaters makes important contribution to the total loads. 113 tons NP is estimated to be discharged without treatment.

In addition to surface waters, land and air are other compartments receiving the pollutant. The most important sources to soil are use of pesticides and veterinary medicines. From these agricultural sources it is estimated that annually 96 tons of ethoxylates reach soil. Releases to air compartment are mostly from volatilization from WWTP and manufacture of textiles. Air emissions can be accepted as minor when compared with releases to water and land.

Table 6-1 Summary of results for the selected scenario

Name of Substance	**Releases to environment (tons/year)**		**Releases to environment (%)**
Nonylphenol	Surface water	340.2	88.2
	Air	31.9	8.3
	Soil	13.5	3.5
Nonylphenol Ethoxylates	Surface water	946.2	86.9
	Air	33.7	3.1
	Soil	109.6	10

The main sources causing NP and NPE input to WWTP are provided in Table 6-2. According to Table 6-2, the main sources of emissions are use of detergents, cleaning agents, washing of textiles, manufacture of paper and paper products, textiles and leather. Especially detergents and cleaning agents result in high loads to wastewater treatment plants corresponding to approximately 80 % of all the NP emissions. For NPE, paper and paper products manufacturing is found to be the prominent source. NP and NPE's should be controlled in cleaning agents and manufacture of paper and paper products in order to decrease pollutant loads to environment.

Table 6-2 Main emission sources identified

Name of Substance	Main sources of emissions to WWTP (tons/year)		%
Nonylphenol (NP_{eq})	Use of detergents and cleaning agents	355	77.8
	Washing of textiles	92	20.2
	Others	9	2
	TOTAL	**456**	**100**
Nonylphenol Ethoxylates	Manufacture of paper and paper products	1604	58.5
	Manufacture of textiles	471	17.2
	Manufacture of leather	385	14.1
	Others	280	10.2
	TOTAL	**2740**	**100**

In conclusion, even with the low emission scenario, with the restriction on the use of substance, still high loads to water environment are observed. Substances are continued to be used in high amounts especially in applications out of scope of the current regulation. Alternative strategies are required for Turkey to reduce NP and NPE usage and emissions to environment.

As a result of the SFA study, the locations which are susceptible to NP and NPE pollution can be identified. The uses of detergents and cleaning agents both for industrial and private use are possible NP/NPE emission sources all over the country. For washing of textiles containing NP/NPE the situation is same. So, for releases estimated in terms of NP_{eq} it is not possible to identify specific locations for highest releases. In areas where industrial activities are dense and in crowded cities, the releases can be assumed as larger compared to other locations. For NPEs, the hotspot locations are determined and given in Table 6-3.

Table 6-3 Hotspot locations for NPE in Turkey

Industrial Sector	Location
Paper and paper products	**Marmara Region** – İstanbul, Trakya Region **Aegean Region** – İzmir
Textiles	**Marmara Region** – Bursa, İstanbul, Çorlu, Çerkezköy **Aegean Region** – Denizli, Aydın, Uşak **Southeastern Anatolia Region** – Kahramanmaraş **Mediterranean Region** - Adana
Leather	**Marmara Region** - İstanbul-Tuzla, Tekirdağ-Çorlu, Bursa, Balıkesir-Gönen **Aegean Region** - İzmir-Menemen, Uşak, Manisa-Kula **Mediterranean Region** – Isparta, Hatay **Black Sea Region** - Bolu-Gerede

According to Table 6-3, it can be concluded that water bodies under risk of NPE pollution are Sea of Marmara, Gönen Creek Ergene River, Nilüfer Creek, Gediz River, Büyük Menderes River, and Ceyhan River. These areas can be accepted as hotspots for NPE pollution as; these water bodies are likely to receive NP/NPE pollution.

CHAPTER 7

RECOMMENDATIONS

In this study SFA of NP and NPEs is conducted. As a result of the nature of substance flow analysis, the conclusions aim to serve for environmental policy making. Therefore, some recommendations can be made for further consideration.

The results of the SFA show that one of the prominent sources of releases from products is washing of textile products. Textile product analyses indicate that in spite of the restriction, NPE are still being used in textile manufacturing. Even if the measured concentrations do not exceed the limits in most of the samples, still, the substance is continued to be released to water after washing. In addition, products imported to Turkey from countries not having limitations on the use of substance are of importance. The studies reviewed, support the release estimations of NP from manufacture and washing of textile products. So, NPE usage in textile manufacturing can be further investigated.

When accumulation of the substance in products is considered, the most significant stock of NP occurs with concrete. Products such as textiles, leather, soap, detergents and cosmetics are consumed faster and a big portion of substance in the product reaches wastewater with first use. The usage of NP in concrete is not phased out in Turkey. This means that the substance is still accumulating. According to calculation results for concrete, about 20,000 tons of nonylphenol ethoxylate accumulated in concrete in 10 years in Turkey. With the developments in construction sector and new roads, bridges constructed, the accumulation of the substance will continue to increase. It is important to note that even if inflow of NPEs is ceased today, concrete will continue to be an important source of environmental load for a long time.

Monitoring of hazardous substances in WWTP effluents and surface waters is also important. The validation of the estimated numbers is possible with measurement. If new measurement results are obtained, the conclusions of the study can be further evaluated.

With SFA, usage and emission data of substance can be represented in one diagram and significant sources of releases and points where measures should be taken can be identified without difficulty. In order to phase out the use of NP and its ethoxylates and to minimize their releases to the environment, alternative measures can be developed as future work.

The results obtained in this thesis can be further evaluated from environmental quality standards perspective. For the industrial activities identified as causing highest NP emissions, discharge standards can be set or existing limits can be reviewed, in order to ensure that environmental quality standards are satisfied.

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