TURUN YLIOPISTON
MERENKULKUALAN KOULUTUS- JA TUTKIMUSKESKUKSEN JULKAISUJA

PUBLICATIONS FROM THE CENTRE FOR MARITIME STUDIES
UNIVERSITY OF TURKU

A 63
2012

TANK CLEANING IN THE BALTIC SEA – ASSESSMENT OF THE ECOTOXICITY OF TANK CLEANING EFFLUENTS

Milja Honkanen

Jani Häkkinen

Antti Posti

European Union
European Regional Development Fund

Leverage from the EU 2007–2013

Tekes

TURUN YLIOPISTON
MERENKULKUALAN KOULUTUS- JA TUTKIMUSKESKUKSEN JULKAISUJA

PUBLIKATIONER AV SJÖFARTSBRANSCHENS UTBILDNINGS- OCH
FORSKNINGSCENTRAL VID ÅBO UNIVERSITET

PUBLICATIONS FROM THE CENTRE FOR MARITIME STUDIES
UNIVERSITY OF TURKU

A 63
2012

TANK CLEANING IN THE BALTIC SEA – ASSESSMENT OF THE ECOTOXICITY OF TANK CLEANING EFFLUENTS

Milja Honkanen
Jani Häkkinen
Antti Posti

Turku 2012

JULKAISIJA / PUBLISHER:

Turun yliopisto / University of Turku
MERENKULKUALAN KOULUTUS- JA TUTKIMUSKESKUS
CENTRE FOR MARITIME STUDIES

Käyntiosoite / Visiting address:
ICT-talo, Joukahaisenkatu 3-5 B, 4.krs, Turku

Postiosoite / Postal address:
FI-20014 TURUN YLIOPISTO

Puh. / Tel. +358 (0)2 333 51
http://mkk.utu.fi

Kopijyvä Oy
Kouvola 2012

ISBN 978-951-29-5173-4 (paperback)

ISBN 978-951-29-5174-1 (PDF)

ISSN 1456–1816

FOREWORD

Far more studies have been conducted on the risks of marine transport of oil than on the risks arising from chemical transportation. Furthermore, most of the studies dealing with either oil or chemical shipping are focused on large spills resulting from shipping accidents. Studies on the impacts of chronic pollution from routine shipping operations, such as tank cleaning and bilge water handling are relatively scarce – particularly regarding chemicals. This is partly due to the "invisible" nature of operational discharges. The amounts of hazardous substances that are released at a time are relatively small and the consequences cannot be seen instantly. In contrast, a spill from a disastrous shipping accident may be over a thousand tonnes at worst, and the consequences can typically be seen immediately (e.g. surfacing of dead fish). All in all, due to its invisibility, the issue of chronic pollution resulting from operational discharges has been, at least to some degree, overlooked by both researchers and the shipping industry. This report reviews the environmental impacts of operational discharges resulting from tank cleaning.

This study was conducted as a part of the Chembaltic (Risks of Maritime Transportation of Chemicals in Baltic Sea) project which gathers information on chemicals transported in the Baltic Sea. The Chembaltic project is implemented in co-operation with the University of Turku Centre for Maritime Studies, Aalto University and Kotka Maritime Research Centre. The project is funded by the European Regional Development Fund (ERDF) and the Finnish Funding Agency for Technology and Innovation (Tekes) as well as the following companies and agencies: Neste Oil Oyj, Vopak Chemicals Logistics Finland Oy, Port of HaminaKotka Ltd, Crystal Pool Ltd, and the Finnish Transport Safety Agency (Trafi). The project has also been supported by the Finnish Port Association and the Finnish Shipowners Association.

The authors of the report would like to thank Jyrki Vähätalo from the Finnish Transport Safety Agency (Trafi), Crystal Pool Ltd and MARPOL surveyors Pentti Keskitalo and Laila Carlson for informative discussions on different aspects of tank cleaning. Further, the authors would like to thank the project partners and the steering group of the Chembaltic project. Lastly, M.Sc. Irina Wahlström and M.Sc. (Tech.) Olli-Pekka Brunila are acknowledged for reviewing the report.

Kotka, 8 October 2012
The Authors
The Centre for Maritime Studies, University of Turku

FUNDING PROVIDERS AND PARTNERS OF THE CHEMBALTIC PROJECT

ABSTRACT

This study was conducted as a part of the Chembaltic project which gathers information on chemicals transported in the Baltic Sea and the risks they present to the environment. In this study, the environmental risks of tank cleaning waters were evaluated by conducting a literature survey and a small-scale risk assessment of five target chemicals following EU methodology laid down in the Technical Guidance Document on Risk Assessment where applicable. The target chemicals were chosen based on existing studies and projects where chemicals were ranked by their hazardousness in the aquatic environment and their shipping volumes in the Baltic Sea. The selected chemicals were nonylphenol ethoxylate (nonylphenol), phenol, sulphuric acid, styrene and xylenes.

In the risk assessment carried out for this study, the Predicted Environmental Concentrations (PECs) of all five target chemicals were determined. The PECs were calculated based on the residual cargo quantity that was estimated to remain in a tank after unloading (=strip) and the water quantity that is used in the cleaning process. The cargo residue that remains in a tank after unloading depends not only on the cargo characteristics but also on the size of the tank and the stripping technique used in a particular ship. Therefore, the PECs were calculated for a hypothetical 1,000 m^3 tank using three different strip sizes: 15 litres, 50 litres and 300 litres. The 15-litre and 50-litre strips are more or less typical for modern tankers. The PECs were calculated with and without the dilution effect caused by prewashing to evaluate the importance of these mandatory in-port prewashes. The PECs obtained for the target chemicals were compared to their corresponding Predicted No Effect Concentrations (PNECs), which were derived from toxicity data in the available literature. Whenever the calculated PEC/PNEC ratio exceeds 1, a risk is indicated.

The results of the risk assessment clearly demonstrated the importance of prewashing cargo tanks ashore before the main washing. Without prewashing the cargo tanks and discharging the generated prewashing effluents into reception facilities ashore, the PEC/PNEC ratios obtained for further washings exceed 1 regardless of the chemical and the quantity of chemical residue (15/50/300 litres). In contrast, if the cargo tanks are prewashed and the remaining prewash residues in the tanks are small ($\leq$ 15 l), the risk arising from tank cleaning effluents stays at accepted levels, and no significant harm seems to be caused to aquatic organisms. When the prewash residue is around 50 litres, the risk arising from further washings mostly remains at accepted levels as well.

Whenever the prewashing is carried out properly, the tank washings only represent a very minor and local risk for water biota. The results of the study showed that prewashing requirements for the most hazardous category of X cargoes and high-viscosity and solidifying Y cargoes are without a doubt necessary to keep the hazards arising from these substances at accepted levels. Further, MARPOL Y class also includes persistent and toxic chemicals whose release in the sea without prewashing is not recommended, even if the regulations might not necessarily require prewashing. Since this study was conducted by modelling, more research is needed e.g. to measure the actual chemical concentrations in the sea after release of tank washings.

TIIVISTELMÄ

Tutkimus on tehty osana Chembaltic-hanketta, jonka tavoitteena on kerätä tietoa Itämerellä kuljetettavien kemikaalien riskeistä. Tässä tutkimuksessa kemikaalisäiliöalusten pesuvesien ympäristölle aiheuttama riski arvioitiin viiden tutkitun kemikaalin osalta noudattamalla ja soveltamalla EU:n teknisiä ympäristöriskinarviointiohjeita. Arvioidut kemikaalit valittiin huomioiden aiemmin tehdyt tutkimukset, joissa kemikaalit on laitettu järjestykseen ympäristövaarallisuutensa ja Itämerta koskevien kuljetusmäärätietojensa perusteella. Tutkimuksessa arvioiduiksi kemikaaleiksi valikoituivat nonyylifenolietoksylaatti (nonyylifenoli), fenoli, rikkihappo, styreeni ja ksyleenit.

Riskinarvioinnin alkuvaiheessa tutkituille viidelle kemikaalille määritettiin ennustettu pitoisuus ympäristössä (PEC). PEC-arvo laskettiin lastin tyhjennyksestä jäljelle jäävän kemikaalin määrän (strip eli jäännös) ja tankkien puhdistukseen käytettävän pesuveden määrän perusteella. Kemikaalijäännöksen määrään vaikuttavat paitsi lastin ominaisuudet, myös säiliön koko ja käytettävä aluskohtainen strippaustekniikka. Tämän vuoksi PEC laskettiin hypoteettiselle 1 000 m^3 säiliölle sekä kolmelle eri kemikaalijäännökselle: 15 litraa, 50 litraa ja 300 litraa. Moderneissa aluksissa 15 l ja 50 l jäännökset ovat tyypillisiä. PEC-arvo laskettiin tutkituille kemikaaleilla sekä ilman esipesua että esipesu huomioiden, mikä mahdollisti satamien suorittamien esipesujen merkityksen arvioimisen ympäristölle aiheutuvien riskien kannalta.

Tutkituille kemikaaleille laskettua PEC-arvoa verrattiin EU-menetelmällä laskettuun ennustettuun vaikutuksettomaan pitoisuuteen (PNEC), joka perustuu kirjallisuudesta kerättyihin arvoihin eri kemikaalien ekotoksisuudesta. EU-ohjeistuksen mukaan aina, kun laskettu PEC / PNEC-suhde on suurempi kuin 1 on olemassa riski ympäristölle. Nyt toteutetun riskinarvioinnin tulokset korostavat selvästi satamassa suoritettavan esipesun ja siinä syntyvien jätteiden maihin jättämisen merkitystä ennen pääasiallista pesua ja tästä syntyvien pesuvesien laskemista meriveteen. Ilman esipesua, saadut PEC/PNEC-suhteet ylittävät arvon 1 – riippumatta kemikaalista tai näiden jäännösmääristä (15/50/300 l). Sen sijaan, jos esipesu suoritetaan ja säiliön esipesujäännökset ovat hyvin pieniä ($\leq$ 15 l), pesuvesistä aiheutuvat päästöt pysyvät alle hyväksyttävän tason ja eikä niistä näyttäisi aiheutuvan merkittävää haittaa vesieliöille. Myös silloin, kun kemikaalijäännös on esipesun jälkeen noin 50 litraa, pesuvesistä aiheutuva riski pysyy hyväksyttävällä tasolla.

Jos esipesu tehdään sääntöjen mukaisesti, kemikaalialusten pesuvedet muodostavat vain hyvin vähäisiä ja paikallisia haittoja vesieliöille. Tutkimuksen tulokset osoittavat, että esipesuvaatimukset vaarallisimman eli MARPOL X -luokan kemikaaleille sekä kiinteytyville ja korkean viskositeetin kemikaaleille ovat perusteltuja. Lisäksi myös Y-luokan kemikaaleissa esiintyy pysyviä ja myrkyllisiä yhdisteitä, joiden päästäminen mereen ilman esipesua ei ole suositeltava, vaikka säännöt eivät tätä edellyttäisi. Tutkimuksessa tulokset saatiin mallintamalla. Tulevaisuudessa tarvitaan lisää tutkimusta esimerkiksi todellisista kemikaalipitoisuuksista meressä pesuvesien purkamisen jälkeen.

TABLE OF CONTENTS

1 INTRODUCTION

The volume of marine shipping has increased significantly in the Baltic Sea in recent years, and it is predicted to increase even further in the future. The Baltic Sea is, in fact, one of the busiest seas in the world, and at any given time, approximately 2,000 sizeable ships are estimated to sail on its routes. The ships sailing the Baltic Sea include large passenger ferries, cargo vessels, and tankers carrying oil and other hazardous substances. In 2009, 51% of these ships were cargo vessels, 17% tankers and 11% passenger ferries (HELCOM 2010a). The traffic is busiest on major routes from ports in the Gulf of Finland to the Danish straits, through which all ships entering and leaving the Baltic Sea must travel (HELCOM 2009). The transport of hazardous substances presents a great diversity of risks. First of all, because of the busy traffic, shallow depth, narrow navigation routes, numerous islands, and ice cover during the winter period, the risk of an accident in the Baltic Sea area while transporting chemicals is ever present. Luckily, major chemical transportation accidents are very rare. In the Gulf of Finland, for example, a collision involving a chemical tanker can only be expected to happen on average once every 45 years (Sormunen 2012). In addition to unintended accidental spills, chemicals may also be introduced in the marine environment deliberately within the limits of the law. Releasing tank cleaning waters containing a chemical into the sea is an example of an activity that falls within this category of "legal discharges". Chemical tankers can carry various kinds of hazardous substances including highly toxic, flammable and/or corrosive chemicals, such as phenol, benzene and ammonia, but they can also carry lighter products, such as ethanol and edible vegetable oils (Posti & Häkkinen 2012). Consequently, cargo tanks need to be efficiently cleaned every time after cargo unloading to avoid contamination of the following cargo and also to keep the tanks and their associated pipelines in good condition (McGeorge 1995).

The cleaning of chemical tanks and the discharge of the resulting washings are controlled by Annex II of the international convention MARPOL 73/78[1] – to which all the Baltic Sea coastal countries (i.e. the HELCOM[2] countries) are parties. Regulation 13 of the Annex states that any tank cleaning waters, or ballast waters, containing chemical residues must be predominantly discharged into a reception facility at the port of unloading – in other words, releasing these cleaning waters (or ballast waters containing a chemical) in the sea is predominantly prohibited. The discharge of tank cleaning effluents in the sea is only allowed if it is done strictly by the guidelines and criteria set out in Annex II. For example, chemical concentrations in the washings must be within the MARPOL limits, and washings can only be discharged in deep waters (MARPOL Annex II reg. 13). In addition, for tanks having contained highly hazardous cargo or certain solidifying or high-viscosity cargoes, the Annex requires mandatory in-port pre-washes – where the slops generated during these prewashes must always be discharged into reception facilities ashore (Kunichkin 2006, MARPOL Annex II reg. 13.6 and 13.7). In practice, only the prewash effluents are discharged to the shore reception facilities, and the main washings are practically always discharged directly into the sea,

[1] The International Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978 relating thereto (MARPOL 73/78).

[2] HELCOM countries: Denmark, Estonia, Finland, Germany, Latvia, Lithuania, Poland, Russian Federation and Sweden.

as it is legal when accomplished as required in the Annex II. If the main slops were to be discharged ashore as well, the costs would skyrocket, as the appropriate disposal and handling of tank cleaning effluents is extremely expensive and time-consuming (HELCOM 1993).

The amount of a chemical that may legally be released into the sea per cargo tank is 75–300 litres depending on the ship's construction year (Appendix 4 to MARPOL Annex II). When chemical remnants are washed away with water, the total quantity of slop generated per tank in the main washing procedure may vary from 10 m^3 to hundreds of cubic meters per tank (HELCOM 1993). This gives us a rough estimate of the amounts of effluents that are released in the sea from a ship that typically has a capacity of 10–60 cargo tanks (Hänninen & Rytkönen 2006). In the Gulf of Finland, particularly in the busy Hamina-Porvoo district, the shallow waters and the nearness of land rather limits the possibilities of discharging tank cleaning effluents (HELCOM 1993). In the main basin of the Baltic Sea where the waters become deeper, however, the releasing of tank washings is not as restricted.

Even though MARPOL Annex II regulates tank cleaning and the disposal of cleaning effluents to some extent, there are still gaps in our knowledge of how the discharged substances behave once they are introduced in the sensitive marine environment and what adverse effects they might have once there. In addition, when solvents or detergents are used in tank cleaning, the resulting washings act as chemical mixtures leading to the possibility of joint toxicity. With the continuously growing volumes of chemical transportation in the Baltic Sea, it is important to evaluate all risk factors relating to chemical shipping, including tank cleaning. Therefore, in this report, the possible environmental effects of releasing tank cleaning waters into the Baltic Sea ecosystem are evaluated based on a literature survey and a small-scale risk assessment conducted for five target substances (nonylphenol ethoxylates, phenol, sulphuric acid, styrene and xylenes) following the methodology set out in the Technical Guidance Document of the EU on Risk Assessment (EC 2003) where applicable.

This report was written as part of the Chembaltic project (Risks of Maritime Transportation of Chemicals in the Baltic Sea). The project gathers information on chemicals transported in the Baltic Sea. The risk of chemical accidents in open water and ice conditions is being modelled in the project. The risks caused by port operations with chemicals are being studied as well. In addition, the impact of other special environmental risk factors that chemical transportation involves is being evaluated. Tank cleaning is one of these special risk factors, and its environmental impact is examined in this report. The Chembaltic project is scheduled to take place between February 2011 and December 2013, and it is being carried out in co-operation with the University of Turku Centre for Maritime Studies, Aalto University and Kotka Maritime Research Centre. The project is funded by the European Regional Development Fund (ERDF) and the Finnish Funding Agency for Technology and Innovation (Tekes) as well as the following companies and agencies: Neste Oil Oyj, Vopak Chemicals Logistics Finland Oy, Port of HaminaKotka Ltd, Crystal Pool Ltd, and the Finnish Transport Safety Agency (Trafi). The Finnish Port Association and the Finnish Shipowners Association have also supported the project. The report was mainly written

by Milja Honkanen, co-authored with and supervised by Jani Häkkinen (Ph.D.) and Antti Posti (M.Sc. Tech.). The publication reflects the views of the authors. The Managing Authority of the project cannot be held liable for the information published in this report.

2 GENERAL BACKGROUND

2.1 The Baltic Sea – a particularly sensitive sea area

The Baltic Sea is an exceptionally sensitive sea area for many different reasons. It is a large but shallow semi-enclosed inland sea with brackish water – meaning that its water is neither saline nor fresh water, but instead has a salinity between the two (approximately 3–15‰) (HELCOM 2010b). In comparison, the salinity in oceans is approximately 35‰ (Hallanaro 2010). The unusual salinity conditions in the Baltic Sea are challenging for the aquatic organisms, as the salinity is too low for most marine species while it is, especially in the main basin, too high for freshwater species. Consequently, only relatively few species have adapted to living in the Baltic Sea. In addition to salinity, the cold winters of the Baltic Sea area strain the biota and thus contribute to the low species richness (Håkanson et al. 2003). Its poor biodiversity makes the Baltic Sea an unstable ecosystem and thus highly susceptible to environmental impacts: if one species is lost, for example due to chemical exposure, there may be no other species to take its place in the ecosystem. The brackish water and cold climate not only affect the abundance of species but also cause physiological stress to them (HELCOM 2010c). Since the Baltic Sea biota is under constant natural stress, it is understandably more susceptible to the effects of hazardous substances.

The Baltic Sea also differs from most of the world's seas in that it is a continental sea (instead of a sea that lies between continents). This feature accounts for the shallowness of the Baltic Sea: its mean depth is only about 54 metres and its maximum depth 459 metres (Landsort deep), which is still relatively shallow (Hallanaro 2010). The mean depth of the Gulf of Finland is only 38 metres. In comparison, the mean depth of the Atlantic Ocean is approximately 4,000 meters, and that of the Mediterranean Sea is about 2,000 metres (Hallanaro 2010, Furman et al. 1998). Consequently, the water volume of the Baltic Sea is relatively small, making the dilution of hazardous substances less efficient compared to deep oceans. In addition, owing to the restricted passage of water via the Danish straits which connect the Baltic Sea to the North Sea, the water exchange time in the Baltic Sea is very slow (half-life of water ca. 30 years; HELCOM 2010c). Therefore, hazardous substances stay in the Baltic Sea for a very long time. The cold climate also contributes to the long turnover rate of hazardous substances, as the degradation processes slow down at low temperatures (Håkanson et al. 2003).

Despite the high vulnerability of the Baltic Sea, it is under a lot of different pressures. The catchment area of the Baltic Sea is heavily populated (about 85 million people live across the catchment area and its shorelines) and it has a lot of industry, busy traffic and intense agriculture. Heavy loads of hazardous substances and nutrients causing eutrophication are emitted or discharged from households, traffic and industrial and agricultural sources, and they enter the Baltic Sea via surface waters or the air. Nevertheless, one of the biggest threats to the Baltic Sea environment is the ever increasing marine transport of oil and chemicals (HELCOM 2010c). Regardless of their source, once released into the Baltic Sea, hazardous substances may remain there for decades, accumulating in the food webs to reach toxic levels and causing harmful

effects on the sensitive ecosystem. Consequently, identifying and mitigating the risks arising from chemical transportation is essential to achieve better protection of the Baltic Sea.

In 2005, the Baltic Sea, with the exception of the Russian waters and the Russian economic zone, was declared a Particularly Sensitive Sea Area (PSSA) by the International Maritime Organization (IMO). A PSSA status is given to sea areas that are especially vulnerable to risks caused by marine transport and other harms. The recognition as a PSSA area allows for specific protective measures to be taken to control maritime activities in the Baltic Sea, such as routeing measures and installation of Vessel Traffic Services (VTS) (IMO 2011a). The Baltic Sea has also been defined as a "special area" according to several annexes to MARPOL 73/78, meaning that it is provided with a higher level of protection than other sea areas (FEA 2012). The MARPOL discharge and equipment requirements for ships, for example, are more stringent in special areas.

MARPOL Annexes under which the Baltic Sea is defined as a special area are (Date of Entry into Force):

- Annex I: Oil (2 Oct 1983)
- Annex IV: Sewage (1 Jan 2013)
- Annex V: Garbage (31 Dec 1988)
- Annex VI: Prevention of air pollution by ships - Emission control area; SO_x (19 May 2005) (MEPC 2008).

Originally, the Baltic Sea, the Black Sea and the Antarctic were all designated as special areas under MARPOL Annex II (Noxious liquid substances). The annex was, however, revised in 2007, and the revision set significantly stricter discharge limits for new ships (constructed or converted after 1 Jan 2007) compared to the previous limits. Consequently, there was no longer any need for special requirements for the Baltic and the Black Sea areas (IMO 2008). Only the Antarctica's status as a special area remained after the revision: the discharge of noxious liquid substances in the Antarctic area is strictly prohibited.

2.2 Transportation of chemicals in the Baltic Sea

Chemicals can be transported by ships either in packages or as bulk cargo. Bulk chemical cargoes can be further dived into solids, liquids and gases, and they can be transported either in chemical carriers or in specialized gas carriers. The carriers transporting liquid bulk chemicals in the Baltic Sea are typically parcel tankers, which can carry from 10 to 60 cargo tanks ("parcels") at a time (Hänninen & Rytkönen 2006). This consequently means that a parcel tanker can carry up to 60 different chemicals simultaneously – although the number of different cargoes on a tanker seldom exceeds 10 (Posti & Häkkinen 2012). The total cargo capacity of chemical tankers varies from 400 to over 40,000 m^3 and that of individual tanks from 70 m^3 to 2,000 m^3 (Hänninen & Rytkönen 2006).

Different cargoes cannot be placed randomly in chemical tankers, and there are several factors that must be taken into account when planning the cargo placement (Kunichkin 2006). Cargo compatibility is one of these factors: cargoes that react dangerously with each other must be separated (e.g. by a cofferdam, a void space or a tank containing compatible cargo). Further, some tank coatings are not compatible with all cargoes. Lastly, the FOSFA (The Federation of Oils, Seeds and Fats Associations) and the NIOP (the National Institute of Oilseed Products) have placed restrictions on what can be carried as previous immediate cargoes before edible animal and vegetable oils and fats (Verwey 2007). These prior cargo restrictions are in place because previous cargo carried in a tank is a potential source of contamination, despite efficient cleaning methods (Kunichkin 2006). Some residues may, for example, be adsorbed into the tank coating or find their way into areas the cleaning machines have trouble reaching and be consequently released into oil or fat even after adequate cleaning. Lastly, the IBC Code grades chemical tankers into type 1, type 2 and type 3 tankers based on their design and construction standards, and defines which substances can be transported in each type of ship (IMO 2008). The most hazardous substances can only be carried in type 1 carriers, whereas type 2 and type 3 tankers are suited for carrying progressively less hazardous substances (IMO 2011b).

The liquid cargo transported in the Baltic Sea consists of various kinds of compounds, some of which are highly toxic, corrosive, and/or flammable and are therefore dangerous to both human health and the environment, and some of which pose no hazard even if released in the environment in large quantities. Of all the hazardous liquid substances transported in the Baltic Sea area, oil is by far transported the most. For example in 2010, approximately 290 million tonnes of the international liquid cargo handled in the Baltic Sea ports were oil and oil products (Holma et al. 2011). The amount of liquid chemicals handled annually in the Baltic Sea ports is over 11 million tonnes – and about one half of that (roughly estimated 5.0–6.3 million tonnes) is handled in Finnish ports (Posti & Häkkinen 2012). Even though the volume of chemical transportation may seem small in relation to oil and oil products, the potential risks relating to chemicals may actually be greater. Firstly, chemicals may be far more toxic than oil, and secondly, the high cargo diversity in chemical carriers poses a special risk in accident conditions, as different chemical cargoes with different reactive properties may be mixed together, forming a chemical mixture significantly more reactive and/or more toxic than its parent compounds (Hänninen & Rytkönen 2006). On the other hand, in reality a spill resulting from a chemical tanker accident is typically significantly smaller than a spill from an oil tanker accident (due to smaller transport volumes per ship and compartmentalisation of the cargo). Either way, it is clear that the risks relating to chemical shipping are more difficult to identify than the risks arising from oil transportation. This stems from the fact that thousands of chemicals with different properties are transported by sea each year, and the environmental risk profiles and potentials of these chemicals, compounds and other substances are very complex and highly variable (Malmsten 2001).

The chemicals handled in greatest quantities in the Baltic Sea ports are methanol, sodium hydroxide solution, methyl tert-butyl ether (MTBE), xylenes, pentanes, ammonia, phosphoric acid, sulphuric acid, and ethanol and ethanol solutions (Posti &

Häkkinen 2012). At least hundreds of thousands of tonnes of all these substances are handled annually – some of the volumes even amounting to over 1 million tonnes per year. The majority of the most frequently handled substances belong to MARPOL's pollution category Y, meaning that they are of a moderate hazard if released in the marine environment. Only MTBE, ethanol and ethanol solutions are category Z substances, i.e. the hazard arising from them, according to MARPOL, is only minor (for a more detailed discussion of MARPOL pollution categories, see the following section).

2.3 MARPOL categorization of noxious liquid substances carried in bulk

The regulations on the transport of liquid bulk chemicals are laid down in SOLAS[3] chapter VII (Carriage of dangerous goods) and in the revised MARPOL Annex II (IMO 2011b). SOLAS is an international treaty which concerns the safety of commercial ships (IMO 2011c), whereas MARPOL is primarily concerned with aspects of maritime environmental protection. Both treaties require chemical tankers built after 1 July 1986 to comply with the International Code for the Construction and Equipment of Ships carrying Dangerous Chemicals in Bulk (IBC Code) (IMO 2011b). The IBC code lays down the construction standards for chemical tankers and identifies and categorises the substances that may be carried in them. MARPOL Annex II originally entered into force in 1983 but has since been revised, and the revision entered into force in 2007. Annex II contains regulations and guidelines on the cleaning and discharge of liquid bulk chemicals carried in ships. The precise requirements for cleaning and discharge depend on the pollution category to which the substance at hand has been categorised in the IBC code. In Finland, MARPOL Annex II is implemented through the Act and Decree on Maritime Environmental Protection (1672/2009 and 76/2010).

The revised Annex II introduced a new four-category classification system for noxious liquid substances carried in bulk (previously, there were five categories: A, B, C, D and Appendix III; Luhtala, 2010). In Regulation 6 of the revised Annex II, noxious liquid substances are now divided into four categories: X, Y, Z and OS according to their potential for harm. Another significant change in the revision is that vegetable oils, which were previously unrestricted, must now be transported in chemical carriers (Kunichkin 2006). All the example substances in the following are from MEPC (2007) – the latest list of substances that can be carried in bulk by ships (Chapter 17 of the IBC-code).

Category X includes liquid chemicals which, if discharged into the sea from tank cleaning or deballasting operations, would present ***a major hazard*** to either marine resources or human health. Therefore, the prohibition on the discharge of these substances into the marine environment is justified. Examples of category X substances are coal tar, pine oil, all isomers of octane, triethylbenzene, and diphenylether.

Category Y chemicals are liquid substances which, if discharged into the sea, would present ***a hazard*** to either marine resources or human health or cause ***harm*** to amenities

[3] The International Convention for the Safety of Life at Sea (SOLAS).

or other legitimate uses of the sea. Therefore a limitation on the quality and quantity of the discharge of category Y substances into the marine environment is justified. For example, methanol, phenol, sodium hydroxide, sulphuric acid, vegetable oils, and xylenes are category Y substances.

Category Z chemicals are not as harmful as the X and Y chemicals: they, if discharged into the sea, would present ***a minor hazard*** to either marine resources or human health or cause ***minor harm*** to amenities or other legitimate uses of the sea and therefore justify less stringent restrictions on the quality and quantity of the discharge. Examples of Z category chemicals are diethyl ether, ethyl acetate, methyl tert-butyl ether (MTBE), isobutyl alcohol and urea solution.

The OS category (Other Substances) contains liquid substances which cannot be divided into any of the above-mentioned categories (X, Y or Z). They are, at present, considered to present no harm to marine resources, human health, amenities or other legitimate uses of the sea. Consequently, there is no compelling need to restrict the discharge of these substances into the marine environment. Substances such as molasses, apple juice, and coal and clay slurries are examples of "other substances". None of the Annex II requirements apply to OS substances.

The categorisation criteria for liquid chemicals mentioned above are rather broad. More precise guidelines for the categorization of hazardous liquid substances and mixtures are, in fact, given in Appendix 1 to Annex II. The actual hazard assessment procedure for liquid substances on which the categorization is based was carried out by the EHS[4] working group of the Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP 2002). The working group evaluates new liquid substances to be transported in bulk by ships based on their toxicity and behaviour in the environment, both of which arise from the intrinsic properties of the chemical at hand. The GESAMP rating scale begins with the value 0 ("non-hazardous" or a "negligible hazard"), and continues through medium values of 1 and 2 to maximum values of 3–6, which indicate a more severe hazard (GESAMP 2002). The GESAMP hazard evaluation procedure for a given liquid substance results in a "hazard profile", and based on these profiles, the IMO assigns the substances to one of the four pollution categories (X, Y, Z and OS). The hazard profiles for liquid substances are published regularly, and the composite list of them is available from the IMO (IMO 2011d).

2.4 Effects and behaviour of chemicals in the environment

The release of chemicals in the environment may result in adverse effects on the environment and its organisms – the flora and the fauna. The actual chemical-organism interactions occur at molecular level (e.g. when a chemical binds to a protein or DNA in a cell), but the effects are reflected on all the higher biological levels, including the ecosystem level (Fent 2004) (Figure 2.1). Because a viable population needs its individuals to survive until reproductive age and to grow mature enough to be able to

[4] EHS Working Group on the Evaluation of the Hazards of Harmful Substances Carried by Ships.

reproduce, any interferences with an organism's physiological processes relating to survival, growth or reproduction can understandably also be seen on the population level. Then, if a population of a species declines in numbers or becomes completely extinct as a result of a chemical exposure, the effects on the community structure may be extensive – especially if the affected species is an ecosystem key species (HELCOM 2010c). For example, the extinction of an important predator fish species may lead to massive algae blooms due to the cascade effects along the food chain (Walker et al. 2006). Changes in community structure, on the other hand, may cause shifts in a whole ecosystem and its functions. As seen in Figure 2.1, the effects of hazardous substances are easiest to define on molecular and organism level, but the further one goes on the biological organization scale, the harder it becomes to determine and predict environmental effects.

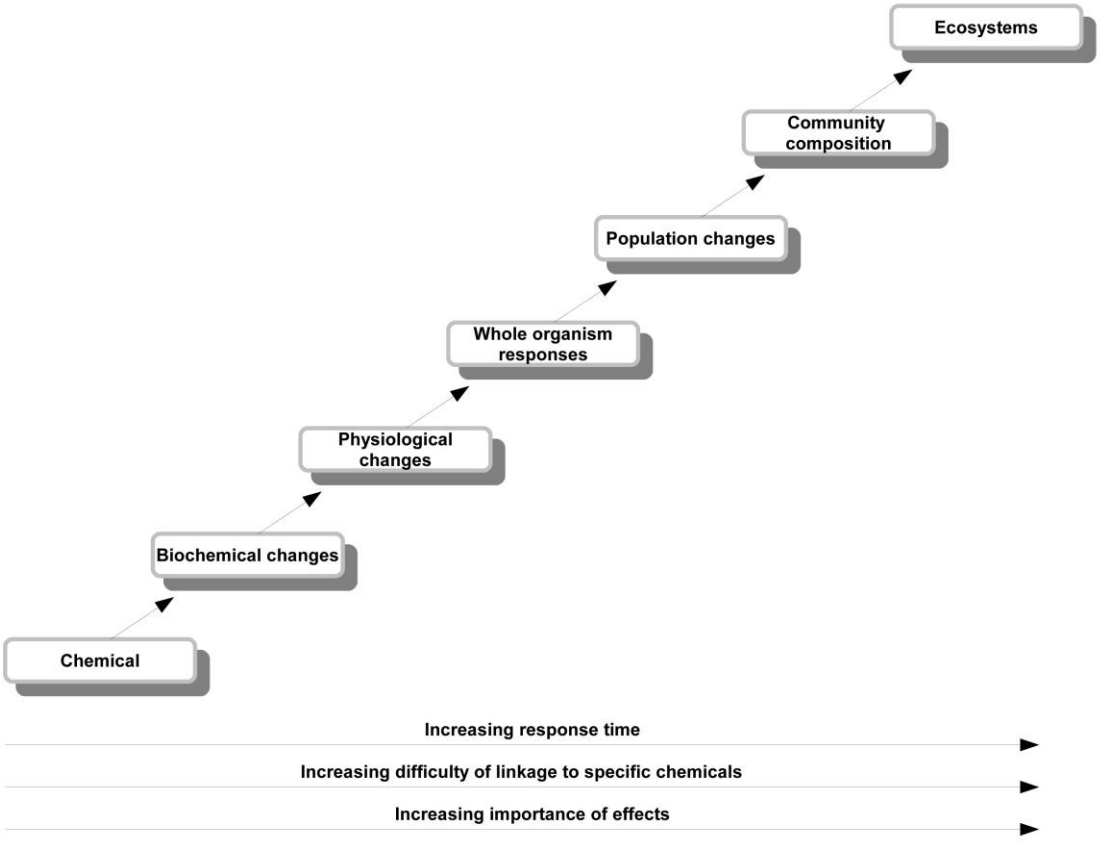

Figure 2.1 Linkages of responses between the biological organizational levels. (Walker et al. 2006)

The environmental effects of a single chemical mostly depend on two factors: the toxicity of the chemical and the degree of exposure (e.g. the amount and frequency of the releases; Walker et al. 2006). Simply put, the chemical poses no hazard in the environment if the exposure is marginal, despite the toxicity of the compound. Similarly, even the most substantial exposure to a chemical is insignificant, if the toxicity of the compound is negligible. Of course, it should be noted that in practice these dose-response relationships are rarely as simple as described above (Walker et al. 2006). In addition to exposure and toxicity, the environmental fate of the chemical (i.e.

its persistency, mobility and tendency to accumulate) contributes notably to the chemical's harmfulness (Fent 2004). The environmental fate of a chemical is determined by both environmental conditions and the properties of the chemical.

2.4.1 Toxicity of a chemical

Mere exposure to a chemical does not necessarily mean that toxic effects will actually occur. To produce toxic effects, a chemical must, first of all, be taken up by an organism, and secondly, find a target site inside it. In case of aquatic organisms, exposure may occur either directly from water or indirectly via food. For example, if a chemical is tightly bound to sediment, it is not easily taken up by organisms living in the water phase (e.g. fish). However, worms living burrowed in the sediments could be exposed to the chemical by consuming contaminated sediment particles. Consequently, the same fish that was not affected before via water could now be affected by consuming contaminated worms. Once a chemical is taken up by an organism, it will be distributed within the organism through the circulatory system (blood or hemolymph), and the toxic effect will manifest when the chemical binds to its specific target site (to a molecule, such as receptor, protein, cell membrane or DNA). If an organism lacks the specific target site for a particular chemical, it will obviously not be affected. Plants and algae, for example, lack a central nervous system (or a corresponding target site) and are therefore not affected by neurotoxins. This consequently means that a chemical may either have a target species, or it may be uniformly toxic to all species, depending on whether its target site is found in one or in all species (or group of organisms) (Walker et al. 2006).

Once in an organism, the chemical will be gradually metabolised (either to a less toxic and water soluble metabolite or to a more reactive and harmful metabolite) and finally, the chemical or its metabolites will be excreted through urea, feces and/or gills. Depending on its properties, parts of the chemical may also be stored within the organism in specific vacuoles in cell membranes or in adipose tissue. When the chemical is stored, it will not be able to cause toxic effects, i.e. it is not bioavailable. However, the stored chemical may be released in time, for example when food is scarce and the stored fat needs to be broken down for energy, and then reach its target site causing delayed toxicity (Walker et al. 2006).

The most useful way to evaluate the toxicity of a substance is to perform dose (concentration) – response (effect) tests on organisms of different trophic levels. In toxicity testing, the relationship between concentration and effect for the test species is studied, and the test results in a toxicity value $LC/EC/IC_{50}$[5], which describes the concentration where 50% of the test population is affected (Walker et al. 2006). The No Observable Effect Concentration (NOEC), which is the highest concentration tested at which no significantly different effects from the control population are observed, may also be obtained from these same tests. In aquatic toxicity testing, the typical test

[5] LC_{50}; Lethal concentration, EC_{50}; Effect concentration (previously defined end point; for example immobilization), IC_{50}; Inhibition concentration (end point may, for example, be growth or reproduction).

species are algae, planktonic crustacean *Daphnia* (water flea) and different species of fish. The studied end points may be, for example, death, growth, development or reproduction – an effect that is relevant on all organism, population, and community and ecosystem levels (SYKE 2004). In acute testing, the test organisms are exposed to high concentrations for a short period of time (typically 24/48/96hrs), whereas in chronic testing, the test organisms are exposed to lower concentrations for a longer time period – for the whole life cycle, or a part of it. In chronic tests, the sublethal responses (growth, behaviour, reproduction etc.) are usually more important, as the concentrations are not typically high enough to cause death in test organisms.

In field conditions, organisms are typically exposed to low concentrations of chemicals more or less frequently. Between acute and chronic testing, the test circumstances in chronic testing are far closer to field conditions. The acute toxicity values, on the other hand, are characteristically so high that such concentrations very rarely occur in nature. Typical situations where organisms are acutely exposed to high concentrations of chemicals are disastrous accidents (e.g. tanker collisions) (Häkkinen et al. 2010). Moreover, the high chemical concentrations after a large spill decrease rapidly in the environment, reaching below acute toxicity levels. Therefore, it is most often preferable to use chronic toxicity data in environmental monitoring and the risk assessment of hazardous chemicals. However, chronic toxicity data for chemicals is hard to obtain because the tests are rather expensive and difficult to perform. Therefore, chronic toxicity data is only available for relatively few chemicals (Häkkinen et al. 2010).

Toxicity tests are typically based on national and international standards (SFS, ISO, EN), and the testing of chemicals is performed by the technical OECD guidelines. The testing guidelines of the United States (EPA, ASTM) and Canada (Environment Canada) can also be applied, even though they differ in some parts from the EN and ISO standards (SYKE 2004).

2.4.2 Movements and distribution of a chemical in the (marine) environment

Once a chemical is introduced in the marine environment, it will, first of all, be diluted in the vast amount of water, and secondly, be degraded by both chemical processes (e.g. hydrolysis, photodegradation) and by microorganisms (biodegradation) – at least to some extent (Walker et al. 2006). Sometimes, in a process called bioactivation, the biodegradation may lead to the formation of degradation products which are more reactive and toxic than the original parent chemical. A good illustration of the effect of dilution is comparing the total content of haloforms in river water (up to 13.4 µg/l) to that in seawater (0.119 µg/l) (Crompton 2007). In addition to dilution and degradation, the chemical may also exhibit other behaviours. Depending on its properties, the chemical will move between different environmental compartments (water, air, sediment and living biota) until it reaches a steady state. This environmental partitioning and harmfulness of a chemical are linked together in a sense that a chemical is only toxic when its concentration exceeds a certain threshold in a given compartment (Walker et al. 2006). For example, if we consider a situation where a chemical is released in water, the final steady state concentration to which the pelagic organisms

will be exposed to will be more or less lower than the original concentration during the release. This is partly due to the fact that parts of the original chemical will, for example, evaporate into the air and parts of it will be bound to sediments. Of course, dilution and degradation have a great influence on the chemical concentration as well.

The environmental partitioning, i.e. the environmental fate, of a chemical is a physical process which is highly dependent on the physico-chemical properties of the chemical, as well as on environmental conditions (Allen 2002). Based on the chemical's physico-chemical properties, it is possible to predict the likely movements and partitioning of a pollutant in the environment (the fugacity approach) (MacKay 1979). The most important physico-chemical properties affecting the environmental fate of a substance are: water solubility, vapour pressure, density, and lipophility (described by the octanol-water partitioning coefficient, K_{ow}). Implications of the different physico-chemical properties on the chemicals' behaviour in the environment are briefly reviewed in the following.

Water solubility S is a central factor determining the environmental fate of a chemical. Water solubility greater than 1,000 mg/l makes a substance highly soluble in water (Nikunen & Leinonen 2002) and thus easily available to pelagic organisms. In comparison, poorly soluble (< 10 mg/l) and hydrophobic substances are typically tightly bound to organic particles and the sediment, and are therefore less available for uptake by pelagic organisms. On the other hand, highly water soluble substances are typically readily biodegraded and do not, therefore, have the tendency to accumulate in organisms and food webs (Häkkinen et al. 2010).

Vapour pressure P_{vp} (Pa) (at 20–25 °C) describes a chemical's solubility in air. When a substance has a vapour pressure greater than 0.1 kPa, it is considered highly volatile, whereas substances with a vapour pressure lower than 10^{-5} kPa are not readily volatilized (Nikunen & Leinonen 2002). When a chemical is highly volatile, its risks in aquatic environments are greatly reduced, as it will volatize into the air and leave the water system. In the air, substances are rapidly diluted and typically more readily degraded than in water (Häkkinen et al. 2010). In relation to their environmental fate, Henry's law constant H (Pa m^3/mol) is also a relevant property, as it characterises the partitioning of a substance between air and the aquatic phase ("evaporation from water"). A Henry's law constant greater than 100 Pa m^3/mol means that the substance evaporates extremely easily; values between 1 and 100 Pa m^3/mol indicate that the substance evaporates relatively easily, and values lower than 10^{-2} Pa m^3/mol indicate that the substance does not evaporate well (Nikunen & Leinonen 2002).

Density (kg/l) is also an important factor determining the final fate of a substance in the aquatic environment. When a substance has a density lower than that of sea water (1.025 g/l at 20°C), it will float, whereas a substance with a greater density than that of sea water will sink (presuming that the compound is neither highly volatile nor water soluble) (GESAMP 2002). Viscosity (cSt) is a property of liquids. Viscosity determines a substance's resistance to flow, and floating substances with a viscosity greater than ca. 10 cSt (at 10–20 °C) have a tendency to form persistent slicks on the water surface

(GESAMP 2002). Besides centistokes (cSt), other units, such as Pa.s (pascal-seconds) and poises (P), can be used for viscosity as well.

The solids-water partitioning coefficient K_{oc} describes the compound's tendency to be adsorbed into suspended matter (e.g. organic particles in the water phase and sediment). When the K_{oc} value is high, i.e. > 5,000, the compound will be tightly bound to organic matter and will not move freely in water. A K_{oc} value between 150–500 indicates that the compound's adsorption to solids is moderate, and K_{oc} values lower than 50 indicate that the compound is not readily adsorbed into particles, and consequently, moves freely in the water phase (Nikunen & Leinonen 2002).

The octanol water partitioning coefficient K_{ow} (typically presented on a logarithmic scale; log K_{ow}) is the ratio of a chemical's solubility in n-octanol and water at a steady state (Nikunen & Leinonen 2002). The log K_{ow} is an indicator of a chemical's lipophility/hydrophobicity, and as n-octanol has similar polarity to animal fats, the log K_{ow} can also be used as an indicator of a chemical's potential to bioaccumulate in organisms. A compound's lipophility and the tendency to bioaccumulate increase with an increasing log K_{ow} value. A log K_{ow} value greater than 4 indicates high and a log K_{ow} value greater than 5 extremely high lipophility (Nikunen & Leinonen 2002). Owing to its high lipophility, a substance that is not originally present in toxic concentrations in the environment may still accumulate in organisms and produce toxic effects in time (Walker et al. 2006). Additionally, some chemicals which accumulate readily in organisms have a tendency to bioconcentrate along the food chain, as the predators receive larger chemical concentrations via food than what the chemical concentration is in the surrounding water (Grey 2002). Therefore, the concentrations of such lipophilic chemicals are typically highest (possibly even up to toxic levels) in top predators, such as fish-eating birds and seals. Even though high lipophility is most often associated with negative consequences for the environment, lipophilic substances are, on the other hand, readily adsorbed into sediment and into organic matter in the water phase. Therefore, lipophilic substances are not necessarily as bioavailable to organisms as highly water soluble substances are. On the other hand, sediment-ingesting and sediment-dwelling organisms, such as oligochaeta worms, may be readily exposed to sediment bound substances (Walker et al. 2006). And, as the oligochaeta worms and other benthos are an important food source for example for fish, even sediment-bound chemicals may be introduced to the pelagic food webs.

As mentioned above, the bioaccumulation tendency of a substance can be roughly estimated from its log K_{ow} value. However, typically more defined and reliable partitioning coefficients are used to evaluate a chemical's bioaccumulation tendency. The bioconcentration factor (BCF) describes the distribution of a substance between the tissues of a fish (or some other organism) and its surroundings (water) (Nikunen & Leinonen 2002). The bioaccumulation factor, on the other hand, is the ratio of a substance between an organism and its food (or ingested water) (Walker et al. 2006). Factors affecting the BCF are: bioavailability, distribution and biotransformation in an organism, and excretion (Nikunen & Leinonen 2002). These processes are typically taking place simultaneously, and it takes some time until a steady state is reached. The biota-sediment accumulation factor (BSAF) is somewhat similar to BCF, only it

describes the distribution of a test substance between sediment-dwelling organisms and their surrounding sediment (OECD 2008). When the test substance concentration in an organism exceeds the concentration in the surrounding medium, i.e. when the BCF or BSAF is greater than 100, this is an indication of bioconcentration (Nikunen & Leinonen 2002). It is recommended that BCF is used in chemical risk assessment over the octanol-water partitioning coefficient, as the former is derived experimentally from fish, whereas the latter is merely a calculated estimation of bioaccumulation. Unfortunately, BCFs are only available for relatively few chemicals and, in addition, there is definitely room for improvement as regards the quality of the existing BCF values (a great deal of uncertainties are associated with the test conditions, for example) (Arnot & Gobas 2006).

Depending on the physico-chemical properties referred to above, a substance that is released in the environment will be distributed between the different environmental compartments. For example, the largest share of a highly water soluble chemical will most likely be found in the water phase, whereas the major share of a highly volatile pollutant will end up in the air phase. Chemicals with a high log K_{ow} (between 4 and 7), on the other hand, are highly lipophilic and will, for the most part, be distributed between the biota and the sediments, as they have a tendency to bioaccumulate in adipose tissue in organisms and be adsorbed into organic particles in the sediment. Typically, water soluble chemicals which are both persistent and bioaccumulative are considered to pose the greatest risk in the aquatic environment (Walker et al. 2006). In addition, when a water soluble chemical has a density higher than that of sea water (i.e. the chemical sinks rather than merely floats on the water surface), it becomes more available to the pelagic biota, which makes the risk of that chemical more evident (Häkkinen et al. 2012). It should, however, be noted that this only holds true in case of "sinker "substances which simultaneously dissolve readily in water. Poorly water soluble sinkers might actually sink all the way to the sea bed and be deposited in the sediments, where they are not very bioavailable for pelagic organisms (GESAMP 2002). Furthermore, floating substances which dissolve readily in water may be as bioavailable as the water soluble sinkers are.

As we have seen, chemicals can behave in a number of ways once they are spilled into the sea. Understanding their behaviour is important; first of all, to recognise the implications chemicals have on human health and the environment, but also to determine the most effective response to chemical spills (ITOPF 2010). Categorizing chemicals based on their behaviour in the sea is a useful tool for these purposes. The European Categorization system classifies chemicals in four main categories based on their theoretical behaviour in the sea. These classes are: gases (G), evaporators (E), floaters (F), sinkers (S) and dissolvers (D) (Bonn Agreement 2007). The basic categories are further divided into sub-categories, and as a result, there are a total of 12 different behaviour categories (Table 2.1). It is important to be aware of the fact that the European classification system only considers the primary behaviour/behaviours relevant to a chemical spill (ITOPF 2010). In reality, however, there are other behaviours a chemical may exhibit in the marine environment due to its properties and environmental conditions (e.g. wind, waves, currents) (CEDRE 2012). Benzene, for example, is classified as an evaporator, but it is also soluble to a certain extent – which

may also have to be considered when predicting its physical behaviour in the sea (ITOPF 2010). Moreover, the European classification system is based on experiments conducted in stable laboratory conditions with pure products, at a temperature of 20 °C and in fresh water (CEDRE 2012). These conditions are far from the natural conditions prevailing at the sea. Therefore, the actual behaviour of chemicals may differ greatly from their theoretical behaviour.

Table 2.1 The European classification system for chemicals. The first letter describes the primary behaviour and the following letter the secondary behaviour. Example substances are given in parentheses. (Modified from Bonn Agreement 2007 and CEDRE 2012)

Main Category	**Gas (G)** (methane)	**Evaporator (E)** (benzene)	**Floater (F)** (palm oil)	**Sinker (S)** (coal tar)	**Dissolver (D)** (phosphoric acid)
Sub-categories	**GD** Gas/Dissolves (ammonia)	**ED** Evaporates/ Dissolves (MTBE)	**FD** Floats/Dissolves (butanol)	**SD** Sinks/Dissolves (dichloroethane)	**DE** Dissolves/ Evaporates (acetone)
			FE Floats/Evaporates (xylenes)		
			FED Floats/Evaporates/Dissolves (ethyl acrylate)		

3 TANK CLEANING IN PRACTICE

Tank cleaning is a routine tanker operation which is carefully controlled by MARPOL Annex II (the Control of Pollution by Noxious Liquid Substances in Bulk). Chemical tanks have to be cleaned whenever new cargo that is not compatible with the previous cargo is to be loaded into the tanks, when tanks need to be gas-free before repairs or maintenance, or when they have to be entered for inspection purposes (Olson 1994). If a tank has not been emptied and cleaned properly, introducing new cargo might result, for example, in an explosion or some other detrimental reaction. In addition, any remaining chemical fumes in a tank would pose a serious safety risk for repair, maintenance or other personnel needing to enter the tank, as the fumes may be both highly toxic and flammable. And lastly, there is a need for efficient cleaning also from the commercial point of view as cargo remnants in a tank might contaminate the following cargo (McGeorge 1995).

Operational cleaning and discharge procedures are outlined in the Procedures and Arrangement manual (P&A manual) which must, as required by MARPOL Annex II, be found on every ship certified to carry noxious liquid substances in bulk (McGeorge 1995). The P&A manual is drawn up in accordance with Annex II and it contains all technical information on the cleaning machinery used in a particular ship, and it outlines the sequence of actions to be taken to ensure that the cleaning procedures and the discharge of hazardous chemical residues is done without threatening the sensitive marine environment (Kunichkin 2006). The tank cleaning process may contain up to seven stages: (1) pre-cleaning, (2) cleaning, (3) rinsing, (4) flushing, (5) steaming, (6) draining and (7) drying (Verwey 2007). Selecting a suitable cleaning practice (e.g. the quantity, temperature, and identity of the washing agent) is highly dependent on both the properties of the cargo that is being cleaned from the tank and the properties of the next cargo that the tank is being cleaned for.

3.1 Cleaning and stripping

A tank can be cleaned from chemical residues by washing it either with fresh or sea water (hot/cold), with a cleaning agent, such as mineral oils and chlorinated solvents, or with a mixture of water and cleaning agent. When the cargo is water soluble, water washing is very efficient, but in case of a hydrophobic cargo, adding detergent is central. Choosing a suitable washing agent is imperative, not only for achieving the best cleaning result, but also because a wrong choice may lead to serious errors and financial losses (Kunichkin 2006). For example, water reactive substances, such as toluene-di-isocyanate (TDI), cannot be cleaned using water, and a solvent must be used instead – using water to clean TDI would lead to formation of insoluble sediments. Moreover, some cargoes may react with certain cleaning agents and form toxic or flammable vapours, or damage the equipment (e.g. pumps) (ICS 2002). The washing media should therefore always be carefully chosen based on cargo properties. Other factors that ought to be considered in choosing the washing media are the type of coating inside the cargo tanks, the size and dimension of the tanks and the loading requirements of the next cargo (Tanker Operator 2008a). A decision on the correct cleaning plan can be made by

consulting the various tank cleaning guides that are available on the market (Kunichkin 2006). The leading independent publication on the subject is the "Tank Cleaning Guide" published by Laboratory Dr. A. Verwey, Rotterdam (Kunichkin 2006), which was also consulted for the purposes of the present study.

Even though it is sometimes necessary to use solvents or small amounts of additives or detergents in the washing water to improve the cleaning effect, water is still the most common washing agent (ICS 2002). It is an efficient cleaner and readily available in large quantities, and it can also be heated in most of the chemical tankers if necessary. As regards the washing media, it should also be noted that when detergents or additives are used to wash cargo tanks, the resulting washings are governed by the provisions of either MARPOL Annex I (oil products) or Annex II, which would apply to the cleaning agent if it had been carried as cargo (Annex II reg. 13.5). Also, if a detergent is added to washing water, additives containing category X components may not be used, except those that are readily biodegradable and present in a total concentration of less than 10% of the cleaning additive (Annex II reg. 13.5). Verwey's Tank cleaning guide (Verwey 2007), for example, recommends that in most cases, 0.05% of detergent be used.

The washings resulting from tank cleaning are typically first transferred into slop tanks on board, from which the residues are later discharged, either into the sea or to a reception facility in a port (McGeorge 1995). Discharge into the sea is predominantly prohibited, while MARPOL Annex II allows it to a certain extent (Annex II reg. 13). First of all, to minimize the risk to the marine environment, the Annex gives a precise description on how the discharge of tank cleaning waters (or ballast waters containing a chemical[6]) into the sea must be performed – the discharge is only allowed if carried out strictly by these guidelines. Moreover, the amount of chemical that is allowed to be discharged per tank is defined in the Annex. For a summary of the discharge requirements for the different MARPOL pollution categories, see Table 3.1.

[6] Chemical tankers typically have segregated ballast tanks, and therefore seldom have ballast waters contaminated with chemicals (HELCOM 1993).

Table 3.1 Summary of the stripping and discharge requirements for noxious liquid substances carried in bulk laid in revised MARPOL Annex II and IBC code. (Modified from INTERTANKO 2006)

Category	**BCH Ships: constructed before 1.7.1986**	**IBC Ships: constructed on or after 1.7.1986 but before 1.1.2007**	**New Ships: keel laid down after 1.1.2007**	**Other than chemical tankers: keel laid down before 1.1.2007**
X	strip 300 + 50 l tolerance prewash max 0.1 % 12 mile 25 m depth 7 knots, en route	strip 100 + 50 l tolerance prewash max 0.1 % 12 mile 25 m depth 7 knots, en route	strip 75 l prewash max 0.1 % 12 mile 25 m depth 7 knots, en route	carriage prohibited
Y – high viscosity / solidifying substance	strip 300 + 50 l tolerance prewash 12 mile 25 m depth 7 knots, en route	strip 100 + 50 l tolerance prewash 12 mile 25 m depth 7 knots, en route	strip 75 l prewash 12 mile 25 m depth 7 knots, en route	carriage prohibited
Y	strip 300 + 50 l tolerance 12 mile 25 m depth 7 knots, en route	strip 100 + 50 l tolerance 12 mile 25 m depth 7 knots, en route	strip 75 l 12 mile 25 m depth 7 knots, en route	carriage prohibited
Z	strip 900 + 50 l tolerance 12 mile 25 m depth 7 knots, en route	strip 300 + 50 l tolerance 12 mile 25 m depth 7 knots, en route	strip 75 l 12 mile 25 m depth 7 knots, en route	Strip to max. extent 12 mile 25 m depth 7 knots, en route
OS	no limitations	no limitations	no limitations	no limitations

First of all, regardless of the pollution category, the discharge operation must be carried out at least 12 nautical miles from the nearest land[7] and at a water depth greater than 25 m (Annex II reg. 13.2). Furthermore, the discharge must be performed at a speed of at least 7 knots en route and below the waterline through underwater discharge outlets to ensure efficient dispersion of the cleaning effluent. As regards category Z chemicals, there are some cases in which less strict requirements are possible (e.g. releasing the washings below the waterline is not mandatory, if the ship is constructed before 1.1.2007; Annex II reg. 13.2.2). And finally, category X, Y and Z chemicals can only be discharged in the sea in dilute concentrations – the degree of which depends on the pollution category of the substance and also on the ship's age, since MARPOL Annex II sets minimum stripping requirements for tankers based on the year of their construction (or conversion) (Appendix 4 to MARPOL Annex II). The smaller the strip (i.e. the amount of chemical that remains in a tank after unloading the cargo), the more dilute the resulting washings will be. For substances belonging to the category OS, there are no restrictions regarding the stripping or discharge of tank cleaning waters, as they are practically harmless in the environment (Annex II reg. 6). In the Antarctic area, which is designated as a "special area" under MARPOL Annex II, any discharge of noxious liquid substances or mixtures containing such substances (e.g. tank washings) into the sea is strictly prohibited (Annex II reg. 13.8).

Because of the advanced technology used in newer ships, the removal of chemical residues from a tank and its associated piping system can be done far more efficiently in comparison to older ships (Hänninen & Rytkönen, 2006). Therefore, more stringent

[7] The term "from the nearest land" means from the baseline from which the territorial sea in question is established in accordance with international law (MARPOL Annex II reg. 1.9).

stripping requirements are set for ships built/converted after 1.1.2007 as well (the maximum strip in all pollution categories 75 l; in comparison, the maximum strip for older IBC ships is 100–300 l) (Table 3.1). The +50 litres mentioned in the criteria summarised in Table 3.1 is an allowable tolerance which should not, however, be interpreted as a standard relaxation (ABS 2006). The tendency of some chemicals (e.g. styrene and palm oil) to form a 0.5–2 mm thick coating on the tank floor and walls is also accounted for in the maximum strip limits (Keskitalo 2012 pers. comm.). When the strip limits are as stringent as they are, the total residual quantity will reach hazardous levels after the possible cargo remnants from tank floor and walls are added to the cargo remnants in the tank well during the washing operation.

The stripping limits given in Table 3.1 apply to an individual tank. A chemical tanker may, however, carry several tankfuls of the same substance simultaneously – all of which may have to be washed. The total amount of discharged chemical residue per ship can be calculated rather simply: if we consider a chemical tanker built before 1 Jan 2007 that is carrying 14 tanks of category Y cargo, the total amount of discharged chemical would be: 14 x 100 l = 1,400 l. This is, however, the *maximum* volume of chemical that is allowed to be discharged within MARPOL's limits. In practice, the strip volume may be somewhat smaller than MARPOL requires. For example, during the stripping test (with water) in one of the sister ships[8] of the Bergen-based shipping company Mowinckel, the remaining cargo residue per tank was found to be 24–50 litres (Tanker Operator 2008b). Consequently, the total chemical residue for that particular ship would be approximately 336-700 l (assuming a cargo capacity of 14 tanks). Moreover, by utilizing the novel *super stripping* technique, it is possible to achieve strips of only 0.5–1 litres in volume (Tanker Operator 2008b). However, as chemical carriers can usually comply with the MARPOL requirements by using the *normal* stripping technique, the somewhat time and effort consuming super stripping technique is seldom used in normal unloading operations. It is generally utilized for a volatile cargo, such as gasoline. In such cases, small cargo residues of 0.5–1 litre can be removed by simple and fast inertion with gas (standard practice). Since any further ventilation (which could take several hours) or mechanical removing of the residues is not needed, time and money are saved.

We should keep in mind that efficient stripping is imperative, not only from the environmental point of view but also because of the purely economic interests of both the owners of the ship and the cargo (GESAMP 2002). For example, if we consider a ship sailing under the BCH Code, under which the maximum strip per tank allowed is 300 l (categories X and Y; Table 3.1), the total chemical residue for the entire ship could in theory be up to 4,060 l (once again assuming a cargo capacity of 14 tanks). The owner of the cargo would probably not appreciate such a large amount of cargo going to waste.

[8] Oil and chemical carriers, keel laid down after 1.1.2007 (Tanker Operator 2008b).

3.2 Prewashing

As seen in Table 3.1, for tanks having contained a highly hazardous cargo (MARPOL category X substances) or high-viscosity or solidifying substances in category Y, MARPOL Annex II requires a prewash procedure. For category X substances, prewashing is required purely due to their hazardousness in the environment, but for the high-viscosity and solidifying substances, prewashing is required mostly because ships carrying these substances could not otherwise meet the stripping requirements (HELCOM 1993). Due to their physico-chemical properties, solidifying and high-viscosity cargoes cannot be pumped as easily from the tanks than other substances. Consequently, the residual quantities of high-viscosity/solidifying substances that remain in the cargo tanks after unloading are much greater than in the case of non-solidifying and low-viscosity cargoes. Without prewashing, the amounts of these chemicals discharged into the sea would be quite extensive.

Prewashing must always be carried out ashore, preferably immediately after unloading (ICS 2002). Generally, the sooner the prewashing is carried out the better the cleaning result. After the prewash is complete, the tank and related pipelines must be thoroughly stripped, and the resulting washings must always be discharged into a reception facility at a port (McGeorge 1995). Chemical residues that remain on tank bulkheads and walls after prewashing can be removed by a subsequent washing operation (which is typically necessary for commercial needs). These "main" washing slops are considered to be dilute enough to be safely discharged into the sea as long as the requirements for the discharge described above are met (McGeorge 1995). Chemical tanks having contained "normal" category Y (other than high-viscosity/solidifying substances) or category Z substances do not, in principal, require a prewash. Prewashing is, however, required if the unloading of these cargoes has not been completed following the ship's P&A manual.

In the prewash procedure, tanks are washed with a suitable washing medium until the chemical content decreases below 0.1 % by weight (Table 3.1). Once the prewash has been completed, a MARPOL surveyor authorized by the Government inspects the cleaning result and verifies that it is, in fact, satisfactory (confirmed by an entry in the Cargo record book[9]) (MARPOL Annex II Reg. 13.6). Moreover, a ship cannot leave the port of unloading until the prewash slops are discharged ashore. This is to ensure that the most hazardous chemical residues will not end up in the sea with further washings. There are no specific stripping requirements for prewash effluents other than that the tank and lines need to be efficiently stripped. In case of high-viscosity and solidifying substances, the tanks must be washed with hot water (temperature at least 60 °C) to facilitate the cleaning process, unless the properties of the substance make washing less effective. The amount of water required in a prewash depends on the quantity of the chemical residue, tank volume, cargo properties, and the maximum concentration required for subsequent washings (Kunichkin 2006). The required water quantity is the greatest for solidifying / high-viscosity category X substances. For cleaning a low-

[9] Every ship to which Annex II applies must have a Cargo Record Book. After completion of any operations relating to loading, unloading, cleaning and discharging of slops etc., the operation shall promptly be recorded in the Cargo Record Book (MARPOL Annex II reg. 15).

viscosity or non-solidifying category X substance, the required water quantity is somewhat smaller, and since category Y substances are considered less harmful than category X substances, the water volume required in a prewash involving them is the smallest. For example, the tank cleaning effluents generated during the prewashing of phenol and styrene are typically 10–30 m^3 per tank (HELCOM 1993).

It is important to be aware of the fact that MARPOL prewashing alone is not a sufficient method for cleaning cargo tanks. The tanks practically always need additional washing due to commercial needs (HELCOM 1993). The commercial (i.e. the main) washing takes at least one hour, but for some cargoes the whole cleaning process may take up to 4–6 hours (flushing, steaming etc. included). As a consequence, the time and therefore also the water quantity required is markedly larger than in prewashing.

3.2.1 Solidifying and high-viscosity substances – definitions and prewash requirements

A solidifying substance is defined in Regulation 1.15 of Annex II as a noxious liquid substance which:

1. has a melting point of less than 15 °C, and which at the time of unloading is at a temperature of less than 5 °C above its melting point; or
2. has a melting point of equal to or greater than 15 °C, and which at the time of unloading is at a temperature of less than 10 °C above its melting point.

Phenol, for example, has a melting point of ca. 41 °C (Lide 2005) and, therefore, the unloading of phenol should take place at a temperature greater than 51 °C (41 + 10 = 51). As this is never true in natural conditions, phenol is defined as a solidifying substance. Other examples of solidifying substances are paraffin wax and slack wax (Kunichkin 2006).

A high-viscosity substance is defined in Regulation 1.17 of Annex II as a noxious liquid substance in category X or Y with a viscosity equal to or greater than 50 millipascal-seconds (mPa.s) at the unloading temperature. Examples of high viscosity substances are sodium hydroxide (viscosity of a 50% solution: 78 mPa.s at 20 °C; CEDRE 2005) and nonylphenol and nonylphenol ethoxylates (viscosity of nonylphenol: 563 mPa.s at 20 °C; HSDB 2012). The definition of viscosity given above means that some vegetable oils may require a prewash procedure. Soft oils, such as rape, soya and sun flower oils, are vegetable oils to which the prewash requirement primarily applies (the BLG working group 2009).

High-viscosity and solidifying category Y substances may avoid MARPOL's requirements for prewash if the cargo is heated during unloading. For solidifying substances, the following requirements must be met to avoid prewashing:

- cargoes with a melting point of less than 15 °C must be unloaded at a temperature of at least 5 °C above its melting point
- cargoes with a melting point equal to or greater than 15°C are to be unloaded at a temperature of at least 10 °C above their melting point (Kunichkin 2006).

We should note that if the unloading temperature of high-viscosity / solidifying substances is lower than required, the prewash becomes mandatory. In practice, high-viscosity and solidifying category Y substances can seldom avoid the prewash requirement even if they were heated during unloading (Keskitalo 2012 pers. comm.). This is because the cargo does not typically stay heated during the entire unloading process due to shortcomings in the available heating techniques. At present, there are two prevailing cargo heating systems: in the first one, heating coils are installed inside a tank, whereas the second system is based on recirculating the cargo through cargo heaters on deck. Of the two systems, the latter is more efficient in keeping the cargo heated. In the former, the heating coils are situated a few centimetres *above* the tank top. Such placement leads to a forming of a cold space below the heating coils, which tends to cool the cargo down. A ballast water tank situated under cargo tanks adds to the cooling effect as well, even when empty. There also is a new heating system that offers an alternative for heating coils and up-deck cargo heaters. In this new system, heating ducts are installed *under* the tank top. This way there are no cold spaces, and the tank top itself acts as a cargo heater. Heating ducts are an even more efficient heating system than recirculating the cargo through the up-deck cargo heaters. With heating ducts, the cargo can be kept liquid and problems with solidifying cargoes are nearly non-existent. However, heating ducts are not only a new but also a fairly expensive system to install. Consequently, they are yet to become more common in chemical tankers of today.

3.3 Ventilation

In case of highly volatile chemicals (whose vapour pressure exceeds 5 kPa at a temperature of 20 °C), the residues from tanks can be removed by ventilation alone (Appendix 7.1 to Annex II). For example, benzene and ammonia, with vapour pressures of ca. 10 kPa (at 20 °C) and 880 kPa (at 21 °C) respectively (EnviChem 2012; CEPA 2001a), are chemicals whose residues can be ventilated. Biofuels and ethanol fuel mixtures are other examples of substances whose residues can typically be removed by ventilation (Vähätalo 2012 pers. comm.). The ventilation procedure is preferable than water washing when possible, as unnecessary cleaning of tanks with water or with other cleaning agents loads the environment. MARPOL Annex II contains no regulations on where the ventilation of cargo residues must be performed, but port authorities may have their own regulations that prohibit it in their docks (Kunichkin 2006). This is the case in almost all Finnish ports (Vähätalo 2012 pers. comm.). This is mainly because some gas vapours are extremely toxic and flammable and can be harmful to human health (Kunichkin 2006). Benzene, for example, is a known human carcinogenic and chronic exposure to its vapours can cause leukaemia even in very low concentrations (few parts per million = ppm) (Majima et al. 2000). Furthermore, when considering the whole transport chain of benzene (loading, navigation, unloading, cleaning), the cleaning of the tanks is the very phase where the largest amounts of benzene gas are emitted into the air (Majima et al. 2000). Considering the safety of port personnel and the fact that ports are typically located near settlement, it is quite understandable that ventilation is not allowed in the docks. When ventilation of chemical residues from tanks cannot be accomplished ashore, it is executed at sea.

In the ventilation procedure, tanks are ventilated until no visible remains of liquid can be observed (Kunichkin 2006). On the completion of the ventilation process, an inspection by a MARPOL surveyor is required before the ship can leave the port (to ensure that the tank is in fact clear of hazardous cargo residues) (Vähätalo 2012 pers. comm.). Any water introduced in the tank subsequent to ventilation is regarded clean, and therefore, any washings subsequent to ventilation are not subject to the discharge requirements of MARPOL Annex II (reg. 13.3). Additional water washing prior to ventilation may be needed in some occasions – typically, when the cleaning result by ventilation alone does not meet the commercial requirements for loading the next cargo (ICS 1995).

4 TANK CLEANING AND THE ENVIRONMENT

To examine the environmental impact of tank cleaning effluents, several reports and scientific papers addressing the environmental impact of maritime transport of chemicals were reviewed. It became clear that the number of studies focusing on the risks of marine transport of oil is far greater than that of studies focusing on the risks arising from chemical transportation. In addition, most of the studies, both on oil and chemical shipping, are focused on large spills resulting from shipping accidents (the size of which typically is on a scale of hundreds or even thousands of tonnes; HELCOM 2002). Studies on the impact of chronic pollution from routine shipping operations, such as tank cleaning and bilge water handling, where smaller spills occur more or less frequently, are relatively few – particularly in case of chemicals. This is partly due to the "invisible" nature of operational discharges (Ng & Song 2010): the amounts of hazardous substances that are released at a time are relatively small and the consequences cannot be seen instantly. In contrast, a spill from a disastrous shipping accident may exceed a thousand tonnes at worst, and the consequences can typically be seen immediately (e.g. surfacing of dead fish[10]). In addition, large tanker accidents are typically well covered by the media, whereas minor discharges resulting from routine shipping operations are rarely considered newsworthy. All in all, due to its invisibility, the issue of chronic pollution resulting from operational discharges has been, at least to some degree, overlooked by both researchers and the shipping industry (Ng & Song 2010). In this Chapter, the environmental impact of operational discharges resulting from tank cleaning is reviewed. The impact of oil was included, as the literature on operational chemical discharges was very limited.

4.1 Oil

Despite its invisible nature, chronic operational pollution from commercial ships may still be a significant threat to the marine environment. It has been estimated that oil discharges resulting from routine shipping operations (including illegal discharges) greatly exceed the amounts of oil that are being released during large tanker accidents (Hampton et al. 2003). In the EU alone, operational oil discharges have been estimated to equal 8 Exxon Valdez sized spills every year (Camphuysen 2007). The worldwide releases of oil have been estimated to be approximately 1 million tonnes per year, which is as a substantial reduction from the ca. 6 million tonnes per year rate in the 1970s. However, we should note that these numbers are rough estimations, as adequate information on the current pollution status is scarce. Even though the amount of oil that is released in the sea in a single incident of operational discharge is small, at least in comparison to accidental oil spills, the overall environmental impact may be quite significant. It is not only the size of the spill that determines the severity of the environmental impact but also the type of oil, weather conditions (e.g. wind and waves) and overall sensitivity of the area where the spill happens that matters. Even small amounts of oil may kill large amounts of sea birds, as noted by Hampton et al. (2003).

[10] In July 2000, 2 tonnes of nonylphenol ethoxylate leaked from an Italian tanker Crystal Rubino in the Port of Hamina due to overloading. Dead fish surfaced almost immediately. Long-term effects, e.g. those affecting birds, may also have occurred (Helsingin Sanomat 2003).

Consequently, chronic oil pollution may actually be far greater a threat to aquatic biota than large oil tanker accidents (Hassler 2011).

Operational discharges of oil have historically resulted mostly from two sources: cargo tank cleaning and oil contaminated ballast waters (Hampton et al. 2003). Nowadays, segregated ballast tanks (SBT) in ships have significantly reduced the problem of oil contaminated ballast waters. Consequently, tank cleaning remains the main source of operational discharges of oil. Moreover, methods such as "load on top" (LOT) and crude oil washing (COW) have significantly reduced the amount of oil that is being released into the environment because of tank cleaning (Hassler 2011). The former refers to a method were oil-water mixtures generated during tank cleaning are not discharged overboard but transferred into a designated slop tank instead. Since oil is lighter than water, it will gradually separate from water during the voyage and settle on top of it. The more or less clean water phase can then easily be pumped out of the tank and discharged into the sea. The next oil cargo in the loading port may then be loaded on top of the previous oil remnants. Crude oil washing, on the other hand, is a cleaning technique where, instead of using sea water, the tanks are washed with crude oil itself. Washing the cargo residues on the tank walls and bulkheads with oil dissolves the residues into the oil, after which they can be pumped out and reunited with the rest of the cargo. Crude oil washing generates practically no cleaning effluents, which makes the COW method profitable from both the environmental and the commercial point of view. Finally, a significant factor that has reduced the problem of chronic oiling is free reception facilities in ports ("no special fee system"). In the Baltic Sea area, for example, major ports are required to supply reception facilities for oily residues from tankers and arrange for the proper disposal of the effluents. Most importantly, the ports are not allowed to charge the vessels any extra fees for using their reception facilities.

The Baltic Sea is defined as a special area under MARPOL Annex I, which means that any discharge of oil or oily mixtures is prohibited there[11] (HELCOM 2010d). Unfortunately, the MARPOL regulations are rather systematically violated. For example, in 2011, there were 122 confirmed illegal oil discharges in the Baltic Sea area (HELCOM 2011). However, the number of discharges detected has been constantly decreasing over the last 20 years, despite the ever growing traffic, so there has definitely been some improvement in terms of compliance with the MARPOL regulations. The total estimated volume of oil spills observed in 2011 was on average 24 m^3, and most of the spills (93%) were smaller than 1 m^3. However, as noted by Hassler (2011), oil spills are detected by means of aerial surveillance, which is typically carried out during the day. Since illegal discharges are more likely to occur during the night, a considerable amount of deliberate discharges may go unnoticed. According to HELCOM (2011), of all the aerial surveillance flight hours in 2011, only 15% were carried out at night (this figure for 2010 being 12%). The scale of chronic oil pollution can, in addition to aerial surveillance and other visual observation methods, be estimated indirectly by following port statistics of, for example, the discharge of oily wastes into reception facilities, and by systematically counting beached sea birds contaminated by oil (Camphuysen 2007).

[11] Outside special areas, an oil tanker of 15,000 dwt could, within the limits of Annex I, release 500 and a tanker of 100,000 dwt, 3,300 l of oil residues into the sea (Tanker Operator 2008b).

Beached bird surveys have been proven to be an effective and sensitive way of estimating the degree of chronic oiling in many case studies in the North Sea (Skov et al. 2011). In the Baltic Sea, similar systematic surveys have been scarce.

Sea birds are the organism group that suffers the most from oil pollution. Birds are affected by oil in many ways, but the most detrimental one is oil's ability to adsorb to feathers and damage the insulating properties of the plumage (Camphuysen 2007). Without insulation from the cold, birds cannot survive in the marine environment. In addition to the acute effects of oil, oil may also affect birds and other organisms in the long term (e.g. by affecting growth and weakening the immunity system; Helle & Kuikka 2010). Bird species living offshore are the most susceptible to the impacts of oil. When Hampton et al. (2003) evaluated the risks of tank cleaning effluents containing oil to sea birds on the Californian coast, they hypothesized that constant discharges of tank cleaning effluents could very well cause significant population-scale effects on offshore birds. Some species of auks and storm-petrels, for example, spend extensive periods of time breeding and foraging in waters which were assumed to be frequently receiving oily tank cleaning waters (Hampton et al. 2003). The authors also concluded that it was possible that bird populations could also be impacted on a regional scale along the busiest shipping routes. Clear examples of this are the coasts of Canada, which are riddled with busy shipping routes. Hundreds of thousands of sea birds living there are killed each year from operational oil discharges from commercial ships (Hampton et al. 2003, Environment Canada 2011).

Sea birds are affected by chronic discharges of oil in the offshore waters of the Baltic Sea as well. In Southern Sweden, chronic oiling has been estimated to be a significant cause of mortality in wintering offshore birds, particularly in long-tailed ducks *Clangula hyemalis* and black guillemots *Cepphus g. grylle* (Skov et al. 2011). The numbers of long-tailed ducks affected by oil have been surveyed in Southern Gotland for 15 years (Larsson & Tydén 2011). In the study period between 1996/97 and 2003/04, it was estimated that in central Baltic Sea, tens of thousands of long-tailed ducks were injured annually by oil (Larsson & Tydén 2005). Moreover, when long-tailed ducks caught in fish nets near Hoburgs Bank (a shallow offshore area to the southeast of Gotland) were analysed, it was found that 11.8% of the 998 birds analysed had oil on their plumage. During the latest study period (from 2007/08 to 2010/11), the number of long-tailed ducks contaminated by oil decreased from the previous years. However, it was not clear whether the decrease stemmed from the decreasing number of operational oil discharges or from an overall declining trend in long-tailed duck populations in the Baltic Sea area. Moreover, since two of the winters during the study period were particularly cold, parts of the study locations were covered by ice in the wintertime. Because the ice prevented the affected birds from washing ashore, the number of oiled birds was most likely underestimated (Larsson & Tydén 2011).

As discussed above, due to such factors as effective surveillance and free reception facilities at ports, illegal operational discharges of oil have been decreasing in recent years in the Baltic Sea waters. However, despite the positive trend, chronic oiling still remains a significant hazard to the Baltic Sea environment, particularly to offshore sea birds.

4.2 Chemicals

Operational discharges of chemicals mainly consist of effluents generated during tank cleaning. According to Maffii (2007), the volume of tank cleaning effluents containing a chemical released into the sea worldwide is estimated to be 7 million tonnes every year. The volumes have increased substantially from the 1970s, when the estimated annual discharge rate of tank cleaning effluents containing a chemical was approximately 10,000 tonnes (Lakey 1975/76). Operational chemical discharges also exceed operational oil discharges quite extensively. Of course, in contrast to oil, the discharge of chemicals in tank cleaning waters is allowed in the Baltic Sea, and in fact, all over the world (excluding the Antarctic) if certain conditions are met (see section 3.1). It is therefore understandable that the volume of operational chemical discharges is larger than the volume of operational oil discharges.

Factors reducing the risk arising from tank cleaning effluents

As regards tank cleaning, the degree of environmental exposure is largely dependent on the quantity of chemicals that remains in a tank after unloading. Because of the special stripping appliances used in chemical tankers today, these "strips" are in practice quite small – typically less than 100 litres (GESAMP 2002). Moreover, with the latest techniques, it is possible to drain the tanks almost completely dry (only a strip of a few litres remaining after super stripping; Tanker Operator 2008a). Unfortunately, at present, this super stripping system is very rarely utilised in unloading.

Cargo tanks are typically made of (or coated with) stainless steel, which makes their inside surface smooth and therefore relatively easy to strip and clean (McGeorge 1995). Easy and fast cleaning minimises the amount of water needed in tank cleaning, and consequently, the amounts of slops generated during the entire cleaning process. Some chemical tanks may also be coated with epoxy, polyurethane, zinc silicate or phenolic resins depending on the cargo to achieve even more efficient cleaning results. The efficient stripping and cleaning techniques have enabled the stringent stripping requirements laid down in the revised MARPOL Annex II that entered into force in 2007.

In addition to setting the maximum limits for strip quantities, the Annex also governs the discharge of effluents: how and where it must be carried out. By following the MARPOL requirements for discharge, an effective immediate dilution of tank cleaning slops can be achieved (Mercier et al. 1973). First of all, when the discharge of tank cleaning slops is done below the waterline and at a speed greater than 7 knots, the flow will carry the slops into the propeller, where they will be broken up and be well dispersed and diluted in the propeller's wake (McGeorge 1995). In theory, the chemical concentration will not exceed 1 ppm after this. If the discharge were not performed as required by MARPOL, e.g. it were carried out from a dragging ship and over the side, the initial dilution would be inefficient and the harmful substances would precipitate on the same location making the environmental hazard considerably greater. However, as regards the dilution of effluents, it must be noted that even though pollutants are considered to disperse and dilute fairly well in the sea (especially when the discharge is

carried out as required by MARPOL), hydrophobic substances which adsorb to particulate matter are carried by water currents and are therefore typically precipitated on the same location (Walker et al. 2006).

The reason behind the MARPOL requirement stating that tank cleaning effluents must be discharged in waters at least 25 metres deep is to ensure that the water volume at the discharge location is great enough to allow a high degree of dilution. In oceans, the dilution and also the degradation of harmful substances is particularly efficient because of their enormous size and water currents, but lakes and small inland seas are of a completely different nature (Walker et al. 2006). The Baltic Sea, in particular, is of great concern regarding chemical (and oil) discharges. The Baltic Sea, being a semi-enclosed inland sea, has a very slow water exchange rate. This combined with the low temperatures of the northern climate makes the Baltic Sea highly vulnerable to hazardous substances, as these factors result in slow dilution and degradation of substances (HELCOM 2010c).

Case studies

No previous assessments of chemical concentrations resulting from operational discharges from chemical tankers in the Baltic Sea were found in this study. This may partly be because evaluating the scale of chronic chemical pollution from ships is quite challenging. First of all, many chemicals dilute and/or volatize very rapidly once they are released into the sea and cannot therefore be detected as easily as, for example, oil (Hurford et al. 1989). Moreover, due to the background pollution in the sea (e.g. from land and atmospheric sources), measuring chemical concentrations in the sea is not the most reliable indication of the scale of chronic pollution caused by shipping. Analysing water samples for chemicals indicates whether the sample is contaminated or not, and by which chemical(s), but it does not, however, specify the origin of the chemical(s). Several general screening surveys have been conducted on chemical concentrations in different parts of the Baltic Sea (e.g. Lilja et al. 2009, HELCOM 2010c, Andersson et al. 2012). However, these screenings focused on chemicals and chemical groups that are of high concern in the Baltic Sea area, many of which originate from atmospheric sources and/or from land, rather than being transported in bulk by chemical tankers (e.g. dioxins, furans and heavy metals). Some of the target chemicals could in theory originate, at least partly, from tank cleaning (e.g. nonylphenol and nonylphenol ethoxylates), but none of the projects have singled out operational discharges from chemical tankers as a possible source of chemical contamination in the Baltic Sea.

In the North Sea, two case studies have been conducted where the risks of discharging tank cleaning effluents into the sea were evaluated. These studies were conducted by Hurford et al. (1989, 1990) who did a sampling survey on the concentrations of certain chemicals in the North Sea that were known to be discharged with tank cleaning waters into the sea. Isopropyl benzene, perchloroethylene, phenol and di (2-ethylhexyl) phthalate were selected as target chemicals in their first study. The sampling survey was accomplished twice – before and after the implementation of MARPOL Annex II – to evaluate whether the MARPOL discharge requirements had a positive effect on chemical concentrations in the North Sea. One objective of the sampling surveys was to

discuss whether there was a need to declare the North Sea a special area (Hurford et al. 1989). At the time, only the Baltic Sea and the Black Sea had been designated special areas under Annex II. In addition to measuring chemical concentrations in locations where discharging of tank cleaning slops was considered to be most likely, the authors produced estimates of discharge concentrations based on the import volumes of the target chemicals to North Sea ports and the residue quantity estimated to remain in a cargo tank after unloading (= the strip). The properties of the North Sea (water volume and exchange time) were also considered in the calculations.

In the first study (conducted in April 1986), the measured chemical concentrations were analysed from samples taken from 32 sampling stations along the Eastern coast of England (near UK ports where target chemicals were typically unloaded) and in the central North Sea. The measured concentrations were in most cases between 0.001 and 0.1 µg/l, and they were generally of a similar magnitude as the modelled concentrations. According to Hurford et al. (1989), the 96h LC_{50} values of the target substances were in the range of 1–100 mg/l. Since the measured concentrations were four or five orders of magnitude lower than the corresponding toxicity values, the authors concluded that the measured concentrations of the target chemicals would not be likely to cause significant harm to the marine environment. However, as the authors noted, in assessing ecological risks from short-term toxicity values determined in stable laboratory conditions in single species tests, a measure of caution is definitely called for. The acute toxicity values are rough estimates of toxicity at best. It is also important to be aware of the fact that the measured concentrations account not only for pollution caused by operational discharges from chemical tankers but for all pollution from various sources (e.g. from land, air and offshore installations, such as oil platforms). The results of the first sampling survey suggested that even before the implementation of MARPOL Annex II, the discharge of tank cleaning effluents into the sea did not cause a significant pollution problem in the North Sea area (Hurford et al. 1989).

The second sampling survey in the North Sea (Hurford et al. 1990) was conducted approximately 18 months after the implementation of MARPOL Annex II (in October 1988). There were a total of 40 sampling stations, and the concentrations of chlorobenzene, ethylbenzene, styrene and xylene were now measured from samples in addition to the four chemicals whose concentrations were also measured in the first survey (Hurford et al. 1989). The results of the second survey reinforced the conclusion inferred in the first survey: the discharging of tank cleaning effluents in the North Sea did not cause significant harm to the North Sea biota. The measured concentrations were once again extremely low, most of the time even below the detection limits of the available technique. The modelled concentrations were in the same range as the measured values. The measured concentrations were three or four orders of magnitude lower than the 96h LC_{50} values of the target chemicals. In other words, the chemical concentrations were now even lower than they were in the first survey. The authors, however, noted that the results of the two surveys could not be compared without reservation, as weather conditions during the second survey were more severe. Wind and waves, for example, may have increased the elimination rates of volatile chemicals from water into the air and amplify the mixing of waters in the water column. Moreover, the transportation volumes of a chemical may have changed between the

surveys, and there may also have been changes in pollution from other sources. However, despite these uncertainties, it could be concluded that the implementation of MARPOL Annex II had decreased chemical concentrations in the North Sea. Consequently, it seemed that tank cleaning effluents were not a significant environmental threat in the North Sea.

Even though the results of Hurford et al (1989, 1990) indicated that tank cleaning did not pose a significant threat to the aquatic organisms in the North Sea, this does not guarantee that tank cleaning does not cause pollution in the Baltic Sea. As noted before in section 2.1, the Baltic Sea is a shallow inland sea with a long water turnover time. Consequently, dilution and dispersion are not as extensive, and degradation is not as rapid in the Baltic Sea as it is in the North Sea. Moreover, as noted by the GESAMP Working group (Portmann 1981), chemicals that have a tendency to bioaccumulate in organisms pose a special risk in the environment, even when singular releases are small. When small amounts of chemicals are released in the sea more or less frequently, the chemical concentrations may bioaccumulate in organisms and eventually reach toxic levels causing delayed toxicity. None of the chemicals targeted by Hurford et al (1989, 1990) were particularly persistent or bioaccumulative. Many of them were highly volatile: only styrene, di (2-ethylhexyl) phthalate and phenol were non-volatile substances. Moreover, phenol degrades rather rapidly in water (CEPA 2000). However, the measured concentrations of styrene and di (2-ethylhexyl) phthalate in the water samples were still very low in general (below 0.01 µg/l for styrene and below 0.05 µg/l for DEHP; Hurford et al. 1990). Also measuring chemical concentrations from fish samples could have told us more about environmental exposure to tank cleaning effluents, especially in terms of the more hydrophobic chemicals. Oost et al. (2003) reviewed the use of fish bioaccumulation biomarkers in environmental risk assessment quite extensively, and according to them, screening chemical concentrations in fish could be an effective way of gaining knowledge of site-specific pollution when used in compliance with other monitoring methods.

Operational discharges of oily non-mineral oil substances

As demonstrated by the sampling surveys conducted by Hurford et al. (1989, 1990), implementing MARPOL Annex II in 1983 lowered the chemical concentrations in the North Sea. The revision of MARPOL Annex II (in 2007) has probably reduced the pollution arising from tank cleaning washings even further, but this is not certain, as the subject has not been studied. The revision contains some important improvements: stricter stripping limits, re-classification of several substances from category D to the scope of MARPOL, and consequently, enforcement of in-port prewashes, not only for the most hazardous category X cargoes but also for many high-viscosity and solidifying cargoes that were previously in category D (ABS 2006).

Prior to the revision, all animal and vegetable oils and fats (e.g. palm oil and paraffin wax) were classified in category D, which meant that they were considered only a minor hazard if released in the sea (Lloyd's Register 2006). In addition, they did not require a prewash procedure. However, these substances behave very similarly to mineral oil in the marine environment: they form floating slicks, they are toxic, and they damage the

cold insulation of bird plumage (Dahlmann et al. 1994). There have, in fact, been several cases where animal and vegetable oils and fatty products discharged into the sea with tank washings have caused substantial bird kills (Camphuysen et al. 1999 and the references therein). For example, when Dahlmann et al. (1994) surveyed beached birds in the North Sea (the coasts of Germany, the Netherlands and Denmark) in 1990–1993, they found that chronic oiling, mostly due to tank washing, was the main cause of bird deaths in the North Sea. However, the surveyed birds were greatly affected by palm oil, paraffin wax and other MARPOL Annex II (category C and D) substances as well. Even highly toxic category A chemicals were detected in the birds' plumage (e.g. dodecylphenols and bisphenols). The phenolic compounds were found to originate from lubricating oil additives. In general during the study period, the German and Dutch coasts suffered constantly from palm oil and paraffin wax pollution. There were several reported pollution incidents involving both substances – all due to legal discharges of tank cleaning effluents (Dahlmann et al. 1994). Some of the reported incidents were more severe than others, and there even was one case on the coast of Netherlands where paraffin wax caused the death of approximately 2,000 seabirds and a significant overall pollution of beaches. In addition, on one occasion, 8 tonnes of paraffin wax had to be cleaned from the beaches. Based on these findings, it is obvious that chronic discharges of animal and vegetable oils and fats can cause substantial damage to marine biota.

The extensive pollution described above was mainly a consequence of the current state of law. At the time, MARPOL regulations did not demand in-port prewashes for tanks that had contained category D substances, regardless of whether they were high-viscosity or solidifying substances or not. However, as noted by the then MARPOL surveyor of Kotka District, Mr. Hannu Lappalainen (HELCOM 1993), residues of high-viscosity and solidifying cargoes may be quite extensive after unloading. There had even been a case where after unloading phenol from two cargo tanks, the amount of phenol remnants had amounted to over 35 tonnes – even though the cargo was heated during unloading. This is a rather good demonstration of the importance of prewashing in keeping pollution from high-viscosity and solidifying cargoes at accepted levels.

The hazards of vegetable oils were recognized in the revision of MARPOL Annex II. At present, all animal and vegetable oils and fats belong to MARPOL category Y (Lloyd's Register 2006), meaning that they are considered a moderate hazard in the marine environment. Moreover, many of these oils and fats are either high-viscosity or solidifying substances and therefore fall under the prewash requirement. Consequently, the amounts of animal and vegetable oils released in the sea with tank washings can be expected to be reduced from the pre-revision times. However, no clear scientific evidence on the subject could be found.

In addition to animal and vegetable oils, many other substances were also re-classified from category D to category Y in the revision. A good example is caustic soda (sodium hydroxide) (Lloyd's Register 2006) – one of the most frequently handled chemicals in Baltic Sea ports (Posti & Häkkinen 2012). Consequently, the amounts of caustic soda and also other re-classified substances that are being discharged into the sea with tank cleaning slops have probably decreased as well, although once again, this is a purely hypothetical assumption. As caustic soda is a high-viscosity cargo, tanks having

contained it must now be prewashed ashore, and the prewash slops must be discharged to a reception facility.

In conclusion, oily non-mineral oil substances (e.g. vegetable oils) and fatty substances seem to be, if not the greatest, at least the clearest hazard arising from discharging tank cleaning effluents in the environment. The discharging of non-persistent (e.g. volatile and/or readily biodegradable) substances with tank cleaning effluents, on the other hand, does not seem to cause a significant hazard to the marine environment. In addition, when considering the reasonably high degree of deliberate oil discharges in the Baltic Sea, we cannot help but wonder how these two individual sources of chronic pollution affect aquatic biota when combined. Further research may be needed to evaluate whether the chronic discharge of tank cleaning slops containing chemical adds to the hazards arising from chronic oiling, or vice versa.

5 EVALUATING THE ECOTOXICOLOGICAL EFFECTS OF TANK CLEANING

The purpose of this study was to re-evaluate the potential environmental effects tank cleaning waters may have once they are released in the Baltic Sea. The impact of in-port prewashing on chemical concentrations in the sea was also studied. The evaluation was carried out based on a literature survey and previous studies. For practical reasons, it was impossible to evaluate the effects of all the thousands of chemicals that are transported by sea and that may consequently be discharged into the sea with tank washings. Therefore, this study first selected a few target substances which were known to be particularly hazardous in the marine environment based on existing literature and which were known to be transported regularly and in high volumes in the Baltic Sea. The risks of each target substance were then characterised by comparing the predicted exposure of the substance (expressed as the Predicted Environmental Concentration, PEC) to the toxicity of the same substance (expressed as the Predicted Non Effect Concentration, PNEC). The risk of each target substance was indicated by the ratio of its PEC and PNEC concentrations – a method also used in the EU risk assessment procedure (EC 2003). For a schematic illustration of the chemical risk assessment procedure, see Figure 5.1.

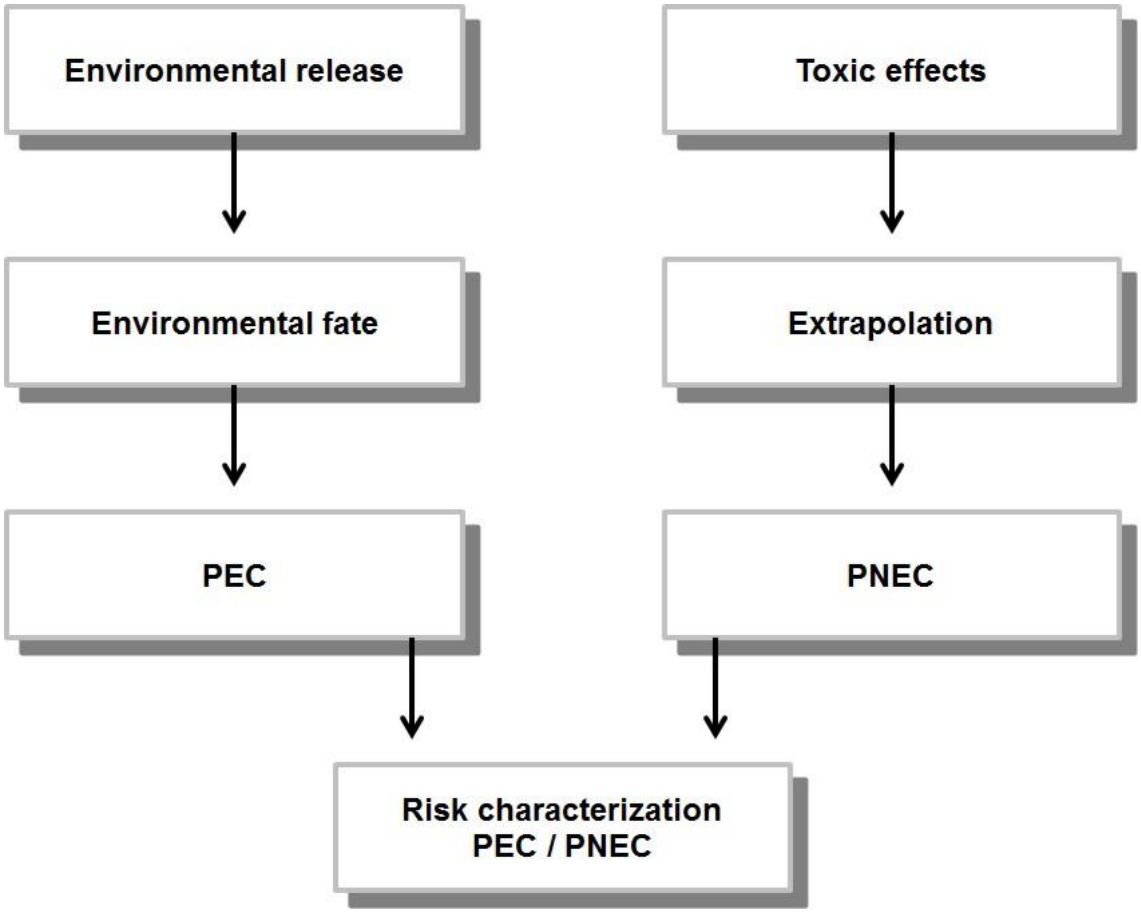

Figure 5.1 Chemical risk assessment procedure. (Nikunen & Leinonen 2002)

5.1 Target substances

The target substances for this study were chosen by utilizing the results of previous studies. Since the scientific definition of a risk includes both the probability of the event (e.g. chemical spill) and the severity of the impact resulting from that event (Helle & Kuikka 2010), these factors were also taken into account when selecting the target substances for the present study. First of all, as Hurford et al. (1989) noted regarding evaluating the impact of tank washing, it is imperative to concentrate on substances which are, in fact, being unloaded in the ports of the studied area. This is because tank cleaning and subsequent discharges are most likely to occur after cargoes are unloaded in ports. Consequently, assessing the environmental impact of hazardous substances that are not unloaded in Baltic Sea ports would be entirely beside the point of this study. However, gathering information on what substances are actually unloaded in Baltic Sea ports, and thus involved in tank cleaning, turned out to be rather problematic. For example, there is a nationwide vessel traffic system called PortNet in Finland which gathers various data on ships that call at Finnish ports (the information that is collected includes routes, cargo, hazardous cargo and maritime fees), but the system is, however, best suited for gathering information on exports rather than imports (Posti & Häkkinen 2012). Therefore, the import data acquired from PortNet may have some deficiencies and should be approached with caution. Moreover, separate import and export data on liquid bulk chemicals was not available from the other Baltic Sea states. Therefore, the next best thing was to concentrate on chemicals which were known to be transported frequently and in high volumes in the Baltic Sea area. Even though the transport volume of a particular chemical may not tell us much about the chemical's role in tank cleaning, at least it indicates that the chemical could in theory be washed into the Baltic Sea.

According to Posti & Häkkinen (2012) who, based on secondary literature sources, conducted a survey of the volumes and identities of liquid bulk chemicals that are being transported by ships in the Baltic Sea region, the most frequently handled chemicals in the Baltic Sea ports are methanol, sodium hydroxide solution, methyl tert-butyl ether (MTBE), xylenes, pentanes, ammonia, phenol, phosphoric acid, sulphuric acid and ethanol and ethanol solutions. In addition to these substances, the authors identified other high volume substances, such as ethylene, propane and butane. Furthermore, large amounts of fertilizers and vegetable oils are shipped in the Baltic Sea area as well (Posti & Häkkinen 2012).

As the magnitude of risk arising from chemical discharges depends greatly on the hazardousness of the chemical, it was reasonable to select target substances which were known to be more or less hazardous in the aquatic environment. As mentioned earlier in section 2.4, the greatest risk to the aquatic environment arises from chemicals that are toxic, highly soluble in water, persistent and with a tendency to bioaccumulate (Walker et al. 2006). In regard to selecting the target substances, there were few chemical risk assessments available in which chemicals shipped in bulk were scored and ranked according to different parameters (e.g. transport volumes and environmental end-points, such as toxicity to aquatic organisms and persistency). However, as the scientific literature on chronic pollution resulting from maritime transport of hazardous

substances is in general rather scarce, all the assessments were based on larger accident-sized chemical spills. However, it was justified to also use these rankings in this study, as the estimated environmental parameters are essentially the same regardless of the size of the spill (which, compared to shipping disasters, is undeniably significantly smaller in case of tank washings).

Regarding methodology, French McCay et al. (2006) estimated the potential ecological consequences of chemical spills of difference sizes (0.5; 10 and 1,000 tonnes) using a predictive spill model together with chemical hazard quotients. The model was run for a selected range of chemicals typically shipped in bulk, and it estimated areas where the predicted no effect concentration (PNEC) might be exceeded after the spill. The authors concluded that of the 25 chemicals assessed, phenol and formaldehyde were the most hazardous to aquatic biota, followed by ammonia, chlorobenzene, tetraethyl lead, acetaldehyde, xylene, ethylbenzene, styrene and carbon tetrachloride. The HASREP (2005) project, on the other hand, focused mainly on the transport volumes of chemicals. The project identified 100 of the most transported harmful chemicals between major EU ports (including trade through the English Channel). The project assessed both the transport volumes and GESAMP hazard profiles, and as a result identified the most hazardous chemicals to the marine environment. Based on their assessment, the HASREP project highlighted substances such as styrene, benzene, vegetable oil, methanol, xylene, molasses, phenol, vinyl acetate, toluene, sulphuric acid and acrylonitrile. However, it was recognized that even though these substances have a relatively high probability of spillage, all of them will not necessarily, if spilled, have a significant impact on the marine environment (HASREP 2005). The priority list composed by Häkkinen et al. (2012) was also helpful in selecting the target substances for the present study. In their list, Häkkinen and his colleagues ranked 30 of the most transported substances in the Baltic Sea region based on their transport volumes and environmental hazardousness. The scoring system had similarities with the other systems mentioned, but it had a clear advantage over the others in that it was devised specifically for the Baltic Sea region. The chemicals that scored highest in the list were nonylphenol, sulphuric acid, creosote, phenol and ammonia (positions in the priority list 1–5, respectively) (Häkkinen et al. 2012). All of these substances present a great hazard if released into the marine environment, and all of them are also transported in relatively high volumes (contributing to the probability of an accident). Besides these five substances, benzene, styrene, xylenes and MTBE ranked relatively high on the list as well.

There were also other valid risk assessments available as regards chemicals and aquatic environments. Guerbet & Jouany (2002), for example, used a simplified risk assessment method (SIRIS) and ranked 90 chemicals based on both exposure (water solubility, lipophility, vapour pressure, persistence) and effect criteria (BCF, LC/EC/LD_{50}) to identify the substances that might present a risk to the aquatic environment. However, the substances evaluated consisted of various kinds of pesticides and industrial chemicals, and only a few of them appeared in the other rankings. Benzene, for example, ranked 6th, ethylbenzene 18th and toluene 74th. Interestingly enough, xylenes, which were ranked reasonably high in other scoring systems, were at the bottom of the list (88th place) composed using the SIRIS method (Guerbet & Jouany 2002).

As we can see from the above, the chemicals that are stressed vary more or less depending on the scoring method used. This is quite understandable as the outcome of the scoring depends greatly on whether emphasis is given to transport volumes, environmental end-points or both. There were, however, some substances that appeared in several of the listings – ammonia, phenol, sulphuric acid, xylenes and styrene, to name a few. For a summary of the chemicals that were, based on the studies and projects mentioned, selected as target substances for this study, see Table 5.1. Only substances that were mentioned more than once were selected. An exception to this rule is nonylphenol, which was selected as a target substance even though it was only mentioned in one of the listings (in Häkkinen et al. 2012). But as it was ranked the most hazardous substance on this list, a decision was made to include it in this study. Moreover, ammonia, benzene, methanol and MTBE were all excluded from the evaluation, even though they were highlighted by several of the scoring systems. All of the substances mentioned are highly volatile, and therefore the primary cleaning method for removing residues of these chemicals from cargo tanks is ventilation, not washing with water. All of the selected substances belong to MARPOL pollution category Y. In addition, three of the target substances, phenol, nonylphenol and sulphuric acid, require a prewash procedure (nonylphenol being high-viscosity and phenol and sulphuric acid being solidifying substances; Table 5.1). As regards nonylphenol, we should note that it is transported as nonylphenol ethoxylates, which belong to category Y. However, once nonylphenol ethoxylates reach the sea, they will be gradually degraded, forming hazardous nonylphenol as a degradation product (Häkkinen et al. 2012).

Table 5.1 Target chemicals chosen for the evaluation of the ecotoxicological effects of tank cleaning.

Substance	**MARPOL category**	**High-viscosity**	**Solidifying**
Nonylphenol -Nonylphenol ethoxylates	X Y	yes yes	no no
Phenol	Y	no	yes
Sulphuric acid	Y	no	yes
Styrene	Y	no	no
Xylenes	Y	no	no

In the following sections, the target chemicals are briefly introduced. The cleaning practices for the target chemicals are also summarised. The cleaning practices discussed are obtained from the "Dr. Verwey's Tank Cleaning Guide" (Verwey 2007). It is, however, important to be aware of the fact that their recommendations are merely an outline. Larger shipping companies, for example, have usually their own requirements, which may differ from Verwey's suggested practices (Kunichkin 2006). Moreover, even though the Verwey recommendations are in compliance with MARPOL and the IBC code, they cannot overrule restrictions arising from local circumstances (Verwey 2007). Therefore the cleaning practices described in the following should not be taken as the only possible choice of a cleaning method. Verwey, for example, suggests steaming with toluene as a subsequent cleaning step after water washing for various acrylates. Steaming with toluene is, in fact, an efficient way to improve the cleaning result, but it is restricted because of safety reasons (many explosions have occurred during toluene steaming) (Kunichkin 2006). Whenever the following sections refer to steaming,

steaming with water is meant. Butterworthing refers to a washing method where the cleaning solution (water or water detergent mixture) is applied to a tank with a rotating one or two-ended nozzle washing machine(s) (Verwey 2007). The water amount used in the washing process depends on the number of washing cycles. The objective of flushing is to remove salts remaining from seawater washing, and therefore, the tanks are always flushed with fresh water (Jo Tankers 1999).

5.1.1 Nonylphenol and nonylphenol ethoxylates

Nonylphenol ethoxylates (NPEs) are not transported in particularly high volumes in the Baltic Sea. For example in 2010, the volume of nonylphenol ethoxylates handled in Finnish ports (imports + exports) was approximately 11,100 tonnes, whereas the volumes of the most handled chemicals (e.g. MTBE and xylenes) were over a hundred thousand tonnes (Posti & Häkkinen 2012). On the other hand, as mentioned in section 5.1, nonylphenol (NP), the predominant biodegradation product of nonylphenol ethoxylates, is particularly hazardous in the environment, and a decision was therefore made to include it in this study. Nonylphenol has several isomers, all of which are moderately persistent and extremely toxic to aquatic organisms. In addition, nonylphenol is a known estrogenic and an endocrine disruptor, meaning that it is capable of interfering with the hormonal systems of numerous organisms (CEPA 2001b, U.S. EPA 2005, Soares et al. 2008).

Nonylphenol is composed of a phenol ring attached to either a straight or, more usually, a branched nonyl group. Under ambient conditions, it is a viscous liquid with a light pale colour, and it is immiscible with water. Nonylphenol ethoxylates are a class of a broader group of compounds known as alkylphenol ethoxylates (APEs) and they have the following general formula: $C_{15}H_{24}O+(CH_2CH_2O)_n$. In the United States, the U.S. Environmental Protection Agency and chemical industry representatives have agreed that the commercial product that best represents "nonylphenol" is a substance composed of branched C_9-alkylphenols with CAS-number 84852-15-3. There are also other CAS-numbers that have been used to describe these compounds commercially (nos. 104-40-5 and 25154-52-3) (CEPA 2001b, Soares et al. 2008). For a summary of the physico-chemical properties of nonylphenol, see Table 5.2.

Table 5.2 Physico-chemical properties of nonylphenol.

Property	**Value**	**Source**
Molecular weight	220.33 g/mol	MacKay et al. 2006
Melting point	-8 °C	OECD 1997
Boiling point	293–297 °C	HSDB 2012
Density	0.950 kg/l (20 °C)	HSDB 2012
Viscosity	563 cP (20°C)	HSDB 2012
Water solubility	6.35 mg/l (25 °C)	Ahel & Giger 1993
Vapour pressure	0.07–0.13 Pa (25 °C)	MacKay et al. 2006
Henry's law constant	11.02 Pa m^3/mol	OECD 1997
K_{oc}	165,959	Isobe et al. 2001
Log K_{ow}	4.1–6.36	MacKay et al. 2006

Nonylphenol ethoxylates and their degradation products are synthetic organic chemicals. NPEs have been used for more than 50 years in detergents, emulsifiers, wetting agents and dispersing agents. NPE-containing products have been used in many sectors such as textile processing, pulp and paper processing, paints, resins and protective coatings, steel manufacturing and pest control products (CEPA 2001).

According to Verwey's Tank Cleaning Guide (Verwey 2007), cargo tanks having contained nonylphenol (ethoxylates) are generally washed with hot sea water (butterworthing, 6 cycles). Since nonylphenol ethoxylates are hydrophobic substances (log K_{ow} 4.1–6.36; Table 5.2), adding small amounts of detergent may in some cases be necessary so that the cleaning result is satisfactory for loading the next cargo. For example, when cleaning for ethanol, a detergent should be added. After the tanks have been washed, they are flushed with fresh water, then steamed, drained, and finally dried. It should be noted that nonylphenol ethoxylates are not accepted as a previous immediate cargo to edible animal and vegetable oils and fats. Since nonylphenol ethoxylates are a high-viscosity cargo, they are subjected to mandatory in-port prewash as required by MARPOL Annex II.

5.1.2 Phenol

Phenol was highlighted in several of the surveyed scoring systems (by French McKay et al. 2006, HASREP 2005 and Häkkinen et al. 2012), and it was therefore selected as a target substance for the present study. Phenol was one of the most frequently handled chemicals in Finnish ports in both 2008 and 2010 (73,040 t and 87,359 t respectively) (Posti & Häkkinen 2012). Phenol is highly toxic to aquatic organisms, particularly to fish, but it is not persistent in aquatic environments, nor is it likely to bioaccumulate in organisms or food webs (HSDB 2012). In ambient conditions, phenol is a solidifying substance, but it is used and transported in liquid form (FIOH 2011a). The transport temperature of phenol is 50–55 °C.

Phenol is an aromatic alcohol with the chemical formula C_6H_6O. It is a white to light pink crystalline solid and has a characteristic acrid smell and a sharp burning taste. For a summary of the physico-chemical properties of phenol, see Table 5.3. Phenol is a common industrial chemical used, for example, in the production of panels, insulation, paints, lubricants, creams, adhesives, brakes, electrical components and electrodes. In addition to these applications, phenol can also be used as a feedstock in the production of other organic substances such as bisphenol A, alkylphenols, anilines, chlorophenols and other chemicals. Phenol is also used as a general disinfectant, anaesthetic and antiseptic, and it is present in a number of consumer products, including many dental care products and antiseptic lotions. Phenol is also produced naturally in water and soil as a decomposition product of vegetation and detritus. Increased natural environmental concentrations of phenol may also result from forest fires (CEPA 2000).

Table 5.3 Physico-chemical properties of phenol.

Property	**Value**	**Source**
Molecular weight	94.111 g/mol	Lide 2005
Melting point	40.89 °C	Lide 2005
Boiling point	181.87 °C	Lide 2005
Density	1.0545 kg/l (both 45 °C and 4 °C)	Lide 2005
Viscosity	3.437 cP (50 °C) 12.7 cP (18 °C)	HSDB 2012 Verwey 2007
Water solubility	82 800 mg/l	ATSDR 2008
Vapour pressure	46.663 Pa	HSDB 2012
Henry's law constant	0.034 Pa m^3/mol	HSDB 2012
K_{oc}	16.22–91.20	ATSDR 2008
Log K_{ow}	1.46	ATSDR 2008, HSDB 2012

The cleaning practice for phenol is similar to that for nonylphenol: after unloading, tanks having contained phenol are washed with hot sea water (butterworthing, 6 cycles), followed by flushing, steaming, draining of the tank, lines and pump, and finally drying. For some following cargoes, a lighter washing procedure is possible (e.g. for crude oil and coal tar). In the short cleaning procedure, 3 washing cycles, instead of 6, are used, and after washing, simply draining and drying the tank is enough. Phenol is not an acceptable previous immediate cargo for edible animal and vegetable oils and fats (Verwey 2007). Since phenol is a solidifying substance, it is subjected to mandatory in-port prewashing as required by MARPOL Annex II.

5.1.3 Sulphuric acid

Sulphuric acid is one of the most frequently transported chemicals in the Baltic Sea (Posti & Häkkinen 2012). The tonnages handled in Finnish ports were 62,822 t in 2008 and 25,172 t in 2010. On the priority list composed by Häkkinen et al. (2012), sulphuric acid was ranked the second most hazardous substance to aquatic environments. The compound was highlighted by the HASREP (2005) project as well. Sulphuric acid is strong acid, and in water it dissociates completely into sulphate and H^+ ions (protons) (CEDRE 2006). Consequently, high concentrations of sulphuric acid in water results in elevated H^+ levels leading to acidification. The ecotoxicity of sulphuric acid is, in fact, entirely based on its acidifying nature (FIOH 2011b). Sulphuric acid is highly corrosive, but it has not been classified as hazardous to the environment (in the instructions by the Finnish Institute of Occupational Health; FIOH 2011b). Neither has it been reported to bioaccumulate in organisms or food webs. Sulphuric acid is transported in liquid form in stainless steel tanks (CEDRE 2006).

Sulphuric acid (H_2SO_4, CAS no. 7664-93-9) is a colourless and odourless viscous liquid which crystallizes at 3–10 °C depending on its water content (from 0 to 2%) (OECD 2001). It may also have a brownish colour and slightly acrid odour (FIOH 2011b). Sulphuric acid is non-flammable, but it may react dangerously with many chemicals, presenting a risk of explosion (e.g. powdered metals) (CEDRE 2006). Adding water to sulphuric acid will also cause a violent reaction. In Finland, sulphuric acid is used in agriculture (in the production of phosphoric acid and fertilizers) and in titanium oxide

and aluminium sulphate synthesis (FIOH 2011b). In addition, sulphuric acid is used in pulp, paper and metal industries, in batteries and as a laboratory chemical (FIOH 2011b).

For a summary of the physico-chemical properties of sulphuric acid, see Table 5.4. Because of its rapid dissociation and reactivity, no measured Henry's law constant, Koc or Kow value is available for sulphuric acid. However, it has been possible to obtain predicted model values for these parameters by utilising the US Environmental Protection Agency's EPISuite software (Table 5.4).

Table 5.4 Physico-chemical properties of sulphuric acid.

Property	**Value**	**Source**
Molecular weight	98.08 g/mol	CEDRE 2006
Melting point	5 °C (98 %) 10.4–10.5 °C (100 %), 3 °C (98 %)	CEDRE 2006 OECD 2001
Boiling point	335 °C (98 %) 290 °C (100 %), 310–335°C (98 %)	CEDRE 2006 OECD 2001
Density	1.835 kg/.	OECD 2001
Viscosity	21 cP (25 °C)	HSDB 2012
Water solubility	Miscible with water 1 000 000 mg/l (predicted and measured, EPISuite)	HSDB 2012 CSID 2012
Vapour pressure	<0.01 Pa (20 °C) ca. 0 Pa (20 °C) 0.019 Pa (predicted), 0.00791 Pa (measured), EPISuite	OECD 2001 FIOH 2011b CSID 2012
Henry's law constant	0.00000257 Pa m^3/mol (predicted)	CSID 2012
K_{oc}	6.124 (predicted, EPISuite) 1 (in sediment, predicted based on K_{ow})	CSID 2012 HUTA CYNKU 2011
Log K_{ow}	-2.20 (predicted, EPISuite)	CSID 2012
pH	0.3 (1 N solution)	FIOH 2011b
pK_a	<0; -1.92 1.98	CEDRE 2006 HSDB 2012

Residues of sulphuric acid are washed from tanks with abundant cold sea water (butterworthing, 3 cycles). Because sulphuric acid is a strong acid, it is imperative to continue the washing until a pH value of at least 7 in the slop water is reached. After the washing is completed, flushing with fresh water should follow immediately without interruption. Next, passivation of stainless steel is performed by nitric acid or a commercial passivation liquid. The cleaning is completed by flushing (pH is checked again), steaming, draining and drying the tank (Verwey 2007). Sulphuric acid belongs to MARPOL category Y, and it is a solidifying substance if not unloaded at 5 °C above its melting point (3–10 °C + 5 °C = 8–15 °C). When the unloading temperature of sulphuric acid is lower than required, MARPOL Annex II requires a prewash procedure ashore after the unloading.

5.1.4 Styrene

Styrene was selected as a target substance for this study, as it appeared on three of the surveyed ranking lists. It was featured in the rankings composed by French McKay et

al. (2006) and Häkkinen et al. (2012), and it was highlighted by the HASREP (2005) project as well. Styrene was evaluated as a particularly hazardous substance because it is shipped in relatively high volumes and it is also dangerous to aquatic biota. In 2008 and 2010, the styrene volumes handled in Finnish ports were 59,423 and 71,934 tonnes, respectively (Posti & Häkkinen 2012). Even though styrene is toxic to aquatic organisms, it is readily biodegraded and therefore not persistent in the environment (FIOH 2011c). Styrene has not been reported to bioaccumulate in organisms or food webs.

Styrene (C_8H_8, CAS no. 100-42-5) is a volatile monoaromatic hydrocarbon which consists of a benzene ring attached to a vinyl group. Synonyms for styrene include vinylbenzene, vinylbenzol, phenylethylene, styrolene, styrol, styrole, ethenylbenzene, cinnamene, cinnamenol and cinnamol (CCME 1999). Styrene is either a colourless or pale yellow liquid and at low concentrations it has a distinct sweet aromatic odour (FIOH 2011c). For the physico-chemical properties of styrene, see Table 5.5. Styrene is used in the manufacture of plastics, synthetic rubbers and latex, such as polystyrene and styrene-butadiene (SB) (CCME 1999). These styrene plastics are for example used in packaging materials, disposable food and drink containers, car tires, paints, resins, in other plastic products, and fibrous glass products.

Table 5.5 Physico-chemical properties of styrene.

Property	**Value**	**Source**
Molecular weight	104.15 g/mol	MacKay et al. 2006
Melting point	-30.65 °C	MacKay et al. 2006
Boiling point	145 °C	MacKay et al. 2006
Density	0.9012–0.9060 kg/l	MacKay et al. 2006
Viscosity	0.696 cP (20 °C)	HSDB 2012
Water solubility	160–330 mg/l (25°C)	MacKay et al. 2006
Vapour pressure	807–880 Pa	MacKay et al. 2006
Henry's law constant	233–297 Pa m^3/mol	MacKay et al. 2006
K_{oc}	513–2,630	MacKay et al. 2006
Log K_{ow}	2.76–3.16	MacKay et al. 2006

The cleaning practice for styrene, according to Verwey's Tank cleaning guide (Verwey 2007), is as follows: as soon as styrene has been unloaded from tanks, a prewash, if required due to commercial needs, is performed. Otherwise, the tank and the associated lines and pump are drained as well as possible and the tank is filled completely with cold sea water and left until the cleaning is started[12]. The cleaning begins by emptying the tank. After that, the tank is butterworthed with cold sea water (9 cycles). The cleaning is completed by flushing, steaming, draining and drying. Styrene is not an acceptable previous immediate cargo for edible animal and vegetable oils and fats (Verwey 2007). It should be noted that in some Finnish ports, styrene is prewashed even though this is not required by MARPOL (e.g. Sköldvik in Porvoo and Port of Oulu;

[12] In the calculations in section 5.2.1, filling a tank completely with water was not accounted for as there was no confirmation that this step was also executed in the Baltic Sea. For example, in the suggested cleaning practice for styrene described in the cleaning guide composed by the German Chemtec Consulting GmBh (1999), such practice was lacking.

NesteOil 2006, Keskitalo 2012 pers. comm.). Cargo owners have requested it due to environmental reasons.

5.1.5 Xylenes

Xylenes were ranked relatively high in three of the surveyed scoring systems (by French McKay et al. (2006), Häkkinen et al. (2012) and HASREP (2005). In addition, xylenes are among the most frequently transported liquid bulk chemicals in the Baltic Sea (Posti & Häkkinen 2012). In Finnish ports, xylenes were the third most frequently handled chemical in 2008 and the fourth most frequently handled chemical in 2010 (206,558 t and 161,894 t, respectively). Consequently, xylene was selected as a target chemical for the present study. Xylenes are volatile flammable liquids that are toxic to aquatic organisms (FIOH 2011d). Xylenes have been reported to only bioaccumulate moderately in organisms, they do not bioaccumulate along the food webs, and they are not persistent in the environment (CEPA 1993).

Xylenes (mixture CAS no. 1330-20-7) are monoaromatic hydrocarbons consisting of two methyl groups attached to a benzene ring (CEDRE 2008). The general molecular formula of xylene is $C_6H_4(CH_3)_2$. There are three positional isomers of xylene: ortho- (o-xylene CAS 95-47-6), meta- (m-xylene CAS 108-38-3) and para-xylene (CAS 106-42-3). Xylenes are clear and colourless volatile liquids with a distinct aromatic odour similar to benzene. For a summary of the physico-chemical properties of xylenes, see Table 5.6. Xylenes are predominately manufactured from petrol or oil, but small amounts of xylenes are also produced from coal tar (HSDB 2012). In a commercial xylene mixture produced from oil, approximately 20% is o-xylene, 44% m-xylene, 20% p-xylenes, and 15% ethylbenzene. In a commercial xylene mixture produced from coal tar, on the other hand, approximately 45–70% is m-xylene, 23% p-xylene, 10–15% o-xylene and 6–10% ethylbenzene. Commercial xylene may also be contaminated with small amounts of, for example, toluene, phenol or benzene (HSDB 2012).

According to ATSDR (2007), 70% of the xylene mixture is used in the manufacture of ethylbenzene and the o-, m- and p-isomers of xylene. The rest of the mixed xylene is used as a solvent in the manufacture of products such as paint, varnish, glue, printing ink, insecticides, and dyes (CEDRE 2008). Mixed xylene is also used in the rubber and pharmaceutical product industries, in histology laboratories and in microscopy. Individual xylene isomers are used, for example, in the synthesis of phthalic acid (o-xylene), isophtalic acid and acide terephtalic acid (m-xylene and p-xylene).

Table 5.6 Physico-chemical properties of xylenes. (Mackay et al. 2006; density and viscosity values from Lide 2009)

Property	**Ortho-xylene**	**Meta-xylene**	**Para-xylene**
Molecular weight	106.16 g/mol	106.16 g/mol	106.16 g/mol
Melting point	-25.2 °C	-47.8 °C	13.25 °C
Boiling point	144.5 °C	139.12 °C	138.37 °C
Density	0.8755 kg/l	0.8598 kg/l	0.8565 kg/l
Viscosity	0.76 cP (25 °C)	0.581 cP (25 °C)	0.603 cP (25 °C)
Water solubility	167–221 mg/l (25 °C)	157–206 mg/l (25 °C)	156–215 mg/l (25 °C)
Vapour pressure	880–892 Pa (25 °C)	1 100–1 115 Pa (25 °C)	1 167–1 200 Pa (25 °C)
Henry's law constant	372–731 Pa m^3/mol (25 °C)	665–675 Pa m^3/mol (25 °C)	614–696 Pa m^3/mol (25 °C)
K_{oc}	47.86–478.63	114.82–426.58	74.13–602.56
Log K_{ow}	2.73–3.35	3.18–3.45	3.10–3.48

Meta- and ortho-xylenes are generally cleaned by first butterworthing the tank with cold sea water (3 cycles) and subsequently with warm fresh water (3 cycles). This is for coated tanks; for stainless steel tanks, the number of cycles is 2 for both sea and fresh water washing. Following the washing, the tank, its associated lines and the pump are drained, and the cleaning process is completed by drying the tank. When a tank has contained m- or o-xylene and it has to be cleaned for crude oil or coal tar, butterworthing with cold sea water, and draining and drying afterwards is sufficient. Moreover, when cleaning for gasoline or naphta, the residues of m- and o-xylenes can be removed by ventilation. Residues of para-xylene are primarily cleaned by butterworthing first with lukewarm sea water (6 cycles) and subsequently with hot water (3 cycles) (this is for coated tanks; for stainless steel tanks, the number of cycles is 4 and 2, respectively). Afterwards, the tank is steamed, drained and dried. When a tank that has carried p-xylene as cargo has to be cleaned for crude oil, coal tar or for few other "heavy" substances, a sufficient cleaning result is achieved by simply butterworthing with warm sea water (3 cycles) followed by draining and drying. Xylenes are not accepted as previous immediate cargo for edible animal and vegetable oils and fats (Verwey 2007).

5.2 EU risk assessment

In this study, the risks of releasing tank cleaning effluents into the Baltic Sea were assessed by using the European Union Technical Guidance Document on Risk Assessment (EC 2003) for the applicable parts. The EU environmental risk assessment of hazardous substances is, for a large part, based on comparing the PEC and PNEC concentrations of the chemical that is being assessed. The PEC/PNEC ratio indicates whether the concentration of a chemical to which organisms are expected to be exposed to will actually be great enough to cause harmful effects in the environment. When the PEC/PNEC ratio is well below 1, the risk is considered to be low, whereas values greater than 1 indicate a substantial risk, and consequently, some risk management actions might be needed (Walker et al. 2006). Also, as might be expected, the risk increases in relation to an increasing PEC/PNEC ratio.

5.2.1 Predicted Environmental Concentration (PEC)

Predicted Environmental Concentration (PEC) is the concentration in which the discharged or spilled chemical is anticipated to appear in the environment. According to technical guidelines by the EU (EC 2003), both the discharge concentration and the chemical's properties relating to the environmental fate should be considered in determining the PEC. Typically, in an exposure assessment, two separate PECs are calculated – the local and the regional value. PEC_{local} is the concentration during the chemical discharge, whereas $PEC_{regional}$ is the steady state concentration in surface water (or in sediment/soil/air). In the present study, only the local PECs for tank washings were determined.

When calculating the PECs, the first step was to determine the initial chemical concentration in the tank washings. The initial concentrations were obtained by dividing the chemical quantity that remains in a tank after unloading (i.e. the strip) with the volume of the added washing medium (water or other cleaning agent). Since the tank capacity of chemical tankers varies between 70 and 2,000 m^3 (Hänninen & Rytkönen 2006), all values were calculated for a medium-sized tank of 1,000 m^3. To be able to study the impact of prewashing on the expected chemical concentration in the sea, the PECs were calculated both with and without the dilution effect caused by in-port prewashing. Since the quantity of the strip varies greatly depending on the ship (see section 3.1), three model PECs were calculated for each target chemical by using different strip values. Based on literature and a consultation with the Finnish Transport Safety Agency (Trafi) (Vähätalo 2012 pers. comm.), 15 litres was selected as the minimum, 50 litres as the medium and 300 litres as the maximum strip value for the hypothetical 1,000 m^3 cargo tank. It seemed that strip values between 25 and 50 litres were quite common among both old and new tankers, whereas 15 litres is at the lower limits of the capability of the typical stripping technique (in larger, ca. 1,000 m^3 tanks). Since 300 litres is the largest amount of chemical which, within the limits of the law, is allowed to remain in a tank after unloading, it was also a justified selection for the maximum strip value for this study. In smaller tanks (e.g. 500 m^3), the strip quantities are in total somewhat smaller than in larger tanks, but as the water amount used in washing smaller tanks is also proportionally smaller, there should not be significant differences between the chemical concentrations in slops generated in cleaning of small and large cargo tanks.

Water volume calculations

The volume of cleaning water in which we assume the chemical to be diluted was somewhat challenging to determine, as water quantities vary greatly depending on the cargo and the properties of the cleaning machine(s) used. In the cleaning process, the cleaning solution (water or water-detergent mixture) is applied to a cargo tank via one or more butterworth tank cleaning machines (Kunichkin 2006). When the double-ended nozzle of the machine rotates a full cycle (360°), the tank walls have been sprayed twice. Accordingly, half a cycle by a double-ended nozzle means that the tank has been sprayed once. The total water quantity used in a tank cleaning process depends on the number of cleaning cycles – which is further dependent on the properties of the cargo

strip that has to be cleaned from the tank (as well as on the properties of the next cargo). For example, in the MARPOL prewash procedure, the number of cleaning cycles varies from ½ to 2, depending on the pollution category of the chemical and whether the chemical in question is a solidifying or a high-viscosity substance (Kunichkin 2006). In the main cleaning process, the number of cleaning cycles is, however, significantly higher. For example, according to Verwey's Tank Cleaning Guide (Verwey 2007), cleaning styrene residues from a tank requires a total of 9 cleaning cycles.

When the number of washing cycles required in a cleaning process, the water discharge rate (m^3/h) and cycle duration of the cleaning machine used are known, it is possible to calculate the total water quantity used in a washing process. Alternatively, if the duration of the whole washing process (h) is known, the total water quantity can be calculated simply by multiplying it by the washing machine's discharge rate (Vadakayil 2010). In this study, only the number of cleaning cycles for cleaning the target substances was available, and therefore the next step was to find out about the discharge rates and cycle durations of a butterworth machine. A Butterworth type LT tank cleaning machine (Butterworth Inc. 2012) was selected as a sample machine, and its technical performance data was utilised in calculating the total water quantities used in a tank cleaning process. It was assumed that the performance data of this particular washing machine does not significantly differ from the data of other manufacturers' machines (in the same size range).

The water discharge rate and cycle duration of a butterworth machine vary depending on its nozzle diameter and the water spray pressure used (Drew Marine 2005). For the water discharge rates and cycle durations at varying inlet pressures for the LT type machine with two 8 mm nozzles, see Table 5.7. We should note that the values given in the table are obtained from a performance curve, a summary in nature, given in the Butterworth LT product data sheet (Butterworth Inc. 2012). The values are therefore rough estimates, not exact values. The mean values of both the discharge rate and cycle duration were used in calculating the total water volumes needed in a cleaning process. As seen in Table 5.7, the mean discharge rate of the LT machine is 13 m^3/h, and the mean duration of one cleaning cycle is 9 minutes. At a seminar on reception facilities in ports (HELCOM 1993), the then MARPOL surveyor in Kotka District (Finland) estimated that the discharge rate of the butterworth machines typically is 10–20 m^3. Consequently, the discharge rate value of 13 m^3/h obtained here seems to be adequate.

Table 5.7 Water quantities used by a butterworth type LT washing machine with 2 x 8mm nozzles (capacity 2–570 m3). (The values are from Butterworth Inc. 2012)

Pressure (psi)	**30**	**75**	**125**	**175**	**225**	**300**	**mean**
Discharge rate (m^3/h)	4	9	12	15	17	21	13
Min/cycle	20.5	10.5	7.5	6.0	5.0	4.5	9.0

To be able to calculate the water quantity used in the entire washing process, the required number of cleaning cycles and the water quantity used per cycle (m^3) need to be known (Vadakayil 2010). In this study, the numbers of cleaning cycles for the target substances were obtained from Dr. Verwey's Tank Cleaning Guide (Verwey 2007). However, as mentioned earlier, it should be noted that there are also other tank cleaning

guides available in the market whose suggested cleaning practices may differ from Verwey's suggestions. Moreover, large shipping companies typically have their own cleaning practices which may also differ from the Verwey practices (Kunichkin 2006). For a summary of the numbers of cleaning cycles required in the cleaning processes of the target substances, see Table 5.8. Of the target substances, the largest amount of water is required for styrene, and the smallest for sulphuric acid. As regards sulphuric acid, it should be noted that the washing must be continued until the pH in the resulting slops is at least 7 (Verwey 2007). Consequently, more cycles than 3 may be needed in practice.

Since tanks are typically flushed subsequent to the actual washing using the same butterworth machine(s), the number of times a tank needs to be flushed had also to be taken into account when calculating the total water quantity used in a cleaning process. For the numbers of "flushings" used in the cleaning processes for the target substances, see Table 5.8. Verwey's tank cleaning guide did not, however, specify the number of *cycles* used in flushing or define the flushing duration in any other way either. Hence, the duration of flushing was assumed to be 0.5 hours as required in the "General Cargo Cleaning Guide" of the Norwegian shipping company Jo Tankers (Jo Tankers 1999).

Table 5.8 Number of cleaning cycles required in the cleaning of the target substances. (Verwey 2007)

Chemical	**Number of cycles**	**Number of flushings**
Nonylphenol	6	1
Phenol	6	1
Sulphuric acid	3	2
Styrene	9	1
o-xylene	6	0

The water quantity per cleaning cycle can be calculated rather simply from the average discharge rate as follows: a discharge rate of 13 m^3/h of the LT washing machine is equivalent to 13 m^3/60min = 0.2166 m^3/min. Consequently, the water quantity applied to a tank per cleaning cycle is 0.2166 m^3/min x duration of one cycle (which is 9 min for the LT machine; Table 5.7) = 1.95 m^3. The total quantity of water applied to a tank in a washing process can then be determined by multiplying the number of cleaning cycles with the water volume applied per cycle. For example, the required number of washing cycles for phenol is 6, and consequently, the water quantity needed to wash phenol residues from a tank (with a Butterworth LT type machine) is 6 x 1.95 m^3 = 11.7 m^3. To work out the total amount of water used in the whole cleaning process, the water quantity used for flushing had to be added to the water quantity used for the main washing. The water quantity used for flushing was determined by multiplying the flushing duration (h) with the washing machine's discharge rate (m^3/h): 0.5 h x 13 m^3/h = 6.5 m^3. For a summary of the water quantities applied to a tank in the washing and flushing steps of the cleaning process of the target chemicals, see Table 5.9. For a summary of the total water quantities (washing + flushing) used for cleaning a tank from residues of the target substances, see Table 5.10. Lastly, it is important to note that the capacity of a Butterworth LT type machine is 2–570 m^3, and therefore, one cleaning machine is well sufficient to clean a small cargo tank (e.g. 500 m^3), but in a larger tank,

several machines would have to be installed. The hypothetical 1,000 m^3 tank used as a model in the present study, for example, would have to be equipped with two of these LT washing machines (Butterworth Inc. 2012). Consequently, when calculating the water quantities required for the cleaning process of a larger cargo tank, the water volumes have to be doubled or even tripled (depending on the number of washing machines used). In Table 5.10, the water quantities are given for both a small (<570 m^3) and a large tank (570–1,140 m^3). The PECs were calculated from the total water quantity needed for the larger tank (570–1,140 m^3). In this study, it was also assumed that the volume of water used in a cleaning process increases linearly in relation to an increasing number of washing machines. In practice, this might not be true, and the increase in the water volume per washing machine might be smaller than x 2. Thus the water volumes calculated here (Table 5.10) for the hypothetical 1,000 m^3 tank might be slightly overestimated.

Table 5.9 Water quantities (m^3) used in washing and flushing a tank from residues of the target chemicals.

Chemical	**Water quantity (m^3), washing** washing duration (h) x flow rate (m^3/h)	**Water quantity (m^3), flushing** flushing duration (h) x flow rate (m^3/h)
Nonylphenol	11.7	6.50
Phenol	11.7	6.50
Sulphuric acid	5.85	13
Styrene	17.6	6.50
o-xylene	11.7	0.00

Table 5.10 Total water quantities (l) used for determining the PECs. The water quantities are given for one and two butterwort machines. The water quantities applied to a tank when washing with two machines were used in further calculations.

	One butterworth machine **Total water quantity (l)**	*Two butterworth machines* **Total water quantity (l)**
Chemical	washing + flushing	washing + flushing
Nonylphenol	18 200	36 400
Phenol	18 200	36 400
Sulphuric acid	18 850	37 700
Styrene	24 050	48 100
o-xylene	11 700	23 400

Concentration calculations

In the following, determination of the initial concentration of phenol in tank cleaning water is described step by step as an example of the method used. The concentration is determined for a chemical residue of 50 litres. First of all, the density of phenol is 1.0545 kg/l (Lide 2005). Consequently, the quantity (kg) of phenol in 50 litres is: 50 l x 1.0545 kg/l = 52.725 kg. The washing water quantity we assume the phenol to be diluted in was 36,400 litres (Table 5.10). Therefore, the initial concentration of phenol in tank cleaning water is: 52.725 kg / 36 400 l = 0.001448 kg/l = 1.448 g/l (50 l strip). This is the "without prewash" concentration. For the calculated chemical quantities (kg)

in the model strip volumes, see Table 5.11, and a summary of the initial "without prewash" chemical concentrations for the five target chemicals, see Table 5.12.

The initial concentrations given in Table 5.12 do not take the dilution caused by prewashing into account, even though of the target substances, phenol, nonylphenol (ethoxylates) and sulphuric acid are, in fact, substances that are subjected to a mandatory prewash procedure. In addition, in some ports in Finland, styrene is prewashed as well, even though it is neither a solidifying nor a high-viscosity substance (Keskitalo 2012 pers. comm, NesteOil 2006). This means that the first tank washings containing phenol, nonylphenol (ethoxylates) and sulphuric acid (and to some extent styrene) are not released into the sea but are discharged to a reception facility at a port instead. Only the subsequent washings are discharged in the sea. When a tank is prewashed, a large share of the chemical residue is removed from the tank and the following main washings are therefore far more dilute than they would be without a prewash. In this study, the "with prewash" concentrations were calculated for all five target substances so enable an evaluation of the effects of prewashing on the predicted environmental concentrations.

As mentioned in section 3.2, it is a MARPOL Annex II requirement that the concentration of a category X chemical must not exceed 0.1 % by weight in the prewash effluent (Annex II reg. 13.6.1). In Finland, the 0.1 m-% limit applies to the category of high-viscosity/solidifying Y substances as well (Chapter 3, Section 3 of Government Decree 76/2010). Since 0.1 m-% = 1,000 ppm = 1,000 mg/l, it was assumed that the water-chemical residue, *the strip*, that remains in a tank after prewashing and thorough draining has a concentration of 1 g/l. The "with prewash" concentrations for the target substances were calculated using the common dilution equation (1) for solutions.

Equation (1):

$C_1V_1 = C_2V_2$

Where
C_1= the starting chemical concentration
V_1= the starting volume
C_2= the final concentration
V_2= the final volume.

By re-arranging equation 1, we obtain $C_2 = C_1V_1 / V_2$. The "with prewash" concentrations for the target substances were obtained by using 1 g/l as the starting chemical concentration C_1, the three model strip values (15/50/300 l) one by one as the starting volume V_1, and the water quantities from Table 5.10 (with the strip volume added to it) as the final volume V_2. For the "with prewash" concentrations obtained, see Table 5.13.

Table 5.11 Chemical quantities (kg) in the model strips.

Chemical	Density (kg/l)	Source	Chemical Quantity (kg) strip volume x density		
			Strip 15 l	**Strip 50 l**	**Strip 300 l**
Nonylphenol	0.950	HSDB 2012	14.25	47.50	285.0
Phenol	1.0545	Lide 2005	15.82	52.73	316.4
Sulphuric acid	1.835	OECD 2001	27.53	91.75	550.5
Styrene	0.906	MacKay et al. 2006	13.59	45.30	271.8
o-xylene	0.8755	Lide 2009	13.13	43.78	262.7

Table 5.12 Initial "without prewash" chemical concentrations in tank washings. Three concentrations were calculated for each chemical using different residual quantities (15, 50 and 300 litres). The water volumes applied in the calculations are from Table 5.10.

Concentration (mg/l) without prewash

Chemical	Strip 15 l	Strip 50 l	Strip 300 l
Nonylphenol	391.5	1 305	7 830
Phenol	434.5	1 448	8 691
Sulphuric acid	730.1	2 434	14 602
Styrene	282.5	941.8	5 651
o-xylene	561.2	1 871	11 224

Table 5.13 Chemical concentrations in tank washings after two washing sequences (prewash and main wash).

Concentration (mg/l) with prewash

Chemical	Strip 15 l	Strip 50 l	Strip 300 l
Nonylphenol	0.4119	1.372	8.174
Phenol	0.4119	1.372	8.174
Sulphuric acid	0.3977	1.325	7.895
Styrene	0.3118	1.038	6.198
o-xylene	0.6406	2.132	12.66

Once the initial chemical concentrations of the (main) washings were determined, the next step, according to the EU methodology, was to consider the immediate dilution and other factors affecting the chemical concentration in the environment. Since tank washings disperse, dilute and degrade rapidly once they reach the sea, it would have been ideal to use a detailed two- or three-dimensional distribution model, similar to that used in French McCay et al. (2006), to predict how far the discharged tank washings travel and how strong an effect dilution, degradation and other elimination processes (e.g. evaporation) have on the initial chemical concentration. Such modelling would have given a more precise indication of how far-reaching and harmful the effects of tank cleaning waters actually are. However, as the present study is merely a preliminary survey on the subject of tank washings, acquiring the required expensive computer software would not have been practical. Therefore the regional distribution of the washings was not modelled in this study. The effect of dilution was, however, estimated by using an overly simplified dilution equation 2 given in the EU's Technical Guidance Document on risk assessment (EC 2003).

Equation (2):

$$PEC_{seawater} = Clocal_{eff} / (1+Kp_{susp} \cdot SUSP_{water} \cdot 10^{-6}) \cdot DILUTION$$

Where
$Clocal_{eff}$ = concentration of the substance in the effluent (mg/l)
Kp_{susp} = chemical's solids-water partitioning coefficient (kg/l)
$SUSP_{water}$ = concentration of suspended matter in the seawater (mg/l)
DILUTION = dilution factor (-) 10 / 100 / 1,000
$Clocal_{seawater}$ = local concentration in seawater during emission episode (mg/l).

Equation 2 addresses both dilution and adsorption to particles. The dilution factor used in the equation is defined based on flow rates of both the watercourse and the chemical effluent (EC 2003). As climatic and geographical conditions differ greatly in the EU countries, the dilution factor also varies over a wide range (1–100,000). The dilution factor is by default 10 for rivers, 100 for coastal waters and 1,000 for seas (Koskela et al. 2006). Mercier et al. (1974) experimentally modelled the dilution of soluble liquids released with tank washings from a towed (model) chemical tanker. By measuring both the initial chemical concentration in the washing water and the peak concentration in the sea immediately after discharge, the authors were able to calculate dilution factors for variable discharge locations. The obtained dilution factors ranged from less than 1,100 to 3,200, and the mean value was approximately 3,000. The dilution factors were for a discharge from a 630-ft vessel with a discharge rate of 330 tons/h (Mercier et al. 1974). To reduce the uncertainty arising from the simplified dilution equation, the PECs for this study were calculated by using both 1,000 and 3,000 as dilution factors. However, it should be noted that the application of values greater than 1,000 is not recommended in the calculation of local PECs in surface waters (EC 2003). High dilution factors are not recommended because the dilution equation assumes complete mixing of the chemical effluent in the surface water, and it does not take into account the fact that in reality, higher concentrations in the mixing zone will occur. When using low dilution factors, the mixing-effect can, however, be accepted.

According to Ferrari et al. (2007), the concentration of total suspended matter in the Baltic Sea ranges from 1 to 4 mg/l. The mean value (2.5 mg/l) was applied in the dilution equation as the $SUSP_{water}$ value. For the solids-water partitioning coefficients (Kp_{susp} values) of the target substances, see Table 5.14 ($Kp_{susp} = K_{oc}$).

Table 5.14 Koc values of the target substances. The lowest values were utilized in calculating local PECs.

Substance	**K_{oc}**	**Source**
Nonylphenol	165 959	Isobe et al. 2001
Phenol	16.22–91.20	ATSDR 2008
Sulphuric acid	1.0	HUTA CYNKU 2011
Styrene	513.0	Mackay et al. 2006
o-xylene	47.86	Mackay et al. 2006

For phenol, the effects of dilution and adsorption can be calculated as follows: the initial phenol concentration (without a prewash) in the washing was determined earlier, and the value obtained was 1,448 mg/l. Consequently, $Clocal_{eff}$ = 1,448 mg/l. As seen in Table 5.14, the Koc of phenol is 16.22–91.20. The lowest value 16.22 was applied as the Kpsusp in the equation. Consequently, the resulting PEC represents the so-called "worst-case scenario". As mentioned above, $SUSP_{BalticSea}$ = 2.5 mg/l, and finally, the dilution factor for seas is 1,000. When all these values are added in equation (2), the resulting "without prewash" $PEC_{seawater}$ for phenol (50 l strip) is 1.448 mg/l. Applying 3,000 as a dilution factor results in a "without prewash" $PEC_{seawater}$ of 0.4828 mg/l. When the "with prewash" concentration of phenol is applied in the dilution equation, the resulting PECs are 1.372 µg/l (dilution factor 1,000) and 0.4572 µg/l (dilution factor 3,000). The local PECs for all five target chemicals are summarised in Tables 5.15 and 5.16.

The $PEC_{seawater}$ represents concentration in seawater immediately after the discharge. In reality, the discharged washings will, of course, continue to dilute even further (and degrade, volatize etc.). Moreover, the dilution equation used assumes that the washings are discharged into a specific location from an unmoving ship. In reality, this is not true, as the washings must be discharged while the ship is sailing at a speed of at least 7 knots en route. When the ship is moving ahead while discharging, the flow will carry the chemical residues into the ship's propeller, where the chemical will be broken up and well dispersed in the propeller wake (McGeorge 1995). Therefore, the washings are actually distributed over a wider area than assumed by the simple dilution equation.

The behaviour and environmental fate of the target chemicals are discussed separately below.

Table 5.15 Local "without prewash" PECs for the target chemicals. In total, six PECs were calculated for each chemical. The PECs were calculated for three different residual quantities (15, 50, 300 l) using two separate dilution factors (1,000 and 3,000).

$PEC_{seawater}$ (mg/l) without prewash (dilution factor 1,000)

	Strip 15 l	**Strip 50 l**	**Strip 300 l**
Nonylphenol	0.2767	0.9223	5.534
Phenol	0.4345	1.448	8.691
Sulphuric acid	0.7301	2.434	14.60
Styrene	0.2822	0.9406	5.643
o-xylene	0.5612	1.871	11.22

$PEC_{seawater}$ (mg/l) without prewash (dilution factor 3,000)

	Strip 15 l	**Strip 50 l**	**Strip 300 l**
Nonylphenol	0.09223	0.3074	1.845
Phenol	0.1448	0.4828	2.897
Sulphuric acid	0.2434	0.8112	4.867
Styrene	0.09406	0.3135	1.881
o-xylene	0.1871	0.6235	3.741

Table 5.16 Local "with prewash" PECs for the target chemicals. In total, six PECs were calculated for each chemical. The PECs were calculated for three different residual quantities (15, 50, 300 l) using two separate dilution factors (1,000 and 3,000).

$PEC_{seawater}$ (mg/l) with prewash (dilution factor 1,000)

	Strip 15 l	**Strip 50 l**	**Strip 300 l**
Nonylphenol	0.0002911	0.0009695	0.005777
Phenol	0.0004119	0.001372	0.008174
Sulphuric acid	0.0003977	0.001325	0.007895
Styrene	0.0003114	0.001037	0.006190
o-xylene	0.0006405	0.002132	0.01266

$PEC_{seawater}$ (mg/l) with prewash (dilution factor 3,000)

	Strip 15 l	**Strip 50 l**	**Strip 300 l**
Nonylphenol	0.00009704	0.0003232	0.001926
Phenol	0.0001373	0.0004572	0.002725
Sulphuric acid	0.0001326	0.0004415	0.002632
Styrene	0.0001038	0.0003457	0.002063
o-xylene	0.0002135	0.0007106	0.004219

5.2.2 Predicted No Effect Concentration (PNEC)

The Predicted No Effect Concentration (PNEC) is the highest chemical concentration considered not to cause any harmful effects to aquatic organisms. The PNEC value for a chemical is determined in the "concentration-effect assessment" stage of the risk assessment procedure. According to the EU methodology (EC 2003), the PNEC value is obtained by utilising available literature toxicity data. However, as most of the toxicity

values are from short-term toxicity tests performed in stable laboratory conditions, these values cannot be directly applied to natural field conditions. To decrease the uncertainty arising from using these somewhat "unrealistic" laboratory results, the acute/chronic toxicity values must be first divided by a safety factor. Using a safety factor ensures that the resulting PNEC value is low enough to cover even the most sensitive species in the aquatic environment.

The magnitude of the safety factor depends on the number of tested trophic groups and the quality of the available toxicity data. If only acute toxicity data for a chemical is available, a safety factor of 1,000 must be used (EC 2003). This is to allow for the great deal of uncertainty that relates to the extrapolating from short-term laboratory results for a single species into field conditions, where several different species are exposed (Walker et al. 2006). The safety factor also takes into account the possible mixture effects (e.g. synergism and antagonism) as in the field, organisms are usually exposed not only to one, but to a number of different chemicals simultaneously (Walker et al. 2006). Because the test conditions in chronic toxicity tests are much closer to natural conditions in the field (compared to short-term toxicity tests), the safety factor for chronic toxicity values does not need to be as conservative as it is for acute LC/EC_{50} values. In general, the safety factor decreases as the number of groups from which chronic NOEC values are available increases. When a chronic NOEC value is available for one species (either *Daphnia* or fish), a safety factor of 100 is used. A safety factor of 50 is used when chronic NOEC values are available for two species representing two different trophic levels (fish and/or *Daphnia* and/or algae). When NOEC values are available for three species representing three trophic levels (fish, *Daphnia* and algae), a safety factor of 10 is used (EU 2003). For a summary of the safety factors for different data sets, see Table 5.17.

In the ChemRisk project, Häkkinen et al. (2010) studied the risks of chemical transportation accidents (by road and rail) in Kymenlaakso area. In this project, 30 chemicals were evaluated using the EUSES method (i.e. characterizing the risk by comparing the PEC and PNEC concentrations). In addition, a novel scoring system developed by the authors was used in the project as well. All target substances selected for the present study were evaluated in the ChemRisk project, and the PNEC values determined in the project were also utilised in the present study. In determining the PNEC concentrations for the chemicals studied, toxicity values from three trophic levels (algae, *Daphnia* and fish) were taken into account (Häkkinen et al. 2010). In selecting the lowest short-term $LC/EC/IC_{50}$- and chronic NOEC values, scientific discretion and source criticism was applied. For algae, the 72-hr test results were considered as chronic values. This is acceptable as the growth and cell division of algae is so rapid that the 72-hr (or longer) values can be considered to represent both short-term and long-term results. The PNECs were derived by dividing either the acute toxicity value ($LC/EC/IC_{50}$) or the chronic toxicity value (NOEC) for the most sensitive species (i.e. the lowest toxicity value of the three tested trophic groups) by an arbitrary safety factor. For nonylphenol, phenol and xylenes, three long-term NOECs were available. Consequently, a safety factor of 10 was used in calculating PNECs for these chemicals. For sulphuric acid and styrene, two chronic NOECs were available, and therefore, a safety factor of 50 was used in calculating the PNECs for them. For a summary of the

data that was selected for the derivation of PNEC values and the resulting PNECs for the target chemicals, see Table 5.18. The PNECs for the target substances utilised in this study are: nonylphenol: 0.0007 mg/l, phenol: 0.0017 mg/l, sulphuric acid: 0.0005 mg/l, styrene: 0.0013 mg/l and xylene: 0.0900 mg/l.

Table 5.17 Safety factors for deriving PNECwater for different data sets. (Modified from Nikunen & Leinonen 2002)

Available toxicity data	**Safety factor**
Short-term LC/EC_{50} from three taxonomic groups (algae, crustaceans and fish) of three trophic levels	1 000
One long-term NOEC (from crustacean reproduction or fish growth studies)	100
Two long-term NOECs from species representing two trophic levels (algae and/or crustaceans and/or fish)	50
Three long-term NOECs from species (normally algae and/or crustaceans and/or fish) representing three trophic levels	10

Table 5.18 PNEC values for the target chemicals and a summary of the data that was selected for PNEC derivation. (Häkkinen et al. 2010)

Chemical CAS number	**Fish, acute (mg/l)**	***D.manga*, acute (mg/l)**	**Algae, acute (mg/l)**	**Fish, chronic (mg/l)**	***D.manga*, chronic (mg/l)**	**Algae, chronic (mg/l)**	**Safety factor**	**$PNEC_{water}$ mg/l**
Nonylphenol 84852-15-3	0.017 96h LC50 (Lussier et al. 2000)	0.104 96h LC50 (Brooke 1993)	0.027 EC50 (Ward & Boeri 1990)	0.0074 33d NOEC (Ward & Boeri 1990)	0.0107 22d NOEC (Fliedner 1993)	0.027 EC50 (Ward & Boeri 1990)	10	0.0007
Phenol 108-95-2	0.15 96h LC50 (Black et al. 1982)	5 48h LC50 (IUCLID 2000a)	1211 24h EC50 (CEPA 2000)	0.017 27d NOEC (IUCLID 2000a)	0.16 16d NOEC (IUCLID 2000a)	7.5 8d NOEL (CEPA 2000)	10	0.0017
Sulphuric acid 7664-93-9	16 pH 3.25 96h LC50 (OECD 2001)	29 24h EC50 (OECD 2001)		0.025 26 °C, pH 6 NOEC (OECD 2001)		0.13 pH 5,59 NOEC (OECD 2001)	50	0.0005
Styrene 100-42-5	2.5 96h LC50 (Qureshi et al. 1982)	4.7 48h EC50 (Cushman et al. 1997)	0.72 96h EC50 (Cushman et al. 1997)	>0.2 7d NOEC (Mamaca et al. 2005)		0.063 96h NOEC (Cushman et al. 1997)	50	0.0013
Xylenes o-xylene 95-45-6 p-xylene 106-42-3	1.7 96h LC50 p-xylene (Benville & Korn 1977)	1.0 24h LC50 o-xylene (Galassi et al. 1988)	3.2 72h EC50 (Galassi et al. 1988)	3.77 27d LC50 (Black et al. 1982)	1.57 21d NOEC p-xylene (CEFIC 2005)	0.9 8d NOEC p-xylene (CEDRE 2008)	10	0.0900

6 RESULTS

6.1 PEC/PNEC ratios

The risk a chemical presents in the environment is characterised by comparing the predicted environmental concentration to the predicted no effect concentration. If the PEC/PNEC ratio is greater than 1, this is an indication of a risk. In this case, there are two possible conclusions to be made: 1) further studies on the subject are needed or 2) the existing risk management measures are not sufficient, and the risk needs to be reduced by additional risk management actions (Nikunen & Leinonen 2002). Moreover, the greater the ratio, the greater the risk. When the ratio is < 1, there is no significant risk, and neither further studies nor risk management measures are needed.

For the PEC/PNEC ratios of the evaluated target substances, see Table 6.1. As we can see in the Table, without a prewash the risk limits are exceeded for every target chemical, regardless of the quantity of chemical residue or the dilution factor used in PEC calculations. In contrast, if a tank is prewashed prior to main washing and the remaining strip (chemical-water mixture) is *15 litres*, the predicted environmental concentration does not exceed the predicted no effect concentration for any of the target substances (regardless of the dilution factor used). When using *50 litres* as the strip value, the risk ratios remain below 1 for most of the target chemicals as well. Only when the smaller (1,000) dilution factor is used, the risk ratios of nonylphenol and sulphuric acid are > 1 (ratios 1.40 and 2.65, respectively).

When the remaining strip in a tank after a prewash is assumed to be *300 litres*, o-xylene is the sole target chemical the PEC/PNEC ratio of which stays below the risk limits. All the other target chemicals have PECs higher than their PNECs (regardless of the dilution factor used). When using 1,000 as the dilution factor, the resulting ratios are: nonylphenol 8.25, phenol 4.81, sulphuric acid 15.79, and styrene 4.76. If 3,000 is used as the dilution factor, the ratios are: nonylphenol 2.75, phenol 1.60, sulphuric acid 5.26, and styrene 1.59.

All in all, the PEC/PNEC ratios were clearly the highest for sulphuric acid and the lowest for ortho-xylene (Table 6.1). When a dilution factor of 1,000 was used in the PEC calculations, the "with prewash" PEC/PNEC ratios for sulphuric acid were: 0.80 (15 l), 2.65 (50 l) and 15.79 (300 l). The predicted seawater concentrations of sulphuric acid greatly exceed its PNECs due to the compound's high density and, on the other hand, due to its low PNEC. If we consider 50 litres of sulphuric acid (density 1.835 kg/l), the mass (kg) of the compound in that given volume is nearly 92 kg. In comparison, 50 litres of styrene (density 0.906 kg/l) contains approximately 45 kg of styrene. Consequently, there is almost twice as much sulphuric acid in a given volume than there is styrene. In addition, the predicted no effect concentration of sulphuric acid is relatively low (0.5 µg/l; Table 5.18), indicating that sulphuric acid concentrations higher than 0.5 µg/l are considered to be harmful in the environment. Of the target substances, only nonylphenol has a lower PNEC concentration than sulphuric acid. The "with prewash" PEC/PNEC ratios for o-xylene calculated with a dilution factor of 1,000 were: 0.0071 (15 l), 0.024 (50 l) and 0.14 (300 l). Compared to the other target

chemicals, the predicted exposure concentration of xylene is rather high (see Table 5.16). However, since xylenes are not as toxic to aquatic organisms compared to the other target substances (PNEC 0.09 mg/l; Table 5.18), its PEC/PNEC ratios stay well below the risk limits. This is, however, only if a tank is prewashed. If not, the PEC/PNEC ratio of o-xylene exceeds 1 even when the strip is only 15 litres and when the higher dilution factor (3,000) is used. As demonstrated above, the magnitude of the risk is dependent on both the magnitude of the exposure and the toxicity of the chemical.

Table 6.1 PEC/PNEC ratios for the target chemicals. Twelve PEC/PNEC ratios for each chemical in total are given, as the PECs were calculated for three different residual quantities (15, 50, 300 l) using two separate dilution factors (1,000 and 3,000), and lastly, with and without a prewash procedure.

PEC/PNEC ratio (dilution factor 1,000)

	Strip 15 l		**Strip 50 l**		**Strip 300 l**	
	without prewash	prewash	without prewash	prewash	without prewash	prewash
Nonylphenol	395.3	0.4159	1318	1.385	7 905	8.253
Phenol	255.6	0.2423	852.0	0.807	5 112	4.808
Sulphuric acid	1 460	0.7954	4867	2.649	29 204	15.79
Styrene	217.1	0.2395	723.5	0.7978	4 341	4.762
o-xylene	6.235	0.007117	20.78	0.02369	124.7	0.1406

PEC/PNEC ratio (dilution factor 3,000)

	Strip 15 l		**Strip 50 l**		**Strip 300 l**	
	without prewash	prewash	without prewash	prewash	without prewash	prewash
Nonylphenol	131.8	0.1386	439.2	0.4617	2 635	2.751
Phenol	85.20	0.08076	284.0	0.2690	1 704	1.603
Sulphuric acid	486.7	0.2651	1 622.5	0.8830	9 735	5.263
Styrene	72.35	0.07983	241.2	0.2659	1 447	1.587
o-xylene	2.078	0.002372	6.928	0.007896	41.57	0.04688

In the following sections, the results (PECs, PNECs, and their ratios) are reviewed in more detail for each target substance individually. The toxicological profiles and the environmental fates of the substances are also discussed.

6.2 Nonylphenol

6.2.1 Exposure (local PEC)

When the impact of prewashing was taken into account, the calculated local predicted exposure concentrations (PECs) for nonylphenol (ethoxylates) ranged from 0.0970 µg/l to 5.78 µg/l, depending on the strip volume and dilution factor used in the calculations ("with prewash" concentrations; Table 5.16). The "without prewash" PECs were considerably higher: 0.0922–5.53 mg/l (Table 5.15). The PECs may, in reality, be somewhat lower as the water quantities used in calculating the initial chemical

concentration may differ from the estimates used in the present study. Moreover, the dilution equation used in calculating the PECs does not, for example, account for dispersion caused by the ship's propeller or the continuous forward movement of the ship. In addition, in practice, the PEC concentrations would obviously be rapidly dispersed and diluted further in the vast sea, and therefore, the calculated local PECs are only *momentary* concentrations.

6.2.2 Effects (PNEC for aquatic environment)

In selecting the PNEC value for nonylphenol, a total of 6 toxicity tests were taken into account (one acute and one chronic test for each trophic group (algae, *Daphnia* and fish). Since no NOEC value could be found for algae, the EC_{50} value of 27 µg/l (Ward & Boeri 1990) was used as both the acute and the chronic value. By examining the toxicity data that was selected for the derivation of $PNEC_{nonylphenol}$, it can be concluded that nonylphenol is highly toxic to all three trophic groups, both acutely and chronically. Fish seem to be the most sensitive species to nonylphenol. The lowest toxicity value among the data was the NOEC value of 7.4 µg/l for fish (Ward & Boeri 1990). Since long-term toxicity data was available for all three trophic groups, 10 could be used as a safety factor. Consequently, the predicted no effect concentration (PNEC) obtained for nonylphenol was 0.7 µg/l (Table 5.18). Lastly, nonylphenol acts as an endocrine disruptor that can mimic oestrogen (Soares et al. 2008). As a result, when male fish are exposed to nonylphenol, they may become feminized and suffer from reduced fertility.

6.2.3 Bioaccumulation

Bioaccumulation of nonylphenol in aquatic organisms varies from negligible to significant. From algae, invertebrates and fish, BCF and BAFs between 0.9 and 10,000 have been reported (e.g. Servos 1999, CEPA 2001b, Vazquez-Duhalt et al. 2005). Bioaccumulation is greatest in the lower trophic levels, particularly in algae. Bioaccumulation in the lower trophic levels is particularly adverse as the higher organisms will also be exposed by consuming contaminated food (Vazquez-Duhalt et al. 2005). Bioaccumulation of short-chained nonylphenol ethoxylates in aquatic organisms has been reported to be moderate (BCFs up to 740) (CEPA 2001b). For longer-chained NPEs, bioaccumulation studies are scarce, but it is generally assumed that the tendency to bioaccumulate decreases when the ethoxylate chain elongates. However, according to Vazquez-Duhalt et al. (2005), in fish there are no significant differences between the bioaccumulation tendencies of nonylphenol, nonylphenol monoethoxylate and nonylphenol dioethoxylate.

6.2.4 Environmental fate and persistence

When tank washings containing nonylphenol ethoxylates are discharged into the sea, nonylphenol will be gradually formed as the ethoxylates are degraded (Häkkinen et al. 2012). Nonylphenol will then partition between the different environmental

compartments based on its physico-chemical properties. Since nonylphenol has a high octanol-water partitioning coefficient (4.1–6.36; Table 5.2) and poor solubility in water (6.35 mg/l), it partitions favourably to organic matter and sediments (John et al. 2000, Soares et al. 2008).

According to fugacity modelling carried out by the Canadian Environment authorities (CEPA 2001b), if nonylphenol is released in water, most of it will be present in water phase (49–59%), slightly less of it will partition to sediment (41–50%), and only a negligible proportion (<1%) of it will end up in air and soil compartments. Nonylphenol will not volatise readily into air, as it has a low vapour pressure (Table 5.2). However, the Henry's law constant of nonylphenol indicates that it evaporates relatively well from water. If nonylphenol evaporated into air once discharged into the sea, it would be rapidly degraded by reactions with hydroxyl radicals (•OH). The measured half-life of nonylphenol in the atmosphere is only 0.3 days (U.K Environment Agency 1997). Since nonylphenol ethoxylates are far less volatile than nonylphenol, it is not predicted that they would be partitioned to the atmosphere (CEPA 2001b). As regards predicting the behaviour of nonylphenol in the environment, we should note that variations in the physico-chemical properties of nonylphenol and nonylphenol ethoxylates, and their rapid conversion to other metabolites, makes their environmental fate extremely complex (CEPA 2001b). The percentages given above, for example, are predictions only, and not based on exact measured values.

The biodegradation rate of nonylphenol is greatly dependent on ambient temperature. When Manzano et al. (1998) studied the biodegradation of nonylphenol in river waters, they noted that the percentages of primary biodegradation varied from 68% at 7 °C to 96% at 25 °C, and that at all the temperatures studied, some metabolites generated during the biodegradation process remained at the end of the 30-day assay. Consequently, nonylphenol is not readily biodegraded at low temperatures. Moreover, the biodegradation rates of nonylphenol seem to be slower in sea water and sea water sediments than in freshwater and freshwater sediments (U.S EPA 2005). According to Ekelund et al. (1993), the half-life of nonylphenol in sea water was 58 days and that in aerobic sea water in presence of sediment was 35 days. Since the Baltic Sea surface waters are warm only shortly during the summer, the biodegradation rate of nonylphenol in the Baltic Sea can be assumed to be very slow. The ultimate sink of nonylphenol is the sediment. When Liber et al. (1999) studied the persistence and partitioning of nonylphenol in an artificial littoral ecosystem, they found that the half-life of nonylphenol was 1.2 days in water, 8–13 days in macrophytes and 28–104 days in sediment. Moreover, according to Shang et al. (1994), when nonylphenol ends up in the sediment it may stay there for as long as 60 years.

Photolysis (i.e. photodegradation) may have an important role in the elimination of nonylphenol, particularly if the compound is released in the surface waters. Ahel et al. (1994) noted that under summer sun conditions, the half-life of nonylphenol was from 10 to 15 hours in the surface layer of natural (filtered) lake water. The photolysis rates at 20–25 cm below the surface were already about 1.5 times slower. The photolysis rates of nonylphenol ethoxylates were shown to be significantly slower than they were in the case of nonylphenol, and consequently, it was estimated that photolysis will only

have a minor role in the overall removal of alkylphenol ethoxylates in aquatic environments (Ahel et al. 1994). Since tank cleaning waters must be discharged below the water line and nonylphenol ethoxylates have a density higher than that of sea water (i.e. NP/NPEs are not likely to float on the surface waters), photolysis is probably not as important an elimination route for nonylphenol and nonylphenol ethoxylates as biodegradation.

6.2.5 PEC/PNEC ratio

In the risk characterization step of nonylphenol, its PEC concentration is compared to its PNEC concentration. The "without prewash" PEC/PNEC ratios for nonylphenol ranged from 132 to 7,905, depending on the quantity of the chemical residue (15/50/300 l) and the dilution factor used in the PEC calculations (1,000 or 3,000; Table 6.1). In other words, the calculated risk ratios indicate that if a tank having contained nonylphenol ethoxylates is not prewashed prior to main washing, the predicted no effect concentration of nonylphenol (ethoxylate) in the sea during the discharge will most likely be momentarily exceeded. However, nonylphenol ethoxylates are high-viscosity cargoes, and therefore subjected to a MARPOL prewash. The "with prewash" PECs are thus closer to the true values when characterizing the risk of tank cleaning waters containing nonylphenol ethoxylate. The calculated "with prewash" PEC/PNEC ratios for nonylphenol varied from 0.14 to 8.25. When a dilution factor of 1,000 was used, the risk ratio stayed at accepted levels only when the volume of the water-chemical mixture remaining in a tank after prewash was assumed to be 15 litres. The calculated PEC/PNEC ratio then was 0.42. If the strip was assumed to be 50 or 300 litres in volume, the risk ratios were 1.40 and 8.25, respectively. When the higher dilution factor (3,000) was used in the calculations, the risk ratios were accordingly lower. In that case, the PEC/PNEC ratio only exceeded 1 when the chemical-water-residue after prewash was assumed to be 300 litres (risk ratio 2.75). For the 15-litre and 50-litre strips, the risk ratios were 0.14 and 0.46, respectively – well below the risk limit.

In conclusion, the calculated risk ratios indicate that there might be a risk relating to the discharge of tank cleaning waters containing nonylphenol into the sea, even though nonylphenol ethoxylates are currently prewashed ashore. The risk is the most evident when the NPE water mixture that remains in a tank after prewash is assumed to be 300 litres. Fortunately, while a strip volume of 300 litres is accepted within the limits of the law, such high strip quantities are rare in practice (GESAMP 2002). Chemical residues lower than 100 litres are far more typical in chemical tankers today. The results indicate that when 50 litres of NPE water mixture (remaining from a prewash) is washed from a tank and subsequently discharged into the sea in the resulting washings, the resulting risk ratio is either 1.40 or 0.46, depending on the dilution factor used. Since there are a lot of uncertainties relating to the used dilution equation and estimated washing water quantities, further studies might be needed to verify whether the risk is relevant for strips in this size range. Based on the PEC/PNEC ratios obtained, it could be argued that if the NPE water effluent quantity in a tank after prewashing is less than 15 litres, discharging the subsequent washings into the sea is not likely to pose a significant risk to the aquatic environment. The results also revealed that prewashing of tanks from

which nonylphenol ethoxylates have been unloaded is extremely important – without prewashing and discharging the first washings to a reception facility at a port, the nonylphenol ethoxylate concentrations in the main washings which may be discharged into the sea would be alarmingly high (0.092–5.53 mg/l; Table 5.15). The persistent nature of nonylphenol and its tendency to bioaccumulate in organisms and food webs are factors that raise nonylphenol's hazardousness in the aquatic environment. Because of the these properties, chronic exposure to even the smallest concentrations of nonylphenol may in time bioaccumulate in organisms, and eventually rise up to toxic levels (Soares et al. 2008). Of course, it should be noted that nonylphenol is acutely toxic even in low concentrations. Moreover, chronic exposure to nonylphenol can cause reduced fertility in male fish.

6.3 Phenol

6.3.1 Exposure (local PEC)

When dilution by prewashing was taken into account, the calculated predicted exposure concentrations for phenol were significantly lower than they were when the impact of prewashing was left out of the calculations. The "without prewash" PECs calculated for phenol ranged from 0.14 to 8.7 mg/l and the "with prewash" PECs from 0.14 to 8.2 µg/l (Tables 5.15 and 5.16). The magnitude of the PECs depended on the assumed residue volume and whether 1,000 or 3,000 was applied as the dilution factor in the calculations.

6.3.2 Effects (PNEC for aquatic environment)

One acute and one chronic toxicity test for each trophic group (algae, *Daphnia* and fish) was considered when determining the PNEC value for phenol. Based on the selected toxicity data, phenol is toxic to all three trophic groups. Fish are the most sensitive species to phenol (96h LC_{50}: 0.15 mg/l; Black et al. 1982), whereas algae seem to tolerate phenol rather well (24h EC_{50} 1,211 mg/l; CEPA 2000a). The long-term NOEC value of 17 µg for fish was the lowest value amongst the toxicity data. Since there were chronic NOEC/NOEL values available for all three trophic groups, 10 was used as a safety factor in deriving the $PNEC_{phenol}$. The obtained PNEC for phenol was 1.7 µg/l.

6.3.3 Bioaccumulation

The bioconcentration factors (BCFs) of phenol reported in fish range from 1.7 to 39. The reported BCF values and the rapid elimination of phenol from organisms suggests that bioaccumulation of phenol is unlikely (HSDB 2012).

6.3.4 Environmental fate and persistence

Phenol is highly soluble in water (82,000 mg/l; see Table 5.3), it has a low organic carbon-water partition coefficient (16.22–91.20) and a low octanol-water partition coefficient (1.46). Therefore, phenol is not expected to significantly adsorb to sediment or suspended matter in water. According to the fugacity modelling performed by the Canadian Environment authorities (CEPA 2000), when phenol is released in water, almost all of it, as predicted by the model, will also stay in the water compartment.

Biodegradation is the major elimination route of phenol in surface waters – assuming that the degradation is not inhibited by the presence of high, toxic concentrations of phenol or by other factors (such as a lack of nutrients or microorganisms capable of degrading phenol) (CEPA 2000). If biodegradation is particularly slow, phenol will typically react rapidly with hydroxyl and peroxyl radicals and singlet oxygen in sunlit surface waters. For the hydroxyl radical reaction, a half-life of 100 hours, and for the peroxyl reaction, a half-life 19.2 hours has been reported. The photooxidation reactions require dissolved organic matter (DOM) that functions as photosensitizer. DOM is, however, rather scarce in sea water. For example, in coastal waters of the Baltic Sea, the DOC concentration is typically <5.5 mg/l (Schumann et al. 2003). This is rather low compared to, for example, boreal lakes where the DOM concentration typically varies between < 5 mg/l and 15 mg/l (Kronberg 1999). All in all, the suggested half-life of phenol in water is 55 hours (CEPA 2000). The degradation of phenol is somewhat slower in sea water than in fresh water, and a half-life of 9 days has been reported in an estuarine river (ATSDR 2008). In sediment, a biodegradation half-life of 550 hours (ca. 23 days) has been suggested (CEPA 2000).

6.3.5 PEC/PNEC ratio

When the risk of phenol was characterised by comparing phenol's PEC concentrations to its PNEC concentration, it became clear that if cargo tanks that have contained phenol were not prewashed prior to main washing, the predicted exposure concentration in the sea would exceed phenol's PNEC in every strip range (15/50/300l). The calculated risk ratios were also significantly higher than 1, regardless whether the dilution factor used in the calculations was 1,000 or 3,000 (Table 6.1).

In contrast, if cargo tanks that have contained phenol are prewashed prior to main washing (as, in fact, required by MARPOL Annex II), the predicted exposure concentrations will most likely stay at accepted levels – at least, if the chemical-water effluent remaining in a tank after prewash is not significantly higher than 50 litres in volume. When only strip quantities of 50 litres are considered, the calculated risk ratios for phenol were 0.27 (dilution factor 3,000) and 0.81 (dilution factor 1,000). As seen in Table 6.1, when the washing effluent that remains in a tank after prewash is assumed to be 300 litres is volume, the risk ratios for phenol are 4.8 (dilution factor 1,000) and 1.60 (dilution factor 3,000). This consequently means that a strip residue of 300 litres of phenol-water effluent might present a risk to aquatic organisms when released into the sea with further washings.

Based on the calculated PEC/PNEC ratios, we can conclude that prewashing of cargo tanks from which phenol has been unloaded is essential before main washing and releasing washing waters to the sea to ensure that phenol concentrations in the sea resulting from these operational discharges stay at accepted levels and do not pose a risk to the aquatic environment. The results also indicate that a prewash strip quantity of 300 litres will result in such high phenol concentrations in tank washings that the washings may, at least momentarily, be hazardous to aquatic organisms. Of course, phenol is quite readily biodegraded, and it does not bioaccumulate in organisms or food webs. Therefore it is not as hazardous as, for example, nonylphenol. On the other hand, it has been estimated that the degradation of phenol is somewhat slowed down in sea waters compared to lakes and rivers (ATSDR 2008), and photodegradation may also be slowed down as phenol has a density lower than that of sea water (density: 1.0545 kg/l; Table 5.3). In other words, it is expected to sink rather than float on the water surface and this, consequently, could decrease the photodegradation rates of phenol. Finally, as noted earlier, the PEC concentrations were calculated by using an overly-simplified dilution equation, which does not account for the dispersion and dilution caused by the conditions that prevail during the discharge (moving ship etc.). The calculated PECs only describe a momentary concentration immediately after the discharge. In practice, the dispersion and dilution of the effluents will continue even further.

6.4 Sulphuric acid

6.4.1 Exposure (local PEC)

The predicted exposure concentrations calculated for sulphuric acid were quite high when the dilution effect resulting from prewashing was not taken into account. When the lower dilution factor (1,000) was used in the calculations, the resulting PECs were 0.73–14.6 mg/l (Table 5.15). When the higher dilution factor (3,000) was used, the calculated local PECs were 0.24–4.9 mg/l. When the effects of prewashing were accounted for in the calculations, the local PECs for sulphuric acid were 0.40–8.2 µg/l (dilution factor 1,000) and 0.13–2.6 µg/l (dilution factor 3,000) (Table 5.16).

6.4.2 Effects (PNEC for aquatic environment)

A total of four toxicity tests were selected for the derivation of predicted no effect concentration for sulphuric acid (Table 5.18). For algae, no acute toxicity data were available, and for *Daphnia*, no chronic toxicity data were available. From the available toxicity data given in Table 5.18, we can conclude that the chronic toxicity of sulphuric acid is pointedly higher than its acute toxicity. The acute toxicity of sulphuric acid to fish, for example, is 16 mg/l (96h $LC_{50,}$ pH 3.5), whereas sulphuric acid's chronic toxicity to fish is 25 µg/l (NOEC 26 °C, pH 6) (OECD 2001). The chronic NOEC of 25 µg/l for fish was also the lowest toxicity value among the selected toxicity data. As chronic toxicity values were only available for fish and algae, a safety factor of 50 was

used in deriving the $PNEC_{sulphuric\ acid}$. The obtained PNEC for sulphuric acid was therefore 0.5 µg/l.

According to a CEDRE (2006) report, when the concentration of sulphuric acid in fresh water is below 0.01 g/l, the impact on pH is small. When sulphuric acid concentration is 0.01–0.1 g/l, the pH of naturally neutral fresh water will range from 5.5 to 7. A concentration of 0.1–1 g/l corresponds to a pH value of 1.8–5.5, and finally, a concentration greater than 1 g/l corresponds to pH below 1.8. However, it should be noted that the effects of sulphuric acid are greatly dependent on the natural pH and buffer capacity of the water system, both of which vary among aquatic systems. In comparison to many lakes, the Baltic Sea has a much greater buffer system (alkalinity), and it is not as prone to acidification caused by anthropogenic activities (e.g. acid rain) (Kumblad & Rydin 2012). The mean total alkalinity of the surface water in the Baltic Sea varies depending on the salinity (Hjalmarsson et al. 2008). Consequently, the alkalinity and the buffering capacity are lowest in the Bothnian Bay and increase towards the Baltic proper and Kattegat as the salinity increases.

6.4.3 Bioaccumulation

Due to its complete ionisation in water, sulphuric acid is not likely to bioaccumulate in organisms or in food webs (OECD 2001). BCFs for sulphuric acid have not been determined (CEDRE 2006).

6.4.4 Environmental fate and persistence

Sulphuric acid is perfectly water soluble: in water, it dissociates completely into sulphate and hydrogen ions (OECD 2001). In the ionisation process, a large amount of heat is released. Due to its complete ionisation, sulphuric acid is not likely to adsorb into organic matter or sediments. Sulphate concentrations in the environment tend to remain at natural levels, and the harmful effects of sulphuric acid are mainly due to acidification caused by an increasing concentration of H^+ ions.

Sulphuric acid is an inorganic chemical, and hence it will not undergo biological degradation in aerobic conditions (CEDRE 2006). However, the compound may be broken down by sulphate reducing bacteria (IUCLID 2000b). Through abiotic degradation at 25 °C, following half-lives have been reported for sulphuric acid: pH 4: even over 1 year and pH 7 or pH 9: less than 1 minute (IUCLID 2000b). In the Baltic Sea surface waters, the pH value typically ranges between 8 and 8.5 (Omstedt et al. 2009).

In aquatic environments, sulphuric acid will also react with other ions (e.g. magnesium and calcium ions) forming sulphate salts (HSDB 2012).

6.4.5 PEC/PNEC ratio

The PEC/PNEC ratios calculated for sulphuric acid exceeded 1 by far when the effects of prewashing were not accounted for in the calculations. Even with the higher dilution factor of 3,000, the resulted risk ratios were at times over a thousand (487–9,735; Table 6.1). Using 1,000 as the dilution factor resulted in even higher risk ratios: 1,460–29,204.

When the impact of prewashing was taken into consideration, the risk ratios of sulphuric acid still remained relatively high. When a dilution factor of 1,000 was used in the PEC calculations, the PEC/PNEC ratio only went down to accepted levels in the strip range of 15 litres. When the PECs were calculated for the 50 and 300 litres sized sulphuric acid strip (consisting of H_2SO_4 water effluent), the ratios were 2.6 and 16, respectively. When 3,000 was used as the dilution factor, the risk ratios for sulphuric acid were, consequently, somewhat lower, only exceeding 1 in the strip range of 300 litres. The calculated risk ratios for sulphuric acid (when using 3,000 as the dilution factor) were: 0.27 (15 l), 0.88 (50 l), and 5.3 (300 l).

As regards characterising the risk arising from tank cleaning waters containing sulphuric acid, based on the calculated risk ratios, it may be concluded that a risk does indeed exist. The risk is the greatest if cargo tanks are not prewashed subsequent to unloading and if the first washings are discharged directly into the sea. It is, however, important to be aware of the fact that the PNEC for sulphuric acid refers specifically to *sulphuric acid.* As noted earlier, sulphuric acid dissociates completely into sulphate and hydrogen ions in water, and therefore, sulphuric acid concentrations stay reasonably low in aquatic environments (OECD 2001). Consequently, the negative effects of sulphuric acid in aquatic systems mainly stem from the acidification effect caused by increasing levels of H^+ ions. However, once tank cleaning waters containing sulphuric acid are released into the sea, the acid concentrations can be expected to rapidly dilute in the vast amount of water (CEDRE 2006). Moreover, the overall buffering capacity (alkalinity) of the Baltic Sea is quite good (Kumblad & Rydin 2012), and therefore, the change in pH would probably be minor. The areas in the Baltic Sea that are most susceptible to acidification (based on the total alkality in surface waters) are the sub-basins in which the salinity is the lowest: the Gulf of Finland, the Gulf of Bothnia, and particularly the Bothnian Bay. The total alkalinity in surface water in the Gulf of Finland is on average 1,200–1,400, in the Gulf of Bothnia 1,000–1,400 and in the Bothnian Bay 800 (Hjalmarsson et al. 2008).

6.5 Styrene

6.5.1 Exposure (local PEC)

The calculated predicted exposure concentrations for styrene varied between 0.10 and 6.2 µg/l when the dilution effect of prewashing was accounted for in the calculations. When prewashing was not accounted for, the calculated PECs were accordingly higher: 0.094–5.6 mg/l. The magnitude of the PECs obtained depended on the strip volume and dilution factor used in the calculations. Styrene is a cargo for which the prewash

procedure is not mandatory. However, there are ports in Finland where commercial prewashes of styrene are performed (Keskitalo 2012 pers. comm; NesteOil 2006), and therefore, in practice, both "with prewash" and "without prewash" concentrations probably occur in the Baltic Sea.

6.5.2 Effects (PNEC for the aquatic environment)

All in all, 5 toxicity tests were selected for determining $PNEC_{styrene}$ (Table 5.18). Both acute and chronic values were available for algae and fish, but for *Daphnia,* only results from short-term toxicity studies were available. Based on the selected toxicity data, styrene is toxic to all three trophic groups, both acutely and chronically, with algae being the most sensitive trophic group (acute 48h EC_{50} for algae 4.7 mg/l; Cushman et al. 1997). Among the selected toxicity data, the lowest toxicity value was the chronic 96h NOEC of 63 µg/l for algae (Cushman et al. 1997). Since only two chronic NOEC values were available for the derivation of $PNEC_{styrene}$, a safety factor of 50 had to be used. The PNEC concentration obtained for styrene was 1.3 µg/l.

6.5.3 Bioaccumulation

A BCF of 13.5 in goldfish has been reported for styrene (HSDB 2012). The value suggests that bioaccumulation of styrene is not significant, despite the relatively high log K_{ow} (2.76–3.16; Table 5.5). The low BCF probably results from the rapid metabolism and excretion of styrene from organisms (CCME 1999).

6.5.4 Environmental fate and persistence

When styrene is released into the aquatic environment, the majority of the compound can be expected to partition into the atmosphere due to its high vapour pressure and Henry' law constant (HSDB 2012) (vapour pressure: 807–880 Pa and Henry's law constant: 233–297 Pa m^3/mol; Table 5.5). Volatilization of dissolved styrene from water is particularly fast from the water surface. However, styrene dissolves into water very slowly (water solubility 160–330 mg/l at 25 °C; Table 5.5) and based on its high Koc (513–2,630; Table 5.5) styrene may also be adsorbed to suspended matter and sediment when released to water (HSDB 2012). Consequently, styrene's elimination from water may be slowed down by these factors.

In the air, styrene is rapidly broken down by reactions with hydroxyl radicals and ozone: half-lives of styrene for these reactions are 7 and 16 hours, respectively (HSDB 2012). Direct photolysis of styrene in the atmosphere is rather slow. Based on modelling, half-lives of styrene have been estimated to be 3 hours in a shallow river system, 3 days in a shallow pond, and 13 days in a lake (CCME 1999). According to Gibbs & Mulligan (1997), the half-life of styrene in water in aerobic conditions is approximately 5 days.

6.5.5 PEC/PNEC ratio

When the dilution effect caused by prewashing was taken into account, the calculated PEC/PNEC ratios for styrene mostly remained at accepted levels. The "with prewash" risk ratios calculated by using 15 litres as the strip quantity were: 0.24 (dilution factor 1,000) and 0.080 (dilution factor 3,000) (Table 6.1). When 50 litres was used as the strip quantity, the "with prewash" risk ratios for styrene were: 0.80 (dilution factor 1,000) and 0.27 (dilution factor 3,000). The "with prewash" risk ratios obtained for styrene were only greater than 1 when calculated using 300 litres as the strip quantity. In that case, the PEC/PNEC ratios obtained were: 4.8 (dilution factor 1,000) and 1.6 (dilution factor 3,000).

Without the effects of prewashing, the PEC/PNEC ratios calculated for styrene exceeded 1 in all strip ranges and regardless of the dilution factor used (Table 6.1). Consequently, the results indicate that prewashing of tanks from which styrene has been unloaded is central in keeping the risk of tank cleaning slops containing styrene at accepted levels. Styrene, however, belonging to category Y and being a low-viscosity and non-solidifying substance, is a cargo that is not subjected to a mandatory in-port prewash. As mentioned earlier, in some Finnish ports styrene is prewashed as there has been environmental concerns from cargo owners relating to discharging styrene into the sensitive environments of the Bothnian Bay and the Gulf of Finland without prewashing (Keskitalo 2012 pers. comm.). However, since prewashing of styrene is not required by MARPOL, the alarmingly high "without prewash" PECs can be assumed to occur at least in some parts of the Baltic Sea area. Based on the findings of this study, it is clear that some risk management actions should be taken to lower the risks of styrene, particularly in the Baltic Sea, where the abiotic circumstances deteriorate the elimination of hazardous substances (shallowness, long water turnover time, cold climate etc.). The problem arising from styrene in the Baltic Sea may be further emphasised due to the fact that styrene is one of the most frequently handled chemicals in the Baltic Sea ports.

6.6 Xylenes

6.6.1 Exposure (local PEC)

The calculated predicted exposure concentrations for ortho-xylene, when the dilution effect caused by prewashing was not considered, were 0.19–11 mg/l, depending on the amount of chemical residue (15/50/300 l) and the dilution factor that was used in the PEC calculations (1,000 or 3,000). When prewashing was accounted for, the obtained PEC concentrations for o-xylene were significantly lower: 0.21–13 µg/l. In total, of the evaluated target substances, o-xylene's predicted exposure concentrations were the second highest. Only sulphuric acid had PEC concentrations higher than o-xylene.

6.6.2 Effects (PNEC for aquatic environment)

In selecting the predicted no effect concentration for xylenes, a total of 6 toxicity tests were taken into account (one acute and one chronic test result for each of the three trophic groups) (Table 5.18). According to the selected toxicity data, it is reasonable to conclude that xylenes are not as toxic chronically as they are acutely. The acute toxicity of xylenes is moderate, whereas the chronic toxicity of xylenes is only slight. Moreover, in acute exposure, *Daphnia* seems to be the most sensitive species to xylenes (24h LC_{50}: 1.0 mg/l; Galassi et al. 1988). The lowest toxicity value among the selected toxicity data was the 8d NOEC of 0.9 mg/l for algae (CEDRE 2008). This value was obtained for para-xylene. Since NOEC values were available for all three trophic groups, a safety factor of 10 was used in deriving the $PNEC_{xylenes.}$ The PNEC concentration obtained for xylenes was 90 µg/l (Table 5.18).

6.6.3 Bioaccumulation

Only moderate bioaccumulation has been reported for xylene. Moreover, xylenes do not bioconcentrate along food chains. For xylenes, the following BCFs have been reported:

- BCF 6 in clam *Tapes semidecussata* (mixed isomers, 8-day exposure) (Nunes & Benville 1979)
- BCF 21.4 / 23.6 / 23.6 in eel *Anguilla japonica* (o-xylene / m-xylene/ p-xylene) (Ogata & Miyake 1978)
- BCF 14–14.7 in rainbow trout (56-day exposure; no increase in the xylene concentrations in fish after day 2) (CEPA 1993).

Bioaccumulation of xylenes is most substantial in algae. In the green algae *Selenastrum capricornutum*, BCFs of 257, 251 and 218 have been reported for para-, meta- and ortho-xylenes, respectively (Herman et al. 1991).

6.6.4 Environmental fate and persistence

Xylenes have relatively high vapour pressures, moderate solubility in water and moderately low octanol-water partitioning coefficients (Table 5.6). Subsequently, xylenes are expected to partition mainly to the atmosphere in case they are released into the environment (CEPA 1993). According to CEDRE (2008), 99.7% of xylene that is released into the environment will end up in the air compartment. Similarly, when xylenes are released into water, they will be rapidly volatised into the atmosphere, particularly if they are released in surface waters (CEDRE 2008). The environmental fate of the different xylene isomers is assumed to be the same, as the physico-chemical properties of the isomers do not significantly differ from each other.

In the air, xylenes are rapidly degraded by reactions with hydroxyl radicals – the half-life of xylenes in the air varies from 1 hour to 2 days (FIOH 2011d). In water, a half-life of only 5.6 hours has been reported for xylenes (in 1-meter deep surface water) (Mackay & Leinonen 1975). The half-life is short due to the rapid volatilisation.

However, the half-life of xylenes varies depending on mixing events and the depth of the water system (the half-life would, for example, be shorter in turbulent water due to increasing volatilisation rates). For lakes, volatilisation rates of 8 days, and for streams and rivers, volatilization rates of 1–2 days, have been calculated (CEPA 1993). However, according to U.S. EPA (1987), volatilisation from streams and rivers takes from 36 minutes to 47 days. The high variability in the reported values is due to differences in depth and flow rates in streams and rivers.

In surface waters, xylenes are also degraded by microorganisms in both aerobic and anaerobic conditions (CEPA 1993). In aerobic systems, half-lives for biodegradation in water have been estimated to be 7–28 days for all three isomers. In anaerobic conditions, the half-lives were longer for all isomers: 180–360 days for o-xylene and 28–112 days for m- and p-xylenes.

6.6.5 PEC/PNEC ratio

The risk relating to tank cleaning waters containing xylenes were characterised by comparing the calculated PEC concentrations of o-xylene to its PNEC concentration. Among the five target substances, the PEC/PNEC ratios calculated for o-xylene were the lowest. The risk ratios ranged from 2.1 to 125 when the impact of prewashing was not considered, and from 0.0024 to 0.14 when the dilution caused by prewashing was considered (Table 6.1). The magnitude of the risk ratio depended on the amount of chemical-/pre-washings residue (15/50/300 l) for which the ratio was calculated and on the dilution factor used in the PEC calculations (1,000/3,000).

Based on the calculated risk ratios, it can be concluded that if cargo tanks are prewashed subsequent to unloading of xylenes, the following main washings can be expected to be dilute enough so that there will be no risk to aquatic organisms. Even if the strip (consisting of remnants of xylene-pre-washings) is as large as 300 litres, the xylene concentration in the main washings can be expected to stay so low that a risk to the environment is unlikely (regardless of the dilution factor) (Table 6.1). This is in contrast to the other target substances: when the strip amount of prewashings containing chemical was assumed to be 300 litres, none of the risk ratios of the other four target substances stayed at accepted levels. However, since there were some uncertainties relating to the PEC calculations and the risk ratios calculated for the 300 litres strip exceeded/were under 1 on such a small margin (Table 6.1, “with prewash” risk ratios), the risk may also need to be refined for this strip range (e.g. by obtaining more detailed exposure data, for example by measuring concentrations in the sea immediately after discharging the slops).

As with nonylphenol, phenol, sulphuric acid and styrene, there is also an indication of a risk when tank cleaning waters containing xylenes are discharged directly into the sea without any previous washing. The risk is most evident if the amount of xylenes remaining in a tank after unloading and stripping is 300 litres or greater. If the strip quantity is around 50 litres, the risk is somewhat lower, and when the amount of chemical residue is 15 litres, the risk is the smallest: risk ratios were 6.2 (dilution factor

1,000) and 2.1 (dilution factor 3,000) (Table 6.1). Due to the uncertainties relating to the method used in obtaining the PECs, the risk may need to be refined for the smallest strip range. Even though risk ratios calculated in the present study indicate the presence of a risk, the margins by which the ratios exceed 1 are relatively small.

In conclusion, if cargo tanks that have contained xylenes are prewashed prior to main washing, the xylene concentrations in the generated main slops seem to stay dilute enough so that there will be no negative consequences to the environment. When these dilute concentrations of xylenes are released into the sea, they will be rapidly diluted and since xylenes, having a density lower than that of sea water[13], are so called "floaters", and their evaporation from the water can be expected to be rapid. Based on the calculated PEC/PNEC ratios, it is also reasonable to conclude that without prewashing and discharging the first washings to ashore reception facilities, the xylene concentrations in the main washings are likely to reach such high levels that the risk to aquatic organisms will become plausible – particularly if the strip quantity is 300 litres.

[13] Density of o-xylenes: 0.8755 kg/l (Lide 2009).

7 SUMMARY AND CONCLUSIONS

This study examined a risk evaluation of tank cleaning wastes in the Baltic Sea area. The risks were evaluated by conducting a literature survey and a small-scale risk assessment on five target chemicals by following EU methodology laid down in the Technical Guidance Document on Risk Assessment (EC 2003) where applicable. The target chemicals were chosen on the basis of existing studies and projects where chemicals were ranked based on their hazardousness in the aquatic environment and their shipping volumes in the Baltic Sea. The selected chemicals for the evaluation were nonylphenol ethoxylate, phenol, sulphuric acid, styrene and xylene.

For various reasons, tanks in chemical carriers are cleaned after they have been emptied of cargo (Olson 1994). Requirements for the discharge of the generated effluents are laid down in Annex II of the international convention MARPOL 73/78 (the Control of Pollution by Noxious Liquid Substances Carried in Bulk). Tanks having contained cargoes that fall in the most hazardous category X must be prewashed ashore until the chemical concentration in the generated effluent is low enough according to MARPOL limits (0.1% by weight). In-port prewashes are also required for high-viscosity and solidifying cargoes in category Y (e.g. animal and vegetable oils) whose residues cannot be pumped out of tanks as effectively as the residues of other substances. All slops generated during prewashing must be discharged to ashore reception facilities. Prewashing is not a sufficient cleaning method by itself, and cargo tanks practically always have to be washed further in a subsequent main washing process, which may take several hours. The slops generated during the main cleaning process can be discharged directly into the sea (HELCOM 1993, Kunichkin 2006).

Literature survey

The literature survey revealed that studies on operational (legal or illegal) discharges from the shipping industry are rather scarce and mainly focus on oil. The environmental effects of chronic oiling have been well studied in the North Sea by means of systematic beached bird surveys (Skov et al. 2011). In the Baltic Sea, however, the number of case studies on the effects of chronic oiling on the environment has been low. On the basis of several existing studies from the North Sea and the few focusing on the Baltic Sea, it can be concluded that chronic operational oil discharges from tankers are a significant threat to the marine environment, probably more so than the operational discharges of chemicals (e.g. Skov et al. 2011; Larsson & Tydén, 2009, 2011).

In addition to mineral oil, oily substances such as vegetable oils had also been found to cause massive bird kills on several occasions in the North Sea before they were included in the scope of MARPOL and its cleaning and discharge requirements (e.g. Camphuysen et al. 1999). At present, no studies have been conducted on the environmental effects of tank cleaning effluents containing chemicals in the Baltic Sea. However, general screening surveys have been carried out in different parts of the Baltic Sea where the concentrations of certain high priority chemicals or chemical groups have been measured in both water and organisms (e.g. Lilja et al. 2009, HELCOM. 2010c, Andersson et al. 2012). Many of the targeted chemicals are not carried in bulk by

chemical tankers (e.g. dioxins, furans, tributyltin and heavy metals). Moreover, operational discharges from chemical tankers have not been identified as a possible source of contamination in any of the projects mentioned above. In contrast to the Baltic Sea, two surveys have been carried out in the North Sea where the chemical concentrations resulting from tank cleaning were evaluated by both modelling and by taking samples from sites near UK ports (Hurford et al. 1989, 1990). Based on these studies, chronic discharges from tank cleaning waters containing chemicals did not cause significant harm to the aquatic organisms in the North Sea. The findings from the North Sea cannot be applied to the Baltic Sea without reservation, as the properties of these seas (e.g. water exchange rates and depth) differ greatly from each other. Therefore, the elimination of hazardous substances in the Baltic Sea can be expected to take longer than it takes in the North Sea (Håkanson et al. 2003). The beached-bird surveys and concentration measurements seem to complement each other, as the former are the best indicator of chronic pollution of hydrophobic substances, whereas the latter is best suited for detecting pollution caused by water soluble substances.

Risk assessment

In the risk assessment of this study, the Predicted Environmental Concentrations (PECs) for all five target chemicals were determined. The PECs were calculated based on the residual cargo quantity that was estimated to remain in a tank after unloading (= the strip) and the water quantity that is used in the cleaning process. The water volume used in tank cleaning depends on many things, most importantly on cargo properties (Kunichkin 2006). The water volumes used for the target chemicals were determined by utilising Dr. Verwey's Tank Cleaning Guide (Verwey 2007). The cargo residue that remains in a tank after unloading varies as well, depending on tank size and the stripping technique used in a particular ship. Therefore, the PECs were calculated for a hypothetical 1,000-m^3 tank using three strips of different sizes: 15 litres, 50 litres and 300 litres. The 15-l and 50-l strips are more or less typical of modern tankers (e.g. Kunichkin 2006, Tanker Operator 2008a). In practice, strips of 300 litres in volume are rare (GESAMP 2002), but as this is the largest chemical volume that is allowed to remain in a cargo tank by MARPOL Annex II, selecting this as the maximum strip value was justified. The PECs were calculated with and without the dilution effect caused by prewashing to evaluate the importance of these mandatory in-port prewashes. Immediate dilution in the sea and adsorption into suspended solids were also accounted for in determining the PECs.

In the risk characterisation, the PECs obtained for the target chemicals were compared to their corresponding Predicted No Effect Concentrations (PNECs) which were derived from toxicity data in available literature (by Häkkinen et al. 2010). Whenever the calculated PEC/PNEC ratio exceeds 1, there is an indication of a risk. In such cases, there are two possible conclusions to be made: 1) further studies on the subject are needed or 2) the existing risk management measures are not sufficient, and the risk needs to be mitigated by additional risk management actions (Nikunen & Leinonen 2002).

The results of the risk assessment clearly demonstrated the importance of prewashing cargo tanks ashore before the main washing. Without prewashing the cargo tanks and discharging the generated prewashing effluents into reception facilities ashore, the obtained PEC/PNEC ratios for the further washings exceed 1 – regardless of the chemical and the quantity of the chemical residue (15/50/300 litres).

In contrast, if the cargo tanks are prewashed and the remaining prewash residues in the tanks are small (≤ 15 l), the risk arising from tank cleaning effluents stays at accepted levels and there seems to be no significant harm to the aquatic organisms. When the prewash residue is around 50 litres, the risk arising from further washings mostly remains at accepted levels as well. However, the results indicate that prewash remnants of 300 litres can in most cases be expected to cause significant harm to the aquatic organisms when they are discharged into the sea with further washings. In practice, residues that remain in a tank after prewashing are virtually never as large as 300 litres; they are more likely to be in the 15–100–litre range, possibly even smaller (GESAMP 2002, Kunichkin 2006, Keskitalo 2012 pers. comm.).

Even though the current study indicates that prewashing is essential to keep the risks arising from tank cleaning wastes at accepted levels, of the target substances only nonylphenol (ethoxylate), mandatory prewashing under MARPOL only applies to nonylphenol (ethoxylate), phenol and sulphuric acid. Styrene and xylenes, on the other hand, do not require prewashing of any kind – at least not by MARPOL.

Adequacy of the current cleaning and discharge requirements

When the current state of cleaning and stripping requirements is considered, of the evaluated target substances the greatest risk seems to arise from styrene and xylenes. Sulphuric acid and nonylphenol ethoxylate may also give rise to a risk in certain cases. The risks of styrene and xylenes stem from the current state of the law: they do not need to be pre-washed, whereas the risks of nonylphenol (ethoxylate) and sulphuric acid are evident, even though they are subjected to a prewash. A risk in case of nonylphenol (ethoxylate) and sulphuric acid may exist when the strip (which consists of prewashing effluent) is in the medium range, i.e. around 50 litres, or larger. Phenol is also subjected to a prewash, but the risk arising from tank cleaning effluents containing phenol remains below the risk limit (assuming that strips of 300 litres after prewashing are non-existent in practice). The sufficiency of the current risk management actions regarding the cleaning and discharge of the target chemicals are summarised in the following. Suggestions to improve the state of risk management are also given where needed.

Phenol

Phenol is subjected to a mandatory in-port prewash, as it is a solidifying substance belonging to MARPOL pollution category Y. The results of this study indicate that a strip value of 300 litres after prewash cannot be accepted from the environmental point of view. At present, there are no requirements applicable to the amount of prewashing effluent that is allowed to remain in a tank after prewashing, but fortunately, a volume of washings as large as 300 litres remaining in a tank after prewash is very unlikely

(GESAMP 2002). All in all, the current cleaning and discharge requirements for phenol seem to be sufficient to keep the environment from harm by tank cleaning wastes containing phenol. However, the results of this study suggest that the prewashing remnants of phenol should not exceed 50 litres, at least not by a large margin.

Nonylphenol (ethoxylates)

At present, nonylphenol (ethoxylate) belongs to MARPOL category Y, and being a high-viscosity substance, it is subjected to a mandatory prewash procedure. The risk ratios that were calculated in this study indicate that prewashing may not be sufficient in all cases to keep the hazard arising from tank cleaning effluents containing nonylphenol ethoxylate at accepted levels. When prewash remnants in a tank are around 50 litres in volume, there may be a risk to the aquatic organisms (risk ratios for this strip size were 0.46 and 1.4 depending on the calculation method). As there were some uncertainties relating to calculating the PEC values, however, the risk may need to be refined. In contrast, the results indicate that prewash residues of $\leq$ 15 litres seem to be small enough in volume not to cause significant harm in the marine environment when released in the sea with subsequent washings. Similarly to phenol, prewash residues of 300 litres are likely to cause harmful effects in the environment, but as mentioned earlier, such strip amounts hardly ever occur in practice. In conclusion, there might be a need to adjust the stripping and cleaning requirements for nonylphenol ethoxylate. At present, there are no requirements applicable to the amount of prewashing effluent that is allowed to remain in a tank after prewashing. The results of this study suggest that the prewashing remnants of nonylphenol ethoxylate should not exceed 15 litres, at least not by a large margin.

Sulphuric acid

Sulphuric acid is at present classified in MARPOL category Y. It is a solidifying substance, and therefore subjected to a prewash procedure. According to the risk ratios calculated in the study, it may be concluded that prewashing might in some cases be insufficient to reduce the risk arising from tank cleaning effluents containing sulphuric acid to a tolerated level. Similarly to nonylphenol ethoxylate in the 50-litre strip range, there might be a risk to the aquatic organisms (risk ratios in this strip size were 0.88 and 2.6, depending on the calculation method). As with phenol and nonylphenol ethoxylate, prewash residues of 300 litres are most likely to cause harmful effects in the environment when released in the sea in the following washings. In practice, however, such large strip quantities are rare (GESAMP 2002). Based on the results, it may be concluded that the current cleaning and stripping requirements are otherwise satisfactory but it could be recommended that the prewashing effluents that remain in a tank after prewashing would not exceed 15 litres, at least not in excess.

Xylenes

At present, xylenes are classified in MARPOL category Y, but they are not subjected to a prewash procedure as they are neither high-viscosity nor solidifying cargoes. Based on the results, without prewashing, the amounts of xylenes that are discharged into the sea with tank washings are great enough to cause harm to aquatic organisms. The risk ratios exceed 1 in all size ranges (15/50/300 litres) if xylenes are not prewashed. The risk to the environment would be significantly reduced if xylenes were prewashed. The risk ratios would then stay well below the risk limits in all strip ranges – even in the 300-litre strip. In conclusion, the risk ratios obtained in this study indicate that the current state of risk management seems to be insufficient to ensure low enough concentrations of xylenes in the sea. An obligation to use tank prewashing for xylenes is recommended.

Styrene

Styrene is currently classified as a category Y substance. It is a low-viscosity and non-solidifying substance, and therefore, not subjected to a mandatory in-port prewash. Based on the risk ratios obtained in this study, tank cleaning effluents containing styrene give rise to a significant risk in the environment. Without prewashing, the amount of styrene that ends up in the sea in tank cleaning effluents is so large that the calculated risk ratios exceed 1 by a great deal, even when the chemical residue that remains in a tank after unloading is as small as 15 litres. Consequently, the harm to aquatic organisms from tank cleaning effluents containing styrene is likely to be substantial. If tanks having contained styrene were prewashed, the risk would be reduced to accepted levels in all but the 300-litre strip class. But once again, 300 litres of prewashing effluents rarely remain in a tank after prewashing (GESAMP 2002). In conclusion, there seems to be a clear shortcoming in the current state of stripping and cleaning requirements for styrene. Based on the results of this study, it is suggested that prewashing of tanks having contained styrene be enforced by a legislative measure. Currently, as requested by cargo owners, voluntary commercial prewashes of styrene are performed in some Finnish ports (Keskitalo 2012 pers. comm., NesteOil 2006), which, in the light of the results of this study, is very positive. However, it would be even better if this good practice was also enforced by law. Moreover, if/when styrene is prewashed, it is also recommended that the prewashing remnants that remain in a tank after prewashing would not exceed 50 litres by a large margin.

Conclusions

In conclusion, the results of the study showed that prewashing requirements for the most hazardous category X cargoes and the high-viscosity and solidifying category Y cargoes are without doubt needed to keep the hazards arising from these substances at accepted levels. Without prewashing, the impact of such substances as vegetable oils on sea birds would be detrimental. Moreover, based on the risk ratio calculations, it is reasonable to suggest that prewashing be made mandatory for all category Y cargoes, at least in the particularly sensitive Baltic Sea area. There are several toxic and persistent cargoes in the Y category (Häkkinen et al. 2012) that at present, being non-solidifying

and low-viscosity, may avoid the prewashing requirements. It can be hypothesised that these substances can cause significant damage in the shallow and sensitive ecosystems of Baltic Sea in the long run, if the discharges continue to be as substantial as they seem to be without in-port prewashes. Alternatively, the high-risk category Y cargoes should be carefully identified by future research and enforce mandatory prewashes only for hazardous chemicals. This way unnecessary and costly prewashing of lower-risk category Y cargoes could be avoided.

Finally, one possible way of reducing the hazards arising from tank cleaning is to minimize the amount of cargo that remains in a tank after unloading. It might be preferable to utilise a so-called super stripping system in the unloading process more frequently. By using super stripping, the tank can be drained almost completely (Tanker Operator 2008a), which would substantially reduce the volume of chemicals that are released in the sea as a result of tank cleaning. Finally, as no case studies concerning the effects of tank cleaning in the Baltic Sea area were found in this study, sampling surveys or some other monitoring might be indicated in the future.

REFERENCES

ABS, American Bureau of Shipping (2006). Understanding the Revisions to MARPOL Annex II and the IBC Code. ABS Guide to Owners. Available at: http://www.scribd.com/doc/69758863/MARPOL-IBCCODE-6219 (Accessed 18 June 2012).

Ahel, M. & Giger, W. (1993). Partitioning of alkylphenols and alkylphenol ethoxylates between water and organic solvents. Chemosphere 26: 1471–1478.

Ahel, M., Scully, F. E., Hoigné, Jr, J. & Giger, W. (1994). Photochemical degradation of nonylphenol and nonylphenol polyethoxylates in natural waters. Chemosphere 28: 1361–1368.

Allen, D. T. (2002). Evaluating environmental fate: Approaches based on chemical structure. In: Allen, D.T. & Shonnard, D.R. (Eds.), Green Engineering: Environmentally Conscious Design of Chemical Processes pp. 93–135, Prentice Hall, Upper Saddle River, NJ, USA.

Andersson, H., Palm Cousins, A., Brorström-Lundén, E., Wickman, T., Pettersson, M., Holmström, K., Fischer, S. & Parkman, T. (2012). Summary report SWEDEN. Work package 4: Identification of sources and estimation of inputs/impacts on the Baltic Sea. 21 p + Appendices. IVL. Stockholm.

Arnot, J. A. & Gobas, F. A. P. C. (2006). A review of bioconcentration factor (BCF) and bioaccumulation factor (BAF) assessments for organic chemicals in aquatic organisms. Environ. Rev. 14: 257–297.

ATSDR, Agency for Toxic Substances and Disease Registry (2007). Toxicological profile for Xylene. 330 p. U.S. department of health and human services. Available at: http://www.atsdr.cdc.gov/ (Accessed 18 June 2012).

ATSDR, Agency for Toxic Substances and Disease Registry (2008). Toxicological profile for phenol. 226 p. U.S. department of health and human services. Available at: http://www.atsdr.cdc.gov/ (Accessed 18 June 2012).

Benville, P.E. & Korn S. (1977). The acute toxicity of six monocyclic aromatic crude oil components to striped bass (Morone saxatilis) and bay shrimp (Crago franciscorum). California Fish and Game 63(4): 204–209.

Black, J. A., Birge, W. E., McDonnell, W. E., Westerman, A. G., Ramey, B. A. & Bruser, D. M. (1982). The aquatic toxicity of organic compounds to embryo-larval stages of fish and amphibians. Research report no 133, University of Kentucky, Water Resources Institute, Lexington, Kentucky.

BLG Working group (2009). Implementation of MARPOL Annex II. BLG Working group. On the evaluation of safety and pollution hazards of chemical 15th Session. Agenda item 8 – IMO. BLG/ESPH 15/8.10/9/2009.

Bonn Agreement (2007). Hazardous Materials. Online. Available at: http://www.bonnagreement.org/eng/html/counter-pollution_manual/chapter26_hazardous%20materials.htm (Accessed 23 August 2012).

Brooke, L. T. (1993). Acute and chronic toxicity of nonylphenol to ten species of aquatic organisms. Report to the U.S. Environmental Protection Agency, Duluth, MN (contract no. 68-C1-0034). Lake Superior Research Institute, University of Wisconsin-Superior, Superior, Wis. Julkaisematon, cited in U.S. EPA 2005.

Butterworth Inc. (2012). Product Data Sheet. Tank Cleaning Machine, Type: LT & LT-FT. Available at: http://www.butterworth.com/Data_Sheets/LT_LTFT_Tank_Clean_DS.pdf. (Accessed 14 August 2012).

Camphuysen, K. C. J., Barreveldà, H., Dahlmann, G. & Van Franeker, J. A. (1999). Seabirds in the North Sea Demobilized and Killed by Polyisobutylene $(C_4H_8)_n$ (PIB). Marine Pollution Bulletin 38: 1171–1176.

Camphuysen, K. C. J. (2007). Chronic oil pollution in Europe. A status report. Royal Netherlands Institute for Sea Research. 85 p. International Fund for Animal Welfare (IFAW). Brussels.

CCME, Canadian Council of Ministers of the Environment (1999). Canadian Water Quality Guidelines for the Protection of Aquatic Life: Styrene. 3 p. Winnipeg.

CEDRE, Centre of Documentation, Research and Experimentation on Accidental Water Pollution (2005). Chemical response guide. Sodium hydroxide 50% solution. 57 p. France.

CEDRE, Centre of Documentation, Research and Experimentation on Accidental Water Pollution (2006). Chemical response guide. Sulphuric acid. 64 p. France.

CEDRE, Centre of Documentation, Research and Experimentation on Accidental Water Pollution (2008). Chemical response guide. Xylenes. 69 p. France.

CEDRE, Centre of Documentation, Research and Experimentation on Accidental Water Pollution (2012). Understanding Chemical Pollution at Sea. Learning guide. Brest. 93 p. Available at: www.cedre.fr, "Publications" section.

CEFIC (2005). *Daphnia magna* reproduction test with p-xylene. DHI water & Environment.

CEPA, Canadian Environmental Protection Act (1993). Priority substances list assessment reports: Xylenes. 32 p. Minister of Supply and Services. Available at: http://www.ec.gc.ca/CEPARegistry/subs_list/Priority.cfm (Accessed 14 August 2012).

CEPA, Canadian Environmental Protection Act (2000). Priority substances list assessment reports: Phenol. 66 p. Minister of Supply and Services. Available at: http://www.ec.gc.ca/CEPARegistry/subs_list/Priority.cfm (Accessed 14 August 2012).

CEPA, Canadian Environmental Protection Act (2001a). Priority substances list assessment report: Ammonia in the Aquatic Environment. 96 p. Minister of Public Works and Government Services. Available at: http://www.ec.gc.ca/CEPARegistry/subs_list/Priority.cfm (Accessed 14 August 2012).

CEPA, Canadian Environmental Protection Act (2001b). Priority substances list assessment report: Nonylphenol and its Ethoxylates. 97 p. Minister of Public Works and Government Services. Available at: http://www.ec.gc.ca/CEPARegistry/subs_list/Priority.cfm (Accessed 14 August 2012).

CHEMTEC Consulting GmbH (1999). CTC-Cleaner- VLC. 25 p. Dassendorf, Germany.

Crompton, T. R. (2007). Toxicants in Aqueous Ecosystems. Springer-Verlag. Berlin Heidelberg. 456 p.

CSID (2012). ChemSpider – The free chemical database. Available at: http://www.chemspider.com/Chemical-Structure.1086.html (Accessed 25.8.2012).

Cushman J. R., Rausina, G. A., Cruzan, G., Gilbert, J., Williams, E., Harrass, M. C., Sousa, J. V., Putt, A. E., Garvey, N. A., St Laurent, J. P., Hoberg, J. R. & Machado, M. V. (1997). Ecotoxicity hazard assessment of styrene. Ecotoxicology and Environmental Safety 37: 173–180. Cited in Häkkinen et al. 2010.

Dahlmann, G., Timm, D., Averbeckt, C. H. R., Camphuysen, C., Skov, H. & Durinck, J. (1994). Oiled Seabirds-Comparative Investigations on Oiled Seabirds and Oiled Beaches in the Netherlands Denmark and Germany (1990–93). Marine Pollution Bulletin 28: 305–310.

Drew Marine (2005). Tank cleaning manual. 5th Ed. 102 p. Ashland Inc. Boonton NJ, USA.

EC, European Commission (2003). Technical Guidance Document on Risk Assessment in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances Commission Regulation (EC) No 1488/94 on Risk Assessment or existing substances Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market Part II. Office for official publications of the European Communities. Luxembourg.

Ekelund, R., Granmo, A., Magnusson, K., Berggren, M. & Bergman, A. (1993). Biodegradation of 4-nonylphenol in seawater and sediment. Environ. Pollut.79: 59–61.

Envichem (2012). Data bank of environmental properties of chemicals. Maintained by Finnish Environment Institute (SYKE). Available at: http://wwwp.ymparisto.fi/scripts/Kemrek/Kemrek.asp?Method=MAKECHEMSEARCHFORM (Accessed 14 August 2012).

Environment Canada (2011). Birds Oiled at Sea. Online. Available at: http://www.ec.gc.ca/mbc-com/default.asp?lang=En&n=C6E52970-1#_1 (Accessed 24 August 2012).

FEA, Finland's Environmental Administration (2012). Protection of the Baltic Sea. Available at: http://www.ymparisto.fi/default.asp?node=17722&lan=en (Accessed 11 July 2012).

Fent, K. (2004). Ecotoxicological effects at contaminated sites. Toxicology 205: 223–240.

Ferrari, G. M., Boa, F. G. & Babin, M. (2003). Geo-chemical and optical characterizations of suspended matter in European coastal waters. Estuarine, Coastal and Shelf Science 57: 17–24.

FIOH, Finnish Institute of Occupational Health (2011a). OVA-ohje: Onnettomuuden vaaraa aiheuttavat aineet: Fenoli [Substances causing accident hazard: Phenol]. In Finnish. Available at: http://www.ttl.fi/ova/fenoli.html (Accessed 11 July 2012).

FIOH, Finnish Institute of Occupational Health (2011b). OVA-ohje: Onnettomuuden vaaraa aiheuttavat aineet: Rikkihappo [Substances causing accident hazard: Sulphuric acid]. In Finnish. Available at: http://www.ttl.fi/ova/rikkiha.html (Accessed 11 July 2012).

FIOH, Finnish Institute of Occupational Health (2011c). OVA-ohje: Onnettomuuden vaaraa aiheuttavat aineet: Styreeni [Substances causing accident hazard: Styrene]. In Finnish. Available at: http://www.ttl.fi/ova/styreeni.html (Accessed 11 July 2012).

FIOH, Finnish Institute of Occupational Health (2011d). OVA-ohje: Onnettomuuden vaaraa aiheuttavat aineet: Ksyleeni [Substances causing accident hazard: Xylene]. In Finnish. Available at: http://www.ttl.fi/ova/ksyleeni.html (Accessed 11 July 2012).

Fliedner, A. (1993). *Daphnia magna*, Reproduction test (OECD No. 202). FraunhoferBInstitute fur Umweltchemie und Okotoxikologie, Postfach 1260, WB5948 Schmallenberg B Grafschaft, Germany. Report No. UBAB002/4B22. Cited in U.S. EPA 2005. Cited in Häkkinen et al. 2010.

French McKay, D. P., Whittier, N., Ward, M. & Santos, C. (2006). Spill hazard evaluation for chemicals shipped in bulk using modelling. Environmental Modelling and Software 21: 156–169.

Furman, E., Dahlström, H. & Hamari, R. (1998). Itämeri – luonto ja ihminen [Baltic Sea – man and nature]. In Finnish. 159 p. Otava. Keuruu.

Galassi, S., Mingazzini, M., Vigano, L., Cesareo, D. & Tosato, M. L. (1988). Approaches to modelling toxic responses of aquatic organisms to aromatic hydrocarbons. Ecotoxicology and Environmental Safety 16: 158–169.

GESAMP, IMO/FAO/UNESCO-IOC/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (2002). The Revised GESAMP Hazard Evaluation Procedure for Chemical Substances Carried by Ships. Rep. Stud. GESAMP No. 64, 126 pp.

Gibbs, B. & Mulligan, C. (1997). Styrene toxicity: An ecotoxicological assessment. Ecotoxicology and environmental safety 38: 181–194.

Guerbet, M. & Jouany, J. M. (2002). Value of the SIRIS method for the classification of a series of 90 chemicals according to risk for the aquatic environment. Environmental Impact Assessment Review 22: 377–391.

Grey, J. S. (2002). Biomagnification in marine systems: the perspective of an ecologist. Marine Pollution Bulletin 45: 46–52.

Hallanaro, E.-L. (2010). Merkillinen Itämeri [The Extraordinary Baltic Sea]. In: Bäck, S., Ollikainen, M., Bonsdorff, E., Eriksson, A., Hallanaro, E-L., Kuikka, S., Viitasalo, M. & Walls, M. (eds.), Itämeren tulevaisuus [The Future of the Baltic Sea]. In Finnish: 23–25. Gaudeamus Helsinki University Press. Tampere.

Hampton, S., Kelly, P. R. & Carter, H. (2003). Tank vessel operations, seabirds, and chronic oil pollution in California. Marine Ornithology 31: 29–34.

HASREP (2005). Response to harmful substances spilled at sea. Task 2. Risk assessment methodology for the transport of hazardous and harmful substances in the European Union maritime waters. CEDRE. Brest. 32 p.

Hassler, B. (2011). Accidental Versus Operational Oil Spills from Shipping in the Baltic Sea: Risk Governance and Management Strategies. AMBIO 40: 170–178.

HELCOM (1993). Seminar on Reception Facilities in Ports. Turku, Finland, 16–19 November 1992. Balt. Sea. Environ. Proc. No. 50. Available at: http://www.helcom.fi/stc/files/Publications/Proceedings/bsep50.pdf (Accessed 20 August 2012).

HELCOM (2002). Response to accidents at sea involving spills of hazardous substances and loss of packaged dangerous goods. HELCOM Manual on Co-operation in Response to Marine Pollution within the framework of the Convention on the Protection of the Marine Environment of the Baltic Sea Area (Helsinki Convention), Volume 2. 184 p. Available at: http://www.helcom.fi/stc/files/ResponseManual/ResponseManualVol_2.pdf (Accessed 24 August 2012).

HELCOM (2009). Overview of the shipping traffic in the Baltic Sea. Online. Available at: http://www.helcom.fi/stc/files/shipping/Overview%20of%20ships%20traffic_updateApril2009.pdf (Accessed 23 August 2012).

HELCOM (2010a). Maritime Activities in the Baltic Sea – An integrated thematic assessment on maritime activities and response to pollution at sea in the Baltic Sea Region. Balt. Sea Environ. Proc. No. 123. 64 p. Available at: http://www.helcom.fi/stc/files/Publications/Proceedings/bsep123.pdf (Accessed 12 July 2012).

HELCOM (2010b). Ecosystem Health of the Baltic Sea 2003–2007: HELCOM Initial Holistic Assessment. Balt. Sea Environ. Proc. No. 122. 63 p. Available at: http://www.helcom.fi/stc/files/Publications/Proceedings/bsep122.pdf (Accessed 2 July 2012).

HELCOM (2010c). Hazardous substances in the Baltic Sea – An integrated thematic assessment of hazardous substances in the Baltic Sea. Balt. Sea Environ. Proc. No. 120B. 116 p. Available at: http://www.helcom.fi/stc/files/Publications/Proceedings/bsep120B.pdf (Accessed 2 July 2012).

HELCOM (2010d). Illegal Discharges of Oil in the Baltic Sea. HELCOM Indicator Fact Sheets 2010. Online. Available at: http://www.helcom.fi/BSAP_assessment/ifs/ifs2010/en_GB/illegaldischarges/ (Accessed 18.7.2012).

HELCOM (2011). Annual 2011 HELCOM report on illegal discharges observed during aerial surveillance. 13 p. Available at: http://www.helcom.fi/stc/files/shipping/spills2011.pdf (Accessed 24 August 2012).

Helle, I. & Kuikka, S. (2010). Itämeren öljykuljetusten riskipeli [The risky business of oil transportation]. In: Bäck, S., Ollikainen, M., Bonsdorff, E., Eriksson, A., Hallanaro, E-L., Kuikka, S., Viitasalo, M. & Walls, M. (eds.), Itämeren tulevaisuus [The Future of the Baltic Sea]. In Finnish: 190–205. Gaudeamus Helsinki University Press. Tampere.

Helsingin Sanomat (2003). Kalat kuolivat Crystal Rubinon myrkkyihin. [Fish died from the poisons of Crystal Rubino in Hamina]. In Finnish. Newspaper Helsingin Sanomat 2.6.2003. Helsinki.

Herman, D. C., Mayfield, C. I. & Inniss, W. E. (1991). The relationship between toxicity and bioconcentration of volatile hydrocarbons by the algae Selenastrum capricornutum. Chemosphere, 22: 665–676.

Hjalmarsson, S., Wesslanderb, K., Andersona, L. G., Omstedtb, A., Perttila, M. & Mintropa, L. (2008). Distribution, long-term development and mass balance calculation of total alkalinity in the Baltic Sea. Continental Shelf Research 28: 593–601.

Holma, E., Heikkilä, A., Helminen, R. & Kajander, S. (2011). Baltic Port List 2011 – Annual cargo statistics of ports in the Baltic Sea Region. A publication from the Centre for Maritime Studies, University of Turku. 180 p.

HSDB, Hazardous Substances Data Bank (2012). Maintained by U.S. National Library of Medicine. Available at: http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB (Accessed 18.7.2012).

Hurford, N., Law, R. J., Payne, A. P. & Fileman, T. W. (1989). Concentrations of Chemicals in the North Sea Arising from Discharges from Chemical Tankers. Oil & Chemical Pollution 5: 391–410.

Hurford, N., Law, R. J., Fileman, T. W., Payne, A. P. & Colcomb-Heiliger, K. (1990). Concentrations of Chemicals in the North Sea due to Operational Discharges from Chemical Tankers – Results from the Second Survey, October 1988. Oil & Chemical Pollution 7: 251–270.

HUTA CYNKU (2011). Material safety data sheet. Sulphuric acid technical. HUTA CYNKU Miasteczko Śląskie S.A. Poland. 12 p. Available at: http://www.hcm.com.pl/sites/default/files/kch_kwas_siarkowy_techniczny_EN_12_12_2011.pdf (Accessed 7 August 2012).

Håkanson, L., Lundin, L.-C., Savchuk, O., Ionov, V., Musielak, S. & Furmanczyk, K. (2003). The Baltic Sea. In: Ryden, L., Migula, P. & Andersson ,M. (eds.), Environmental Science: 120–146. The Baltic University Press. Uppsala.

Häkkinen, J., Kiiski, A., Malk, V., Myyrä, M. & Penttinen, O.-P. (2010). Kemikaalikuljetusonnettomuuteen varautuminen Kymenlaaksossa – ympäristöriskien arviointi ja puhdistusmenetelmien vertailu [Preparing for a chemical transport accident in the Kymenlaakso area – comparison between different risk assessment and remediation methods]. In Finnish. 142 p. Yliopistopaino, Helsinki.

Häkkinen, J., Malk, V., Penttinen, O.-P., Mäkelä, R. & Posti, A. (2012). Environmental risk assessment of most transported chemicals in sea and on land – an analysis of Southern Finland and the Baltic Sea – In: Töyli, J., Johansson, L., Lorentz, H., Ojala, L. & Laari, S. (eds.), Nofoma 2012 – proceedings of the 24th Annual Nordic logistics research Network conference. 313–328.

Hänninen, S. & Rytkönen, J. (2006). Transportation of liquid bulk chemicals by tankers in the Baltic Sea. VTT Technical Research Centre of Finland. VTT Publications 595. 155 p. Available at: http://www.vtt.fi/inf/pdf/publications/2006/P595.pdf (Accessed 27 June 2012).

ICS, International Chamber of Shipping (1995). Tanker Safety Guide (Liquefied Gas) 2nd Ed. Edward Mortimer Ltd. Halifax. West Yorkshire. 259 p.

ICS, International Chamber of Shipping (2002). Tanker Safety Guide (Chemicals) 3rd Ed. Edward Mortimer Ltd. Halifax. West Yorkshire. 207 p.

IMO, International Maritime Organization (2008). IMO Marine Environment Policy. Background paper. International Maritime Organization. Marine Environment Division. 20 p. In : Sixteenth OSCE Economic and Environmental Forum - Part 1: "Maritime and inland waterways co-operation in the OSCE area: Increasing security and protecting the environment" Vienna, 28–29 January 2008. Available at: http://www.osce.org/eea/30453 (Accessed at 23 August 2012).

IMO, International Maritime Organization (2011a). Particularly Sensitive Sea Areas. Online. Available at: http://www.imo.org/OurWork/Environment/PollutionPrevention/PSSAs/Pages/Default.aspx (Accessed 11 July 2012).

IMO, International Maritime Organization (2011b). International Code for the Construction and Equipment of Ships carrying Dangerous Chemicals in Bulk (IBC Code). Online. Available at: http://www.imo.org/OurWork/Environment/PollutionPrevention/ChemicalPollution/Pages/IBCCode.aspx (Accessed 11 June 2012).

IMO, International Maritime Organization (2011c). International Convention for the Safety of Life at Sea (SOLAS), 1974. Online. Available at: http://www.imo.org/about/conventions/listofconventions/pages/international-convention-for-the-safety-of-life-at-sea-%28solas%29,-1974.aspx (Accessed 23 August 2012).

IMO, International Maritime Organization (2011d). Chemical reporting forms. Online Available at: http://www.imo.org/ourwork/environment/pollutionprevention/chemicalpollution/pages/chemicalsreportingforms.aspx (Accessed 8 June 2012).

INTERTANKO (2006). The Revisions to MARPOL Annex II - A Practical Guide. 42 p. Available at: http://eliteblacksea.com/files/article/marpolannexiiguide.pdf (Accessed 23 August 2012).

Isobe, T., Nishiyama, H., Nakashima, A. & Takada, H. (2001). Distribution and behaviour of nonylphenol, octylphenol, and nonylphenol monoetoxylate in Tokyo metropolitan area: Their Association with aquatic particles and sedimentary distributions. Environ. Sci. Technol. 35: 1041–1049.

ITOPF, The International Tanker Owners Pollution Federation (2010). About Marine Spills. Online. Available at: http://www.itopf.com/marine-spills/about-hns/#fate (Accessed 11 July 2012).

IUCLID dataset (2000a). Phenol, Substance ID: 108-95-2. 175 p. European Commission, European Chemicals Bureau.

IUCLID Dataset (2000b). Sulphuric acid, Substance ID: 7664-93-9. 178 p. European Commission, European Chemicals Bureau.

Jo Tankers (1999). General tank cleaning guide. Jo Tankers B.V. 48 p.

John, D. M., House, W. A. & White, G. F. (2000). Environmental fate of nonylphenol ethoxylates: differential adsorption of homologs to components of river sediment. Environmental Toxicology and chemistry 19: 293–300.

Koskela, S., Seppälä, J., Hiltunen, M.-R. & Mattila, T. (2006). Kemikaalin häiriöpäästön ympäristöriskinarviointi EUSES-mallilla. [Assessing the environmental risk of a chemical release with the EUSES-model]. In Finnish. Suomen ympäristökeskuksen raportteja 5/2006.

Kronberg, L. (1999). Content of Humic Substances in Freshwater. – In: Keskitalo, J. & Eloranta, P. (eds.), Limnology of Humic Waters: 9–10. Backhuys Publishers, Leiden. 284 s.

Kumblad, L. & Rydin, E. (2012). Restoration measures in Björnöfjärden. Online. Available at: http://www.balticsea2020.org/english/bibliotek/33-living-coast/199-permanent-fixing-of-phosphorus-in-sediment (Accessed 28 August 2012).

Kunichkin, V. (2006). Chemical Tanker Notes. 234 p. Seamanship International Ltd. Lanarkshire, UK.

Lakey, R. (1975/76). The 1973 Marine pollution convention's impact on ships transporting hazardous materials. Journal of Hazardous Materials 1: 113–128.

Larsson, K. & Tydén, L. (2005). Effekter av oljeutsläpp på övervintrande alfågel *Clangula hyemalis* vid Hoburgs bank i centrala Östersjön mellan 1996/97 och 2003/04. [Effects of oil spills on wintering Long-tailed Duck *Clangula hyemalis* at Hoburgs bank in central Baltic Sea between 1996/97 and 2003/04]. In Swedish. ORNIS SVECICA 15: 161–171.

Larsson, K. &Tydén, L. (2009). Inventeringar av oljeskadad alfågel längs Gotlands sydkust under perioden 1996/97 till 2008/09. [Surveys on oiled long-tailed ducks in the Eastern coast of Gotland from 1996/97 to 2008/09]. In Swedish. 13 p. Report. Gotland University.

Larsson, K. & Tydén, L. (2011). Inventeringar av oljeskadad alfågel längs Gotlands sydkust under perioden 1996/97 till 2010/11 [Surveys on oiled long-tailed ducks in the Eastern coast of Gotland from 1996/97 to 2010/11]. In Swedish. 13 p. Report. Gotland University.

Liber, K., Knuth, M. & Stay, F. (1999). An integrated evaluation of the persistence and effects of 4-nonylphenol in an experimental littoral ecosystem. Environmental Toxicology and Chemistry 18: 357–362.

Lide, D. R. (2005). CRC handbook of chemistry and physics. 86th Ed. 2544 s. CRC Press. Boca Raton. Florida.

Lide, D. R. (2009). CRC handbook of chemistry and physics. 89th Ed. CRC Press. Boca Raton. Florida.

Lilja, K., Norström, K., Remberger, M., Kaj, L., Egelrud, L., Junedahl, E., Brorström-Lundén, E., Ghebremeskel, M. & Schlabach, M. (2009). Screening of Selected Hazardous Substances in the Eastern Baltic Marine Environment. 57 p. IVL. Stockholm.

Lloyd's Register (2006). Revised MARPOL 73/78 Annex II and IBC Code – A guide to changes for tankers and offshore supply vessels. 17 p. Lloyds register. Classification News No 14/2006.

Lussier, S. M., Champlin, D., LiVolsi, J., Poucher, S. & Pruell, J. R. (2000). Acute toxicity of para-nonylphenol to saltwater animals. Environmental Toxicology and Chemistry 19: 617–621.

Luhtala, H. (2010). Maritime transport of chemicals in the Baltic Sea, Publications from the Centre of Maritime Studies, University of Turku. 47 p.

McGeorge, H. D. (1995). Marine Auxiliary Machinery 7th Ed. 525 p. Butterworth-Heinemann, Elsevier Ltd. Great Britain.

Mackay, D. (1979). Finding fugacity feasible. Environmental Science & Technology: 13: 1218–1223.

Mackay, D. & Leinonen, P. J. (1975). Rate of evaporation of low solubility contaminants from water body to atmosphere. Environ. Sci. Technol. 9: 1178–1180.

Mackay, D., Shiu, W. Y., Ma, K. C., Lee, S. C. (2006). Handbook of physical-chemical properties and environmental fate for organic chemicals. 2nd Ed. 4182 p. Taylor & Francis Group/CRC Press. Boca Raton. Florida.

Maffii, S. (2007). External costs and climate impacts of maritime transport. Note. – Policy Department B. Structural and Cohesion Policies. Transport and tourism. Note PE 379.227. 43 p. Bruxelles. European Parliament. Available at: http://www.trt.it/english/Schede-progetti/European-parliament/External%20Costs%20of%20Maritime%20Transport.pdf (Accessed 24 August 2012).

Majima, T., Yamaguchi, K., Yamanouchi, H., Fujii, S. & Sakamoto, S. (2000). Experiment using Scale Model of Cargo Tank to Estimate the Concentration of Benzene Gas Emitted from Chemical Tanker During Loading Operation. 7 p. SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, 26–28 June 2000, Stavanger, Norway.

Malmsten, C. L. (2001). Vaaralliset kemikaalionnettomuudet. [Hazardous chemical accidents]. In Finnish. 330 p. Tammi. Tampere.

Mamaca, E., Bechmann R. K., Torgrimsen, S., Aas, E., Bjørnstad A, Baussant, T. & Le Floch, S. (2005). The neutral red lysosomal retention assay and Comet assay on haemolymph cells from mussels (*Mytilus edulis*) and fish (*Symphodus melops*) exposed to styrene. Aquatic Toxicology 75(3): 191–201. Cited in Häkkinen et al. 2010.

Manzano, M. A., Perales, J. A., Sales, D. & Quiroga, J. M. (1999). The effect of temperature on the biodegradation of a nonylphenol polyethoxylate in river water. Water research 33: 2593–2600.

MEPC, Marine Environment Protection Committee (2012). List Of Special Areas Under MARPOL And Particularly Sensitive Sea Areas. – IMO. MEPC.1 Circ. 778. 26/1/2012. 6 p. Available at: http://www.imo.org/blast/blastDataHelper.asp?data_id=30979&filename=778.pdf (Accessed 23 July 2012).

Mercier, J. A., Hires, R. I. & Wu, M. (1974). Model study on the dilution of soluble liquids discharged from tankers. Final report. 106 p. Stevens Inst. of Tech. Davidson Lab. Hoboken. New Jersey.

NesteOil (2006). Ympäristölupapäätös. Länsi-Suomen Ympäristölupavirasto. Ympäristöpäätös Nro 29/2006/2. Dnro LSY-2004-Y-120.

Ng, A. K. & Song, S. (2010). The environmental impacts of pollutants generated by routine shipping operations on ports. Ocean & Coastal Management 53: 301–311.

Nikunen, E. & Leinonen, R. (2002). Ympäristölle vaaralliset kemikaalit – riskinarviointi ja luokitus [Environmentally hazardous chemicals – Risk assessment and classification]. In Finnish. 142 p. Chemas Oy. Helsinki.

Nunes, P. & Benville, P. (1979). Uptake and depuration of petroleum hydrocarbons in the Manila clam (Tapes semidecussata). Bulletin of Environmental Contamination and Toxicology 21: 719–726.

Ogata, M. & Miyake, Y. (1978). Disappearance of aromatic hydrocarbons and organic sulphur compounds from fish flesh reared in crude oil suspension. Water Research 12: 1041–1044.

OECD, Organization for Economic Co-operations and Development (1997). SIDS (Existing Chemicals Program) Initial assessment report for 6th SIAM. Prepared by M. Thomas, Environment Agency, National Centre for Ecotoxicology and hazardous substances. London. UK.

OECD, Organization for Economic Co-operations and Development (2001). SIDS. Sulphuric Acid CAS N°: 7664-93-9. UNEP Publications.

OECD, Organization for Economic Co-operations and Development (2008). OECD guidelines for the testing of chemicals. Bioaccumulation in Sediment-dwelling Benthic Oligochaetes. OECD/OCDE Test No. 315.

Olson, P. (1994). Handling of Waste in Ports. Marine Pollution Bulletin. 29: 6–12: 284–295.

Omstedt, A., Gustafsson, E. & Wesslander, K. (2009). Modelling the uptake and release of carbondioxide in the Baltic Sea surface water. Continental Shelf Research 29: 870–885.

Oost; R., Beyer, J & Vermeulen, N. P. E. (2002). Fish bioaccumulation and biomarkers in environmental risk assessment: a review. Environmental Toxicology and Pharmacology 13: 57–149.

Portman, J. E. (1981). Recent activities of GESAMP working group on the evaluation of hazardous substances carried by ships. Ecotoxicology and Environmental Safety 5: 56–71.

Posti, A. & Häkkinen, J. (2012). Survey of transportation of liquid bulk chemicals in the Baltic Sea. Publications from the Centre for Maritime Studies University of Turku, A 60. 78 p.

Qureshi, A. A., Flod, K. W., Thompson, S. R., Janhurst, S. M., Inniss, C. S., & Rokosh, D. A. (1982). Comparison of a luminescent bacterial test with other bioassays for determining toxicity of pure compounds and complex effluents – In: Pearsonm J.G, Foster, R.B., & Bishop,W.E. (eds.): Aquatic Toxicology and Hazard Assessment, 5th Conference. 179–195 p. American Society for Testing and Materials, Philadelphia. Available at: http://www.astm.org/DIGITAL_LIBRARY/STP/PAGES/STP36718S.htm (subject for a fee, Accessed 25.7.2008).

Schumann, R., Rieling, T., Görs, S., Hammer, A., Selig, U. & Schiewer, U. (2003). Viability of bacteria from different aquatic habitats. I. Environmental conditions and productivity. Aquatic Microbial ecology 32: 121–135.

Servos, M. R. (1999). Review of the aquatic toxicity, estrogenic responses and bioaccumulation of alkylphenol and alkylphenol polyetoxylates. Water Quality Research Journal of Canada 34: 123–177.

Shang, D. Y., Macdonald, R. W. & Ikonomou, M. G. (2008). Persistence of nonylphenol ethoxylate surfactants and their primary degradation products in sediments from near a municipal outfall in the strait of Georgia, British Columbia, Canada. Environmental Science & Technology 33: 1366–1372.

Skov, H., Heinänen, S., Žydelis, R., Bellebaum, J., Bzoma, S., Dagys, M, Durinck, J., Garthe, S., Grishanov, G., Hario, M., Kieckbusch, J. J., Kube, J., Kuresoo, A., Larsson, K., Luigujoe, L., Meissner, W., Nehls, H. W., Nilsson, L., Krag Petersen, I., Mikkola Roos, M., Pihl, S., Sonntag, N., Stock, A. & Stipniece, A. (2011). Waterbird populations and pressures in the Baltic Sea. TemaNord 2011: XX. Nordic Council of Ministers, Copenhagen 2011.

Soares, A., Guieysse, B., Jefferson, B., Carntmell, E. & Lester, J. N. (2008). Nonylphenol in the environment: a critical review on occurrence, fate, toxicity, and treatment in wastewaters. Environment International 34: 1033–1049.

Sormunen, O. (2012). Spill estimation of chemical tanker collisions in the Gulf of Finland. Master's thesis. Aalto University School of Science. Espoo 116 p.

SYKE, Finnish Environment Institute (2004). Suomessa käytetyt vesientutkintamenetelmät. Suomen Ympäristö [Research methods used in water research]. In Finnish. SY683. 119 p.

Tanker Operator (2008a). The Science of Cargo Tank Cleaning. TankerOperator Magazine. Vol 7 No 8. 2008. London.

Tanker Operator (2008b). Discharge requirements should be simplified. TankerOperator Magazine. Vol 7 No 8. 2008. London.

U.K. Environment Agency (1997). Draft comprehensive risk assessment report for nonylphenol. National centre for ecotoxicity and hazardous substances. London. U.K.

U.S. EPA, Environmental Protection Agency (1987). Occurrence of synthetic organic chemicals in drinking water, food and air. 175 p. PB89-192520. Office of drinking water Washington, D.C.

U.S. EPA, U.S. Environmental Protection Agency (2005). Aquatic life ambient water quality criteria – nonylphenol. Final. U.S. Environmental Protection Agency. Office of water. Office of Science and Technology. Washington, DC.

Vadakayil, A. (2010). Marpol Rules For Annex 2 Chemical Tankers-- Capt Ajit Vadakayil. Online. Available at: www.ajitvadakayil.blogspot.com (Accessed 24 August 2012).

Vazquez-Duhalt, R. Marquez-Rocha, F., Ponce, E., Licea, A. F. & Viana, M. T. (2005). Nonylphenol, an integrated vision of a pollutant. Scientific review. Applied Ecology and Environmental Research 4: 1–25.

Verwey, Dr. A. (2007). Tank Cleaning Guide 7th Ed. 454 p. Verwey Chemical Laboratories & Superintendence Company. Rotterdam.

Walker, C. H., Hopkin, S. P., Sibly, R. M. & Peakall, D. B. (2006). Principles of Ecotoxicology 3rd Ed. 303 p. Taylor & Francis Inc. New York.

Ward, T. J. & Boeri, R. L. (1990). Acute static toxicity of nonylphenol to the marine alga (Skeletonema costatum). Prepared for the Chemical Manufacturers Association by Resource Analysts, Hampton, New Hampshire (Study No.8970-CMA). Cited in U.S. EPA 2005.

University of Turku
CENTRE FOR MARITIME STUDIES

FI–20014 TURUN YLIOPISTO

http://mkk.utu.fi

Turun yliopisto
University of Turku