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Review of Maritime Accidents Involving Chemicals – Special Focus on the Baltic Sea

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ABSTRACT: Transport and handling of hazardous chemicals and chemical products around the world's waters and ports have considerably increased over the last 20 years. Thus, the risk of major pollution accidents has also increased. Past incidents/accidents are, when reported in detail, first hand sources of information on what may happen again. This paper provides an overview of the past tanker accidents in the Baltic Sea and chemical related accidents in seas worldwide. The aim is to find out what can be learned from past accidents, especially from the environmental point of view. The study is carried out as a literature review and as a statistical review. The study revealed that the risk of a chemical accident is highest in seas where the highest tonnes of chemicals are transported, the density of maritime traffic is highest and, of course, in the ship-shore interface where unloading/loading takes place. Incidents involving chemical spills are statistically much less likely to occur than oil spills. However, chemical cargoes can be more dangerous to humans and property because chemicals can be more combustible, poisonous, irritating and reactive. The most important difference between a chemical and an oil spill may be related to response actions. In case of a chemical accident, the air quality or the risk of explosion should be more carefully evaluated before any response actions are taken. In case of chemical spills, the response is more limited in comparison to oil. Actually, very little is known about the actual marine pollution effect of most of highly transported substances. From the environmental point of view, the previous studies have highlighted accidents in which pesticides were released to water, but also substances considered as non-pollutants (vegetable oils) seem to have a negative effect on biota in the water environment.

1 INTRODUCTION

Transport and handling of hazardous chemicals and chemical products has considerably increased over the last 20 years, thus increasing the risk of major pollution accidents. Worldwide, about 2000 chemicals are transported by sea either in bulk or packaged form. Only few hundred chemicals are transported in bulk but these make up most of the volume of the chemical sea-borne trade (Purnell 2009). Chemical releases are thought to be potentially more hazardous than oil. As to marine spills, chemicals may have both acute and long-term environmental effects, and may not be as easily recoverable as oil spills. In addition, public safety risks are more severe in chemical releases (EMSA 2007).

The Baltic Sea is one of the busiest sea routes in the world – 15 % of the world's cargo moves in it. In 2010, the international liquid bulk transports in the Baltic Sea ports contained around 290 million tonnes of oil and oil products, at least 11 million tonnes of liquid chemicals, and 4 million tonnes of other liquid bulk (Holma et al. 2011; Posti & Häkkinen 2012). In addition, chemicals are transported in packaged form, but tonnes are not studied. Navigation in the Baltic

Sea is challenging due to the relative shallowness, narrow navigation routes, and ice cover of the sea. Oil and chemicals are a serious threat to the highly sensitive Baltic Sea ecosystems. Recently, both the number and the volume of the transported cargo have increased significantly in the Baltic Sea (HELCOM 2009), concomitantly raising the spill/ship collision risk in the Baltic Sea areas (Hänninen et al. 2012). The results of previous studies (EMSA 2010, Hänninen & Rytkönen 2006, Bogalecka & Popek 2008, Mullai et al. 2009, Suominen & Suhonen 2007) indicate that both the spill risks and chemical incidents are not as well-defined than those concerning oils. The expected spill frequency and spill volumes caused by ship-chemical tanker collisions in the Gulf of Finland (GoF) collision probability are much less in case of chemical tankers than in case of oil tankers (Sormunen et al. 2011, Sormunen et al. 2014). Nevertheless, among the wide range of chemicals transported, the potency to cause environmental damage cannot be overlooked.

At their best studies about historical chemical accidents may offer valuable lessons about the reasons leading to the accident, its environmental or health-related consequences or even the costs of the accident. First studies concerning past maritime or port-related HNS accidents were already made two decades ago (Rømer et al. 1993; 1995; Cristou 1999). More recently, many excellent papers and reports concerning maritime accidents have been written, concentrating mainly on the probability and environmental consequences of accidents (e.g. Marchand 2002; Wern 2002) Response to harmful substances spilled at sea (Drogou et al. 2005; EMSA 2007; Mamaca et al. 2009). Oil accidents have been studied more than other HNS accidents, but this is simply because of the higher incident numbers and larger spills (Burgherr 2007). One of the most important issues studied is the difference in response actions in the case of oil and chemical accidents (Marchand 2002; EMSA 2007; Purnell 2009).

The study and analysis of past accidents with consequences to the environment and humans can be a source of valuable information and teach us significant lessons in order for us to prevent future shipping accidents and chemical incidents. The purpose of this study is to provide a review of the past tanker accidents in the Baltic Sea, and chemical-related accidents in seas worldwide, thus aiming at finding out what can be learned from these past accidents, including e.g. occurrence, causes, general rules and particular patterns for the accidents. The study focuses mainly on chemicals transported in liquefied form, but chemical accidents involving substances in packaged form are also studied. Conventional oil and oil products are observed only on a general level. The special scope in the study is put on environmental impact assessment.

2 MATERIALS AND METHODS

The study was carried out in two stages. First, *a literature review* on maritime accidents involving hazardous substances and especially chemicals was made to find out what kind of studies have previously been conducted on the topic, and what are the main results of these studies. Both scientific articles and research reports were taken into account. The studies were mainly searched by using numerous electronic article databases and a web search engine.

Second, *a statistical review* on maritime tanker-related accidents in the Baltic Sea was carried out to find out the amount and types of tanker accidents that have occurred in the Baltic Sea in recent years, and to examine what kind of pollution these accidents caused and have caused since. All types of tankers (e.g. oil tankers, oil product tankers, chemical tankers, chemical product tankers and gas tankers) were included in the review. An overview of the tanker accidents in the Baltic Sea was made by using maritime accident reports provided by the Helsinki Commission (HELCOM) and by the European Maritime Safety Agency (EMSA). More detailed information about maritime accidents involving a tanker was searched using maritime accident databases and reports provided by the authorities and/or other actors responsible for collecting maritime accident data in each Baltic Sea country. More detailed maritime accident investigation reports on accidents were found from Denmark, Finland, Germany, Latvia and Sweden; basic information about accidents was found from Estonia and Lithuania; and no maritime accident data was found from Poland and Russia.

3 MARITIME ACCIDENTS INVOLVING CHEMICALS

There are few more recent impact assessment studies for chemical spills in the scientific literature in comparison to those for oil spills. Recently, there have been some good papers and accident analyses concerning chemicals and other hazardous materials (conventional oil omitted), such as Cedre and Transport Canada 2012, EMSA 2007, HASREP 2005, Mamaca et al. 2009, Marchand 2002 and Wern 2002. In addition, the Centre of Documentation, Research and Experimentation on Accidental Water Pollution (Cedre) collect information about shipping accidents involving HNS for an electric database by using various data sources (Cedre 2012). None of those aforementioned sources are, or even try to be, exhaustive listings of all accidents involving chemicals and other hazardous materials, but they have gathered examples of well-known accidents with some quality information. By compiling accident data from aforementioned sources, 67 famous tanker/bulk carrier accidents involving chemicals and/or other hazardous materials were detected. These accidents frequently involved chemicals or chemical groups like acids, gases, vegetable oils, phenol, ammonia, caustic soda and acrylonitrile. Using the same information sources, 46 accidents involving packaged chemicals or other hazardous materials were listed. In comparison to bulk chemicals, it can be seen that the variety of chemicals involved in accidents is much higher in the case of packaged chemicals. In this section, key findings and lessons to be learned from in relation to vessel chemical accidents are discussed in more detail, the analysis being based on original key studies.

3.1 *Overview of maritime chemical accidents worldwide*

One of the earliest scientific analyses of the past maritime accidents was made by Rømer et al. (1993; 1995). Based on 151 marine accidents involving dangerous goods, Rømer et al. (1993) calculated accident frequencies for the different accident types (collisions, groundings, fire/explosions and structural damage). All types of accidents were rare, ranging from 1 x 10-3 to 2 x 10-2. In their analysis, the accidents involving oils were twice as frequent as accidents involving chemicals. In Rømer et al. (1995), the consequences measured by the number of fatalities from marine accidents (n=1780) during the transport of dangerous goods were investigated and compared with those from other modes of transport (n=1001). Accidents concerning the marine transport of dangerous goods were found to comprise a larger proportion of accidents with fatalities in the range of 10–50 than other transport modes. Almost all accidents with more than 40 fatalities were collisions and accidents with more than 100 fatalities were collisions between (oil)tankers and ferries. Surprisingly, the cargo type, containment type, geographical location or time period had no effect in this study (Rømer et al. 1995).

Rømer et al. (1996) researched, on the basis of 1776 descriptions of water transport accidents involving dangerous goods, the environmental problems relating to releases of this kind. It was found that the most detailed descriptions of environmental consequences concerned oil accidents, although most of the consequences were described as reversible changes. It was shown that crude oil releases, on average, are approximately five times larger than the releases of oil products, and that oil product releases are approximately five times larger than those of other chemicals. Only 2% of the 1776 accidents described in the study contained information on consequences to living organisms, and only 10% contained any information on consequences to ecosystems. A relationship between the minimum kilometres of shore polluted and the tonnes oil released was found in oil accidents. Oil slicks were shown to be five times their breadth in length. Gravity scales used to describe and evaluate environmental consequences were discussed in the study as well.

Gunster et al. (1993) studied petroleum and other hazardous chemical spills in Newark Bay, USA, from 1982 to 1991. A record obtained from the United States Coast Guard (USCG) included 1453 accidental incidents that had resulted in the release of more than 18 million US gallons of hazardous materials and petroleum products in the Newark Bay area. Most accidents had occurred with fuel oils and gasoline. The authors reviewed many environmental studies and concluded that with regards to the amount and frequency of these spills, the elimination of entire species and a reduction in biotic diversity have typically been observed among benthic communities after major releases. Many compounds are also long-lived in the environment and thereby pose a chronic threat to aquatic organisms long after the acute initial effects of the spill have abated (Gunster et al. 1993).

Marchand (2002) presented an analysis of chemical incidents and accidents in the EU waters and elsewhere, and stated that 23 incidents had information written down on related facts, such as accident places and causes, chemical products involved, response actions and environmental impacts. The study categorized the accidents into five groups according to how the substance involved behaved after being spilled at sea: products as packaged form; dissolvers in bulk; floaters in bulk; sinkers in bulk; and gases and evaporators in bulk. Based on Marchand's (2002) analysis, most of the accidents happened in the transit phase at sea, that is, while the vessel was moving. Only four accidents happened in ports or in nearby zones. Most of the accidents happened with bulk carriers (62 per cent of all the incidents), and less often with vessels transporting chemicals in packaged form (38 %). Bad weather conditions and the resulting consequences were the main cause of the accidents (in 62 per cent of all the cases). Marchand (2002) highlighted several issues concerning human health risks in the case of maritime chemical accidents. He also pointed out that in most accident cases the risks affecting human health come usually from reactive substances (reactivity with air, water or other products) and toxic substances. The evaluation of the chemical risks can be very difficult if a ship is carrying diverse chemicals and some of those are unknown during the first hours after the accident. A more recent study, Manaca et al. (2009) weighted the same chemical risks as Marchand (2002). Certain substances such as chlorine, epichlorohydrine, acrylonitrile, styrene, acids and vinyl acetate are transported in large quantities and may pose a very serious threat to human health being highly reactive, flammable and toxic. Both Marchand (2002) and Mamaca et al. (2009) pointed out that consequences and hazards to the environment have varied a lot, considering chemical tanker accidents. Both studies stated that, in light of accidents, pesticide products are one of the biggest threats for the marine environment. If pesticides enter the marine environment, consequences for the near-shore biota, and simultaneously for the people dependent on these resources could be severe. On the other hand, even substances considered as non-pollutants, such as vegetable oils (in accidents like Lindenbank, Hawaii 1975; Kimya, UK 1991; Allegra, France 1997), can also have serious effects for marine species like birds, mussels and mammals (Cedre 2012, Marchand 2002).

By surveying 47 of the best-documented maritime transport accidents involving chemicals in the world from as early as 1947 to 2008, Mamaca et al. (2009) gathered a clear overview of lessons to be learned. Even though the data was too narrow for it to be used in making any statistical findings, the study presented some good examples of maritime chemical accidents. 32 of those accidents occurred in Europe. The list of chemicals that were involved in the accidents more than one time included sulphuric acid (3), acrylonitrile (3), ammonium nitrate (2), and styrene (2). Only 10 of the 47 accidents occurred in ports or in nearby zones. Moreover, 66 per cent of the accidents involved chemicals transported in bulk, whereas 34 per cent involved hazardous materials in packaged form. Primary causes for the reviewed accidents were also studied. Improper maneuver was most frequently the reason for the accident (in 22 per cent of all the cases), shipwreck came second (20 %), and

collision was third (13 %), closely followed by grounding and fire (11 % each).

Based on past accident analysis considering packaged chemicals, Mamaca et al. (2009) pointed out that, in light of packaged goods, as a consequence of high chemical diversity present on the vessel, responders must know environmental fates for different chemicals individually as well as the possible synergistic reactions between them. Even though smaller volumes are transported, packaged chemicals can also be extremely dangerous to humans. This could be seen when fumes of epichlorohydrine leaking from the damaged drums on the Oostzee (Germany 1989) seriously affected the ship´s crew and caused several cancer cases that were diagnosed years after (Mamaca et al. 2009). However, these types of accidents involving packaged chemicals have only a localized short-term impact on marine life. As to accidents caused by fire, there are difficulties in responding to the situation if the vessel is transporting a wide variety of toxic products. It is important yet difficult to have a fully detailed list of the transported products for the use of assessing possible dangers for rescue personnel and public. Based on the analyses of the reviewed accidents, Mamaca et al. (2009) showed that the highest risk for human health comes mainly from reactive substances (reactivity with air, water or other products). They also noted that many chemicals are not only carcinogenic and marine pollutants, but can form a moderately toxic gas cloud which is often capable of producing a flammable and/or explosive mix in the air. Acrylonitrile is a toxic, flammable and explosive chemical, and if it is exposed to heat, a highly toxic gas for humans (phosgene) is formed. Vinyl acetate, in turn, is a flammable and polymerizable product that in the case of Multi Tank Ascania incident (in United Kingdom, in 1999) caused a huge explosion. Little is known about the actual marine pollution effects of most of these substances. If hazardous chemicals and oil are compared, it can be said that the danger of coastline pollution is a far greater concern for oil spills than it is for chemical spills. On the other hand, the toxic clouds are a much bigger concern in the case of chemical accidents (Mamaca et al. 2009).

In their HNS Action Plan, EMSA (2007) reviewed past incidents involving a HNS or a chemical. About 100 HNS incidents were identified from 1986 to 2006. These incidents included both those that resulted in spill and those that did not. EMSA (2007) stated that caution should be applied to the data concerning the total sum of the incidents as well as the amount of spills, because there is variability in the reports from different countries. Statistics showed that the principle cause for both release and non-release incidents were foundering and weather (in 22 per cent of all the incidents), followed by fire and explosion in cargo areas (20 %), collision (16 %) and grounding (15%). Majority of the accidents involved single cargoes (73 %), in which most of the material was carried in bulk form (63 %). Moreover, 50 % of all studied incidents resulted in an HSN release. As to these release accidents/incidents, most of them happened in the Mediterranean Sea (40 %); some in the North Sea (22 %) and Channel Areas (20 %), whereas only 8 per cent occurred in the Baltic Sea. The foundering and weather was again the principle cause of these release incidents in 34 per cent of the cases, followed by fire and explosion in cargo areas (18 %), collision (14 %), and grounding (10 %). The majority of the incidents resulting in HNS release involved single cargoes (78 %) of which 61 per cent was in bulk form (EMSA 2007).

HASREP project listed major maritime chemical spills (above 70 tonnes) in the EU waters from 1994-2004 (HASREP 2005). The project found 18 major accidents altogether, and most of them happened in France or Netherlands. Interestingly, 8 accidents listed in HASREP (2005) were not mentioned in the study of Mamaca et al. (2009). The average occurrence of a major maritime chemical accident in the European Union was nearly 2 incidents per year (HASREP 2005). By comparison, the statistical study made by the U.S. Coast Guard (USCG) in the United States over 5 year-span (1992–1995) listed 423 spills of hazardous substances from ships or port installations, giving an average of 85 spills each year. The 9 most frequently spilled products were sulfuric acid (86 spill cases), toluene (42), caustic soda (35), benzene (23), styrene (20), acrylonitrile (18), xylenes (18), vinyl acetate (17) and phosphoric acid (12). Over half of the spills were from ships (mainly carrier barges), and the rest from facilities (where the spill comes from the facility itself or from a ship in dock). A complementary study made over a period of 13 years (1981–1994) on the 10 most important port zones reported 288 spills of hazardous substances, representing on average, 22 incidents each year (US Coast Guard 1999). Small spillages in Europe were not recorded with a similar care because they were not detected and/or there was a lack of communication between environmental organizations and competent authorities (HASREP 2005).

Cedre and Transport Canada (2012) analyzed a total of 196 accidents that occurred across the world´s seas between 1917 and 2010. The substances that were most frequently spilled and that had the greatest quantities were sulphuric acid, vegetable oils, sodium hydroxide solutions and naphtha. Quite surprisingly, the study showed that structural damage (18 %) was the main cause of accidents involving hazardous materials, followed by severe weather conditions (16 %), collision (13 %), and grounding (11 %). Loading/unloading was the cause for only 7 per cent of the accidents (Cedre and Transport Canada 2012).

3.2 *Animal and vegetable oils*

Even though vegetable oil transport volume remains 200 times smaller than the volume of mineral oil transport, it has increased dramatically (Bucas & Saliot 2002). Thus, the threat of a vegetable oil spill due to a ship accident or accidental spill is presently increasing. Even though vegetable oils are regarded as non-toxic consumable products, they may be hazardous to marine life when spilled in large quantities into the marine environment. Bucas & Saliot (2002) observed that there are 15 significant cases of pollution by vegetable or animal oils that have been reported during the past 40 years worldwide. Rapeseed oil was involved in five cases, soybean oil and palm oil in three cases each, coconut oil, fish oil and anchovy oil in one case each, and in

two cases the product was unknown. The largest amount of vegetable oil was spilled in Hawaii in 1975 when M.V. Lindenbank released 9500 tonnes of vegetable oils to coral reef killing crustaceans, mollusks and fishes. It also impacted green algae to grow excessively as well as caused tens of birds to die. Similarly, the fish oil accident had also a serious effect on marine environment, killing lobsters, sea urchins, fishes and birds (Bucas & Saliot 2002).

Based on past cases, Bucas & Saliot (2002) described the environmental fate of vegetable oil spills. The specific gravity of vegetable oils is comprised between 0.9 and 0.97 at 20º Celsius. After spilled into the sea, these oils remain at the surface of the sea and spread forming slicks. The further fate of these oils depends on the nature of the oil, the amount spilled, the air and sea temperatures etc. In open seas or in ports, the consequences are often severe because of local and tidal current movements. The slick can easily spread over several square kilometers. Few hours or days after a spill, the slick is usually no longer regular. A part of the oil may be mingled with sand, some of it may have polymerized and sunk, and in the open sea, mechanical dispersion of the oil slick makes it more available to bacterial degradation. Overall biological degradation can be achieved within 14 days, whereas it takes 25 days for a petroleum product to degrade. If the accident happens in a shallow bay, this bacterial degradation may result in lack of oxygen in the water column (Bucas & Saliot 2002).

Bird loss is usually a major consequence of vegetable oil spills. Slicks are often colorless with a slight odor, and thus they are not easily detected by birds. Several mechanisms lead birds to death after oiling: For example, the loss of insulating capacity of wetted feathers makes birds die from cold; the loss of mobility makes them as easy catch; the loss of buoyancy due to coated feathers results in drowning; the laxative properties of the oil ingested during self-cleaning cause lesions; and the clog of nostrils and throat can result to suffocation. As to crustaceans, the invertebrates have died, for instance, from asphyxiation of clogging of the digestive track. Anoxia of the whole water column may also be the cause of these deaths, and there is also evidence that e.g. sunflower oil can be assimilated on tissues of mussels, as it has happened in the case of the Kimya accident (Bucas & Saliot 2002, Cedre 2012). Bucas & Saliot (2002) stated that it is necessary to quickly collect the oil after spillage by using usual methods like booms and pumps.

3.3 *Risk assessment of different chemicals*

Risk posed by maritime chemical spill depends also on accident scenario and environmental conditions besides inner properties of the spilled chemical. Basically, accidents involving chemical tankers can be classified into four groups. Offshore, in the open sea area, chemical spill has space to have a larger effect or to dissolve and be vaporized. This mitigates the negative effects of the spill. On the other hand, response actions can take a longer time and environmental conditions can be challenging, as well. The incident occurring closer to shoreline can be easier or faster to reach, even if the impact to the environment can potentially be more disastrous. The third scenario portrays a casualty that happens in a closed sea area, like in a port or in a terminal area. In these cases, the spill is usually localized and effectively restricted. However, even smaller spill may elevate toxicity levels in a restricted area. Ports are also situated near city centers, and there is an elevated risk for the health of the public and workers in the area. The fourth possibility is an accident during winter in the presence of ice and snow (Hänninen & Rytkönen 2006). The properties of the chemicals may change in cold water. Some chemicals may be more viscous or even become solids, and thus, easier to recover. On the other hand, hazardous impacts of some chemicals may multiply in the cold environment because the decomposition of the chemicals becomes slower. Thus, chemicals may drift to larger areas. They may also accumulate to the adipose tissues in animals which decreases the probability of an animal to survive beyond winter (Riihimäki et al. 2005).

The marine pollution hazards caused by thousands of chemicals have been evaluated by, for example, the Evaluation of Hazardous Substances Working Group which has given GESAMP Hazard Profile as a result. It indexes the substances according to their bio-accumulation; bio-degradation; acute toxicity; chronic toxicity; long-term health effects; and effects on marine wildlife and on benthic habitats. Based on the GESAMP evaluation, the IMO has formed 4 different hazard categories: X (major hazard), Y (hazard) and Z (minor hazard) and OS i.e. other substances (no hazard) (IMO 2007). Over 80 per cent of all chemicals transported in maritime are classified as belonging to the Y category (GESAMP 2002; IMO 2007). This GESAMP categorization is very comprehensive, but different chemicals having very different toxicity mechanisms, environmental fate and other physico-chemical properties may end up to same MARPOL category. The GESAMP hazard profile, although being an excellent first-hand guide in a case of a marine accident, will not answer the question of which chemicals belonging to the same Y category are the most dangerous ones from an environmental perspective.

Many risk assessment and potential worst case studies exist to help find out what impacts different chemicals might have if instantaneous spill were to happen (Kirby & Law 2010). For example, Law & Campell (1998) made a worst case scenario of circa 10 tonnes insecticide spill (pirimiphos-ethyl), and concluded that it might seriously damage crustacean fisheries in an area of 10,000 km^2 with a recovery time of 5 years. In the case of marine accidents, the greatest risk to the environment is posed by chemicals which have high solubility, stay in the water column, and are bioavailable, persistent and toxic to organisms. Based on the analysis of chemicals transported in the Baltic Sea, Häkkinen et al. (2012) stated that nonylphenol is the most toxic of the studied chemicals and it is also the most hazardous in light of maritime spills. The chemical is persistent, accumulative and has a relatively high solubility to water. Nonylphenol is actually transported in the form of nonylphenol ethoxylates but it is present as nonylphenol when spilled to the environment, and in the aforementioned

study the worst case scenario was evaluated. Other very hazardous substances were sulphuric acid and ammonia (Häkkinen et al. 2012). Similarly, the HASREP (2005) project identified top 100 chemicals which are transported between major European ports and involved in trade through the English Channel to the rest of the World. The assessment was based both on transport volumes and the GESAMP hazard profile. The project highlighted chemicals such as benzene, styrene, vegetable oil, xylene, methanol, sulphuric acid, phenol, vinyl acetate, and acrylonitrile. It was concluded that these chemicals were the ones that have high spillage probability but may not result in significant environmental impact. Similarly, French McKay et al. (2006) applied a predictive modeling approach for a selected range of chemicals that are transported by sea in bulk and concluded that phenol and formaldehyde present the greatest risks to aquatic biota. Harold et al. (2011) evaluated human health risks of transported chemicals, based on the GESAMP ratings for toxicity and irritancy. This gives more weight to chemicals that are floaters; form gas clouds; or are irritable and toxic like chlorine (Harold et al. 2011). It is clear that different weightings have a certain impact on the difference in results in these studies. However, the chemicals of real concern vary depending on the sea area for which the risk assessment is conducted since the amounts and types of chemicals differ in different sea areas as do marine environment and biota (Kirby & Law 2010).

The impacts of a release or a spill depend on the behavior of the chemical or chemicals in question. It can be concluded that the most harmful chemicals for human health have quite opposite properties to those that are most hazardous for water biota. For human health, the most hazardous chemicals are those that are very reactive, form either very toxic or irritating (or explosive) gas clouds, and also have possible long-term effects, such as carcinogenic effects. From the environmental point of view, the most hazardous chemicals are those that sink, have a high solubility, possibly stay at the water column, are persistent, bioavailable and very toxic and can have possible long-term effects (French McKay et al. 2006, Häkkinen et al. 2012, Harold et al. 2011).

3.4 *Response actions in case of maritime chemical spills*

There are many excellent reviews (e.g. Marchand 2002, EMSA 2007, Purnell 2009), based on lessons learned from past accidents, which also contain data about response actions in case of chemical spills. Even if response actions taken differ in every accident case according to special conditions and chemicals involved, it is nevertheless possible to demonstrate certain significant or specific elements valid in all chemical incidents at sea (Marchand 2002).

Firstly, like the information concerning the ship cargo, an evaluation of chemical risks is of primary importance before any operational decisions are to be made, especially if the ship is carrying a wide variety of chemicals (Marchand 2002). Following the chemical spill at sea, the response authorities must immediately take measures in order to minimize the chemical exposure to the public as well as contamination of the marine environment. The primary factors which determine the severity and extent of the impact of the accident are related to the chemical and physical properties of the chemicals in question. It should be noted that in the case of oil spills, the hazard to human health is generally considered to be low, and the more toxic and lighter fractions often evaporate before response actions are able to be started. However, in case of chemical accidents, an initial assessment and monitoring of potential hazards should be undertaken first in order to ensure a safe working environment. In that stage, the primary hazards and fate of the chemical in that marine environment are evaluated. The monitoring techniques need to be designed to measure the key parameters that could give rise to a hazard. It should also be noted that in some cases doing nothing might be the best option, as long it happens under observation (Marchand 2002, Purnell 2009). Le Floch et al. (2010) stated that in case of an instantaneous chemical spill, response usually follows three accepted scenarios: 1) response is not possible, because the spill occurred in a geographical environment that is incompatible with reasonable response times, 2) response is not possible due to reactivity of the substances (major, imminent danger), and 3) response is possible. Gases and evaporators, very reactive substances, and explosives are the biggest concern for human health and safety. Several monitoring devices and dispersion models exist which may aid decision making and help protect responders and the public. The floaters can be monitored by using the same techniques that are used for oil spills. Chemicals that prove to be the most difficult to be monitored are sinkers and dissolvers (such as acrylonitrile in the case of Alessandro Primo in Italy in 1991), even if some techniques e.g. electrochemical methods and acoustic techniques exist (EMSA 2007, Purnell 2009).

Several international, regional and national authorities have published operational guides to describe the possible response options in case of a chemical spill. For example Cedre and IMO have made manuals providing information about different response techniques that can be used in case of chemical spills (Cedre 2012, HELCOM 2002, IMO 2007). Usually response techniques depend on the behavior of a chemical in the environment, and on whether it is released or still contained in packaged form. In practice, the response action varies substantially. Techniques that are applicable in case of oil accidents may be suitable for only some floating chemicals. However, it should not be forgotten that some floating chemicals can also potentially create toxic and maybe explosive vapor clouds (e.g. diesel, xylene and styrene). If this happens, the spark/static-free equipment should be used. Moreover, foams or sorbent materials can also be used near the spill source. Risks associated with evaporators or gases, such as ammonia and vinyl chloride, could be diminished by diluting or using release methods (Purnell 2009). In shallow water areas, neutralizers, activated carbon, oxidizing or reducing agents, complexing agents, and ion-exchangers can be used. Chemicals that are heavier than seawater, in turn, may contaminate large areas of the seabed. Recovery methods that are used include mechanical, hydraulic or pneumatic dredges, but the recovery work is time-

consuming and expensive and results in large quantities of contaminated material. Other option is capping the contaminated sediment in-situ (Purnell 2009).

As Marchand (2002) listed, the time involved in response operations can vary from 2–3 months (Anna Broere, Holland; Cason, Spain; Alessandro Primo, Italy); to 8 months (Fenes, France); to 10 months (Bahamas, Brazil); or to even several years as in the case of the research carried out on a sunken cargo (Sinbad, Holland). Cold weather and ice cover may create further problems to response actions in the Baltic Sea in the winter. The viscosity of chemicals may change in cold, and they can be more persistent. Collecting techniques based on fluid-like masses are no longer effective, if fluids change and act more like solid masses. Moreover, it is difficult for a recovery fleet to operate, if it is surrounded by ice and snow. If chemicals have spread under the ice cover, detecting the spill is more difficult, and the use of dispersing agents is ineffective. However, ice breakers may be used to break the ice cover and to improve mixing chemicals with larger water masses (Hänninen & Rytkönen 2006).

4 STATISTICAL REVIEW ON TANKER ACCIDENTS IN THE BALTIC SEA

4.1 *Accident statistics by HELCOM and EMSA*

The Helsinki Commission (HELCOM) has reported that during the years 1989–2010 approximately 1400 ship accidents happened in the Baltic Sea. Most of the accidents were groundings and collisions, followed by pollutions, fires, machinery damages and technical failures (Fig. 1). One in ten of the accidents are defined as other types of accidents (HELCOM 2012).

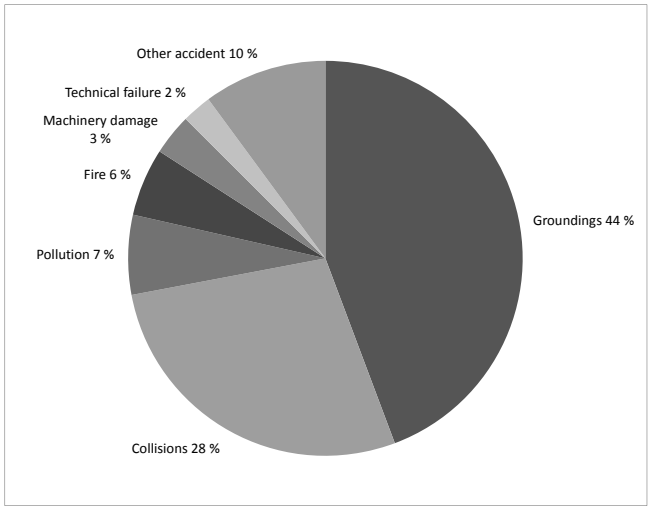

Figure 1. Vessel accidents in the Baltic Sea in 1989–2010 by accident types. (HELCOM 2012)

According to HELCOM (2012), 1520 vessels in total have been involved in the accidents occurred in the Baltic Sea during the years 1989–2010. Almost half of the vessels were different types of cargo vessels excluding tankers (Fig. 2). Large number of other vessel types (e.g. pilot vessels, tugs, dredgers) was also involved in the accidents. One in seven of the accidents involved a tanker and a passenger vessel.

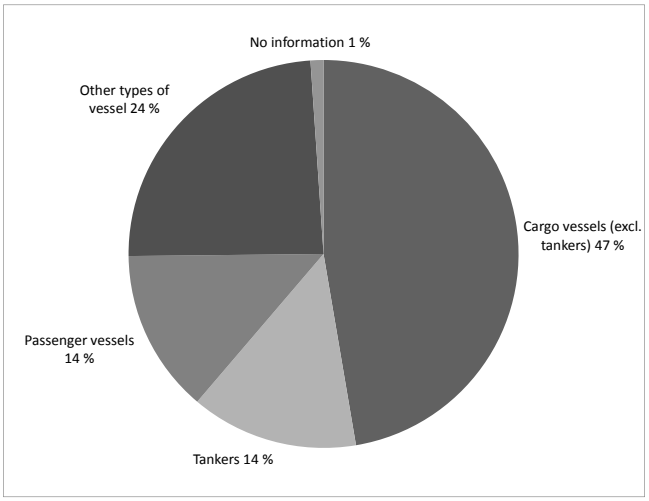

Figure 2. Vessel accidents in the Baltic Sea in 1989–2010 by vessel types. (HELCOM 2012)

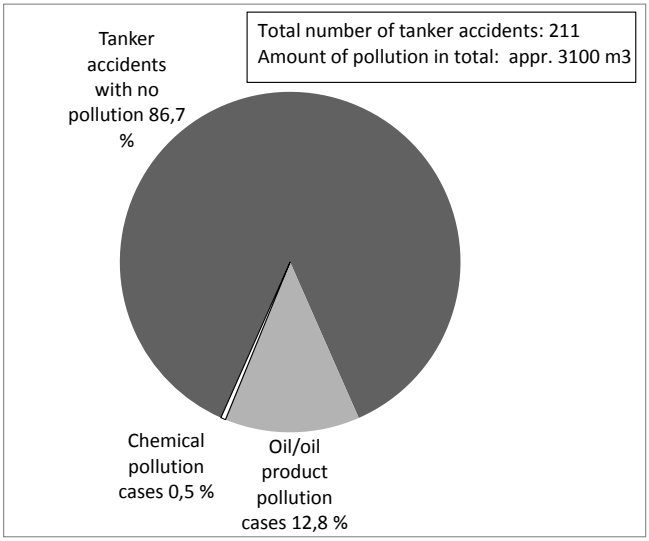

Figure 3. Tanker accidents and the share of pollution cases in the Baltic Sea in 1989–2010. (HELCOM 2012)

Based on the HELCOM's accident statistics, 210 tankers (including crude oil tankers, chemical tankers, oil/chemical product tankers, gas carriers and other types of vessels carrying liquid bulk cargoes) were involved in the accidents that occurred in the Baltic Sea during the years 1989–2010. During this period, 28 of all tanker accidents in the Baltic Sea led to some sort of pollution. Due to these 28 pollution cases, approximately 3100 m^3 of harmful substances in total spilled in the sea. In almost all of the pollution cases, spilled substance was conventional oil or an oil product (e.g. crude oil, gasoline oil, fuel oil, diesel oil) (Fig. 3). In one pollution case only, the spilled substance was a chemical (a leakage of 0.5 m^3 of orthoxylene in Gothenburg on 13 February 1996). 13 out of the 28 tanker pollution cases in the Baltic Sea that were reported by HELCOM have been classified as spills/pollutions; 5 were classified as collisions; 3 as groundings; 2 as technical failures; 1 as machinery damage; 1 as contact with bollard; 1 as hull damage; 1 as loading accident; and 1 as an accident caused by broken hose. Over one-third (11) of all these tanker pollution accidents happened on the Swedish coast; 4 accidents happened in Lithuania; 3 accidents in Latvia; 2 accidents in Estonia; 2 accidents in Russia; 1 accident in Finland; 1 accident in Poland; 0 accidents

in Germany; and 4 accidents in other areas of the Baltic Sea. The largest pollution case involving a tanker in the Baltic Sea during the period of 1989–2010 happened in the Danish waters on 29 March 2001 when approximately 2500 m^3 of oil spilled into the sea as a result of a collision between a tanker and a bulk carrier (HELCOM 2012).

Based on the EMSA's Maritime Accident Reviews (EMSA 2007, 2008, 2009, 2010), the annual number of accidents in the Baltic Sea has varied between 75 and 120 accidents over the period of 2007–2010. In each of these years approximately 15 per cent of all maritime accidents in the EU happened in the Baltic Sea. During the reviewed period, the main causes of the accidents have been groundings (32–52 per cent of all accidents), followed by collisions/contacts (23–35 %), fires and explosions (10–17 %) and sinkings (2–5 %). In every year, the largest proportion of accidents happened in the south-western approaches off the Danish and Swedish coasts, with these accounting for around 70–77 per cent of the regional total. Groundings off the Danish and Swedish coasts accounted for around 80–88 per cent of the total Baltic Sea region groundings in the years 2007–2010. Most of the accidents in the region happened in the heavily trafficked approaches around eastern Denmark, which can be more difficult to navigate than many other areas. The recorded figures show that the Finnish and Estonian coastlines accounted for around 15–17 per cent of the total number of accidents happened in the Baltic Sea in this 4 year period. Accidents recorded by EMSA in the years 2007–2010 include 4 significant pollution events in total. As a consequence of these pollution events, at least 695 tonnes of oil/oil products spilled into the Baltic Sea (the size of pollution in one accident was not available). No significant chemical accidents happened in the Baltic Sea during the reviewed period. In addition to these significant pollution events, some smaller accidental spills were recorded by EMSA in the years 2007–2010. For example, in 2007 EMSA's daily research recorded about 30 accidental oil spills of different sizes in and around EU waters (EMSA 2007).

HELCOM and EMSA mainly provide coarse-level information about each maritime accident. Therefore, more detailed information on maritime accidents involving a tanker was searched using maritime accident databases and reports provided by the authorities and/or other actors who are responsible for collecting maritime accident data in each Baltic Sea country. More detailed maritime accident investigation reports were found about Denmark, Finland, Germany, Latvia and Sweden, and basic information about accidents was found about Estonia and Lithuania. There was no maritime accident data found about Poland or Russia.

4.2 *National accident statistics*

According to the Danish Maritime Authority's (DMA) annual marine accident publications (Danish Maritime Authority 2009), the total of 42 accidents involving a tanker registered under the Danish or Greenlandic flag happened during the period of 1999–2008. When examining foreign vessels, it can be seen that 63 foreign tankers in total were involved in the accidents that happened in Denmark's territorial waters in the reviewed period. 51 of these foreign tankers are classified as oil tankers, 9 as chemical tankers, and 3 as gas tankers. In addition to the DMA's annual marine accident publications, Danish Maritime Authority and the Danish Maritime Accident Investigation Board (DMAIB) have published, on their Internet sites, 142 maritime accident investigation reports or investigation summary reports on merchant ships during the years 1999–2011 (Danish Maritime Authority 2012, Danish Maritime Accident Investigation Board 2012). Study of these investigation reports revealed that 21 accidents involving a tanker in total were investigated by the DMA and the DMAIB. 9 of these accidents can be classified as personal accidents, 6 as collisions, 4 as groundings, 1 as an explosion, and 1 as an oil spill. Over half (11) of the accidents occurred in the Baltic Sea, 1 accident in the North Sea, and the rest of the accidents in other sea areas around the world. Only 2 of the investigated accidents led to pollution: 1) 2700 tonnes of fuel oil spilled in the sea as a consequence of a collision between two vessels in Flensburg Fjord in 2001 and 2) 400–500 litres of heavy fuel oil spilled into the sea during bunkering near Skagen in 2008.

Accident investigation reports provided by the Finnish Safety Investigation Authority shows that 10 tanker-related accidents in total happened to vessels in Finland's waters and to those that were sailing under Finnish flag during the period of 1997–2011. 4 of these accidents were groundings, 3 collisions, 2 spills and 1 personal injury. Two of the accidents led to spill: 1) on 20th July 2000 in the Port of Hamina, about 2 tonnes of nonyl phenol ethoxylate leaked on the quay area and into sea during loading, and 2) on 27th February 2002 in the port of Sjöldvik, about 2 m^3 of flammable petrol leaked into sea during unloading (Finnish Safety Investigation Authority 2012).

The study of the marine casualty statistics (BSU 2012a) and maritime casualty investigation reports (BSU 2012b) provided by the Federal Bureau of Maritime Casualty Investigation (BSU) revealed that during 2002–2011 the BSU recorded 27 marine casualties involving a tanker that happened in Germany's territorial waters or to vessels sailing under the German flag. 16 of these casualties were collisions, 7 personal accidents, 2 groundings, 1 water contamination, and 1 carbon monoxide exposure. 17 chemical tankers, 10 tankers, 1 river tanker and 1 motor tanker in total were involved in the accidents. Most of the accidents occurred in the Kiel Canal, in the Elbe River, in the Port of Hamburg, or outside Germany's waters. Only one of the accidents happened in the Baltic Sea, north of Fünen. Information about possible pollution as a consequence of an accident was not available in all cases. However, at least 18 of 27 accidents involving a tanker did not cause pollution and only 1 of the accidents was reported to have led to pollution (appr. 960 tonnes of sulphuric acid in the Port of Hamburg on 6 June 2004).

According to the maritime accident statistics of the Latvian Maritime Administration, the total of 30 accidents involving a liquid bulk vessel happened in Latvia's territorial waters or to vessels sailing under the Latvian flag during the period of 1993–2010. 17 of

these accidents were classified as collisions, 3 as groundings, 3 as personal injuries, 2 as fires/explosions, 2 as pollutions, and 3 as other types of accidents. Unfortunately, the Latvian Maritime Administration's accident statistics do not provide information on whether the accidents caused pollution or not (Latvian Maritime Administration 2012).

The Swedish Transport Agency's annual maritime accident/incident reports (Swedish Transport Agency 2012a) revealed that the total of 90 accidents and 14 incidents involving a tanker occurred in the Swedish territorial waters during the period of 2002–2010. Machine damages (24 per cent of all the tanker accidents), groundings (22 %), collisions with other object than a vessel (19 %), and collisions between vessels (17 %) have been the most common reasons for tanker accidents. Approximately 51 per cent of the tankers involved in the accidents were vessels sailing under the Swedish flag and 49 per cent were foreign vessels. There was some lack of information, but it could be determined that at least 4 of these accidents led to pollution (Swedish Transport Agency 2012a, 2012b): 1) 500 litres of fuel oil spilled from a fuel tank during bunkering in Gothenburg in 2005; 2) 100 litres of gas oil spilled into the sea as a consequence of a collision between two vessels in Gothenburg in 1998; 3) approximately 45 m^3 of gas oil spilled from a fuel tank due to vessel grounding in Brofjorden in 1999; and 4) approximately 600 tonnes of hydrochloric acid were released into the sea under the control of the Swedish Maritime Administration near Öresund in 2000 as a consequence of a collision between two vessels.

According to the Estonian Maritime Administration, the total of 16 accidents involving a tanker happened to vessels in Estonia's territorial waters, or to vessels which have been sailing under Estonia's flag during the period of 2002–2011. 7 of these accidents were groundings, 3 fires, 4 contacts with a quay, and 2 collisions. None of the accidents have caused pollution (Estonian Maritime Administration 2012).

According to the maritime accident statistics of the Lithuanian Maritime Safety Administration, 12 accidents involving a liquid bulk vessel happened in Lithuania's territorial waters or to vessels sailing under the Lithuanian flag during the period of 2001–2010. 4 of these accidents can be classified as spills, 3 as collisions, 2 as contacts with a quay/other vessel, 1 as fire, and 2 as other types of accidents. As a consequence of the 4 spill types in the accidents, at least 3.5 tonnes of oil and 0.06 tonnes of diesel fuel leaked into the sea in the Lithuanian waters. The amount of oil spilled in the water is probably higher since regarding the 2 oil spill cases, there was no information available about the level of pollution (Lithuanian Maritime Safety Administration 2012).

5 SUMMARY AND CONCLUSIONS

This paper provided an overview of the past tanker accidents in the Baltic Sea and HNS accidents in seas worldwide. It also aimed at finding out what can be learned from past accidents, especially from the environmental point of view.

The results of this study showed that chemical tanker accidents are very rare, even though there is always the possibility that such incident may happen. Many other studies have shown that the most commonly transported chemicals are the ones most likely to be involved in an accident. Moreover, the risks are different and vary in different sea areas. The risk of an accident is the highest in water areas where the largest amounts of chemicals are transported, the density of the maritime traffic is at its highest point, where bad weather conditions exists, as well as the ship-shore interface in ports where unloading/loading take place. Incidents involving chemical spills are statistically much less likely to occur than oil spills.

Actually, very little is known about the actual marine pollution effect of most of highly transported substances. From the environmental point of view, the previous studies have highlighted accidents in which pesticides were released to water, but also substances considered as non-pollutants (vegetable oils) seem to have a negative effect on biota in the water environment. When comparing hazardous chemicals with oil, it can be said that the danger of coastline pollution is a far greater concern in oil spills than in chemical spills. It is very difficult to evaluate chemical risks if a ship is carrying diverse chemicals and some of those substances are unknown during the first hours after the accident. This aforementioned situation is often faced when a vessel is carrying packaged dangerous goods. The most important difference between chemical and oil spill may be related to response actions. The air quality or the risk of explosion does not usually cause concern for response personnel in case of oil spills, but for chemical spills, it should be carefully evaluated if some response actions are made. In case of chemical spills, the response may be limited, in most cases, to initial evaluation, establishing exclusions zones, modeling and monitoring, followed by planning of a controlled release, recovery or leaving in-situ. This process will take many weeks or even months.

Both literary and data mining showed that neither major chemical spills nor oil spills, such as Erika or Prestige, have happened in the Baltic Sea. However, every year over 100 shipping accidents (all cargoes included) take place in the Baltic Sea. Collisions and groundings are the main types of accident/incidents in the Baltic Sea. Human factor is the main cause for the accidents, followed by technical reasons. The largest proportion of accidents happens in the south-western approaches off the Danish and Swedish coasts. Annually, on average, 15 per cent of all shipping accidents in the Baltic Sea have involved a tanker. Less than 5 per cent of the tanker accidents have led to spill/pollution. The spilled substance has in most cases been oil or an oil product – only very few chemical spill cases have been reported in the Baltic Sea. Considering both chemical and oil tankers, only very small spills have happened and their environmental impact has been neglected. Since there have been no major accidents in the Baltic Sea, it is not possible to learn about accident cases. However, there are some excellently described international tanker accidents which give valuable lessons to be learned from by different stakeholders and rescue services.

There are many parties in the Baltic Sea Region, including e.g. HELCOM, EMSA and the national authorities, which are collecting/producing data on the maritime accidents that have occurred in the Baltic Sea. In addition, some European or worldwide databases (e.g. Cedre) contain data of accidents that have occurred in the Baltic Sea. However, in the future, the maritime accident databases on the Baltic Sea Region should be improved and harmonised. Regarding accident investigation reports, each Baltic Sea country should publish these reports publicly in electronic format. It would be worth to contemplate whether all accident investigation reports concerning accidents that have occurred in the Baltic Sea waters or to vessels sailing under a Baltic Sea country's flag could be gathered under one public information service.

Data of the marine pollution effects of most transported chemicals is limited, mainly because of the rarity of maritime chemical accidents. Even though the probability of major chemical tanker accidents is very small, much more studies are still needed on the risks of different chemicals to both the environment and humans, as well as on the economic risks of possible accidents.

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