Chemical munitions off the Belgian coast : an evaluation study

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Abstract - After World War I an estimated 35,000 tons of war material was dumped on the 'Paardenmarkt', a shallow sand flat just off the Belgian coast. Probably about one third consists of chemical munition. The dumping site extends over 3 km^2, ranging in water depth between 1.5 and 5.5 m. The munition has been sagging and is largely covered under accumulating fine-grained sediments, mainly due to the construction of the outer port of Zeebrugge. The munition is most likely not too heavily corroded; complete corrosion could take hundreds of years. The most important threats seem to be related to mechanical disturbance of the munition shells (e.g. due to vessel grounding) and direct contact (with Yperite lumps). At this moment there are no strong indications for acute danger and the best option therefore seems to be to leave the dump site untouched - under the condition of regular monitoring. Geochemical sampling should involve specific screening for munition-related heavy metals, TNT, Yperite, Clark, and their respective breakdown products. Sea-bed monitoring is needed to map the erosion/accumulation processes and detect possible objects on the sea floor, whereas in-depth monitoring can gain further information on the internal structure of the dump site and its evolution. If monitoring would indicate potential surfacing of the munition the construction of an artificial island could be considered.

Introduction

After the first World War a considerable amount of war material was dumped on a shallow sand flat called "Paardenmarkt", offshore Knokke-Heist, Belgium. The dump site extends over 3 km^2, and is indicated on hydrographic maps with a pentagon where neither fishing nor anchoring is allowed.

Geophysical investigations in 1995-1996 showed the extreme complexity of the area, not only related to the dumped material (partly non-metallic, and thus "invisible" for magnetic methods) but also in relation to the natural settings and the (recent) evolution of the site. Despite these good results it was clear that complementary research techniques were necessary to analyse the full complexity of the Paardenmarkt in all its facets.

In 1999-2001 an integrated multi-disciplinary evaluation study took place combining geophysical, geochemical, sediment-dynamical, biological, engineering and ecological expertise. The main objectives of the evaluation study included the following:

- Detailed analysis and scientific evaluation of all available data related to the area, in order to make a correct evaluation of the actual dimension of the encountered problems.
- Analysis of possible strategies of scientific research with respect to the dumped munition and natural setting, and the possible perspectives for continuous monitoring of the area.
- Re-evaluation of the present-day ‘status quo’ policy and the evaluation of different options for possible engineering solutions, including a nature conservation area.

History and general characterisation of the munition dump site

After the first World War large amounts of war material were left behind in Belgium. The clean-up operation was slow and very dangerous, and numerous accidents occurred. Because the situation was getting out of control and dismantling proved too risky, the Belgian government decided to dump war material into the sea.

The dumping operation started in November 1919. Each day during 6 months a shipload of munition (Fig. 1) was dumped in the proximity of the Zeebrugge harbour, just offshore Knokke-Heist, on the western edge of the Paardenmarkt tidal sand flat.

This dumping operation may not be the only one. Newspaper articles and parliamentary records from 1919 suggest an earlier dumping operation carried out by the British Admiralty in the middle of 1919 (indeed part of the country - including Mons and the greater part of the Province of Hainaut - was still under British rule). It is not sure however whether this British operation was carried out near the Belgian coast or further offshore - if carried out at all.

In 1971 dredging ships struck upon several objects on the sea floor during maintenance works for the Zeebrugge harbour. Diving operations carried out by the Belgian Navy in 1972 revealed the presence of munition on the sea floor, among which several toxic shells.

As a result the area was marked on hydrographic maps as a "no anchorage or fishing zone" with a total surface of ±1.5 km^2 (Fig. 2). During these diving operations a number of shells were recovered. According to the reports the state of the shells was "remarkably good".

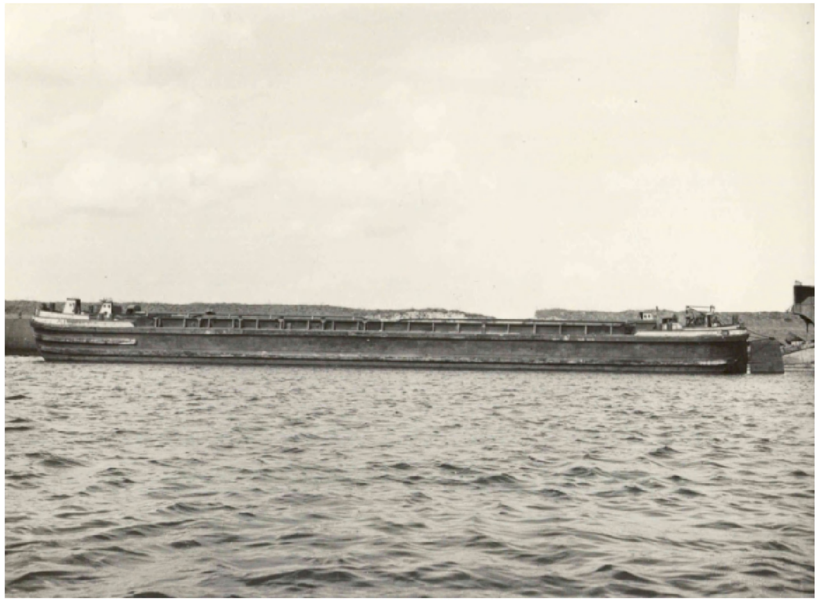

Fig. 1. *Typical "klepbakschip" used for the dumping operations on the Paardenmarkt.*

Magnetometric investigations carried out in 1988 confirmed the presence of metallic objects at the site (Tijdelijke Vereniging Bergingswerken 1989). Due to the limited positioning accuracy and the absence of digital acquisition only a qualitative distribution of the magnetic zones could be obtained (Fig. 2).

A large number of the magnetic zones was located outside the first rectangular delimitation zone. Based on these results the no-fishing zone from 1972 was finally enlarged (mainly towards the west) to a pentagon with a total surface of ±3 km^2 (Figs. 2 and 3). For the time being no other measures were considered.

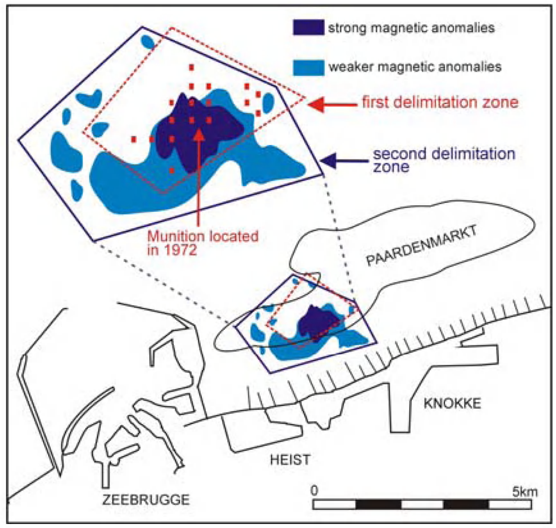

Fig. 2. *Location of the first and second delimitation zone of the Paardenmarkt dump site and results of the 1988 magnetometric survey.*

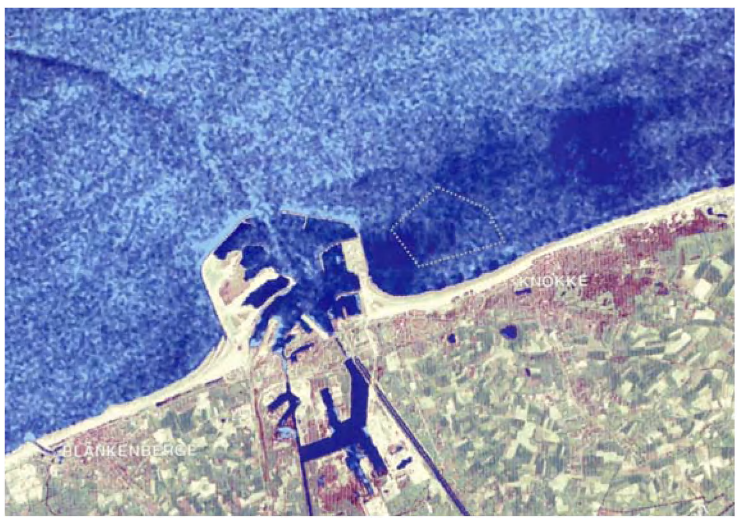

Fig. 3. *Satellite image of the coastal area near Zeebrugge. The pentagon marks the location of the munition dump site.*

Nature of the dumped warfare

The total amount of dumped warfare is estimated to be 35,000 tons. Most likely it involves German ammunition, for the larger part 77mm shells, and to a lesser extent 105 mm and 150 mm shells, as indicated by the diving operations in 1972. Other war material such as guns and explosives however cannot be excluded.

It remains unknown exactly how much of the dumped munition is toxic. German production figures from WW1 indicate that chemical weapons made up 6 to 7 % of the total amount of warfare produced (Lheuruex 1990). However this expresses an average over the whole war period, thereby overlooking the fact that during the final stage of the war increasing amounts of chemical weapons were used. Statistics show that over 50 % of the total production of toxic agents was used in 1918 (Table 1). In Germany alone 92 % of the chemicals was used in artillery shells (Lheureux 1990).

Table 1. *Total production of chemical warfare agents per year (in %) (Source: V. Lheureux, L'utilisation du gaz de combat sur le front Belge pendant la guerre 1914-1918).*

	GERMANY	FRANCE	UK
1915	5.5	1.1	1.3
1916	13.3	13.3	11.1
1917	28.3	28.5	34.1
1918	52.9	57.1	53.5

These figures clearly indicate that toxic shells made up a much larger part of the artillery ammunition during the final months of the war. Furthermore it does not seem unlikely that some selection may have been carried out prior to the dumping operation, with emphasis on the "urgent" toxic ammunition. Keeping all this in mind, an estimation of about one third (of toxic ammunition) seems to be quite reasonable. Regarding the whole of 35,000 tons of dumped ammunition, this would imply a total amount of toxic shells of roughly 12, 000 tons.

German toxic shells from World War I were most commonly filled with (di)phosgene, chloropicrin, Clark and Yperite (mustard gas). According to their content they were referred to as blue, yellow or green cross shells (Fig. 4). The ratio between the different toxic shells dumped on the Paardenmarkt remains unknown. However, it is assumed that Clark and Yperite shells form the main part of the dumped toxic munition.

The munition shells roughly weigh between 7 and 40 kg and have a steel casing. The toxic shells are hard to distinguish externally from conventional shells. The originally painted green, yellow or blue markings have eventually disappeared by erosion.

The chemical warfare agents in general make up roughly one tenth of the total weight of the shells (blue cross shells form an exception: they contain a smaller quantity of toxic agent, Clark). For the Paardenmarkt this would imply a total amount of roughly 1200 tons of chemical compounds.

In addition to the warfare agents one should also take into account the explosive compounds (mainly TNT) which can be equally toxic. Although their part in toxic munition is very low (a few hundred grams per shell typically - except for Clark shells which contain more explosives), they make up one tenth or more of the weight of conventional shells. The total amount of explosives on the Paardenmarkt is estimated to be at least 2500 tons.

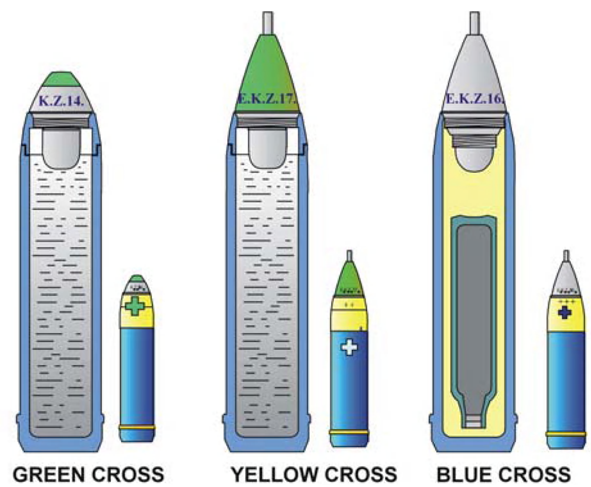

Fig. 4 . *Schematic representation of German toxic WW1 munition. Blue cross shells differ from the other toxic shells in the fact that the toxic agent is stored in a glass bottle (Source: DOVO).*

Geophysical / chemical investigations

In 1995-1996 a number of high resolution seismic, side-scan sonar and magnetometric measurements were carried out on the munition dump site. The results of these surveys indicated the high complexity of the area (Henriet *et al.* 1996), which was due to:

- the complex natural setting: nearshore zone with a high sediment input and strong sedimentation, presence of natural gas, small depressions;
- the complexity of the dumped material: both magnetic and non-magnetic;
- the complex evolution of the dump site: an early evolution (sagging of the dumped munition) and more recent evolution (dumping of dredged material and beach restoration works).

The magnetometric data confirmed the presence of different dump zones (G-Tec 1996):

- a central zone with several very large magnetic anomalies. Most likely this area represents the main part of the dumped material. The strong anomalies are separated by small, anomaly-free areas;
- a wide zone surrounding the central zone marked by a large number of anomalies, generally weaker. It is possible that some of these anomalies are not related to the dumped war material but have a different origin (e.g. small ship wrecks, iron objects).

A geometric model was created for a number of anomalies (Missiaen *et al.* 2001). The use of the vertical gradient of the magnetic field resulted in an important improvement of the horizontal resolution (Fig. 5). This made it easier to separate the different dumps and gave a more accurate position of the exact location of the different dumps.

Vertical gradient data also allowed a more accurate estimation of the actual burial depth of the dumped material (Missiaen et al 2001). The obtained models indicated that in the central zone the munition is completely buried by more than two meters of sediment. Dredging operations carried out in 1988 seem to confirm this recent burial: only one time an obstacle was encountered in the dump area.

A number of side-scan anomalies were observed in the extreme SE corner of the dump site (Magelas 1996). However these could not be related directly to the magnetic anomalies, suggesting that the latter were due to buried objects. The side-scan anomalies were possibly caused by wooden ship wrecks or dumped rubble related to the construction of nearby breakwaters.

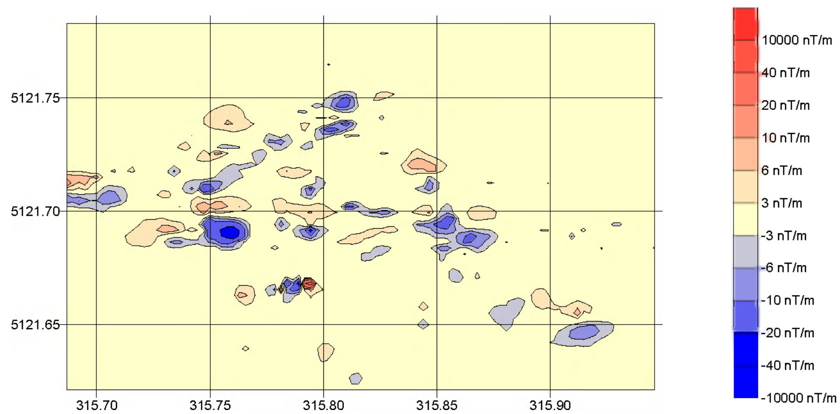

Fig. 5. *Vertical gradient of the magnetic field in the central part of the dump site.*

Over 70 sediment cores and water samples were taken at the site by Navy divers. The sampling locations were chosen based on the results of the geophysical investigations. The sediment cores were 50 cm long and 6 cm in diameter. Water samples were taken 1.5 m above the sea floor, at the same location as the sediment cores. In most cores samples were taken from the top and the bottom of the sediment core (Biorgan 1997).

Analysis included general organic screening and specific screening for Yperite and its main breakdown product thiodyglicol (TDG). None of the analysed water samples showed any contamination. The sediment samples did not indicate contamination except for one sample in the extreme southeast showing a low concentration of Yperite. Additional sampling in the vicinity of this point could however not confirm this.

Sediment dynamics

The Paardenmarkt dump site forms part of a shoal extending from the harbour of Zeebrugge to the Belgian-Dutch border. The site has a hydrodynamically sheltered position adjacent to the harbour jetties (tidal currents up to 1.5 m/s). The sea bottom slopes gently towards the NE and varies between 5.5 m MLLWS (mean lowest low water at spring tide) in the north and 1.5 m in the southwest corner forming a sediment wedge (Fig. 6 - top).

The surficial sediments in the area are generally very fine to fine sands with a strong enrichment of mud (Charlet 2001). They are marked by the presence of biogenic (methane) gas, most likely related to the presence of a thin peat-rich layer. Seismic data suggest a low concentration of gas, probably less than 1 % (Missiaen *et al.* 2002).

The munition dump site is located in a turbidity maximum area hydraulically trapping the muddy deposits. Residual transport directions indicate a coast-ward transport near the dump site. Towards the east the ebb tidal current seems to induce an important bedload transport likely enhanced by the outflow of the Westerschelde (Charlet 2001).

Topographic analysis has indicated that prior to the development of the Zeebrugge outer harbour in 1976 periods of erosion alternated with periods of sedimentation, resulting in important changes in seafloor morphology. Still the sediment volume at the dump site in 1976 was nearly similar to that observed in 1954. Between '54 and '76 a section of the dump site was subject to erosion. This explains the munition observed on the sea floor in 1972.

The extension of the Zeebrugge harbour induced an explicit sedimentation at the dump site and an erosion zone NW of the site. The sediment increase is not spread evenly across the entire site. Fig. 6 clearly shows that the increase is greatest in the southwest corner (up to 4 m), gradually decreasing towards the north. The most recent data seem to suggest a slow migration of the erosion zone towards the east and a trend towards stagnation in the sedimentation/erosion process. However, further verification is still needed.

Ecological value of the dump area

The infaunal communities found along the eastern part of the Belgian coast (Oostende to the Dutch border) are poorer in species than those on the western part (Cattrijsse & Vincx 2001). The latter is not only due to the sedimentological heterogeneity of the western coast , but also to the pollution and the deposition of fine sediments by the Westerschelde (Vincx & Herman 1989). Also the dredge disposal activities along the eastern Belgian coast have a negative influence on the richness of the benthos species.

In September 2000, 24 stations located NW of the munition dump site were sampled for the macrobenthos using a Van Veen grab. At 63 % of the stations macrobenthos was completely absent. If macrobenthos was present, densities never exceeded 233 ind./m^2, with an average density of 62 ind./m^2. The bivalve *Abra alba*, present in 78 % of the samples with macrobenthos present, was the most abundant species. This impoverishment is not due to the presence of chemical munition but is most likely caused by the high mud content of the sediment, which is known to drastically decrease the density and diversity (Degraer *et al.* 1999c).

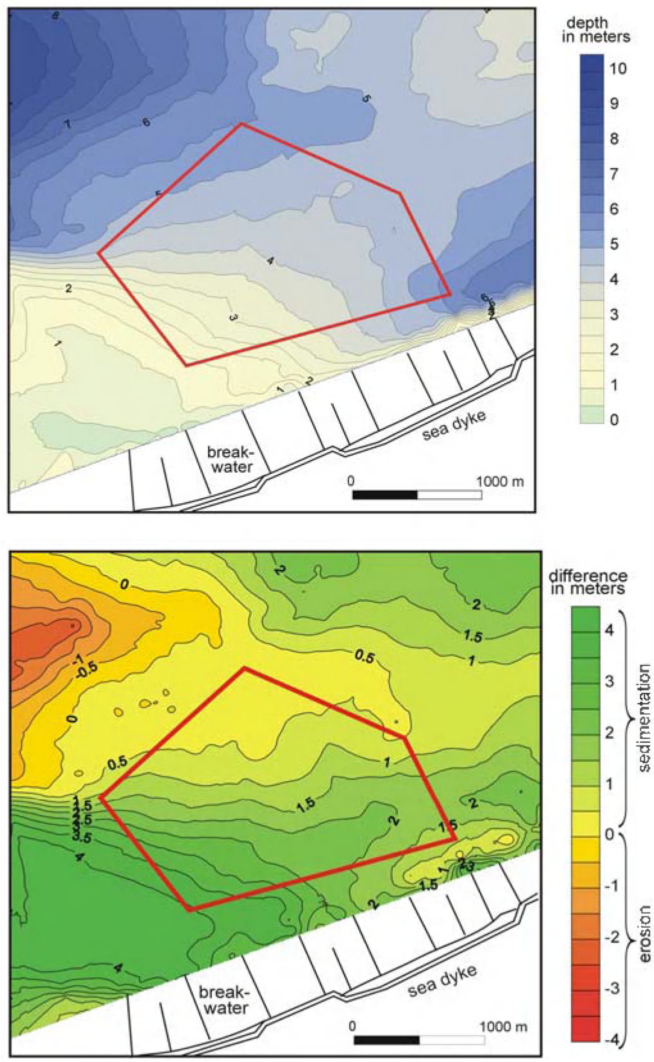

Fig. 6. *Top: bathymetric map of the study area based on sounding from 1996. Bottom: difference map between soundings carried out in 1954 and 1996. The red pentagon marks the location of the munition dump site.*

Some twenty bird species are regularly found at the dump site, another ten species only occasionally (mainly as migrants). The area is poor in species in autumn and winter with only gulls present in reasonable, though relatively small numbers. The major ornithological value seems to be its function as a feeding area for terns breeding in the outer harbour of Zeebrugge and at the "Baai van Heist" nature reserve, a protected beach east of the harbour. Maximal numbers of breeding Little Terns at Zeebrugge amounted to 425 pairs, i.e. 2.5 % of the biogeographical population of this highly threatened species.

The most important fish stocks in the area include flatfish (plaice, sole and dab), shrimp, and to a lesser extent whiting and cod. Commercial fishing in the munition dump area is relatively limited, and mostly involves small boats, often fishing for shrimps (large fishing vessels usually operate further offshore).

Toxic agent behaviour and ecotoxicological aspects

The (long-term) behaviour of the munition-related toxic compounds is not only determined by their physico-chemical characteristics, but also depends on external factors such as temperature, pH, salinity, physical surroundings, etc.

Already in the shell the toxic agent can be degraded. This process will depend on the physical stability of the agent, its chemical purity, and the corrosive action. For instance phosgene has no significant corrosive action when pure, but when hydrolysed it produces HCl which enhances corrosion. Diphosgene is unstable in anything but glass; most metals will catalyse diphosgene in phosgene. Clark compounds have no significant corrosive action with metals when dry, and they are very stable in pure form. Yperite has little corrosive action; it is very stable in steel or aluminium.

Once the munition has corroded and the agent is released into the marine environment the detoxification rate will largely be governed by the agent’s behaviour in water (this is most likely also the case for buried munition because shallow marine sediments will be largely saturated by water). The most important factor will be the solubility of the agent in water. The latter will largely depend on the water temperature, pH, oxygen content, and current velocity.

Most chemical compounds (including phosgene, diphosgene and chloropicrin) are marked by a relative fast hydrolysis. Therefore, and also due to the large dilution involved, these compounds will most likely not pose a large threat to the marine environment. The main threats seem to be related to the presence of Clark, Yperite, TNT and heavy metals.

Clark

Clark I (diphenyl arsine chloride) and Clark II (diphenyl arsine cyanide) are highly toxic compounds. Finely divided they will hydrolyse rather quickly, in larger quantities however they will hydrolyse very slowly. They will decompose into the equally toxic tetra-phenyldiarsine oxide and HCl or HCN respectively.

Both Clark I and II and their breakdown product tetra-phenyldiarsine oxide can persist in seawater for months before being degraded to inorganic arsenic. Clark compounds are also known to adsorb easily onto sediments, and therefore form a potential risk to marine organisms living on or near the sea floor.

Yperite

Yperite will dissolve extremely slow. Once dissolved, however, it will hydrolyse relative rapidly into primarily thiodiglycol (TDG) and HCl. The solubility process is the determining factor in the degradation of Yperite. It will depend on a variety of external factors including temperature and water turbulence.

In still water a concentrated TDG layer will build up at the Yperite-water interface acting as a protective coating. As a result the agent can remain unaffected for a long time (even decades). If the water is subject to disturbance (currents, sand grating) the protective coating is likely to form less easily.

Yperite exposed on the sea floor will exist as a viscous liquid or solid. Small drops will tend to dissolve, but larger lumps can survive for a very long period (decades or longer). The contamination radius is likely to be local: studies have indicated that for a lump of 1 kg the Yperite concentration in sea water reaches the non-toxic level at maximum 14 cm from the source (MEDEA 1997).

In the case of buried shells the volume of sediment that will be affected by a release of Yperite will most likely be very small. The main threat therefore seems to be related to the direct contact of organisms with lumps of Yperite. The magnitude of this effect is a function of the probability of such contact and the injury that results.

TNT

TNT is known to break down very slowly in water, but once dissolved it will decompose easily. In the absence of oxygen TNT may break down rapidly. Some of its breakdown products (such as DNT) are also highly toxic. DNT dissolves more easily in water than TNT, but this effect will decrease for lower temperatures. DNT also has a tendency to adsorb onto sediment. Studies in The Netherlands indicate that DNT may be subject to biological degradation (Van Ham *et al.* 2000). It seems unlikely that high concentrations of TNT or DNT may be expected at or near the dump site.

Heavy metals

Heavy metals do not degrade, and adsorb easily onto sediments and suspended matter in the water column. Therefore they could form a long-lasting environmental burden. Studies of conventional munition dump sites in the Netherlands have shown a clear increase in the concentration of nickel, copper and zinc (Van Ham *et al.* 2000). Peak concentrations can therefore not be excluded in the vicinity of the munition. Due to the high dilution involved the encountered concentrations in the water column are expected to be low.

Risks related to the munition dump site

Corrosion and agent leakage

Most likely the munition is not yet too heavily corroded. The oxygen-poor conditions related to the presence of biogenic gas in the muddy sediments are expected to slow down the corrosion process. It could take hundreds of years, possibly 1000 years, before all of the munition has corroded completely.

But even a slow corrosion process cannot prevent long-term leakage of the toxic agents. Upon corrosion the chemical compounds will most likely be released very slowly. Peak concentrations may happen in case of mechanical disturbance (anchoring, fishing, recovery operations).

The release of Clark compounds may cause long-lasting contamination of the sediments, threatening the organisms living near or in the bottom. In general the threat will be relatively local and therefore rather limited, although a larger contamination radius is possible through sea-floor erosion.

Yperite is expected to largely remain in the shell after corrosion of the munition. However, due to mechanical disturbance lumps may be released, which could possibly reach the shore.

Accidents

Because the munition seems to be largely buried at this moment, the chance for shells to wash ashore is therefore very small. Nevertheless this cannot be excluded completely.

The Paardenmarkt dump site is located near one of the busiest harbours of NW Europe, in the vicinity of main shipping routes. The risk of shipping disasters (e.g. during severe storms) has to be considered. Indeed accidents with stranded ships on the beach have been known to occur over the last years in Belgium (Fig. 7).

Fig. 7. *A German container ship stranded on the beach near Blankenberge, November 2001.*

Attention should also be paid to the long-term effects of global warming and sea-level rise. Global warming will enhance the storm frequency, thus increasing the risk for shipping disasters. Sea-level rise could result in salt water intrusion due to an induced groundwater flux from sea to land, causing a long-term effect on enhanced pollutants pathways (Van Meir 2001).

Detonation

Recent studies carried out by TNO suggest that the risk for spontaneous ignition is very small (Van Ham 2002). However there may still be a slight chance that intact shells, especially larger calibres, could react under severe mechanical stress (such as due to grabbing, dredging or vessel grounding).

Fish contamination

The contamination of fish seems mainly related to arsenic. Fish feeding on sea-floor organisms are likely to have a greater increase in arsenic in their bodies. However under the present conditions (sediment cover, relatively intact shells, poor infauna) the changes for such increase are very small.

Studies have also shown that approximately 99 % of the arsenic in fish would be in organic form that is not carcinogenic (Goldman & Dacre 1989). Organic arsenic is not converted to inorganic forms by humans and is excreted unchanged in form. The present threat to human health related to the consumption of arsenic-contaminated fish is therefore likely to be almost negligible.

Future policy

At this moment a large number of factors remain unknown. Correct evaluation of the munition dump site and the risks involved requires additional in-situ measurements and monitoring. In order to evaluate the actual condition of the munition and their state of corrosion, it is necessary to recover a (representative) number of shells. The recovered munition can be used to model the degradation process.

Regular geochemical sampling is indispensable. The analysis of water and soil samples can give information on the actual state of potential leakage and detoxification processes. Specific screening should be done for munition-related heavy metals, TNT, Yperite, Clark, and their respective breakdown products. Samples should also be taken in the surrounding area for reference. Bioaccumulation of chemical compounds in benthic invertebrates can be used as an additional monitoring tool for munition leakage.

Sea-bed monitoring is crucial to map the erosion/accumulation processes and detect possible objects on the sea floor. Particular attention should be paid to the erosion zone NW of the dump site. Additional in-depth monitoring is needed to map the internal structure of the dump site and its evolution.

One of the main problems of the Paardenmarkt is its close proximity to the coast. Therefore it may be useful to keep a chemical watch (e.g. chemical sensors) between the dump site and the beach as a basic safety measure.

Together with the in-situ measurements and monitoring further fundamental research is needed. For example very little is known about the dynamical behaviour (pollutant release processes and transport pathways) of toxic agents in the marine sediments, and the influence of changing hydrodynamic controls and depositional or erosional fluxes on these processes.

More research is also needed to accurately estimate the short- and long-term ecotoxicological threat of the agents, the chronic and sub-lethal effects on the marine environment and toxicological effects of organisms living and feeding on the sediment. The latter is currently the subject of research performed in Sweden (Waleij 2002); the results of these studies could be of importance for the Paardenmarkt.

Technological developments are equally important. Up to recently, geophysical investigations of marine dump sites have been carried out independently. The use of combined and integrated geophysical techniques can provide an important improvement in high-resolution detection and localisation of dumped munition.

At this moment there do not seem to be strong indications for immediate danger. The best option therefore seems to be to leave the dump site untouched - under the condition of regular monitoring. The latter is needed to track the evolution of the site and to detect any possible hazards in the future.

Recovery of the dumped munition is in theory the only way to solve the problem at heart. However this will be a costly and highly risky operation, and may cause the release of unverifiable amounts of toxic compounds into the environment. Moreover, it requires an extensive dismantling capacity, and adequate transport. Recovery is therefore not considered to be the best solution.

Possible engineering options

If monitoring would indicate the possible surfacing of munition (e.g. due to erosion of the sediment cover), or in the case of present danger, the option to cover the dump site may be considered. The construction of an artificial island offers major opportunities as a nesting and feeding site for terns, gulls and plovers (which are now doomed to disappear due to increasing harbour development) and a roosting site for seals.

In order to construct an artificial island used as possible breeding place the site must be filled up to a level of Z+6.50 m. A "horseshoe" structure seems preferable: 3 sides formed by a rubble mound structure, 2 sides by a sand slope (Fig. 8). Still, the construction of an island does not totally solve the long-term environmental threat of the leaking agents, and monitoring will therefore still be needed.

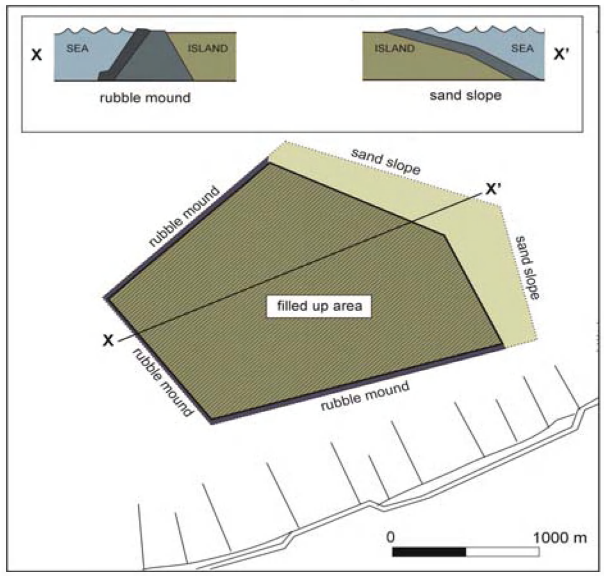

Fig. 8*. Schematic overview of an artificial island covering the munition dump site (not on scale).*

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