A Case Study in Modeling Dispersion of Yperite and CLARK I and II from Munitions at Paardenmarkt, Belgium

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Modeling Dispersion of Toxic Chemicals from Ammunition: Paardenmarkt Site (Belgium)

Historical Background

After the First World War, a large amount of war material was left behind on Belgian territory. Collecting and temporary storage in munition depots lead to hazardous situations that frequently resulted in fatal accidents. The situation became slowly but surely intolerable, and as dismantling the munitions involved too many risks, the Belgian government decided in 1919 to dump the munitions at sea. For six months, several wagonloads a day would arrive in the Zeebrugge harbor to be transferred on and dumped by hopper barges on a shallow shoal called "Paardenmarkt," situated ~1.5 km offshore Knokke-Heist (Figure 1). The dumping operation was soon forgotten. It was during dredging activities in 1971 that the munitions were found. Surveys conducted in 1972 revealed 17 locations with munitions, and based on these results, a rectangle with

ABSTRACT

A case study focused on modeling the dispersion of Yperite (Sulfur Mustard) and arsenical chemical agents CLARK I and II in sediment from munitions disposed at the Paardenmarkt site, Belgium, is discussed. Based on conceptual models, simulations were run for the dispersion of Yperite and CLARK I and II in marine sediments, generating concentration data for temporal and geographical scales in the event of a leakage from an idealized munition. Based on the simulation, leakage of Yperite from a munition into the surrounding marine sediment will give toxic effects only up to a few centimeters from the munition casing. Utilizing a munition with an estimated 44 g of arsenic for the CLARK I and II simulations, the arsenical degradents at the level of Estimated No Effects Concentration or higher gives a volume of sediments in the shape of a sphere with a radius of 0.5 m in a time period of 10 years; increasing threefold in volume over a period of 100 years.

Keywords: Yperite, CLARK I and II, Inorganic arsenic, Dispersion modeling, Marine sediments

a surface area of 1.5 km^2 was henceforth indicated on hydrographical maps as an area where anchoring and fishing were prohibited. At three of these locations, chemical munitions were found; the condition of the shells was found to be remarkably good. Following a magnetometric survey, the delineated area was enlarged in 1990 to a pentagon with a surface area of 3 km^2 (Figure 1; Missiaen et al., 2001; Martens, 2005).

Although no official records were kept, the amount of disposed munitions reported by the Belgian government to the 1991 Standing Advisory Committee for Scientific Advice meeting was 35,000 metric tons of shells based on eyewitness reports (OSCOM, 1991). As the percentage of chemical munitions at the end of the war was about 30% of all munitions then used, the amount of toxic

material is estimated at 500 metric tons (OSCOM, 1991) or 12,000 metric tons of toxic shells (Missiaen et al., 2001). As these numbers are estimations, they should be treated with the utmost care.

Site Characterization

At the Paardenmarkt site, the seafloor gently slopes toward the N-NE, with water depths ranging between 1.5 and 5.5 m below mean lower low water springs. The slope was created by the changed hydrodynamics caused by the extension of the Zeebrugge harbor, increased beach nourishment works and nearby dumping sites for dredging activities in the harbor and access channels (Missiaen et al., 2001). The recent sediments overlaying the dumped munitions consist of fine to very fine sand, muddy sands and mud (Francken, 2006). The muddy sediments are char-

FIGURE 1

Paardenmarkt site near the harbor of Zeebrugge with delimited areas in 1972 and 1988 where anchoring and fishing are prohibited.
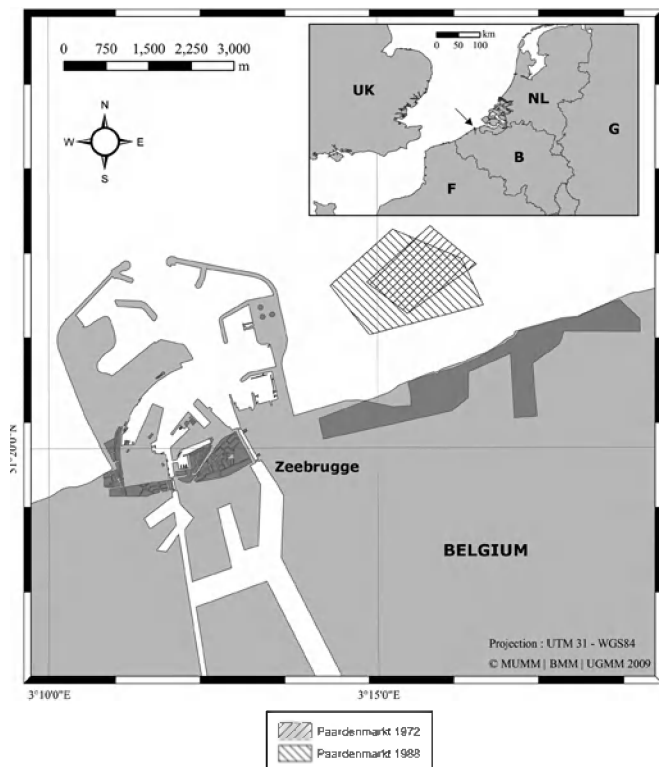
acterized by a high content of organic material (up to 4% in surface sediments) and hence create an anoxic medium, delaying the corrosion of the shells.

There are no data available on individual dumpings, and navigation at the time used fixed points of reference on land (churches and buildings). Even if exact co-ordinates had been kept, currents, trawling and dredging could likely have dispersed the munitions from their original location. Besides the 1972 surveys by navy divers, magnetometric surveys in 1988 and 1996 confirmed the presence of metal objects in the area (Missiaen et al., 2001). The strongest and most frequent magnetic anomalies are situated slightly east from the center of the delineated pentagon. The 1996 survey included measur-

ing a vertical gradient, which permitted an estimate of the depth of burial for individual dumpings. The results indicated that the munitions in the central part of the area are likely buried under a layer of at least 2 m of sediment.

The chemical munitions dumped at the site probably contain the types of shells used in the last months of the war. Typical weapons used were mainly 77 mm shells with tear gases like chloropicrin, choking agents such as phosgene and diphosgene, vomiting agents like CLARK I and II and blistering agents like Yperite (sulfur mustard). Both phosgene and diphosgene hydrolyze rapidly in water and were not selected for further modeling studies (Bizzigotti et al., 2009).

Because of their high toxicity, extremely slow hydrolysis and the equally

toxic breakdown products, CLARK I and II and Yperite pose a long-lasting threat to the marine environment. These chemical agents were therefore selected for further modeling of their dispersion in marine sediments in the event of leakage. The two main questions in case of such an event are (i) how large a volume of sediments will be contaminated, and (ii) how long will each contaminant last? We will try to answer these questions in the subsequent sections.

Yperite or mustard "gas," (also known as H, sulfur mustard, Kampfstoff Lost) is actually a viscous liquid with the chemical name 1,1'-thiobis[2-chloroethane], the molecular formula $C_4H_8Cl_2S$ and a formula weight of 159.08. Despite the relative rapidity of the hydrolysis reaction, mustard has been found to persist in soil or even under water for decades (Bizzigotti et al., 2009). In such incidents of long-term persistence, the common thread is the presence of bulk mustard. While the hydrolysis of *dissolved* mustard is relatively fast, the dissolution of mustard does not occur rapidly (Franke, 1967). Thus, in order to perform environmental fate assessments for Yperite in water, both the hydrolysis rate in seawater and the dissolution rate must be considered (Bizzigotti et al., 2009).

The chemical warfare agents diphenylchlorarsine (also known as CLARK I, DA) and diphenylcyanoarsine (also known as CLARK II, DC) belong to a group of chemicals classified as vomiting agents. DA is the organoarsenic compound with the formula $(C_6H_5)_2AsCl$ and a formula weight of 264.59, and similarly DC is an organoarsenic compound with the formula $C_{13}H_{10}AsN$ and a formula weight of 255.15. CLARK I and II both react very slowly with water compared to phosgene or diphosgene.

Dispersion in Sediments

The main process for dispersion in marine bottom sediments is molecular diffusion. We neglect processes such as bioturbation (burrowing by animals, see below), mechanical disturbance (e.g. dredging activities), resuspension of sediments (shells buried close to the surface) or other wave or current perturbations of interstitial water as pressure induced advection is not the rule in muddy aquatic sediments because of their low permeabilities (Boudreau, 1997).

The effective coefficient for diffusion in interstitial water of marine sediments was estimated by Ullman and Aller (1982) as

$$D_{eff}^{(i)} = \frac{D^{(i)}}{\theta^2}$$

where $D^{(i)}$ is the molecular diffusion coefficient of substance i, and the tortuosity θ can be written as a function of porosity ϕ by (Boudreau, 1997)

$$\theta^2 = 1 - \ln(\phi^2)$$

For the top few tens of centimeters of the seabed, bioturbation may increase considerably the diffusion coefficient (Robbins, 1986). However, for the present model, such processes are not considered explicitly because the effect will be similar to simulations with constant $D^{(i)}$ and the release occurring closer to the seabed.

As an approximation, the molecular diffusion coefficient of salt in water, $D^{(NaCl)} \approx 2 10^{-9}$ m^2 s^{-1}, can be used for CLARK I and II and Yperite. For the purposes of this model, the vertical gradient of porosity is assumed to decrease linearly to a depth of 2 m. Sediment porosity in this region can be estimated from bulk density measurements of sediment cores given by

Malherbe et al. (1983). A typical range of values for use in the model simulations is estimated as $\phi_{2m} = 0.8 \pm 0.1$.

Chemical Reactions

The primary fate of Yperite in water is hydrolysis resulting in hydrochloric acid and thiodiglycol. The degree in which the reaction proceeds via the sulfonium chloride intermediates depends on the concentration of Yperite in the aqueous solution (Yang, et al., 1987). Figure 2 illustrates the hydrolysis of Yperite via a sulfonium chloride in-

FIGURE 2

Hydrolysis of Yperite via a sulfonium chloride intermediate.
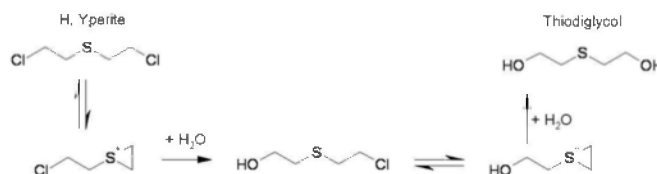
termediate. Hydrolysis is also dependent on the temperature, density, viscosity, pH value and pressure. The rate of Yperite hydrolysis in seawater ($t_{1/2}$ = 175 min at 5°C) is considerably slower than the rate of hydrolysis in pure water (because of aqueous chloride ions equilibrium between the Yperite and the episulfonium chloride (Epstein et al.,

1973). In addition to the slow dissolution of mustard in sea water, other processes such as the formation of oligomeric/polymeric layers can occur further halting the dissolution and hydrolysis (Stock, 1996).

CLARK I hydrolysis in water will lead to diphenylarsenious acid (DPAA) and hydrochloric acid and CLARK II will lead to hydrogen cyanide and diphenylarsenious oxide (DPAO) (Figure 3). Both acids are toxic; nevertheless they will be detoxified quickly in water. Both arseno-organic compounds from the

hydrolysis can later be decomposed into inorganic arsenic compounds and will remain toxic. As for all arsenic compounds, the possible bioaccumulation is of concern (Stock, 1996).

Hydrochloric acid is neutralized by water, while cyanide is quickly broken down. Diphenylchloroarsine is unstable in water and will subsequently

FIGURE 3

Hydrolysis of CLARK I and II to inorganic arsenic compounds.
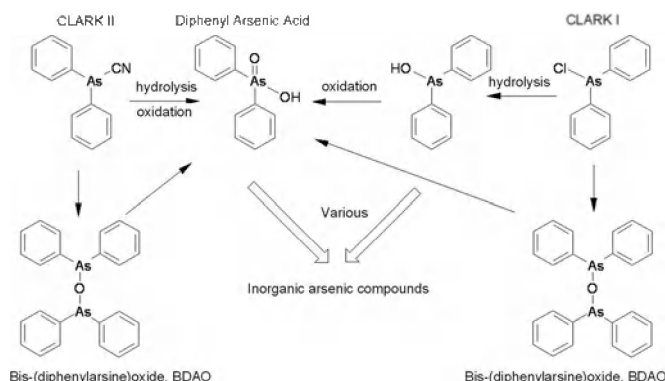
form the highly stable tetraphenyl diarsine oxide. The available information about tetraphenyl diarsine oxide is sparse, but based on its toxicity, it remains a hazard (Stock, 1996). Even if CLARK I and II become fully degraded, the product will still contain an undegradable arsenic component that is toxic to humans. Since CLARK I and II are not soluble in water, have a higher density than water and adsorb to sediments, they are expected to spread very slowly and cause local contamination of sediments close to the point of release.

Once CLARK I and II are hydrolyzed and converted to arsonous acid, the arsenic from them will be indistinguishable from arsenic from other sources and undergo the characteristic environmental reactions of ubiquitous environmental arsenic acid. In natural waters, the predominant species are H_2AsO_4, $HAsO_4^{-2}$ and H_3AsO_3; in sediment, $HAsO_4^{-2}$ and H_3AsO_3 will predominate (MEDEA, 1997).

Conceptual Models

A conceptual model takes into account the different possible scenarios that can take place for the various toxic substances. These scenarios are mainly determined by the local fundamental physical processes that can take place, e.g. hydrolysis to toxic and non-toxic compounds and transport and dilution by diffusion in bottom sediments.

The reactions taking place can be broken down to the following types:

CWA $\xrightarrow{k}$ SNTS

CWA $\xrightarrow{k_1}$ $(1 - e_1)$SNTS $+ e_1$UTS

UTS $\xrightarrow{k_2}$ $(1 - e_2)$SNTS $+ e_2$STS
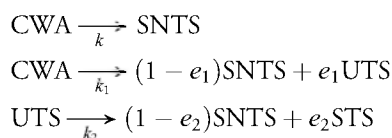
where e stands for the mass fraction, determined by the stoichiometry of the reaction, and k is the reaction rate

coefficient. The abbreviations stand for chemical warfare agent (CWA), stable non-toxic substance (SNTS), unstable toxic substance (UTS) and stable toxic substance (STS).

The mathematical equations require a number of assumptions. These are the following:
1. In solid state, the spatial diffusion of the toxic chemicals is neglected.
2. Transport of pollutants within the sediments is assumed to be dominated by molecular diffusion of the substance dissolved in interstitial water.
3. The geometry of a shell is idealized in the model, which assumes that release occurs from the surface of a rectangular box.
4. The dissolution of the toxic pollutant in the interstitial water will be represented by assuming that chemical equilibrium is reached at the surface of the shell.

The first assumption excludes unlikely events of submarine landslides as well as certain potential human activities such as munitions recovery or inspection operations and sea bottom dredging and fishing activities. The second neglects processes such as interstitial water advection driven by pressure gradients within the seabed, which, except perhaps in the top few centimeters of sediments, generally occurs over much slower, e.g. decadal, timescales (Huettel and Webster, 2000; Burdige and Zimmerman, 2002) than are relevant here. The last assumption indicates that the pollutant is released from the shell at a concentration corresponding to a saturated solution in the interstitial water.

Mathematical Models

The transport equation for Yperite in sediments beneath the sea takes on the following form:

$$\frac{\partial(\phi Y)}{\partial t} = \frac{\partial}{\partial} \left(\phi D_{\text{eff}}^{(Y)} \frac{\partial Y}{\partial x} \right) + \frac{\partial}{\partial} \left(\phi D_{\text{eff}}^{(Y)} \frac{\partial Y}{\partial y} \right) + \frac{\partial}{\partial} \left(\phi D_{\text{eff}}^{(Y)} \frac{\partial Y}{\partial z} \right) - k^{(Y)} \phi Y$$

where ϕ is the porosity of the sediments, $D_{\text{eff}}^{(Y)}$ is the effective diffusion coefficient for Yperite in the sediments and $k^{(Y)}$ is the rate of loss by hydrolysis.

The diffusion of BDAO and DPAA in marine sediments can be written as follows:

$$\frac{\partial\left(X_{\text{BDAO}}^{\text{tot}}\right)}{\partial t} = \frac{\partial}{\partial x} \left(\phi D_{\text{BDAO}}^{\text{eff}} \frac{\partial X_{\text{BDAO}}^{\text{diss}}}{\partial x} \right) + \frac{\partial}{\partial y} \left(\phi D_{\text{BDAO}}^{\text{eff}} \frac{\partial X_{\text{BDAO}}^{\text{diss}}}{\partial y} \right) \\ + \frac{\partial}{\partial z} \left(\phi D_{\text{BDAO}}^{\text{eff}} \frac{\partial X_{\text{BDAO}}^{\text{diss}}}{\partial z} \right) - \phi O_X$$

$$\frac{\partial\left(X_{\text{DPAA}}^{\text{tot}}\right)}{\partial t} = \frac{\partial}{\partial x} \left(\phi D_{\text{DPAA}}^{\text{eff}} \frac{\partial X_{\text{DPAA}}^{\text{diss}}}{\partial x} \right) + \frac{\partial}{\partial y} \left(\phi D_{\text{DPAA}}^{\text{eff}} \frac{\partial X_{\text{DPAA}}^{\text{diss}}}{\partial y} \right) \\ + \frac{\partial}{\partial z} \left(\phi D_{\text{DPAA}}^{\text{eff}} \frac{\partial X_{\text{DPAA}}^{\text{diss}}}{\partial z} \right) + \phi O_X$$

where $X_{\text{BDAO}}^{\text{tot}}$ is the total volume concentration of BDAO (sum of dissolved and adsorbed components divided by total volume), $X_{\text{BDAO}}^{\text{diss}}$ is the concentration of BDAO dissolved in seawater, $X_{\text{DPAA}}^{\text{tot}}$ is the total volume concentration of DPAA

(sum of dissolved and adsorbed components divided by total volume), X_{DPAA}^{diss} is the concentration of DPAA dissolved in seawater and $D_{BDAO}^{eff} = D_{DPAA}^{eff}$ are the effective diffusion coefficients of dissolved BDAO and DPAA in interstitial water. Adsorption of BDAO and DPAA to the sediments is given by

$$X_{BDAO}^{diss} = \frac{1}{K_{BDAO}^{ow}} X_{BDAO}^{ads}$$

and

$$X_{DPAA}^{diss} = \frac{1}{K_{DPAA}^{ow}} X_{DPAA}^{ads}$$

where X_{BDAO}^{ads} and X_{DPAA}^{ads} are the concentrations of, respectively, BDAO and DPAA adsorbed to sediments. The oxidation of BDAO to DPAA is represented by $O_X = k_{BDAO}^{ox} X_{BDAO}^{diss}$.

The equations of the mathematical model have been discretized in a numerical model using a three-dimensional (3-D) grid of unknown concentrations. Consequently, the model has been programmed in FORTRAN 90.

Simulation in Sediments

A numerical simulation was made for the coupled sediment-water system with a grid size of 0.002 m for the sediments (with 200 × 200 × 200 computational points) and a grid size of 0.2 m for the water column (with 50 × 50 × 1 computational points).

FIGURE 4

Simulation of dispersion of Yperite in marine sediments, from initial release (top left, 0 h) to 16 h after (bottom right). Results show contours of Yperite concentration in a vertical cut through an idealized shell. Position A is inside the shell, B on surface, and C, D, E and F at 1, 2, 3 and 4 cm distance from the shell's surface, respectively.
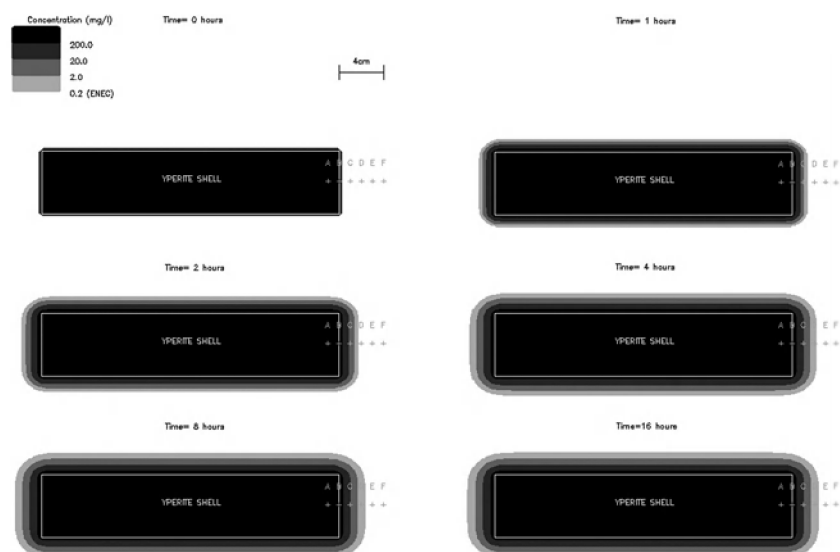
A shell leaking over its entire surface was located at a depth beneath the sediments of 0.2 m.

Yperite

A first control simulation showed that only for shells within a few centimeters of the sediment-water interface will there be any significant flux of Yperite into the water column. Results are thus shown only for concentrations within the sediments. This simulation was made for a duration of 24 h, after which a quasi-steady state was reached until depletion of the shell occurs. The concentration of Yperite in and around the shell is shown for a horizontal cut through the shell in the sediments in Figure 4 at different times after release. Results in a vertical plane are similar since dispersion by dissolution and molecular diffusion is isotropic and no significant gravitational dispersion is expected to occur for Yperite. In these figures, concentrations below the Estimated No Effects Concentration (ENEC) are not shown. Results show that dispersion occurs over a few centimeters in the first hours before significant hydrolysis occurs. Thereafter, hydrolysis balances dissolution and molecular diffusion of Yperite from the shell giving a quasi-steady state.

Figure 5 shows a time series of Yperite concentration for the fixed points A (inside the shell), B (at the surface of the shell) and C, D, E and F (respectively at 1, 2, 3 and 4 cm from the shell), which are marked on Figure 4. These time series show that the quasi-steady state is established after about 10 h (relating to the hydrolysis timescale) and that only for the fixed points C and D in these sediments is the ENEC reached. Thus, pollution of the sediments in this simulation is limited to less than 3 cm

FIGURE 5

Time series of Yperite concentration at fixed position A, B, C, D, E and F (see Figure 4) at different distances from the surface of the shell compared to the ENEC limit.
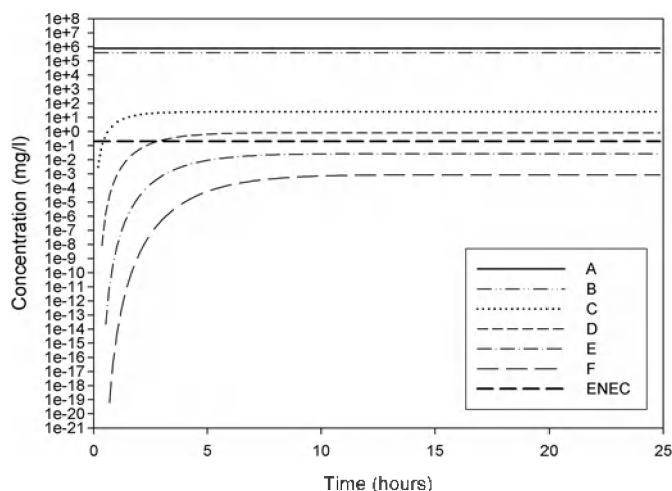
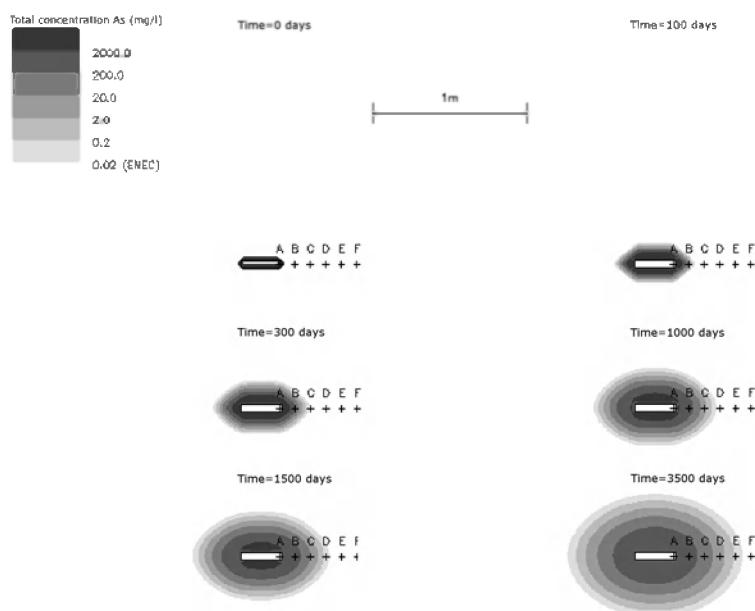from the surface of the shell and persists at least 1 day.

CLARK

In the simulation of CLARK dispersion, the results are shown as the total concentration of arsenic. The simulation is performed for a duration of 10 years, during which time all the arsenic originally contained inside the shell has leaked into the surroundings by dissolution of BDAO into the sea

water at the surface of the shell and subsequent transport by diffusion in the interstitial water, slowed by adsorption to sediments. The resulting concentrations of arsenic found in the sediments (including the small fraction dissolved in the interstitial water) are shown in Figure 6 at different times after the initial release. Time series at fixed locations from the shell are shown in Figure 7.

Sensitivities and Uncertainties

Since some input parameters are poorly known and may vary with factors such as temperature, sediment type, etc., it is necessary to consider how such variations will affect the results. This could be achieved, albeit at high computational cost, by performing many numerical simulations with different input data sets and presenting all results. However, examination of the results of the basic simulation suggest that further approximations to the mathematical model can be made allowing analytical rather than numerical solution.

In view of the very small distance from the shell over which possible toxic impact may occur, the 3-D problem may be simplified into a locally one-dimensional problem. Moreover, except for the initial transient within the first few hours of release, a steady state solution is quickly reached where dissolution of Yperite at the shell surface and its transport by diffusion in the interstitial water are balanced by degradation by hydrolysis. The equations then simplify to the one-dimensional steady state model

$$\frac{\partial}{\partial}\left(\phi D_{eff}^{(Y)}\frac{\partial Y}{\partial r}\right) = k^{(Y)}\phi Y$$

where r is the distance in the sediments measured from the shell surface. For

FIGURE 6

Simulation of dispersion of CLARK in marine sediments, from initial release (top left, 0 days) to 3,500 days after (bottom right). Results show contours of total arsenic concentration (as dissolved in interstitial water included) in vertical cut through idealized shell. Position A is on the shell's surface and B, C, D, E and F at 10, 20, 30, 40 and 50 cm distance from the shell's surface, respectively.

FIGURE 7

Time series of arsenic concentration at fixed positions B, C, D, E and F (see Figure 6) at different distances from the surface of the shell compared to the ENEC limit.
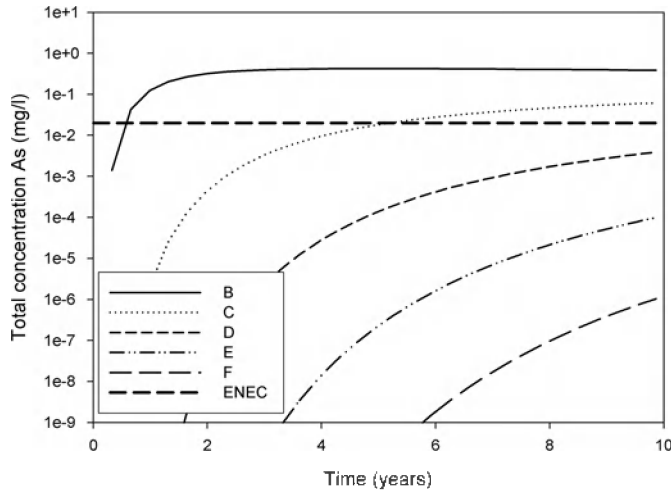
uniform porosity over the length scales considered and initial condition $Y = Y_{sat}$ at $r = 0$, this equation can be solved very simply to give

$$Y = Y_{sat}e^{-r\sqrt{k/D_{eff}}}$$

Thus, the steady state concentration of Yperite in the sediments decreases exponentially with distance from the shell with an e-folding length scale of $\sqrt{D_{eff}/k}$. The ENEC is reached at a distance, δ_Y, from the pollution source, where

$$\delta_Y = \ln\left(\frac{Y_{sat}}{Y_{ENEC}}\right)\sqrt{\frac{D_{eff}}{k}}$$

In our case, this yields a distance of 0.024 m.

The flux of Yperite dissolving from the shell, F, (in kg/m²/s) is then

$$F = Y_{sat}\phi\sqrt{kD_{eff}}$$

The time over which such pollution occurs, τ_Y, can then be estimated roughly as the total mass of pollutant initially contained within the shell, taken as $Y_{in}V$ where V is the volume

of the shell, divided by this flux integrated over the shell surface area, A:

$$\tau_Y = \frac{Y_{in}}{Y_{sat}}\frac{V}{A}\frac{1}{\phi\sqrt{kD_{eff}}}$$

This can be seen as the product of factors relating to Yperite concentration within the shell relative to the saturation concentration, a length scale V/A relating to the size of the shell and the inverse of the velocity scale $\sqrt{kD_{eff}}$ relating to the diffusion-hydrolysis balance. Solving this equation with the same input parameters as for the numerical model, this yields 2.6×10^7 s or 304 days.

For CLARK, the first theoretical approximation supposes that the toxic pollutant disperses uniformly over a volume of sediments given by a perfect sphere of radius r and that the concentrations are zero outside this sphere. In reality, and in the numerical simulation given here, the concentration does not change abruptly in this way but is smooth because diffusion processes reduce the original sharp gradient of concentration found at the shell boundary. However, this first approximation gives already a useful maximum length scale

for pollution. Thus, supposing that the total mass of arsenic inside a 77 mm shell is represented by M^{tot}, the concentration within a uniformly polluted sphere, X_{unif} is given by

$$X_{unif} = \frac{M^{tot}}{4/3\ \pi r^3}$$

For the case of a shell containing 44.05 g As, the consequent concentration, X_{unif}, is plotted for polluted volumes of different radius in Figure 8. This shows that a single shell could potentially contaminate at the ENEC concentration a sphere with a radius of about 8 m if the arsenic is dispersed uniformly over such a volume. Of course, if dispersion occurs over smaller length scales, then the resulting concentrations will be correspondingly higher.

For a diffusion problem without adsorption, a typical length scale over which dispersion occurs, δ_{As}, can be estimated as

$$\delta_{As} = \sqrt{D_{BDAO}^{eff}t}$$

where $D_{BDAO}^{eff} = 2 \times 10^{-9}$ m² s⁻¹ is the effective pore water diffusion coefficient and t is the time. For times $t = 300$ days and $t = 10$ years, this gives $\delta_{As} = 25$ cm and $\delta_{As} = 79$ cm. However, in the present case, the adsorption to sediments provides buffering of the diffusion, and the length scale is correspondingly reduced to
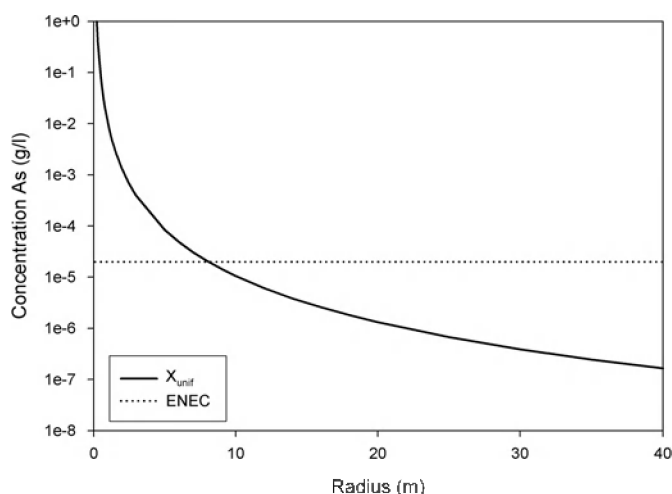
$$\delta_{As} = f_{ad}\sqrt{D_{BDAO}^{eff}t}$$

where

$$f_{ad} = \left(\phi + [1 - \phi]K_{BDAO}^{ow}\right)^{-0.5}$$

In the present simulation, $K_{BDAO}^{ow} = 1000.0$ and $\phi = 0.9$, giving $f_{ad} = 0.1$

FIGURE 8

Concentration arsenic within a uniform polluted sphere with different radii. The ENEC caulue (20 µg/l) is presented as a dotted line.

and δ_{As} = 2.5 cm and δ_{As} = 7.9 cm for times t = 300 days and t = 10 years, respectively. This distance corresponds to about twice the distance from the shell to the highest concentration contour in the results of Figure 6.

The analytical equations given for the length and timescales δ and τ allow a rather simple examination of how these conclusions vary with different input data sets.

Thus, for Yperite, considering k, a slower hydrolysis of Yperite (e.g. as can be expected at lower temperatures) will increase the length scale of the polluted region, but not dramatically. Consequently, a hydrolysis rate ten times slower than that used here gives pollution length and timescales about three times larger. Taking into account D_{eff}, a poorly known parameter, a molecular diffusion coefficient ten times larger gives a pollution length scale about three times larger (and a timescale about three times shorter). Sediment porosity, ϕ, which could vary between about 0.6 and 1.0, affects only slightly the length and timescales of pollution. In the case of localized

corrosion of the shell casing, leakage will occur only over a limited surface area of the shell. In such a case, the pollution length scale (now measured from the exact leakage position) is the same as that given above for a generalized corrosion of the shell casing, although the corresponding timescale, until all the toxic contaminant within the shell has been hydrolyzed, will be considerably increased.

For CLARK, the numerical simulation was stopped after 10 years. Continuation of the simulation for another 90 years would give essentially similar results to those found in Figure 6, but with a larger ellipse for the concentration contours. As time progresses, the elliptical contours will become more spherical as the precise geometry of the initial leak becomes less relevant. From consideration of the relationship between time and length scales, an increase in the simulation duration by a factor of ten gives a corresponding increase in the diffusion length scale by a factor $\sqrt{10}$. Thus, the radius at which concentrations reach or exceed the ENEC concentration is

on the order ~1 m after 100 years. Apart from oxidation, considered below, no other chemical processes are known to affect the dispersion of BDAO within this time frame, although enhanced diffusion from bioturbation might occur. Using the upper limit for the oxidation rate of BDAO to DPAA that can be deduced from the experimental data of Hanaoka et al. (2005), a timescale for the half-life of oxidation can be calculated as

$$T_{ox} = \frac{1}{k_{ox}} = 2.58 \times 10^8 \text{s} = 8.2 \text{ years}$$

Thus, oxidation could start to become significant within the time frame of the numerical simulation presented here and certainly within the duration of the 90 years that has elapsed since dumping of chemical weapons. However, the dispersion and adsorption of DPAA will be very similar to that of BDAO, and the simulation presented here can be considered to represent the total arsenic, i.e. the sum of arsenic found as BDAO and DPAA. The low solubility of BDAO in sea water restricts essentially the speed at which arsenic is released into sea water. With the present value of S_{BDAO} = 1.43 gAsl^{-1}, this release was total within the first year of simulation. After total release has occurred, the solubility plays no further role in the dispersion process. While seemingly rather low, the specified solubility is such that the volume of water (63 l) required to entirely dissolve all the arsenic present in a single shell is not so great. While it is clear that the chosen value of solubility has a very large uncertainty, a value by a factor of 10 smaller would make little difference to the dispersion over the timescale of 10-100 years. Only in the case of extremely low solubility (e.g. 1,000

times smaller than that used here) or zero solubility would the dispersion be significantly different or even non-existent. The strong adsorption of BDAO to organic sediments limits significantly the speed of diffusion. By considering conservation of total mass of arsenic, it is obvious that if diffusion is thus restricted, high concentrations will prevail in the immediate vicinity of the shell in the sediments. Concentrations of arsenic in the interstitial water will, however, be much lower than concentrations found in the sediments. The partitioning coefficient of K_{BDAO}^{ow} = 1000.0 used for simulations is already rather low compared to the stated partitioning coefficients for the CLARK I and CLARK II compounds found in the literature. However, use of higher partitioning coefficients is likely to be unrealistic because adsorption of BDAO (or DPAA) to sediments is likely to also be limited by the concentration of organic sediments available. If adsorption to sediments is less in reality than in the present simulation, then diffusion will be correspondingly faster and more arsenic will be found in the interstitial water than in the present simulation.

Conclusions

The objective of this study was to establish the time and length scales for pollution in the event of leakage of toxic products from chemical weapons dumped at sea on the Paardenmarkt site. A 3-D model of the sediments has been developed and applied to simulate the dispersion of toxic chemicals leaking from a single shell. By linearity, these results can be scaled up to the case of many shells. This study was motivated by two key questions, namely, in the event of leakage from a shell, what is the volume of sediments and water affected by the toxic pollutants and how long does such toxicity persist?

The model results and the theoretical generalization suggest that thanks to slow diffusion in interstitial waters over the timescale necessary for hydrolysis, leakage of Yperite from a shell into the surrounding marine sediments will give toxic effects only up to a few centimeters from the shell casing. The volume affected is thus less than the volume of the shell itself. The timescale for persistence of such toxicity is at least in the order of a year and possibly much longer, depending on the shell surface area where leakage occurs.

A numerical simulation has been made showing how BDAO disperses over a time period of 10 years. In the present case, it is estimated that a single shell with total content of 44 g arsenic will pollute at the level of the ENEC or higher, a volume of sediments given approximately by a sphere with a radius of 0.5 m in a time period of 10 years. This will increase by a factor of about three over a period of 100 years. Compared with the results for Yperite dispersion, the situation for dispersion of CLARK degradation products is very different because there is no known process that will render these products non-toxic. For Yperite, the dispersion length scale was limited by the short timescale (a few hours) before hydrolysis renders the product non-toxic. For the CLARK degradation products, there is no such time limit to the dispersion, which will continue indefinitely, albeit slowly. The main effective limit to the polluted volume is the total mass of arsenic contained within the shell and the concentration for which no acute toxicity can be expected.

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