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**SUPPLEMENT TO THE METHODOLOGY FOR RISK  
EVALUATION OF NON-AGRICULTURAL PESTICIDES  
(ESPE) 2., INCORPORATED IN THE UNIFORM SYSTEM  
FOR EVALUATION OF SUBSTANCES (USES).**

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## II

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## SUMMARY

In 1993 an evaluation system for non-agricultural pesticides was presented (ESPE 2, Luttk *et al.*). The largest part of the method for non-agricultural pesticides was incorporated in the Uniform System for the Evaluation of Substances, USES 1.0 (RIVM, VROM, WVC 1994). In the ESPE 2 report several open ends were still present, because methods for all routes were not available at that time. This report provides models, for incorporation in the Uniform System for Evaluation of Substances (USES), for the following scenarios:

- disinfectants for swimming water,
- leaching from impregnated wood to soil and ground water,
- household products used for fogging.

In addition to these three emission modules a concept is presented with which diffusion of metal ions from the water phase to the sediment can be simulated. This concept is introduced because as the result of a difference in heavy metal concentration in the porewater of the sediment and the surface water, heavy metals may diffuse from one compartment to the other. For anoxic sediments in the presence of "available" sulfide diffusion will mainly take place from the surface water into the sediment. Thus, the metal concentration in the surface water will decrease, which could have consequences for the risk assessment for the aquatic ecosystem. This part of the document is not meant for incorporation in USES but as a starting point for the development of a hazard/risk assessment for the sediment.

The development of risk assessment methodologies for non-agricultural pesticides will continue in the coming years and is intended to result in a second (national) version of USES in 1996.

## SAMENVATTING

Met het gereed komen van deel 2 van het beoordelingssysteem ESPE (Evaluation System for Pesticides, part 2, Non-agricultural pesticides) in 1993 (Luttik et al.) werd de eerste stap tot een methodiek van de toelatingsbeoordeling van niet-landbouwbestrijdingsmiddelen afgerond. Het grootste deel van ESPE 2, werd ingebouwd in het Uniform Beoordelingssysteem (UBS). In het ESPE 2 rapport waren nog verschillende open plekken vorhanden, omdat in de literatuur nog niet voor alle routes een voldoende geaccepteerde methode beschikbaar was.

Dit rapport geeft modellen, die kunnen worden ingebouwd in het Uniform Beoordelingssysteem (UBS), voor de volgende scenario's:

- desinfectantia die gebruikt worden in zwembaden,
- uitlozing van geïmpregneerd hout (palen/schuttingen) naar de bodem en het grondwater,
- fumigantia die gebruikt worden in silo's, gebouwen, etc.

Naast deze drie emissie modellen wordt een concept gepresenteerd waarmee de diffusie van metaalionen van de waterfase naar het sediment kan worden gesimuleerd. Dit concept wordt geïntroduceerd omdat als gevolg van verschillen in de concentratie van zware metalen in het oppervlaktewater en het poriewater van het sediment, zware metalen kunnen diffunderen van het ene compartiment naar het andere. Diffusie van zware metalen in anaërobe sedimenten in de aanwezigheid van "beschikbaar" sulfide zal hoofdzakelijk optreden vanuit het oppervlaktewater naar het sediment. Ten gevolge van dit proces zal de concentratie in het oppervlaktewater verminderen, hetgeen consequenties kan hebben voor de risicoschatting voor het aquatische ecosysteem. Dit deel van het rapport is niet bedoeld om direct in UBS te worden opgenomen, maar meer als een aandachtspunt voor de ontwikkeling van een risicoschattingsmodel voor het sediment. De ontwikkeling van methoden voor het inschatten van de risico's van niet-landbouwbestrijdingsmiddelen zullen in de komende jaren voorgezet worden en het is de bedoeling dat dit zal resulteren in een tweede (nationale) versie van UBS in 1996.

## 1. INTRODUCTION

When in 1990/1991 the national policy for agricultural pesticides was discussed in parliament, it was recognized that the arrears of the development of policy on non-agricultural pesticides should be made up. In 1994 a start was made with the preparation of a long-term policy plan (MJP-H) that will be proposed to parliament in 1996 and a status report was issued. Ahead of the MJP-H, policy options for so called focal points, i.e. specific groups of biocides, will be described in 1995. Risk assessment is considered to be prerequisite for the definition of emission reduction strategies. Therefore, the development of tools for risk assessment of non-agricultural pesticides runs parallel to the described policy development.

The first step towards a full-scale evaluation system for pesticides (ESPE) was made in 1992 with the presentation of an evaluation system for agricultural pesticides (ESPE 1, Emans *et al.*). In 1993 an evaluation system for non-agricultural pesticides was presented (ESPE 2, Luttk *et al.*). The method for agricultural pesticides was completely incorporated in the Uniform System for the Evaluation of Substances, USES 1.0 (RIVM, VROM, WVC 1994). USES 1.0 is a tool that can be used for rapid, quantitative assessments of the general risks of substances. Risk assessment methods for various categories of substances were integrated, as much as was possible, into one assessment scheme. USES 1.0 was developed through the elaboration of an action point of the Dutch National Environmental Policy Plan of 1989, in close consultation with other research Institutes and Industry, experts from the Ministry of Housing, Spatial Planning and the Environment, the Ministry of Welfare, Public Health and Cultural Affairs, and the National Institute of Public Health and Environmental Protection worked together on this project. USES 1.0 can be applied to risk assessments and to set priorities for new substances, existing substances, plant protection products and biocides within the scope of the Dutch Chemical Substances Act and the Dutch Pesticide Act. The protection targets in USES 1.0 are: humans (exposed via the environment and via consumer products), micro-organisms in sewage treatment plants, the aquatic and terrestrial ecosystem, and

top predators.

For the non-agricultural pesticides the following scenarios were incorporated in USES 1.0:

- biocides in the textile industry,
- biocides in the paper and cardboard industry,
- biocides in the process and cooling-water installations,
- preservatives in the metal industry,
- wood preservatives: creosote impregnation,
- wood preservatives: salt impregnation,
- wood preservatives: drenching and dipping,
- remedial timber treatment in buildings,
- leaching from impregnated wood to surface water, and
- antifoulings.

In the ESPE 2 report several open ends were still present, because methods for all routes were not available at that time. This report will provide, models for the following scenarios:

- disinfectants for swimming water,
- leaching from impregnated wood to soil and ground water,
- household products used for fogging.

In addition to these three emission modules a concept is presented with which diffusion of metal ions from the water phase to the sediment can be simulated. This concept is introduced because as the result of a difference in heavy metal concentration in the porewater of the sediment and the surface water, heavy metals may diffuse from one compartment to the other. For anoxic sediments in the presence of "available" sulfide diffusion will mainly take place from the surface water into the sediment. Thus, the metal concentration in the surface water will decrease, which could have consequences for the risk assessment for the aquatic ecosystem.

The development of risk assessment methodologies for non-agricultural pesticides will continue in the coming years and is intended to result in a second (national) version of USES in 1996. Results of this work in the Netherlands will be submitted in current international discussions on this topic.

## 2. MODEL DESCRIPTIONS

### 2.1 Disinfectants in swimming water

#### 2.1.1 Introduction

Swimming pools can be divided in many types, as can be seen from Table 2.1 (excluding natural swimming pools). Swimming pools which are not natural pools, usually are so called circulation baths. This means that the swimming water is pumped round via a water treatment installation. Only in the case of (small) private swimming pools probably non-circulation baths occur. Water treatment is needed to obtain and maintain the desired chemical/bacteriological quality of swimming water. One aspect of the treatment is to supply the swimming water with a certain dose of disinfecting agent. Disinfection usually takes place at a point in the circulation pipe just before the water enters the pool.

**Table 2.1** Types, number of swimming pools and average number of visitors per pool per year in the Netherlands (Loos and Guis, 1994)

Type of swimming pool	Number	Number of visitors
Public pools		
- indoor	299	148,000
- outdoor	290	44,000
- combined	117	214,000
Therapeutic baths		No information available
Saunas		No information available
Whirlpools		No information available
Hotel pools/ camping pools		No information available
Private pools		No information available

For oxidation of contaminants present in swimming water and disinfection of swimming water, disinfectants based on hypochloride are used, and sometimes ozone. According to Loos and Guis (1994) in the Netherlands there are four public swimming pools where ozone is used for treatment of the water, mainly

for oxidation. Disinfection of the swimming water in the pool by chlorine based chemicals remains still necessary, because of the high toxicity of ozon. The other public swimming pools use chlorine based chemicals for both oxidation and disinfection. It is (in principle) possible to use chlorine from cylinders or pressurized containers. Another possibility is the use of chlorine prepared on the spot by electrolysis of a sodium chloride solution. For reasons of safety nearly all swimming pools are using sodium hypochlorite. In smaller swimming pools and private swimming pools often calcium hypochlorite is used.

Superfluous swimming water (drain water and the whole content of the pool discharged at periods of maintenance or unoccupancy) in most cases will be discharged into the sewage system. In 1985 an estimated 6% of the public swimming pools discharged directly to surface water and in 2000 it is expected that it has dropped to 0% (SPEED, 1992). Only private pools then still may discharge to surface water directly. It is unknown in how many cases this will occur.

### **Ozone**

It is not allowed to add ozone to swimming water directly. So, oxidation with ozone has to be carried out in the purification section. Any remaining ozone after oxidation has to be removed, for example with an activated carbon filter, before allowing the water into the swimming basin (VROM, 1981).

The air/ozone or oxygen/ozone mixture from the ozonizer is added to the water in a special apparatus. Due to the low solubility of ozone, a sufficient large contact area and the duration of the contact must be long enough for oxidation and disinfection (VROM, 1981).

### **Chlorine based chemicals**

The order on hygiene and safety of swimming facilities (Government Gazette, 1984) requires a certain concentration of freely available chlorine in swimming water. For 1990 the estimation of the amount applied for this purpose was 2,700 tonnes (expressed as active chlorine) (TNO/CML, 1994).

As hypochlorite is transformed rapidly, discharges of swimming water into the

sewage will normally reach the municipal sewage treatment plant (MSTP) free or nearly free of hypochlorite. If any hypochlorite reaches the MSTP, complete degradation will take place before the effluent will reach the receiving surface water.

### 2.1.2 Model description

Although the chance that disinfectants like ozone and chlorine based chemicals will reach the MSTP is very small, it is possible that metabolites and/or reaction products, like for instance  $\text{CHCl}_3$ , chlorphenols and chloramines, will reach the MSTP. Moreover, in the future other disinfectants may be used that will reach the MSTP. For those situations and for discharging into surface water the following scenarios are modelled:

- A discharge of swimming water by public swimming pools into the sewage system:
  - a the "acute" situation (the whole pool is emptied completely in the sewage system),
  - b the "chronic" situation (a fixed amount of water per visitor is discharged to the sewage system),
- B discharge of swimming water by public and private swimming pools into the surface water.

A) Discharge of swimming water by public swimming pools in the sewage system

**Table 2.2** Model for calculating concentrations in the MSTP and surface water of compounds/metabolites/ reaction products used or formed in swimming water.

Variable/parameter (unit)	Symbol	Default	C/R/E/O
<b>Input:</b>			
Water surface (m <sup>2</sup> )	L <sub>surf</sub>	440	C
Average depth of water (m)	W <sub>depth</sub>	1.8	C
Number of visitors per day (-)	N <sub>visit</sub>	400	C
Concentration compound/metabolite/ reaction product (mg/m <sup>3</sup> )	C <sub>swimw</sub>		R
Water replaced per visitor (m <sup>3</sup> )	Q <sub>repl</sub>	0.05	C
Quantity of water in MSTP (m <sup>3</sup> /d)	Q <sub>stp</sub>	1800	C
Fraction removed in STP (-)	R <sub>stp</sub>		O
Dilution factor of receiving surface water (-)	F <sub>dilut</sub>	32	C
<b>Output:</b>			
C <sub>surfI</sub> = Concentration of compound/metabolite/reaction product in surface water at release of the whole bath capacity (mg/l)			
C <sub>surfII</sub> = Concentration of compound/metabolite/reaction product in surface water at release of 50 litres per visitor (mg/l)			

**Model calculations:**

$$C_{\text{surfI}} = L_{\text{surf}} * W_{\text{depth}} * C_{\text{swimw}} * (1 - R_{\text{stp}}) * 10^3 / (Q_{\text{stp}} * F_{\text{dilut}})$$

$$C_{\text{surfII}} = N_{\text{visit}} * Q_{\text{repl}} * C_{\text{swimw}} * (1 - R_{\text{stp}}) * 10^3 / (Q_{\text{stp}} * F_{\text{dilut}})$$

Note 1 USES 1.0 was not designed to assess degradation and/or reaction products. If a substance like chloroform has to be assessed the concentration of chloroform in the swimming water should be entered at C<sub>swimw</sub> together with the toxicity data and all the other parameters for chloroform.

Note 2 Volatilization of compounds/degradation and or reaction products is not taken into consideration, because it is assumed that the

concentration of the compounds in the waste water of the swimming pools will be low. Therefore, the role of volatilization will be of minor importance.

B) Discharge of swimming water by public and private swimming pools into the surface water.

**Table 2.3** Model for calculating concentrations in the surface water for compounds used or formed in swimming water for "acute" situations.

Variable/parameter (unit)	Symbol	Default	C/R/E/O
<b>Input:</b>			
Concentration in swimming water (mg/l)	$C_{swimw}$		R
Dilution factor of receiving surface water (-)	$F_{dilut}$		
Public swimming pools		4	C
Private swimming pools		2	C
<b>Output:</b>			
$C_{surf}$ =	Concentration of compound/metabolite/reaction product in surface water at release of the whole pool capacity (mg/l)		
<b>Model calculations:</b>			
$C_{surf}$ =	$C_{swimw} / F_{dilut}$		

## 2.2 Leaching from impregnated wood to soil and ground water

### 2.2.1 Leaching from impregnated wood to ground water

For fencing impregnated wooden poles are used extensively in the Netherlands. By far the largest part of the Netherlands can be described by the soil types *sand* and *clay*; the average ground water tables vary from 0.4 m bgl (below ground level) in winter to 0.8 m bgl in summer in *sand* soils, and from 0.8 m bgl in winter to 1.2 m bgl in summer in *clay* soils (Meinardi, 1994). This means that

wooden poles in sand soils will be in "dry" sand for a part of the year, while in winter about 0.1 m will be in the upper part of the ground water. In clay the poles are not in direct contact with the ground water, but in clay always some stagnant water is present in the clay; this stagnant water will exchange substances with water passing through the clay, by diffusion (Meinardi, 1994).

The flux of substances leached from the impregnated poles will be dependent on time and the specific substance. Freshly impregnated and applied poles will have a higher flux in the beginning than after a couple of years. From leaching experiments with creosote (WEI type A, CCO440) it appeared that fluxes of the four most important polycyclic aromatic hydrocarbons (phenanthrene, anthracene, fluoranthene and pyrene) decreased from 4.5 mg/m<sup>2</sup>.day to 1-2 mg/m<sup>2</sup>.day after 1 month; for short term experiments no relation was found between the retention in the wood of the impregnated components and the emission (Schollema, 1992).

The scenario described here is for *sand soils*, as only in this soil type (a part of) the pole is in contact with the ground water (during winter). In clay soils also in winter the poles are not in contact with the ground water. As said before clay soils, however, contain a considerable amount of stagnant pore water, which may exchange substances with the water flow passing through (vertical transport of rain water). This has not been worked out yet; for future work on calculations of concentration of compounds leached from poles in soil a report on quick information with respect to the penetration of substances into the soil (Veling, 1993) may be very useful.

#### sand soils

For the situation in the Netherlands the vertical and horizontal ground water flow rates in the shallow ground water are usually at the same level of about 1 m/year (Meinardi, 1994). Assumptions made for this scenario are:

- wooden poles consist of round timber with a diameter of 0.1 m;
- the poles are positioned at a depth of 0.5 m below ground level (bgl);
- the ground water table is 0.4 m bgl;

- the flux of the substance assessed is constant;
- only the horizontal flow rate of is of importance;
- leaching by rain fall from the part above the ground water table may be neglected.

In this case the concentration in the (shallow) ground water can be calculated simply from the flux of the substance and the (horizontal) flow rate of the ground water (table 2.4).

**Table 2.4** Model for calculating concentrations in ground water for compounds used for impregnating wood used in sand soils

Variable/parameter (unit)	Symbol	Default	C/R/E/O
<b>Input:</b>			
Mean flux of compound (mg/m <sup>2</sup> .day)	$F_{comp}$		R
Ground water flow rate (m/year)	$V_{grndw}$	1	E
<b>Output:</b>			
Concentration in ground water ( $\mu$ g/l)	$C_{grndw}$		
<b>Model calculations:</b>			
$C_{grndw}$	$= F_{comp} / V_{grndw}$ $= 365 F_{comp}$		

## 2.2.2 Leaching from impregnated wood to soil

For calculating the impact of leaching to soil a situation of a fence consisting of impregnated poles and planks with the following characteristics and assumptions is regarded:

- the soil loaded with leached substances is a rectangular box, with a default value for the width of 0.025 m and a depth of 0.05 m (the standard value in USES 1.0 for application of agricultural pesticides without mixing);
- the amount leached over one year is present in the soil box specified above;
- the default value for the number of days that leaching occurs has been set at 35 (chosen on the basis of the day totals of rainfall in 1980 at KNMI, De Bilt,

The Netherlands: 65 days  $\geq 5.0$  mm and 26 days  $\geq 10.0$  mm (van der Linden and Boesten, 1989));

- the surface of the fence exposed to leaching is two times (both sides of the fence) the area of the fence, excluding the surfaces of the poles and the sides and headers of the planks.

**Table 2.5** Model for calculating concentrations in soil for compounds used for impregnating wood

Variable/parameter (unit)	Symbol	Default	C/R/E/O
<b>Input:</b>			
Depth of soil layer (m)	$W_{\text{depth}}$	0.05	C
Width of soil layer (m)	$W_{\text{width}}$	0.025	E
Number of days with leaching (day)	$T_{\text{rain}}$	35	E
Mean flux of compound (mg/m <sup>2</sup> .day)			
over 1 year	$F_{\text{comp}}$		R
Height of the fence (m)	$W_{\text{height}}$	2	E
Density of soil (kg/m <sup>3</sup> )	$\text{RHO}_{\text{soil}}$	1500	E
<b>Output:</b>			
Concentration in soil after 1 year (kg <sub>comp</sub> /kg <sub>soil</sub> )		$C_{\text{soil}}$	

#### Model calculations:

Leaching surface of impregnated fence per m length:

$$L_{\text{surf}} = 2 * W_{\text{height}} * 1 = 2 \text{ m}^2$$

Quantity leached per m length of fence:

$$\begin{aligned} L_{\text{comp}} &= L_{\text{surf}} * F_{\text{comp}} * T_{\text{rain}} \\ &= 2 * F_{\text{comp}} * T_{\text{rain}} \text{ mg} \end{aligned}$$

$$\begin{aligned} C_{\text{soil}} &= 10^{-6} * L_{\text{comp}} / (W_{\text{depth}} * W_{\text{width}} * 1 * \text{RHO}) \\ &= 2.10^{-5} * L_{\text{comp}} / W_{\text{width}} \text{ kg}_{\text{comp}}/\text{kg}_{\text{soil}} \end{aligned}$$

For the calculation of leaching from the soil to the ground water the PESTLA tables may be used uniform to USES 1.0 if the load per hectare is in the range of 0.01-100 kg. The load per hectare is then calculated as:

$$10^{-6} * L_{\text{comp}} * 10,000 / (W_{\text{width}} * 1) = 10^{-2} * L_{\text{comp}} / W_{\text{width}} \text{ kg/ha.}$$

### 2.3 Household products used for fogging

One of the application methods of both rodenticides and insecticides is fogging, in which the product is applied gaseously. Fogging is used against insects in storage places, silos and shipyards, against pests in rooms where bates or sprays cannot be applied (like aeroplanes), and against pests in various materials, like wooden packing material. Especially methylbromide is regularly used so far. Table 2.6 shows the amounts used for fumigation purposes in the period 1990-1993 [VROM/HIMH, 1994]. The average per fumigation was 28.7 kg in 1993 [VROM/HIMH, 1994]. From these data, it could be calculated that on 27 locations on average 100 kg or more is used, the highest average on 1 location was 617.9 kg. As realistic worse case approach for the use of methylbromide an amount of 100 kg per event seems reasonable. No data on the size of the space treated were available.

**Table 2.6 Use of methylbromide in the Netherlands for fumigations in the period 1990-1993 (kg)**

1990	1991	1992	1993
64,471	43,008	38,366	29,495

Alternative substances are hydrocyanic acid (HCN, not allowed any more in the Netherlands) and phosphine (PH<sub>3</sub>). This report will deal with the application of fumigants applied in stock protection at storage places for products like grains. In the scenario for fumigation of buildings, silos, etc. the opportunity has been given to account for retention of the fumigant in goods (i.e. the fraction of fumigant retained in the material treated) and disintegration (i.e. the fraction of

fumigant decomposed or converted into other substances). The calculation of  $C_{air}$  (concentration of fumigant in air compartment) will be calculated according to the standard method of USES 1.0 (OPS model).

**Table 2.7.** Model for calculating release to the air for compounds used for fumigation of buildings, silos, etc.

Variable/parameter (unit)	Symbol	Default	C/R/E/O
<b>Input:</b>			
Amount used (kg)	$Q_{subst}$		R
Fraction of retention in goods (-)	$F_{ret}$	0.02	E
Fraction of disintegration (-)	$F_{disin}$	0.001	E
<b>Output:</b>			
Emission to the air at degassing (kg)	$Q_{emis}$		
<b>Model calculations:</b>			
$Q_{emis}$	$= Q_{subst} * (1 - F_{ret}) * (1 - F_{disin})$ $= Q_{subst} * (1 - 0.02) * (1 - 0.001)$ $= Q_{subst} * 0.979 \text{ kg}$		

### 3. SEDIMENT AS A BUFFER FOR HEAVY METALS

#### 3.1 Introduction

Recent toxicity studies show that the ratio of the acid extractable metals (Simultaneously Extracted Metals, SEM) and the "available" amount of sulfide (Acid Volatile Sulfide, AVS) plays an important role in the prediction of toxic effects for sediment dwelling organisms (Di Toro *et al.*, 1992). In fact, the researchers failed in estimating the toxicity on the basis of the total content of the sediment. Under anoxic conditions in the presence of sulfide, metals are able to form very insoluble metal-sulfide precipitates. Hence, the concentration of the free metal in solution decreases till the nanogram per litre level. Just for illustration, solubility products of several metal sulfides are presented in table 3.1.

**Table 3.1** Solubility products ( $K_s$ ) of various metal sulfides (CRC 1993-1994).

Precipitate	Log $K_s$	Precipitate	Log $K_s$
$\text{Ag}_2\text{S}$ (alpha)	-49.17	$\text{NiS}$	-20.97
$\text{Ag}_2\text{S}$ (beta)	-48.96	$\text{PbS}$	-28.04
$\text{Bi}_2\text{S}_3$	-98.74	$\text{PdS}$	-57.69
$\text{CdS}$	-28.85	$\text{PtS}$	-73.00
$\text{CoS}$	-25.52	$\text{SnS}$	-27.49
$\text{CuS}$	-35.90	$\text{ZnS}$	-24.53
$\text{HgS}$	-52.19		

The "available" amount of sulfide in the sediment is an operational defined parameter, which can be determined quite easily through an acid extraction procedure (Den Hollander and Van den Hoop, 1994). AVS levels in Dutch marine and freshwater sediments vary in between non-detectable and

approximately 50  $\mu\text{mol}$  per gram dry sediment, with an average value of circa 15  $\mu\text{mol g}^{-1}$  (Van den Hoop *et al.*, submitted). This means that anoxic sediments with "available" sulfide may serve as a buffer for heavy metals. For example, a sediment containing 1  $\mu\text{mol AVS g}^{-1}$  is able to bind about 112  $\text{mg kg}^{-1}$  cadmium, which is circa 150 times more than the present Dutch target value (VROM, 1990-1991).

As the result of a difference in heavy metal concentration in the porewater of sediment and the surface water, heavy metal may diffuse from one compartment to the other. For anoxic sediments in the presence of "available" sulfide diffusion will mainly take place from the surface water into the sediment. Thus, the metal concentration in the surface water will decrease, which could have consequences in estimating toxicity risks for surface water.

In the present chapter an estimation will be made of the flux of metals from surface water into sulfide rich sediments on the basis of diffusion only. From these data a disappearance rate will be derived. Hence, we are able to compare this transport with the other important flow current in risk assessment of surface water, namely the refreshment rate of the water.

### 3.2 Calculation of the flux

The flux ( $J$ ) of compounds from a system with a high concentration to a system with a low concentration is given in the most simple form by the first law of Fick:

$$J = -D_M \frac{dc}{dx} \quad 3.1$$

where  $D_M$  is the diffusion coefficient of the compound in  $\text{m}^2 \text{ sec}^{-1}$  and  $dc/dx$  is the concentration gradient in  $\text{gram m}^{-4}$ , respectively. The flux is expressed in  $\text{gram m}^{-2} \text{ sec}^{-1}$ . Diffusion coefficients for heavy metals in pure water solutions at 25°C are available in the literature (CRC 1993-1994). For divalent cations diffusion coefficients are in the order of  $7 \cdot 10^{-10} \text{ m}^2 \text{ sec}^{-1}$ . For monovalent cations they increase by a factor of 2. Under field conditions, the temperature of the

sediment water system is usually smaller, resulting in a smaller value for the diffusion coefficient. For example, for a temperature of 12°C, which is a reasonable estimate for the average of Dutch sediments, the diffusion coefficient appears to be approximately  $5 \cdot 10^{-10} \text{ m}^2 \text{ sec}^{-1}$  (Carignan and Tessier, 1985). The concentration gradient can be estimated as the difference between the concentration of the metal in the surface water and in the porewater of the sediment divided by the thickness of the diffusion layer. On the basis of the solubility products of metal sulfides (see table 3.1) it is expected that the metal concentration in pore water is at least three magnitudes of order lower than in surface water. Hence, it becomes negligible in the calculation of the concentration gradient in equation (3.1). Concentrations of zinc in porewater of sulfide rich sediments in Lake Clearwater and Lake Tantaré in Canada are found to be in the order of  $6 \cdot 10^{-5} \text{ g m}^{-3}$  (Carignan and Tessier, 1985). The thickness of the diffusion layer in sediments are approximately 0,02 m (Carignan and Tessier, 1985). Taking the above values into account we may rewrite equation (3.1) in a more general form:

$$J = D_m \frac{dc}{dz} = \frac{5 \cdot 10^{-10}}{2 \cdot 10^{-2}} * c_w = 2.5 \cdot 10^{-8} * c_w \quad 3.2$$

where  $c_w$  denotes the metal concentration in surface water in  $\text{g m}^{-3}$ . For the sake of completeness, we mention that the porosity of the sediment may influence the effective length of the diffusion layer and, hence, the value of the resulting flux through the term  $dz$  in equation (3.2). In general, the porosity of the top layer of sediment is expected to be large (>50%). This means that the flux will decrease by a factor of two at maximum.

### 3.3 Disappearance rate

To evaluate the importance of the metal flux based on diffusion into sediment in risk assessment of surface water it seems useful to derive a first order "disappearance rate" through:

$$V_o \frac{dc_w}{dt} = -A * J = -A * 2.5 * 10^{-8} * c_w \quad 3.3$$

where  $A$  and  $V_o$  are the surface area of the sediment and the volume of the surface water, respectively. Rewriting equation (3.3) gives:

$$\frac{dc_w}{dt} = -\frac{A}{V_o} * 2.5 * 10^{-8} * c_w = -\frac{2.5 * 10^{-8}}{d} * c_w \quad 3.4$$

where  $d$  is thickness of the water layer. The first order disappearance rate ( $k^{1e}_{diff}$ ) equals  $2.5 * 10^{-8}/d$  ( $s^{-1}$ ) and, hence, is a function of the thickness of the water layer above the sediment. In the example harbour, as described in ESPE2 ( $d=2.5$  m; Luttk *et al.*, 1993)  $k^{1e}_{diff}$  becomes  $10^{-8} s^{-1}$ . The first order refreshment rate of the surface water in this harbour is approximately a factor two larger ( $1.6 * 10^{-8} s^{-1}$ ).

In conclusion it can be stated that the diffusion based transport process of metals from surface water to sulfide rich sediment is of importance in risk assessment for these systems.

#### 4. DISCUSSION AND CONCLUSIONS

USES 1.0 was designed to be able to work with very limited data sets. Missing data will, in most cases, be filled with estimates or defaults. In case new models are made available for incorporation into USES, one should consider the possibility that existing defaults are not really applicable for these new situations. For instance the capacity of the municipal sewage treatment plant (MSTP) is 1800 m<sup>3</sup>/d which is equivalent to 12,000 inhabitants. The release of 800 m<sup>3</sup> swimming water in a short period will probably reduce the efficiency of the purification of the waste water in the MSTP. In this case it is perhaps better to use 7500 m<sup>3</sup>/d which is equivalent to 50,000 inhabitants.

In the models for leaching from impregnated wood (poles and/or fences) to soil and ground water it is necessary to have information on the mean flux of the compound over a certain period. No special experiments are available for the lixiviation of compounds to ground water, but instead the results of the lixiviation experiments with impregnated wood in water can be used. For the overground lixiviation of compounds test designs are available, and the results can be used for the hazard/risk assessment.

In the model for calculating the release to the air for compounds used for fumigation of buildings, silos, etc., only the emission to the air at degassing is calculated. The calculation of the concentration of the fumigant in the air will be calculated according to the standard USES 1.0 method, i.e. the OPS model. A more relevant model (Gaussian plume model) is available in the literature. For the time being it was decided not to provide a new model, because TNO is preparing a document on distribution models for the air.

A first attempt to take into account sediment in risk assessment of heavy metals is made by the introduction of the Acid Volatile Sulfide concept. This approach plays an important role for the case of anoxic sulfide-rich (marine and freshwater) sediments, which are expected to be in excess over oxic sediments for the

Dutch situation. Furthermore, since the availability of heavy metals under these conditions is related to one parameter only, introduction of the AVS-concept in risk assessment is quite simple. In the case of modelling the leaching behaviour of heavy metals from the sediment of Lake Ketelmeer into ground water, precipitation of heavy metals with sulfides was already taken into account by Delft Hydraulics (De Rooy, pers. commun.). Nowadays the concept becomes more widely accepted, which can be illustrated by several applications of the AVS-concept recently presented in the literature (see volume 13 of Env. Tox. & Chem., december 1994). For the case of oxic sediments the partitioning of heavy metals becomes quite involved mainly due to the variety of binding processes which may take place. In addition the number of controlling parameters (like clay, organic matter, pH and (hydr)oxides of iron, manganese and aluminium) increases significantly. Hence, estimation of free metal ions in these systems becomes rather complex. However, it seems worthwhile to investigate the possibility of incorporation of these processes into risk assessment in order to apply the present models too for the case of oxic conditions.

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