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## Scientific progress in sediment and water quality assessment

### Implementation of practical case studies

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# **Scientific progress in sediment and water quality assessment**

**Implementation of practical case studies**

Arjan Jeroen Wijdeveld



# **Scientific progress in sediment and water quality assessment**

## **Implementation of practical case studies**

### **Dissertation**

for the purpose of obtaining the degree of doctor at Delft University of Technology

by the authority of the Rector Magnificus prof.dr.ir. T.H.J.J. van der Hagen

chair of the Board for Doctorates

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# Summary and outline

## Summary

The management of sediment, soil and water in the Netherlands dates back to the first settlements in the lower Northern and Western parts of the Netherlands. Around 500 B.C. farmers constructed 'terps' (artificial dwelling mounds) to protect against floodwater. The Romans (50 B.C. – 250 A.C.) reshaped natural waterways, to improve transport by ship. This also meant that river embankments were constructed and waterways and harbours had to be dredged. With the construction of river dikes in the period 700 – 1200 A.C. the sediment challenge began. The peatlands behind the dikes dried out, creating land below the average sea level. Dikes and dike maintenance therefore became crucial and since 1255 A.C. the first official governmental bodies, public utility boards (waterschappen) were created. These public utility boards together with the Dutch government, provinces and cities are still responsible for sediment and water quantity and quality.

With this timeframe in mind, the scope of this thesis, examining developments in sediment and water quality management in the Netherlands over the past 25 years (1993 – 2018) is relatively short. A critical focus during these past 25 years was the heritage of industrial pollution of waterways and sediments from the early twentieth century. During the past 25 years changes took place in the way risks of contaminants in sediment and water were evaluated, partly due to scientific progress on the ecotoxicological impact of contaminants. As important as the scientific progress were the policy and legislation changes. These changes are driven by a broader spectrum of societal needs, like safety against flooding, scarcity of public funds and the need to change to a more circular economy using sediment as a resource.

The goal of this thesis is to help water managers to understand the mechanisms that change the ecotoxicological risks in their water and sediment systems, providing tools that go beyond the legislation requirements to assess these risks.

## Outline

**Chapter 1** gives a short background on the legislation developments in the Netherlands over the past 25 years and the current legislation from an EU perspective. Chapter 1 highlights the different EU Frameworks that determine if sediments are considered suitable for (re)use or are considered as waste.

**Chapter 2** summarizes the scientific models including the speciation and ecotoxicological models used in Chapter 3 - 6 to evaluate ecotoxicological risks.

The hypothesis and corresponding research questions are formulated at the end of chapter 2.

The development of legislation and the improvements in scientific insights over time are separate processes. In the **Chapters 3 - 5** examples are given on how the application of scientific models can improve the insight in water and sediment ecotoxicity for legislators.

In **Chapter 3** the bio-available fraction of metals is studied using speciation models (both the Free Ion Activity Models (FIAM) and the Biotic Ligand Model (BLM)). By applying these models for lake Ketelmeer it is demonstrated that the potential ecotoxicity of the dissolved metals are location specific within the lake. To quantify these local differences based on the water quality within the lake, a site-specific Risk Characterization Ratio (RCR) is defined based on both the FIAM and BLM model. It should be noted that the RCR for the FIAM model differs from the BLM model. The  $RCR_{FIAM}$  is mainly correlated to the pH of water, while the  $RCR_{BLM}$  is more correlated to the DOM concentration. The discrepancy between the RCR's in what causes a relative increase or decrease in ecotoxicity needs more scientific research. More supportive information (in the form of location specific bioassays or location specific bioaccumulation data) is needed.

In **Chapter 4** the multi substances, Potentially Affected Fraction (msPAF) model, is applied for the Western Scheldt waterbody. With this model the relation between ecological quality and chemical quality, as defined by the Water Framework Directive (WFD), is explored. A 2D hydrodynamic model in combination with a water quality model for the contaminants is used to calculate the contaminant concentration in different parts of the Western Scheldt, looking a seasonal trends in the water quality. The outcome is used to calculate the msPAF. Within the Western Scheldt the study focuses on the area 'Verdronken land van Saeftinghe'. The msPAF results for this area are compared with the macro fauna ecological quality index. Instead of using the (WFD) 'one out - all out' principle for the chemical status, the msPAF is used to describe the combined impact of contaminants on the chemical status. This results in the recommendation to include the msPAF as a second level tier in the WFD.

**Chapter 5** focusses on the transition from sediment to soil. When sediments are used on land they become a soil. The change in mineral composition also changes the availability of metals. By using a FIAM model in combination with a groundwater and unsaturated zone hydrological model, the impact of this change over a timespan of a decade is calculated. It is shown that the ecotoxicological risks, as defined by the msPAF, significantly changes over time and is dependent on redox processes in the sediment/soil.

**Chapter 6**, focusses on the scientific progress in sediment and water quality standards in the Netherlands in the period 1993 – 2018. The analysis is divided in four periods.

- 1) The first period, from 1993 till 2000, explains the Dutch legislation for contaminants in water and sediment as established in 1993. The legislation framework is explained based on the scientific models at that time (PAF and equilibrium partitioning). These models were used to determine the ecotoxicological risk for organisms in water and sediment and to set water and sediment quality standards. There was an integral approach on how to deal with contaminated sediments. This included cost scenarios, removal and clean up options and a timeline for implementation (Bvb, 1993). At that time contaminated sediments were mainly seen as a problem influencing the water quality and hampering dredging.
- 2) The progress in scientific knowledge with regard to the contaminant behaviour in water and sediment has progressed over the past 25 years. In part due to the further development and validation of models such as FIAM, BLM and msPAF. The second period, from 2000 till 2008 is characterized by the improvement of these models. A trigger was the introduction of the WFD, challenging water managers to validate the link between water quality standards and the ecological status of a water body.
- 3) In 2008, the legislation (period 2008 – 2018) has been adapted to incorporate different societal challenges such as safety against flooding and use of sediments in a circular economy (more in the period 2018 - ...). The policy goal shifted from a site specific prevention of contaminant exposure to organisms to a more water body global standstill principle. The assumption was that with the stand still principle a good ecological functioning of the waterbody could be maintained. This assumption is partly supported by the improved scientific knowledge on the bioavailable fraction in both water and sediment. But scientific progress also predicted and demonstrated ecotoxicological risks not considered by legislation, like the impact of local water quality parameters and changes in the sediment or soil redox conditions.
- 4) During the years that followed the concept that sediment is primary a resource, even when contaminated, became politically and socially accepted in the Netherlands. Beneficial use is the standard practice in the Netherlands (period 2018 - ...). The sediment quality is not only evaluated based on total contaminant concentration standards, additional leaching tests give insight in the contaminant emission. Most sediments and soils are used. The stand still principle determines where sediments can be used (not so much if sediments can be used). Acceptable contaminant concentrations in sediments use are linked to the current land use. Chapter 6 shows how sediment standards based on a beneficial use policy within the Soil Directive in The Netherlands (and Flanders) differ from the sediment classification systems based on the EU Waste Directive (as is the case in Ireland, France, Germany).

**Chapter 7** reflects on the legislation and water and sediment quality standards in the Netherlands over the past 25 years, divided into four periods, based on development of scientific insights during this timeframe. Chapter 7 recommends on how policy makers and water managers can use the improved scientific insights in potential ecotoxicological risks in a way fitting with legislation, and recommends where further research is needed, especially for sediments under changing redox conditions. In conclusion the extent to which the research questions (as stated in Chapter 2) are answered is discussed.

The viewpoint that sediment is primary a resource is nowadays shared by many, such as EU Sediment Network (SedNet) and the CEntral Dredging Association (CEDA). Therefore, CEDA took the initiative to write a position paper on the use of contaminated sediments (**Appendix A**).

However, for some water bodies and for some applications of sediments there is a mismatch between the scientific progress made over the past 25 years regarding the evaluation of ecotoxicological risks in water and sediment and the implementation in legislation to prevent or mitigate these risks. **Appendix B** (in Dutch) gives an example for a Dutch lake where it would have been beneficial to take into account the scientific insight at that time in the implementation strategy for a sediment clean-up operation.

## Keywords

Sediment, water quality, metals, ecotoxicology, quality standard, legislation

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# 1

## Introduction

This PhD. thesis presents the experience of 25 years (1993 – 2018) working with contaminants in water and sediments from an applied research perspective. During this time period the insights into how contaminants are released from sediments towards the water phase, and how the exposure of organisms to contaminants take place, have not changed significantly for both metals and organic contaminants. The fundamental scientific basis on how to test the relation between the sediment quality and the impacts on water quality and ecotoxicity was laid in the 1980s and 1990s and published by governmental organisations such as the United States Environmental Protection Agency (US EPA, 1992) and RIVM in the Netherlands (RIVM, 1988). The last 25 years of research have resulted in improved analytical detection methods under field conditions and validated models predicting the ecotoxicological risks. Nowadays the risks can be predicted for multiple contaminants under non-equilibrium and changing conditions, in both water and sediments.

Legislation on water and sediment quality standards, with the purpose of protecting the environment against unacceptable ecotoxicological risks, needs to be regularly adapted to remain in sync with scientific progress. However, this does not always occur in a timely manner. While much of the scientific progress has been adapted in water and sediment legislation, some warnings were ignored. This thesis shows how scientific insights and legislation have developed over the past 25 years, sometimes in parallel and sometimes with different priorities or different focus areas. The matches and mismatches this yields between the application of water and sediment quality standards based on legislation versus the actual ecotoxicological risks, as characterized by improved scientific insights, are demonstrated for case study sites.

The focus here is on the uptake of scientific progress in legislation for water and sediment quality standards in The Netherlands. Since the introduction of the EU Water Framework Directive (WFD) (EU COM, 2000; EU COM, 2008b) Dutch water quality standards are linked to EU directives. The EU Waste Framework Directive (EU COM, 2008a) forces The Netherlands to assess sediment use in a broader EU perspective of resource versus waste criteria. Water quality standards and ecotoxicological stress caused by contaminants in water have been part of transboundary EU rulings before the introduction of the WFD. The lawsuit by Dutch farmers against a state-owned salt mine (Les Mines de Potasse d'Alsace) in France, to be compensated for their crop damage caused by an increase in the contamination level of the river Meuse (European Court Reports, 1976), can be seen as a milestone for the European view that an international water quality policy was needed.

While EU member states could have chosen to follow the US policy regarding 'the polluter pays', as for the US Superfund sites (based on (CERCLA, 1980)), the European

Commission (EC) chose to focus on the development of a shared directive. One reason for this shared approach is that many of the larger European rivers (Danube, Rhine, Meuse, Elbe) are transboundary. The introduction of the Water Framework Directive (WFD) in 2000 (EU COM, 2000) was a milestone in international cooperation to improve the environment, focusing not only on water quality, but mainly on the ecological function of waterbodies<sup>1</sup>.

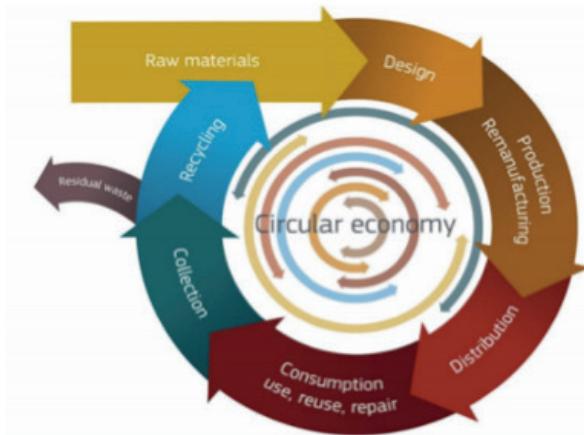
With the definition of ‘good water quality’ based on water concentration standards for priority substances, and the description of ‘good ecological status’ by comparison with reference habitat conditions, the WFD lays a solid basis for the assessment, and potential for improvement of the water quality and ecological status of waterbodies. These improvements have been made by setting up River Basin Management Plans (RBMP), based on a Common EU Implementation Strategy (see Figure 1). Currently (2018), the second RBMP plans are implemented, building on the lessons drawn from the first generation of Plans and include the measures required to speed up progress towards achieving the Directive’s objective.



**Figure 1** Status of implementation of the WFD in the Member States (EU COM, 2018). All EU member states expect Spain have adopted a second River Basin Management Plan

<sup>1</sup> The WFD term ‘waterbodies’ is defined in the directive (article 2 – definitions (10, 12, 13 and 15)). This totality of waters (the body) is, for the purpose of the implementation of the directive, attributed to geographical or administrative units, in particular the river basin (district).

Water quality and sediment quality are closely related. One of the key ambitions of Europe is to transform Europe's economy into a more sustainable one, as stated in the Circular Economy Action Plan (EU COM, 2015), as expressed in Figure 2.



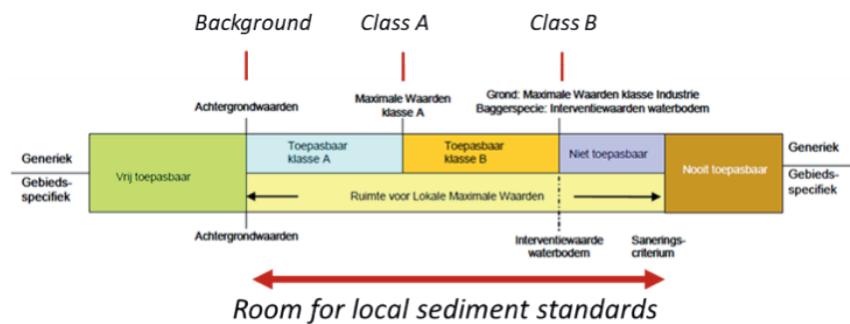
**Figure 2** Conceptual diagram illustrating the circular economy in a simplified way (EU COM, 2015)

Sediments can be used as a substitute for building materials. Sand and clay are important raw materials for the building industry. Sediments are made of these materials and can therefore play an import role in a more circular economy. Often the presence of contaminants prohibits the use of sediments as a resource (EU COM, 2008a), resulting in sediment often being categorized as waste (Figure 3).



**Figure 3** Uncontaminated sediments are a product (non-waste) according to (EU COM, 2008a). Exceeding a contaminant threshold value (one out all out principle) means that sediment is defined as a waste. If sediment treatment is not possible disposal is necessary.

Reallocation of sediments is also considered an application of sediment as building material. Since 2008, the Netherlands have adopted a different approach in the use of sediments as a building material (Bbk, 2008), emphasizing the role of sediments removal and use to increase the safety against flooding and to mitigate for land subsidence and sea level rise. The emphasis is on the stand still principle for overall system quality. Sediment (or soil) use is allowed so long as the overall system quality improves or remains the same. Therefore, local sediment standards can be applied, as is illustrated in Figure 4.



**Figure 4** Sediment classification according to the Dutch soil directive (Bbk, 2008). In green the sediments below background levels, always freely usable. In light blue the lightly contaminated class A sediments (tier 1). In orange the moderately contaminated sediments (tier 2). In purple the contaminated non-useable fraction (with exceptions). In brown the heavily contaminated non-useable fraction. Legislation (Bbk, 2008) allows for location specific standards based on the stand still principle, ranging from background levels up to or even above the intervention level (the area in between the red arrows).

The Dutch soil legislation framework (Bbk, 2008) was adapted to implement the stand still principle. This adaptation is the exception within Europe, other countries have an absolute upper value for the sediment or soil standard. Therefore, the beneficial use of contaminated sediments differs within the EU member states. Some of the Dutch adaptations to set local sediment/soil standards are based on the scientific progress over the past 25 years (1993 – 2018). Other adaptations of sediment/soil quality standards are more questionable from a scientific point of view. Choices to adapt water and sediment legislation are no longer solely based on a scientific ecotoxicological risk assessment, as was the case in 1993 (INS, 1997). Choices are also partly based on prioritizing other social needs like safety against flooding and nature development at societal acceptable cost.

The match and mismatch between scientific progression versus the implementation in legislation on a national (Dutch) and international (EU) level is explored in this thesis. In this thesis improved models (as compared to the models used for legislation) are applied to improve the ecotoxicological risk assessments for water and sediment. To help policy makers and water managers to use these improved models in a relative simple way, tools are presented which can be used in combination with legislation standards. Sometimes the use of these tools show that ecotoxicological risks in the past were exaggerated when it comes to the bioavailable concentration. But there are also examples that show that the implementation of the stand still principle in the Dutch soil directive underestimated the potential ecotoxicological risk.

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# 2

Used ecotoxicological  
risk evaluation  
models, hypotheses  
and research  
questions

## 2.1 Maximum Tolerated Risk (MTR) Levels based on the Potentially Affected Fraction (PAF)

Standards for contaminants are derived from ecotoxicological data in water (US EPA, 1976). To understand the background of the water quality standards at the beginning of this thesis (INS, 1997), a short background is given in how these water quality standards were derived.

Water quality standards are based on ecotoxicological data from dose effect relations for single contaminants and different organisms. To determine the point of ecotoxicological impact a reference condition has to be set. Often the observed median lethal concentration [LC50] is used for acute exposure, and the no-observed-effect concentration [NOEC] for chronic exposure. The value of LC50 for a contaminant is the dose required to kill half the members of a tested population after a specified test duration (often 72 hours). Each test organism has a different sensitivity for a contaminant. Plotting the LC50 values on the x-axis against the number of organisms (as percentage) impacted gives the Species Sensitivity Distribution (SSD) for that contaminant. Normally it is observed that some organisms are extremely sensitive for a contaminant while some organisms have a high tolerance. Most organisms are in between. The shape of the SSD can be described by a s-curve based on the geometric mean of the toxicity data and the standard deviation of the LC50 toxicity values. This resulted in the Potentially Affected Fraction (PAF) at concentration  $C_{diss}$  (De Nijs et al., 2008). Equation 4 gives the formula to calculate the PAF.

$$PAF(C_{diss}, \mu, \sigma) = \int_{-\infty}^{C_{diss}} \frac{1}{\sigma\sqrt{2\pi}} e^{-\left(\frac{(C-\mu)^2}{2\sigma^2}\right)} dC \quad (4)$$

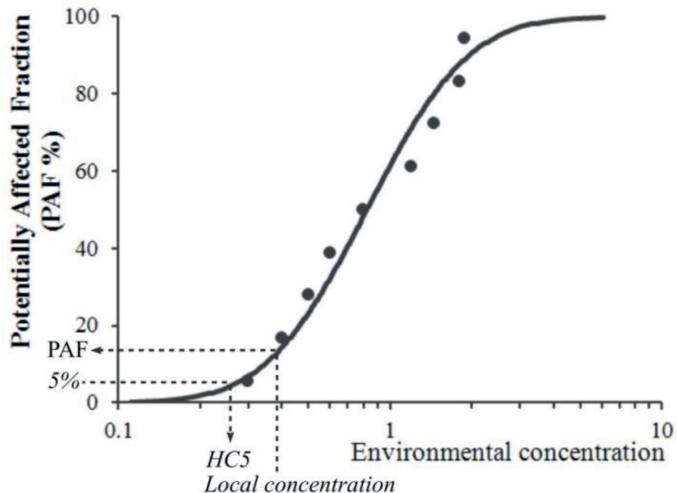
PAF = Potentially Affected Fraction (-)

$C_{diss}$  = concentration contaminant dissolved in water (mg/l)

$\mu$  = geometric mean of toxicity concentration data (mg/l)

$\sigma$  = standard deviation of log transferred toxicity concentration data (mg/l)

The distribution of the sensitivity for an individual toxic components for different individual species is given by the Species Sensitivity Distribution (SSD) (Posthuma et al., 2002). Figure 1 by (Del Signore, 2015) illustrates the SSD curve, where the PAF (no defined point of impact) is plotted against the  $\log(C_{diss})$ .



**Figure 1** Example of SSD, the PAF (y-axis) is plotted as function of the concentration (x-axis), where  $HC_5$  is the concentration were 5% of the species have a potential impact by the contaminant based on NOEC levels (point of impact) for the species (Del Signore, 2015).

The Maximum Tolerable Concentration (MTR) in water (INS, 1997) was chosen at the 5% PAF level ( $HC_5$ ) based on the LC50 impact point (Posthuma et al. 2002). For safety reasons this  $HC_5 C_{diss}$  was divided by ten to set the MTR water quality standard.

Currently many countries within the EU use a similar  $HC_5$  based legislation for the Environmental Quality Criteria (EQC) according to the Water Framework Directive (EU COM, 2000). Instead of the LC50 value, the No Observed Effect Concentration (NOEC) is used as the impact criterium to derive the  $HC_5$ . This has the advantage that an extra safety factor as used for the LC50 derived  $HC_5$  concentration is not needed. A  $HC_5$  is already based on no observed effects.

## 2.2 Multi Substances - Potentially Affected Fraction (msPAF)

Water quality standards based on ecotoxicological data are derived for individual contaminants. The actual exposure of organisms in natural waters is often due to the presence of multiple contaminants. Therefore an ecotoxicological risk model is needed that combines the potential impact of multiple contaminants on the ecotoxicological risk; the multiple substances Potential Affected Fraction (msPAF).

The msPAF method is described by (Posthuma, 2002) and used in the Dutch policy on the application of sediments on land since 2008 (RIVM, 2008).

The potential toxic risk for multiple substances is calculated using the distribution of the LC50 or NOEC values (Posthuma et al., 2002; Newman et al., 2000) following the methodologies as proposed by (de Zwart and Posthuma, 2005): by

- (i) Response Addition (RA), or
- (ii) Concentration Addition (CA).

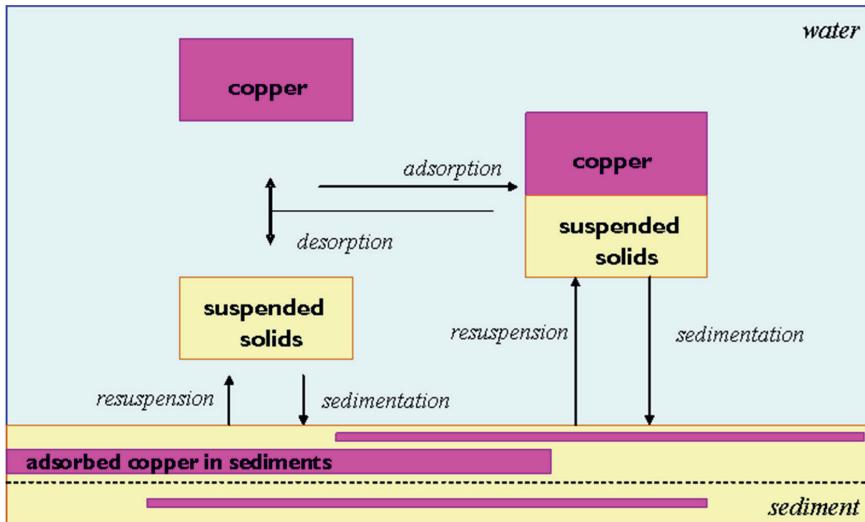
The type of addition that can be applied depends on the mode of action. Response Addition is based on the absence of interaction between toxicants on the target site of toxic action. The mixture toxicity can be described by calculating the combined effect, assuming that there is no correlation between the uptake of compounds. Concentration Addition is based on the same mode of action of the contaminant. It is then possible to calculate and summarize the Hazard Units (HU) for each toxicant (Posthuma et al., 2002).

## **2.3 Equilibrium Partitioning between water and sediment**

Ecotoxicological data is derived from experiments with organisms in water. Therefore a translation of the water quality based standards towards sediment standards has to be made. In 1993 this translation was based on equilibrium partitioning between the water phase and the (suspended) sediment.

It is observed that equilibrium partitioning of contaminants between sediment and water depends on the organic matter and lutum (clay) content of the sediment. To take these sediment dependant into account the standard soil correction method is used (INS, 2007).

The basic model to translate concentrations in the water phase to solid concentrations (suspended solids, sediments or soils) is the use of equilibrium partitioning. Figure 2 gives an overview on the interaction between water and suspended solids and water and sediment for the ad- and desorption of copper. The interaction between suspended solids and sediment by resuspension and sedimentation illustrates that in equilibrium the suspended solid and sediment concentration for copper are the same (based on the copper concentration in the water).



**Figure 2** Equilibrium partitioning between water and suspended solid and water and sediment (Wijdeveld, 2007).

Equation 1 gives the basic partitioning for metals and Equation 2 for organic pollutants.

$$K_d = \frac{C_{solid}}{C_{dissolved}} \Rightarrow C_{solid} = C_{dissolved} \times K_d \quad (1)$$

$K_d$  = partition coefficient between sediment and water (l/kg)

$C_{dissolved}$  = concentration in water (mg/l)

$C_{solid}$  = concentration in sediment (mg/kg)

$$K_{oc} = \frac{K_d}{OC} \quad (2)$$

$K_{oc}$  = partition coefficient between organic carbon in sediment and water (l/kg)

OC = organic carbon content of the sediment (fraction)

The partition coefficients for over a 100 contaminants are given in (INS, 1997), see Table 1 in 'Supportive information – 2. Chapter 2' for the partition coefficients for 15 metals and 10 PAH's. The partitioning between water and solid depends on the capacity of the solid to adsorb contaminants. To describe the adsorption a Langmuir model is used, correcting the solid adsorption rate based on the organic matter and clay (lutum) content (INS, 1997). Equation 3 gives this 'standard soil' correction as

used in the Netherlands. The standard Dutch soil is defined as having 25% lutum and 10% organic matter. See 'Supportive information – 2. Chapter 2' Table 2 for the soil correction values for the 15 metals.

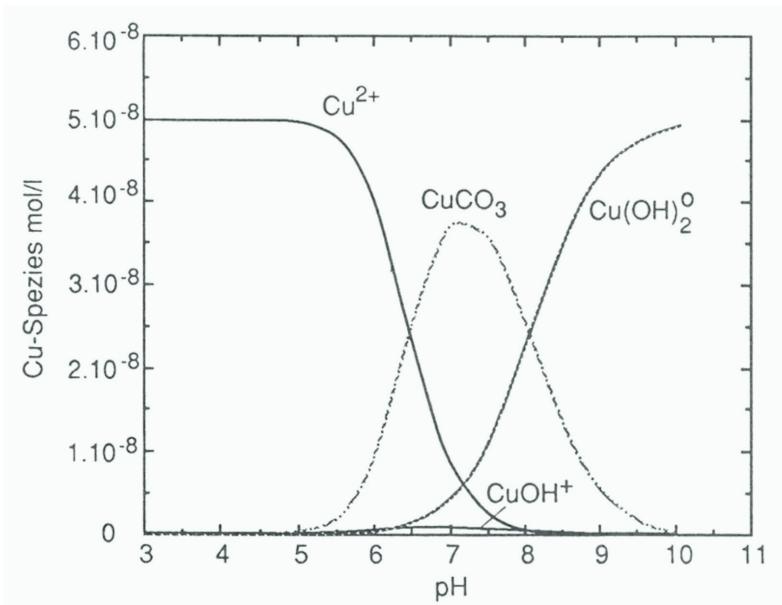
$$S_{soil} = S_{default\ soil} \times \frac{A + [B .(\% \ lutum)] + [C .(\% \ OM)]}{A + [B .25] + [C .10]} \quad (3)$$

$S_{soil}$	= standard for soil or sediment to be evaluated	(mg/l)
$S_{default\ soil}$	= standard for default soil	(mg/kg)
%lutum	= measured lutum content of soil or sediment	(%)
% OM	= measured organic matter content of soil or sediment	(%)
A, B, C	= constant dependant of contaminant	

## 2.4 Free Ion Activity Model (FIAM)

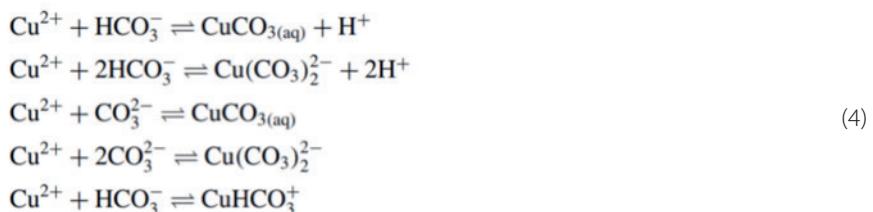
The fact that ecotoxicity in water depends on more than the total dissolved contaminant concentration in water is well known in 1993. Already in 1976 the observed relationship between the toxicity of copper to aquatic life as function of the water alkalinity is described in (US EPA, 1976). The reason of this dependency on other water quality parameters (like the alkalinity, salinity, pH and dissolved organic matter) is based on the binding of dissolved contaminants (metals) to other dissolved ions to form metal ligands. This reduces the bioavailable fraction. A Free Ion Activity Model (FIAM) is able to calculate these binding reactions of metals and other ions (called ligand formation) based on thermodynamic equilibrium constants. The FIAM model assumes that the freely dissolved contaminant fraction has a better correlation with the ecological risk then the total dissolved contaminant fraction. While elements of FIAM modelling have been adapted in water quality standards, like the hardness correction for cadmium in the Water Framework Directive (EU COM, 2000), FIAM models are not widely used by policy makers for water quality standards due to their complexity and difficulty to validate with experimental data.

The Free Ion Activity Model (FIAM) calculates the metal-ligand formation and free metal ion concentration, taking into account the interaction of metals with macro chemical ions present in natural water (Stumm and Morgan,1970; Campbell, 1995; Stumm and Morgan,1996; Parker and Pedler, 1996). In Figure 3 an example is given how dissolved metals are divided in metal ligands and the free metal ion.



**Figure 3** Example of copper speciation as function of pH (Stumm et al, 1970)

A FIAM model calculates the combination of the equilibrium reaction constants for a metal and ligands (speciation). The sum of all reactions strive for a minimal Gibbs free energy. An example based on Figure 3 is the speciation of copper with carbonates (Equation 4).



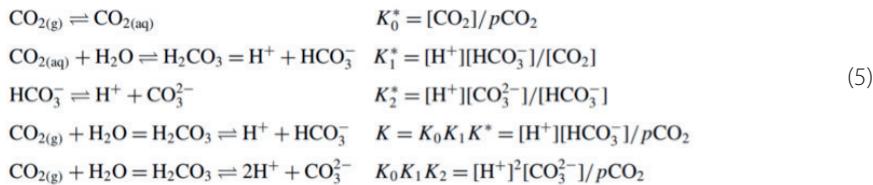
The equilibrium reaction constants can be found in literature (Powell et al., 2005; Powell et al., 2007). Table 1 gives the logarithmic value of the reaction constants for copper with carbonate species (Powell, 2007).

**Table 1** Equilibrium reaction constants for copper carbonate ligands (Powell, 2007)

Recommended values for the  $\text{Cu}^{2+}-\text{H}^+-\text{CO}_3^{2-}$  system at 298.15 K, 1 bar, and  $I_m = 0 \text{ mol kg}^{-1}$ .  
 R = Recommended, P = Provisional.  $\Delta\epsilon$  values for  $\text{ClO}_4^-$  medium.

Reaction	Constant	Evaluation
$\text{Cu}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CuCO}_3(\text{aq})$	$\log_{10} K_1^\circ = 6.75 \pm 0.03$ $\Delta\epsilon = -(0.18 \pm 0.04) \text{ kg mol}^{-1}$	R
$\text{Cu}^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Cu}(\text{CO}_3)_2^{2-}$	$\log_{10} \beta_2^\circ = 10.3 \pm 0.1$ $\Delta\epsilon = (0.3 \pm 0.2) \text{ kg mol}^{-1}$	R
$\text{Cu}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{CuHCO}_3^+$	$\log_{10} K^\circ = 1.84 \pm 0.10$ $\Delta\epsilon = (0.14 \pm 0.15) \text{ kg mol}^{-1}$	R
$\text{Cu}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{CuCO}_3 + \text{H}^+$	$\log_{10} K^\circ = -3.56 \pm 0.03$ $\Delta\epsilon = -(0.19 \pm 0.04) \text{ kg mol}^{-1}$	R
$\text{Cu}^{2+} + 2\text{HCO}_3^- \rightleftharpoons \text{Cu}(\text{CO}_3)_2^{2-} + 2\text{H}^+$	$\log_{10} K^\circ = -10.3 \pm 0.1$ $\Delta\epsilon = (0.3 \pm 0.2) \text{ kg mol}^{-1}$	R
$\text{Cu}_2\text{CO}_3(\text{OH})_2(\text{s}) \rightleftharpoons 2\text{Cu}^{2+} + \text{CO}_3^{2-} + 2\text{OH}^-$	$\log_{10} K_{s0}^\circ = -33.16 \pm 0.08$	P
$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2(\text{s}) \rightleftharpoons 3\text{Cu}^{2+} + 2\text{CO}_3^{2-} + 2\text{OH}^-$	$\log_{10} K_{s0}^\circ = -44.9 \pm 0.2$	P

The concentration of (bi)carbonate in water not only depends on the ligand formation with the metal (copper), but also on the interaction with the atmospheric  $\text{CO}_2(\text{g})$  and the pH of the water (Equation 6).



In the FIAM model it is assumed that the free metal ion activity ( $\text{Cu}^{2+}$  in Equation 5) better describes the observed toxicological effect on organisms (Weng et al., 2001). A numerical FIAM program like CHARON (De Rooij, 1991) can solve these equations. Figure 4 gives an example of the distribution of copper in water (as percentage) as free metal ion ( $\text{Cu}^{2+}$ ) and copper ligands with carbonate and hydroxide species.

2

CU++ : browse percentual occ of CU++	
	x solve output partit comple compon CU++
CU++	19.8757995
H+	
CO3--	
OH-	
H2O	
HC03-	
H2C03	
CUC03	36.4031650
CUC032	0.0113222
CUHCO3	5.0076090
CUOH-	3.9684439
CUOH2	0.1145373
CUOH4-	0.0000000
CU2OH2	34.6191231
CO2A	
STH+	

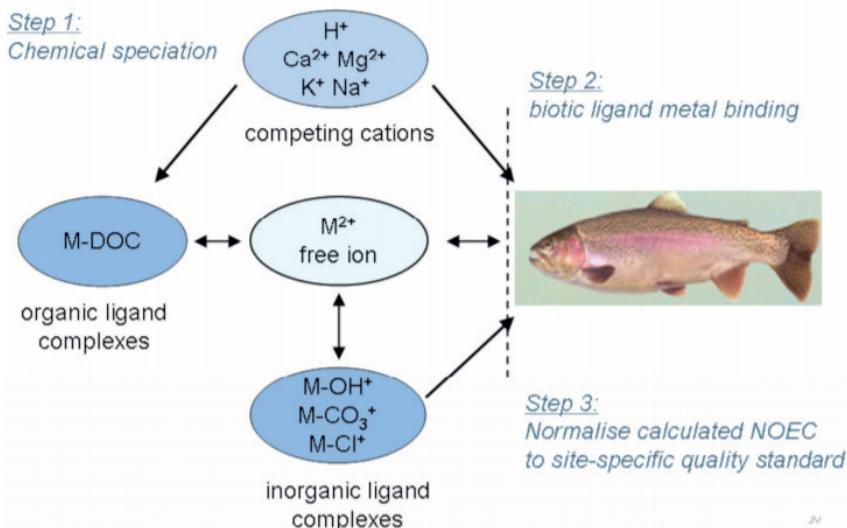
**Figure 4** Example of copper speciation in water at pH 7.0 in the presence of carbonate (equilibrium with CO<sub>2</sub>(g) atmosphere), percentual distribution of dissolved copper species. 19,9% of the copper is freely dissolved (Cu<sup>2+</sup>), the rest of the dissolved copper forms ligands with carbonates and/or hydroxides . CHARON model result (Rooij, 1991).

## 2.5 Bio Ligand Model (BLM)

Bio Ligand models (BLM) are combination of the FIAM model concept and biological uptake models. The BLM model combines the interaction of both the free metal ion and different metal ligands (see the FIAM model) with a living organisms. The concept of BLM's is accepted by the European Water Framework Directive, but the practical implementation stays behind because of model complexity, data requirement, uncertainty about the validity for field predictions and the consequences of BLM's for risk assessment (Verschoor, 2013).

The conceptual framework for the Bio Ligand model (BLM) is an adaptation of the gill surface interaction model, originally proposed by Pagenkopf (Pagenkopf et al., 1974; Pagenkopf, 1983), and the free ion activity model of toxicity (FIAM) (Campbell (1995). The general framework is illustrated in Figure 5 (Verschoor, 2013).

## Biotic Ligand Model



**Figure 5** Concept of biotic ligand model, which includes calculation of chemical speciation, binding to biota and a normalisation procedure to calculate site-specific quality standards (Verschoor, 2013). Step 1 is the FIAM calculation. Step 2 includes the interaction with the biotic ligand (the gill). Step 3 normalizes the No Observed Effect Concentration (NOEC) for local water quality parameters (pH, Hardness, Dissolved Organic Carbon) to derive a site specific Predicted No Effect Concentration (PNEC).

The model is based on the hypothesis that toxicity is not simply related to total aqueous metal concentration but that both metal-ligand complexation and metal interaction with competing cations at the site of action of toxicity need to be considered (Pagenkopf, 1983; Meyer, 1999). Mortality occurs when the concentration of metal bound to the biotic ligand exceeds a threshold concentration.

The BLM replaces the fish gill as the site of action with a more generally characterized site, the biotic ligand. It is likely that these principles apply to any organism for which the site of action is directly in contact with the external aqueous environment.

Due to the need to validate the BLM model with biotic ligand binding (the fish gill) the test conditions have to consider the general water quality needs of the test species (like limited salt for a fresh water species, or a certain range of pH's to avoid damage to the test species due to non-metal related effects). Therefore a BLM model is defined within a range of environmental conditions. Table 2 gives the range of conditions for the BLM model 'HydroQual' (Hydroqual, 2015).

**Table 2** Application range of HydroQual BLM model in natural water, parameter boundary's (Hydroqual, 2015)

Parameter		Lower boundary	Upper boundary
Temperature	°C	10	25
pH		4.9	9.2
DOC	mg/l	0.05	29.6
Humic Acid Content	%	10	60
Ca	mg/l	0.204	120.2
Mg	mg/l	0.024	51.9
Na	mg/l	0.16	236.9
K	mg/l	0.039	156
SO <sub>4</sub>	mg/l	0.096	278.4
Cl	mg/l	0.32	279.7
Alkalinity	mg/l	1.99	360
DIC	mmol/l	0.056	44.9

By applying the combination of FIAM modelling (step 1), the interaction with biota (step 2) and the correction for local water quality parameters (step 3) a site specific Predicted No Effect Concentration (PNEC) is derived for a metal. Currently (2018) the BLM-PNEC method has been validated for Nickel, Copper and Zinc.

## 2.6 Simultaneous Extracted Metals (SEM) to Acid Volatile Sulphides (AVS) ratio (SEM/AVS)

The model concepts used in paragraph 1 - 5 are based on equilibrium. For the interaction between the water and sediment phase the equilibrium is described by adsorption. This equilibrium state is not true for metals in sediments. The availability of metals in sediments depends on the formation and dissolution of minerals. In anaerobic sediments with a high sulphide content, all metals are precipitated as metal sulphide and there is no dissolved metal in the sediment pore water. The absence of dissolved metals means there is no ecotoxicological risk. The Simultaneous Extracted Metals (SEM) to Acid Volatile Sulphides (AVS) ratio (SEM/AVS) expresses the capacity of a sediment to fixate all metals as metal sulphide. In 2000 it was proposed to include the SEM/AVS method for sediment evaluation (Hooper, 2000).

The bioavailability of trace metals in sediments can be predicted with the Simultaneous Extracted Metals (SEM) to Acid Volatile Sulfides (AVS) ratio (SEM/AVS) approach (Di Toro et al., 1992; Berry et al., 1996; Van den Hoop et al., 1997). It is based

on the fact that these metals form insoluble metal sulfides by reacting with the iron sulfide (FeS) in sediments. Acid-volatile sulfides and SEMs are the measures used for reactive sulfide and reactive metal present in the sediment. If AVS exceeds the sum of the SEMs present ( $\Sigma SEM = SEM_{Cd} + SEM_{Cu} + SEM_{Ni} + SEM_{Pb} + SEM_{Zn}$ ), excess sulfide exists in the sediment, and all the metals are present as insoluble nontoxic metal sulfides. Studies using the SEM/AVS ratio as indicator for the bioavailability of metals in sediments tend to rule out metal ecotoxicity in sediments when the SEM/AVS ratio is low (Van Griethuysen et al., 2004; Vangheluwe et al., 2003; Di Toro et al., 2005). Di Toro's group has implemented an improvement of the existing AVS method in predicting not only the lack, but also the onset, of metal toxicity in field contaminated sediments. By taking the partitioning of metals to sediment organic carbon in combination with the AVS into account, the AVS fraction adds to the metal binding capacity of the organic carbon present in the sediment. Using this information it was shown that the organic carbon normalized excess SEM can be used to predict sediment toxicity (Di Toro, 2005) (Equation 6 - 9).

$$SEMx, oc = \frac{\Sigma SEM - AVS}{f_{oc}} \quad (6)$$

SEM is the metal concentration that is simultaneously extracted with the AVS extraction (mmol/kg dry weight)

AVS is Acid-Volatile Sulphides (mmol/kg dry weight)

X is the specific metal

OC is the organic carbon content in the sediment (gram/kg)

$f_{oc}$  is the organic carbon fraction in the sediment (-)

When an ecotoxicological reference point is chosen, like the LC<sub>50</sub> (50% mortality) concentration (based on the SSD), the sediment toxicity can be predicted (Equation 8 – 10).

$$SEM^* x = AVS + K_p C_w^* \quad (7)$$

$K_p$  is the partition coefficient between pore water and sediment solids (l/kg)

$C_w^*$  is the LC50 pore water concentration (mmol/l)

$$K_p = f_{oc} \cdot K_{oc} \quad (8)$$

$$SEM^* x, oc = AVS + f_{oc} \cdot K_{oc} C_w^* \quad (9)$$

$K_{oc}$  is the organic carbon based partition coefficient (l/kg OC)

If  $SEM_{x,oc} > SEM^*_{x,oc}$  then the LC50 for that sediment would be exceeded.

## 2.7 Ongoing model developments to describe the interaction between contaminants and organisms

The model concepts presented in paragraph 1 – 6 are an incomplete overview of all scientific models developed over the past 25 years to improve the understanding between the presence of contaminants in water and sediment and their actual or potential ecotoxicological impact. Some of the other important developments are shortly described below. These models are used in Chapter 3 – 6 and in Appendix A. For the description of the correlation between the scientific progress and the adaptation in legislation with regard to water and sediment quality standards, the model concepts described in this paragraph are not explicitly mentioned.

### 2.7.1 NICA-DONNAN

An example of a further improvement of the FIAM model is the Non Ideal Competitive Adsorption (NICA) model based on the Donnan potential (Milne, 2003). The development of the NICA-Donnan model was started by Prof. dr. W.H. van Riemsdijk (1931 – 2011) and nowadays continued by Prof. dr. R.N.J. Comans, Wageningen University & Research. Improvements are made on the metal-ligand formation with organic matter based on the NICA-Donnan model and the diffuse electrical double layer model.

### 2.7.2 Slow reaction kinetics of ad- and desorption

Many of the Dutch sediment remediation projects in the past 25 years were triggered by the presence of organic pollutants like PAH's and PCB's (DG Rijkswaterstaat. 1992a. DG Rijkswaterstaat. 1992b. ; Best, 2006). Slow reaction kinetics strongly impact the ad- and desorption of especially organic contaminants. Cornelisse (Cornelisse, 1999) and Hulscher (Hulscher, 2005) validated and modelled the desorption rate and bioavailable fraction of these group of contaminants with long term batch experiments and Tenax extraction. Koelmans (Koelmans, 2005) quantified the interaction of hydrophobic organic compounds and soot like materials referred to as carbonaceous materials to correct sediment total concentration for hydrophobic organic compounds for an irreversibly bound soot fraction.

## 2.8 Overview of model developments

From an ecotoxicological risk perspective the water phase is the dominant phase that determines the risk for organisms to be exposed to contaminants. Over the past 25 years models are developed to better describe the interaction of contaminants bound to

sediments versus contaminants available in (pore)water. This is done by characterising mechanisms that determine the bioavailable contaminant fraction in both water and sediment. The differentiation of model concepts in separate paragraphs (1-7) suggest a chronologic development of improved model concepts over time. In reality there is overlap and co-development on the different model concepts.

As an example, the quality criteria for water in paragraph 1 are based on ecotoxicological data from (US EPA, 1976). It is already mentioned that there exists a dependency between the metal toxicity in water and the water alkanity and salinity. The FIAM model (paragraph 4) and BLM model (paragraph 5) are able to quantify these dependencies, improving the Annual Average Environmental Quality Standard (AA-EQS) for different water types. To express the impact of the local water quality as calculated by the FIAM and BLM models, Risk Characterization Ratio's (RCR's) are calculated (see paragraph 3.2.5). A RCR>1 means that the local contaminant concentration is above the predicted no effect concentration.

Another example is the SEM/AVS model (paragraph 6), introducing non-equilibrium partitioning behaviour of sediment toxicity in the nineties of the twentieth century (DiToro, 1992). This model was developed in the same time period as the introduction of sediment standards in the Netherlands based on sediment and water equilibrium partitioning (paragraph 3). The development of the BLM models (paragraph 5) in the beginning of the twenty-first century boosted the further development of the SEM/AVS models to include the organic matter bound metal fraction (Di Toro, 2005). The combination of SEM/AVS with soil organic matter seems a feasible alternative for a sediment BLM model approach based on porewater concentrations and can be used to predict toxic sediment concentrations without modelling the complete pore-water chemistry. This makes the SEM/AVS BLM model more accessible for legislation since less parameters have to be measured and extensive water body specific model calibration is avoided.

Current (2018) water and sediment ecotoxicological risk models are capable to explain the observed and potential water and sediment ecotoxicity. The extent to which these models are incorporated in legislation is a balancing act between environmental policy ambitions, other drivers that influence the ecological status of a waterbody and the willingness of a society to pay for solutions to decrease the ecotoxicological risk for organisms in water and sediment.

## 2.9 Hypotheses and research questions

### 2.9.1 Hypothesis; local water and sediment conditions influence the potential ecotoxicity

The hypothesis for this thesis is that water and sediment standards based on total concentrations of contaminants can be improved to better predict the ecotoxicological impact of contaminants by using the local water and sediment conditions like pH, salinity, dissolved organic matter and alkalinity. This in contrast to the current practice in which the impact of water quality is mostly disregarded in legislation.

Changes in the local water quality parameters can impact what is called the speciation of contaminants. Contaminants interact with organic and inorganic components in water, forming ligands. These ligands are in general not available for uptake by organisms. Therefore the exposure of organisms to contaminants depends on water quality parameters that determine the ligand formation. The impact of water quality parameters can be predicted based on scientific models like the Free Ion Activity Model (FIAM) and the Bio Ligand Model (BLM) (both explained earlier in Chapter 2). There is a role for both FIAM and BLM to describe the impact of local water quality parameters on the bioavailable contaminant fraction. The BLM model improves upon the FIAM model by including the interaction of contaminants with living organisms, but require extensive validation.

Both the FIAM and BLM model can be used to define the impact of local water quality parameters by calculating the local Risk Characterization Ratio's (RCR's). For sediments, the same concept can be applied by calculating the freely dissolved contaminant fraction in pore water. By using RCR's the generic water and sediment quality standards do not have to be adapted. Water managers can therefore gain additional insight if these standards are over or under protective for their situation.

### 2.9.2 Hypothesis; slow reaction kinetics under changing sediment conditions influence the potential ecotoxicity

The distribution between the dissolved contaminant and the solid phase cannot always be described by equilibrium partitioning based on a linear relation between the sediment and water concentration (as defined in Chapter 2). Since equilibrium partitioning is the link between water and sediment legislation (see Chapter 6), processes that influence this non equilibrium partitioning play an important role in the evaluation of the potential ecotoxicity of sediments.

This is especially the case in systems undergoing a strong change in redox conditions, like when soil is used in shallow lakes (see Chapter 6) or when sediment is used on adjacent land (see Chapter 5). In both cases the ecotoxicological risks are significantly higher during a transition period, varying from weeks to years.

### **2.9.3 Research questions:**

These hypotheses are tested through three research questions:

- What is the progress and limitations of current scientific models to quantify ecotoxicological risks bases on water and sediment quality? These models are discussed in Chapter 2.
- What are the boundaries of current legislation in terms of ecotoxicological risks assessment? Do they underestimate or overestimate the risk? This will be demonstrated in Chapter 3 to 5 with the help of concrete examples.
- How can scientific models be used in the context of water and sediment legislation? Chapter 6 places scientific progress and changes in legislation in the framework of the past 25 years of Dutch experience, looking at the scientific progress versus adaptation in legislation.

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# 3

## Variation in the availability of metals in surface water, an evaluation based on the dissolved, the freely dissolved and Biotic Ligand Model bioavailable concentration

## Abstract

In this study the spatial distribution of dissolved metals in surface water is studied at nine locations in Lake Ketelmeer (the Netherlands). The measured dissolved metal concentrations are combined with the local water quality parameters for salinity, pH, alkalinity and DOC to calculate a FIAM Free Ion Activity Model (FIAM) and the Biotic Ligand Model (BLM) based bioavailable metal concentration. The BLM model is used for Cu, Ni, Pb and Zn and the FIAM model for Cd, Cr, Cu, Ni, Pb and Zn.

To be able to compare the dissolved metal concentration with the FIAM or BLM based bioavailable metal concentration, an accepted reference standard can be used which is also corrected for the bioavailable concentration. Here the Water Framework Directive (WFD) Annual Average Environmental Quality Standard (AA-EQS) is used, corrected for the FIAM and BLM based bioavailable metal concentration under reference conditions. This yielded a site specific Risk Characterization Ratio ( $RCR_{FIAM}/RCR_{BLM}$ ).

The FIAM model shows an exceedance of the site specific AA-EQS for Cu ( $RCR_{FIAM}$  of 1.8) and Pb ( $RCR_{FIAM}$  of 1.5) in the northern middle part of the lake. This is due to a lower pH in this part of the lake. The BLM model was inconclusive with regard to spatial trends for Cu and Ni due to out of boundary conditions for the model. For locations where the BLM model was within the model boundary conditions, the  $RCR_{BLM}$  could be as high as 7.5 for Cu and 3.2 for Ni. The main water quality parameter causing the high  $RCR_{BLM}$  was the low DOC concentration.

To establish if the locally increased RCR for Cu and Pb (FIAM) or Cu and Ni (BLM) poses an eco-toxicological risk to organisms the multi substances Potentially Affected Fraction (msPAF) model is used. The FIAM based msPAF indicates that the northern middle part of the lake has the highest chronic metal exposure risk, with an msPAF of 27%. The BLM based msPAF has a maximum of 45%, but lacks a spatial trend due to the missing BLM corrected Cu and Ni concentrations for some locations.

### 3.1 Introduction

The overall purpose of this study is the combined use of measured dissolved metal concentrations and local water quality dependant bioavailable metal concentration to improve the potential ecotoxicological risk evaluation.

In 2008 the European Commission set environmental water quality standards for 33 priority substances and 8 other substances in water as part of the WFD (EU COM, 2000a; EU COM, 2000b). The list of priority substances was updated in 2011 with 15 additional priority substances (EU COM, 2011). Water quality standards for metals in surface water, like the Annual Average Environmental Quality Standard (AA-EQS), are based on the total dissolved metal concentration. The dissolved concentration is defined by the metal concentration in water passing through a 0.45 µm filter.

In reality metals interact with other dissolved components in the water, resulting in metal-ligand formation. Only a fraction of the total dissolved metal concentration is available as free metal ion. The division of the dissolved metal concentration into metal ligands and the free metal ion is called speciation. The ecotoxicity of metals depends on the speciation of the metal (Long and Angino, 1977; Scott et al., 2001; Hattum et al., 1996). The metal-ligand formation in natural water bodies is impacted by water quality parameters like pH, salinity, dissolved organic carbon (DOC) and alkalinity. The bioavailable metal concentration is impacted by this metal ligand formation (Long and Angino, 1977; Scott et al., 2001; Hattum et al., 1996). Many metal ligands are not taken up by organisms, and therefore are less bioavailable (Brown and Markich, 2000). The Free Ion Activity Model (FIAM) calculates the metal-ligand formation and free metal ion concentration, taking onto account the natural water quality (Stumm and Morgan, 1970; Campbell, 1995a; Stumm and Morgan, 1996; Parker and Pedler, 1996). In the FIAM model it is assumed that the free metal ion activity better describes the observed toxicological effect on organisms (Weng et al., 2001). Although the use of FIAM models has been criticized (Campbell, 1995b) and improved upon (Brown and Markich, 2000), the conceptual approach to study the behaviour of the free metal ion and metal-ligands for exposure of biota to metals is the basis for the development of more advanced models to describe the toxicity of metals (Rüdel et al., 2015).

The next step in understanding the ecotoxicity of metals is to consider the interaction of the metal with the organism by the formation of a biotic ligand. The biotic ligand is a biological receptor that is used as the target site at which metals bind for uptake by organisms. These types of numerical models are called BLM models (Verschoor and Vink, 2010), and are conceptually more complex and require up to 10 input parameters to quantify all interactions (Bootsma and Vink, 2016). At the moment, BLM models have

been derived for Cu, Ni, Zn and Pb (Verschoor et al., 2012; Scientific Committee on Health and Environmental Risks, Risk Assessment Report on Zn (2007), Ni (2009) and Cu (2009)). BLM's are recognized as useful and robust methods to determine site-specific risks. They are accepted as second tier risk assessment of monitoring data (Rüdel et al, 2015).

In this study all three methods (the measured total dissolved metal concentration, the FIAM calculated free ion concentration and the BLM bioavailable metal concentration) are compared, taking into account the dissolved metal concentration and the local water quality parameters in a lake. To compare the results for each method a reference point is needed to define an unacceptable metal concentration. For the dissolved concentration, the reference point is the AA-EQS, for the FIAM model the AA-EQS corrected for the local water quality and for the BLM model the Predicted No Effect Concentration (PNEC) is used. Both the FIAM and BLM models calculate a Risk Characterization Ratio (RCR) for each metal at each location in the lake.

To be able to define if the RCR based in either the FIAM or BLM increases or decreases, the reference risk condition should not only reflect the concentration (AA-EQS), but also the reference water quality conditions for this risk concentration. Most of the AA-EQS standards within the WFD are based on ecotoxicological dose-effect response curves (Wijdeveld, 2007). These ecotoxicological tests are carried out under standardized conditions, including water quality parameters like pH, alkalinity, salinity and DOC. Water quality parameters for standard water are defined by Dutch Standard Water (DSW) (Janssen, 2004). The FIAM model calculates the free metal ion concentration in standard water based on the AA-EQS metal concentration, which gives the reference risk concentration for the FIAM model. The  $RCR_{FIAM}$  is calculated by using the measured dissolved metal concentration and the local water quality parameters to calculate the location specific free metal ion concentration and divide this by the free metal ion concentration for AA-EQS in standard water. The  $RCR_{BLM}$  divides the PNEC calculated exposure levels for the measured dissolved metal concentration by the predicted no-effect concentrations based on the local water quality (Muñoz et al., 2009).

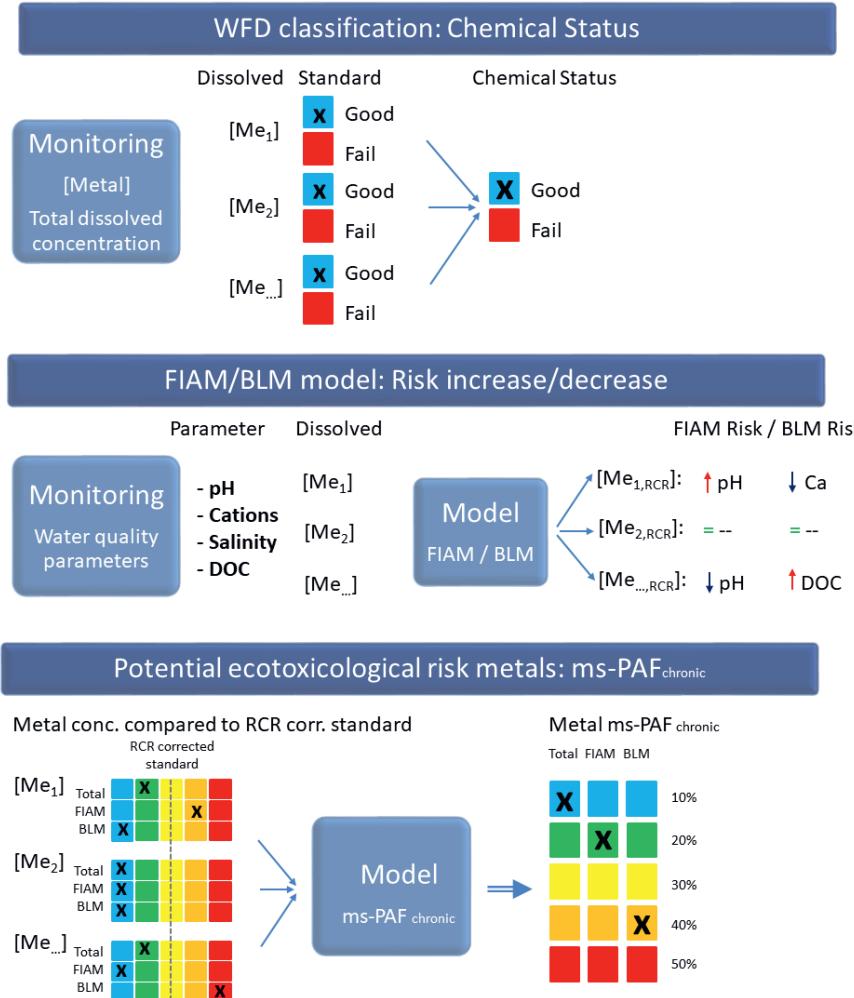
Both the  $RCR_{BLM}$  and  $RCR_{FIAM}$  indicate if the metal exposure is higher or lower compared to reference standard water conditions. Each metal concentration for each calculation method can now be compared by expressing the deviation from the reference point as the Risk Characterization Ratio ( $RCR_{dissolved}$ ,  $RCR_{FIAM}$  and  $RCR_{BLM}$ ). This approach has been adopted by the European Union System for the Evaluation of Substances (EUSES) (Vermeire, 1997).

Ecotoxicological risk assessments are carried out by establishing the concentration-effect relation for individual chemical components like metals and individual test

species under reference water quality conditions (Posthuma et al, 2002). The PAF calculations are based on the observed median lethal concentration [LC50] or no-observed-effect concentration [NOEC] for individual toxic components and individual species. The water quality test conditions for the LC50 and NOEC are carried out in standard water (DSW). Individual (metal) risks can be added to a multi-substance Potentially Affected Fraction (msPAF) by either (i) Response Addition (RA) or (ii) Concentration Addition (CA), depending on the mode of action (De Zwart and Posthuma, 2005). The msPAF does not take into account the variation in the bioavailable fraction based on local water quality parameters. By applying the RCRFIAM correction factor to the measured metal concentration, the msPAF can be corrected for the local water quality.

An alternative approach to study the direct relation between contaminant concentrations and the impact of local water quality conditions would be the use of mortality percentages in bioassays (Lahr, 2003). However the bioassays for this site, Lake Ketelmeer, were carried out in sediment and not in surface water. Sediment toxicity is based on historical pollution, and does not have to be representative of the current surface water quality, and hence is not directly related to the WFD 'good chemical status' objective. (Botwe, 2017) used sediment bioaccumulation bioassays, correlating bioaccumulation to different sediment metal fractions (the exchangeable (carbonate-bound), reducible (iron/manganese oxide-bound), oxidable (organic/sulphide-bound) and residual/refractory (silicate/mineral-bound) phase). These sediment phases are partly impacted by local water quality conditions. For the current Lake Ketelmeer site, the required sediment metal fraction data is missing. Therefore, this study will not investigate sediment based bioassays.

The water quality based metal risk evaluation based on the FIAM or BLM corrected (RCR) concentrations can be summarized by the flow chart in Figure 1. This flow chart summarizes the overall goal of this study, how to assist water managers to assess the impact of local water quality conditions on the potential ecotoxicity of the water body so that the measures they take to improve the surface water quality and meet the WFD objective 'good chemical status' are effective. For this purpose, the first step in Figure 1 is to calculate the WFD chemical status based on the individual metal concentrations. In the next step, the local water quality parameters (pH, Ca and DOC) are used to calculate if the location specific risk according to either the FIAM or BLM model is higher or lower than for standard water. In the last step of Figure 1 the potential ecotoxicity (expressed by the msPAF) is illustrated for all three scenario's. This results in (in this specific case) a higher location specific potential ecotoxicity for the FIAM and BLM based msPAF. This means that for this water body the local water quality has to be taken into account.



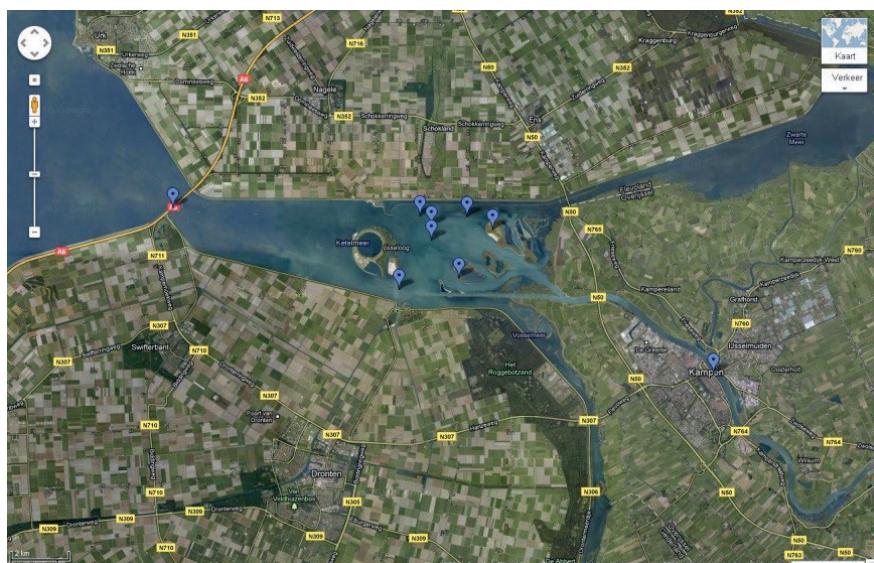
**Figure 1** Overview of three steps to take to translate monitoring data on the dissolved metal concentrations and local water quality towards a msPAF based ecotoxicological risk characterization for metals using either the dissolved metal concentration, a FIAM model corrected RCRFIAM or a BLM corrected RCRBLM. **Step 1** shows the WFD classification of the chemical status based on dissolved metal concentrations. **Step 2** uses the local water quality in combination with either the FIAM or the BLM model to indicate if there is an increase or decrease in the location specific metal risks based on local water quality parameters, indicated by an upward (higher risk) or downward (lower risk) arrow. In **Step 3** the msPAF is calculated for all three methods, scoring the potential ecotoxicological impact on a scale of 0% to 50% potential mortality. In this example the dissolved metal based msPAF is 10%, not taking into account the local water quality parameters. The FIAM based msPAF is 20%, caused by a higher RCRFIAM for metal 1. The RCRFIAM for metal 1 is increased due to a locally lower PH as compared to standard water (see step 2). The BLM based msPAF is 40% due to an increased RCRBLM for metal 3. This increase is caused by a deviation of the DOC concentration (lower) as compared to standard water (see step 2).

### **3.2 Material and methods**

The WFD chemical status of a water body is derived from the individual metal concentrations compared to the AA-EQS. By using the FIAM / BLM model, the RCR corrected concentrations are calculated based on the local water quality, and the main parameters increasing or decreasing the risk are determined. The RCR corrected concentrations can then be used in the ecotoxicological msPAF risk model. This results in a msPAF for metals based on the total dissolved, the FIAM free ion and BLM bioavailable metal.

### 3.2.1 General description of the sample location

Lake Ketelmeer is a Dutch lake at the end of the river IJssel (a branch of the River Rhine), and flows into Lake IJsselmeer. The choice for Lake Ketelmeer is due to the presence of a strong pH gradient. The pH shifts from 7.5 to 8.5 from east to west. This is caused by the River Rhine, which is oversaturated with regard to dissolved CO<sub>2</sub> (mainly as HCO<sub>3</sub><sup>-</sup>) when entering the Netherlands (Gaillardet et al, 1999). The degassing of CO<sub>2</sub> increases the pH and decreases the alkalinity. There is also a mixing of two different sources of water, from the River IJssel and Lake Zwarte Meer. Therefore Lake Ketelmeer shows a spatially varied macro chemical water quality (pH, alkalinity, DOC). The position of Lake Ketelmeer in relation to the water quality sample locations is presented in Figure 2.



**Figure 2** Position of Lake Ketelmeer with the modeled system boundaries (most eastern and western blue dots) and monitoring points for water quality (blue dots). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Seven water quality samples were taken in 1999 and analysed by OMEGAM, a Dutch accredited testing laboratory. The samples were filtered on a 0.45 µm filter to remove suspended matter, and acidified with 0.1M nitric acid for conservation. The water sample depth was 1 meter below the surface water level. The original water temperature of the samples is no longer available. Storage of the water samples was at lower than 10 °C at the day of sampling (ice packs), and transported to the lab on a daily base (lab storage at 4 °C). Detection on the ICP-MS was within 72 hours according to (NEN-EN-ISO 17294-2, 2004).

### 3.2.2 The AA-EQS and the original water quality test conditions

The Annual Average Environmental Quality Standard (AA-EQS) for Cd, Cu, Ni, Pb and Zn were taken from the Fraunhofer Institute fact sheets for fresh surface water in Europe (Lepper, 2002; Lepper, 2004). For Cd, Cu and Zn the water hardness is taken into consideration (Meyer, 1999; Technical Advisory Group on the Water Framework Directive, UK, 2008). For the current analysis the AA-EQS for water hardness class 4 is chosen, based on the average water hardness in The Netherlands. For the Cr no AA-EQS was available, therefore the Dutch surface water standard (Commissie Integral Waterbeheer, 2000) was used. The WFD AA-EQS water quality standards for surface water are presented in Table 1.

**Table 1** AA-EQS standards for surface water (in µg/l) for the modelled metals.

	AA-QS for surface water (µg/l)	Source
Cd	0.15	WFD AA-QS, medium hardness (100 - <200 mg/l CaCO <sub>3</sub> )
Cr	0.30	NW4
Cu	10	WFD AA-QS, medium hardness (100 - <200 mg/l CaCO <sub>3</sub> )
Ni	20	WFD
Pb	7.2	WFD
Zn	75	WFD AA-QS, medium hardness (100 - <200 mg/l CaCO <sub>3</sub> )

By dividing the measured dissolved concentration (presented in Table 2) by the AA-EQS an 'uncorrected' Risk Characterization Ratio ( $RCR_{dissolved}$ ) can be calculated for reference purposes (equation 1).

$$RCR_{dissolved} = \text{Dissolved} / \text{AA-EQS} \quad (1)$$

Dissolved: metal concentration in water after filtration (µg/l)

AA-EQS: annual average quality standard (µg/l)

**Table 2** Location of seven monitoring stations for Lake Ketelmeer plus two monitoring stations on the lake boundaries. Year average results for the water quality and total dissolved metals (after filtration) in 1999.

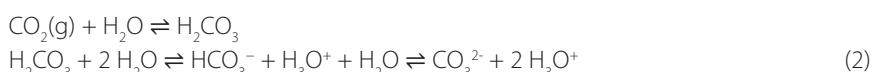
Location			pH	Alka linity	DOC	Salin ity	Dissolved concentrations after filtration (0.4 1999 (Omegam)				
			(*)	(**) meq/l	mg/l	%	µg/l	µg/l	µg/l	µg/l	µg/l
			x	y							
<i>Monitoring stations lake</i>											
Ketelmeer K2	182.16	511.30	8.5	2.0	3.8	--	<0.1	<1	5.0	2.0	<5
Ketelmeer K3	180.10	510.90	8.3	2.3	3.7	--	<0.1	<1	4.5	2.0	<5
Ketelmeer Oost 2	180.80	513.44	8.2	2.5	6.1	--	<0.1	<1	5.0	2.5	<5
Ketelmeer Oost 3	182.44	513.42	8.6	1.8	3.8	--	<0.1	<1	4.0	2.0	<5
Ketelmeer Oost 6	183.32	512.98	8.2	2.5	3.5	--	<0.1	<1	3.5	2.0	<5
Ketelmeer Oost 8	181.20	513.10	7.9	3.0	3.3	--	<0.1	3.0	7.0	2.5	<5
Ketelmeer IJm BRT	181.20	512.60	7.8	3.1	3.0	--	<0.1	<1	6.0	<1	<5
<i>Monitoring stations boundaries</i>											
Kampen (East boundary)	190.99	508.06	8.0	2.8	3.6	0.3	0.07	1.6	3.5	2.0	2.5
Ketelmeer West 1 (Western boundary)	172.26	513.68	8.3	2.3	4.6	0.3	0.06	1.7	3.2	2.0	1.8

(\*)The alkalinity is calculated ,based on the pH and the HCO<sub>3</sub>/CO<sub>2</sub> equilibrium  
(\*\*) no data for salinity, average Rhine value is taken

### 3.2.3 FIAM model CHARON

The FIAM model CHARON (De Rooij, 1991) is used to calculate the free metal ion concentration. CHARON stands for the Chemistry Applied to the Research Of Natural systems. CHARON is an extended and modified version of the chemical equilibrium model CHEMEQ developed by the Rand Corporation (Shapley and Cutler, 1970) and is currently developed and maintained by Deltares. The metals Cd, Cu, Ni, Cr and Zn are selected for the CHARON model.

One of the parameters needed to carry out the FIAM calculation is the alkalinity. The alkalinity is not measured in Lake Ketelmeer. Since the pH gradient in the lake is caused by CO<sub>2</sub> degassing (and therefore the HCO<sub>3</sub><sup>-</sup><sub>(aq)</sub> concentration), the measured pH change can be used to calculate the change in carbonate and bicarbonate concentration (equation 2), and hence the change in alkalinity (equation 3).



$$\text{Alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] + [\text{Si(OH)}_3\text{O}^-] + [\text{MgOH}^+] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] - [\text{H}_3\text{O}^+] \quad (3)$$

The other ions determining the alkalinity are also not measured (except for the pH). It is considered that the concentrations in Si, B, Mg and P are similar in every samples in the lake and then have no influence on the calculated value on alkalinity using equation 3.

The FIAM model is calibrated for Dutch Standard Water (RIKZ, 2004). The free ion risk model is applied to each of the nine locations in Lake Ketelmeer, based on the measured total dissolved metal concentrations and the local water quality parameters (see Section 3, Results, Table 2). By comparison with the reference water conditions (DSW), the RCRFIAM is calculated. The FIAM model results for the free metal ion concentrations and the RCRFIAM are given in Table S.1 (supportive information).

### 3.2.4 BLM model PNEC-PRO v6

PNEC-pro calculates local, water type specific, predicted no-effect concentrations (PNEC) of Cu, Ni, Zn, and Pb based on BLMs. Local PNECs are used for compliance checks in higher-tier risk assessments (Rüdel et al., 2015). PNEC-pro has been implemented in legal frameworks for EQS-compliance testing and WFD-reporting.

PNEC pro uses the cation concentration ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$ ) to calculate the PEC and PNEC concentrations. For Na, a fixed value of 69.0 mg/l is chosen based on the average Rhine concentration (DSW). Changes in Ca and Mg concentration are due to the dissolution of calcium/magnesium carbonate. Assuming a linear relationship between the change in bicarbonate concentration (due to the pH shift) and the change in Ca/Mg-carbonate dissolution rate, the Ca and Mg concentration change can be linked to the change in alkalinity (equation 4).

$$\begin{aligned}\Delta(\text{Ca}^{2+}) &= 0.5 \times \Delta(\text{alk}) \\ \Delta(\text{Mg}^{2+}) &= 0.5 \times \Delta(\text{alk})\end{aligned}\quad (4)$$

### 3.2.5 Risk Characterization Ratio (RCR)

Both the FIAM and BLM model yield a water quality specific risk based on the bioavailable metal concentration. The correction factor can be expressed by the Risk Characterization Ratio (RCR) (Verschoor, 2010), see equations 5 and 6. For the FIAM model, the  $\text{RCR}_{\text{FIAM}}$  is calculated by dividing the free metal ion concentration based on the water quality by the AA-EQS free metal ion concentration for standard water.

$$RCR_{FIAM} = [\% \text{ free metal ion in water body}] / [\% \text{ free metal ion AA-EQS} \\ \text{in standard water}] \quad (5)$$

free metal ion water body: (mmol/l)  
free metal ion AA-EQS in standard water: (mmol/l)

The  $RCR_{BLM}$  is calculated by dividing the predicted environmental concentration (PEC), which is based on the measured dissolved metal concentration and the local water quality, by the water quality specific predicted no effect concentration (PNEC).

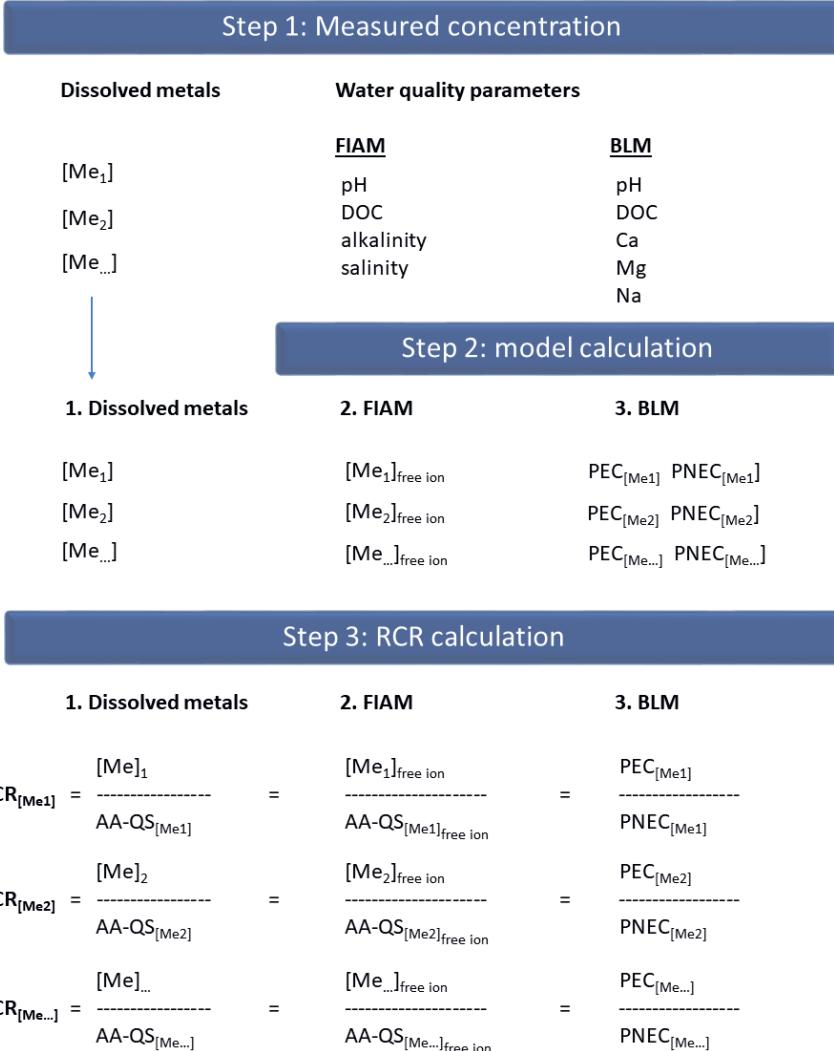
$$RCR_{BLM} = PEC / PNEC \quad (6)$$

PEC: Predicted Environmental Concentration (µg/l)  
PNEC: Predicted No Effect Concentration (µg/l)

If the  $RCR_{FIAM}$  is  $> 1$ , the site specific free metal ion concentration is higher than the FIAM corrected AA-EQS under standard water quality conditions (DSW). The site exceeds the risk associated with the AA-EQS. If the  $RCR_{BLM}$  is  $> 1$ , the site specific predicted environmental metal concentration is above the predicted no effect concentration. The site might negatively impact organisms (ECHA, 2016).

In addition to the dissolved concentration for the metals Cu, Ni, Pb and Zn the PNEC-pro model requires input for DOC, pH, Ca, Mg and Na. The DOC, pH and alkalinity are given in Section 3, Results, Table 2. The calculation of the Ca, Mg and Na concentration based on the alkalinity is explained above. The BLM model results for the PEC and the RCRBLM are given in Table S.1 (supportive information).

The RCR calculation based on the dissolved concentration, the FIAM model and the BLM model is summarized in Figure 3.



**Figure 3** Summary of steps leading to the calculation of the RCRdissolved, RCRFIAM and RCRBLM. **Step 1** contains the monitoring data needed for the calculation, both the dissolved metal concentrations and the water quality parameters needed for each model. In **step 2** the FIAM and BLM model calculations are carried out, yielding the free ion metal concentrations (FIAM) and PEC/PNEC metal concentrations (BLM) based on the local water quality parameters. In **step 3** the RCR for each metal and according to each method is calculated. Both the dissolved metals and the FIAM method require the AA-EQS metal concentration. The FIAM model calculates the AA-EQS free metal ion concentration for standard water as the reference concentration. The BLM model corrects both the measured metal concentrations and the no effect metal concentrations for the local water quality parameters.

### 3.2.6 MsPAF model OMEGA

The concept of calculating the Potentially Affected Fraction (PAF) is based on the observed median lethal concentration [LC50] or no-observed-effect concentration [NOEC] for individual toxic components and individual species. The potential toxic risk for multiple substances is then calculated using the distribution of the LC50 or NOEC values (Posthuma et al., 2002) following the methodologies as proposed by (De Zwart and Posthuma, 2005):

- (i) Response Addition (RA), or
- (ii) Concentration Addition (CA).

The numerical model 'Optimal Modelling for Ecotoxicological Assessment' (OMEGA) incorporates these methodologies to calculate the ecotoxicological risk for multiple contaminants (Hendriks and Van de Guchte, 1997). The model used the ecotoxicological data for approximately 200 substances (Bruin de, 1998). The data is derived by establishing dose effect relations for a toxicant under standard water conditions defined by DSW (Aldenberg, 2001).

The dissolved metal concentration is used as input. Based on the method of correction the input concentration is calculated by equations 7 - 9.

$$\text{Metal(dissolved)} = \text{RCR}_{\text{dissolved}} * \text{AA-EQS} \quad (= \text{Metal(dissolved)}) \quad (\mu\text{g/l}) \quad (7)$$

$$\text{Metal(FIAM)} = \text{RCR}_{\text{FIAM}} * \text{AA-EQS} \quad (\mu\text{g/l}) \quad (8)$$

$$\text{Metal(PNEC)} = \text{RCR}_{\text{BLM}} * \text{AA-EQS} \quad (\mu\text{g/l}) \quad (9)$$

### 3.2.7 Spatial distribution of metals in lake Ketelmeer

For the nine sample locations (see Table 2) a triangulation interpolation between data points is used with linear interpolation between the data points (Surfer, version 11.3.862). The choice for triangulation above Kriging interpolation is to limit the data interpolation to the area between the system boundaries. The resulting spatial pattern is plotted on a Google map, using the Dutch coordinate system (RD-coordinates).

### 3.2.8 Combined use of the models

The monitoring data (Table 2) and AA-EQS standards (Table 1) contain the information needed to calculate the FIAM free metal ion concentration based on the local water quality. The monitoring data can also be used for the BLM model to calculate the Predicted Environmental Concentration and Predicted No Effect Concentration. Therefore the  $RCR_{FIAM}$  and  $RCR_{BLM}$  can be calculated and the correlation between (i) the dissolved concentration and  $RCR_{FIAM}$  corrected concentration, (ii) the dissolved concentration and the  $RCR_{BLM}$  corrected concentration and (iii) the  $RCR_{FIAM}$  corrected concentration and  $RCR_{BLM}$  corrected concentration can be studied.

The msPAF calculation is based on dissolved concentrations, without taking into account local water quality parameters. By using the  $RCR_{FIAM}$  corrected concentration, the msPAF<sub>FIAM</sub> calculation becomes dependent on local water quality parameters.

## 3.3 Results

### 3.3.1 Site specific metal concentration and local water quality parameters

Table 2 summarizes the coordinates of the sampling location (Dutch RD), the measured dissolved metals concentration and the water quality parameters pH, alkalinity, dissolved organic carbon (DOC) and salinity. The eastern boundary (inflow) is represented by the location 'Kampen'. The western boundary (outflow) is represented by 'Ketelmeer West 1'. 70% of the reporting standard is used for analysis if the measured value is below the reporting standard.

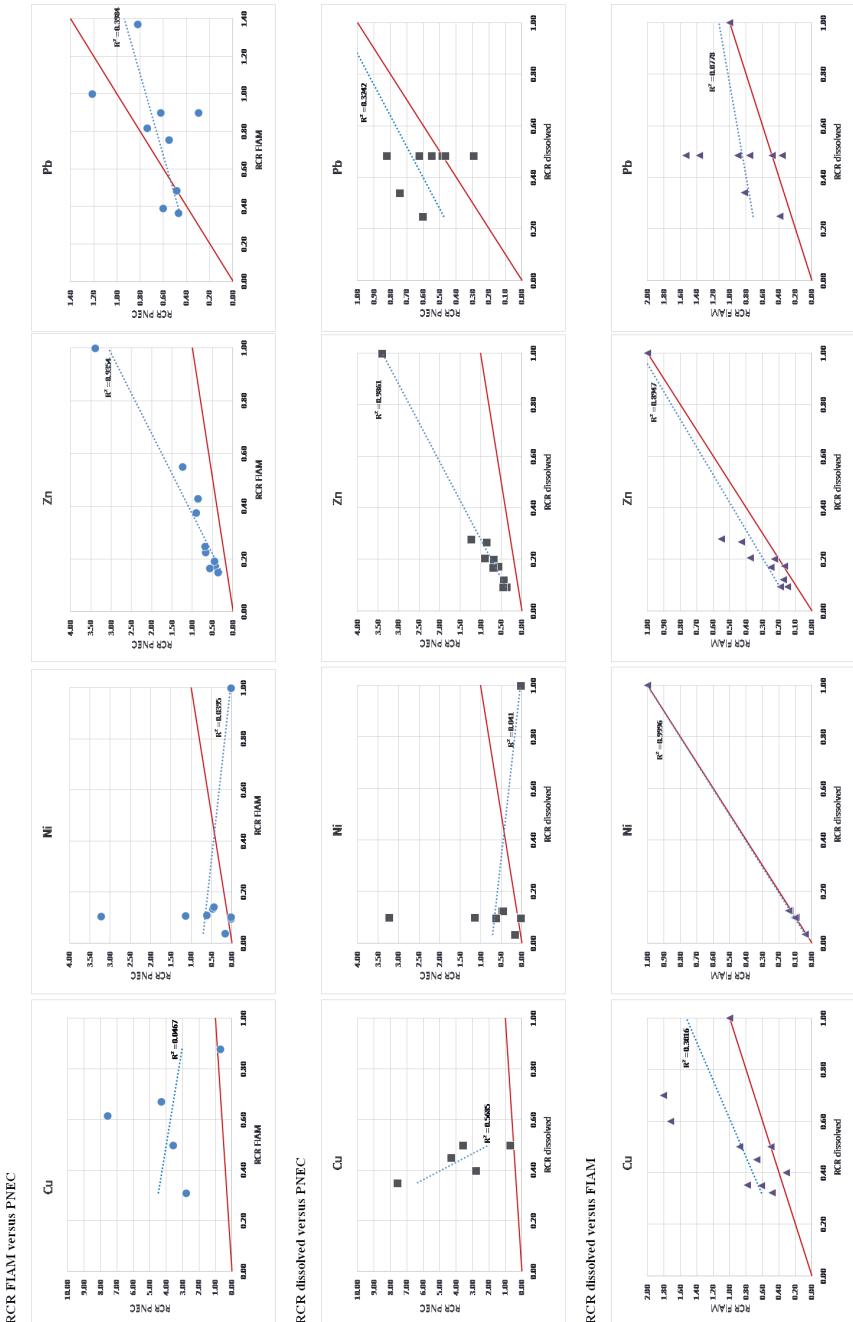
Some of the metals are below the reporting level for the locations within the lake (Cd, Pb, Cr for most locations). Only Cr exceeds the AA-EQS standard on one location (Ketelmeer Oost 8). This relatively good (below AA-EQS) water quality for metals is in line with findings in other studies. With the exception of location Ketelmeer Oost 8, the lake is classified as a WFD water body with good chemical quality.

The FIAM model results for the free metal ion concentrations and the RCRFIAM are given in Table S.1 (supportive information). A parameter analysis, using only one of the four local water quality parameters, shows that the pH is the main parameter to determine if the free metal ion concentration is lower or higher than for reference conditions (DSW). The middle-north part of the lake has a relatively low pH, resulting in a higher free metal ion concentration.

The BLM model results for the PEC and the  $\text{RCR}_{\text{BLM}}$  are given in Table S.1 (supportive information). A parameter analyses for the BLM model reveals that DOC is the main parameter determining an increase in the bioavailable metal concentration at low DOC concentrations. For Ni, a DOC concentration of < 4 mg/l leads to non-valid results for the BLM model. The north-eastern part of the lake has the lowest DOC concentrations, and therefore the highest bioavailable metal concentrations. Also hard water (as defined by the  $\text{Ca}^{2+}$  concentration, with values of 80 - 90 mg/l) often results in non-valid results for the BLM model for Cu.

### **3.3.2 Comparison between the measured dissolved metal concentration, the FIAM free ion metal concentration and the PNEC Pro calculated metal concentration at risk.**

For each of the locations in the lake a  $\text{RCR}_{\text{dissolved}}$ ,  $\text{RCR}_{\text{FIAM}}$  and  $\text{RCR}_{\text{BLM}}$  is calculated for the metals Cu, Ni, Zn and Pb. The RCR's indicate how far below or above the dissolved metal concentration is, compared to a critical concentration (the AA-EQS for  $\text{RCR}_{\text{dissolved}}$ , the AA-EQS<sub>FIAM</sub> for  $\text{RCR}_{\text{dissolved}}$  and the PNEC for  $\text{RCR}_{\text{BLM}}$ ). Each of the RCR's take water quality parameters into account in a different way. Figure 4 plots the correlation between the three different combinations of RCR's for each of the nine locations to see if there are similarities or differences in the increase or decrease of the RCR.



**Figure 4** Comparison of RCR factors for the measured dissolved concentration, the FIAM calculated concentration and the PNEC (BLM) calculated concentration. The dots are the calculated RCR's (dissolved, FIAM and PNEC) for each location, the dotted line the linear best fit (with  $R^2$ ) and the red line gives the 1:1 correlation between two RCR factors.

Figure 4 shows that trends between RCR factors, based on the measured dissolved metal concentrations and water quality parameters, as calculated by the different RCR methods (see equation 1, 5 and 6) often do not correlate ( $R^2 < 0.75$ ; less than 50% of standard deviation explained). The correlation between the  $RCR_{dissolved}$  and  $RCR_{PNEC}$  (BLM) for Cu and Ni is even negative. This is due to the lack of model results for the BLM model due to out of boundary conditions for four (Ni) to five (Cu) locations. This also explains the lack of correlation between the  $RCR_{FIAM}$  and  $RCR_{PNEC}$  for Cu and Ni. When focusing on the correction between the  $RCR_{dissolved}$  and  $RCR_{FIAM}$  it stands out that for Cu, Zn and Pb, the  $RCR_{FIAM}$  is higher than the  $RCR_{dissolved}$ . For most locations within the lake the local water quality increases the free metal ion concentration as compared to standard water.

### 3.3.3 MsPAF

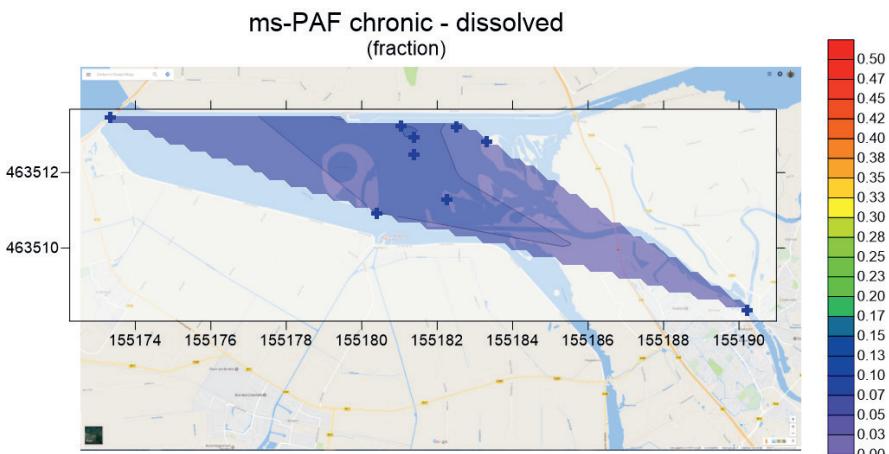
The results of the msPAF analysis for each location in the lake are given in Table S.2 (supportive information). The msPAF results indicate how many of the organisms are at risk of experiencing an observable toxicological impact due to the presence of a mixture of metals. The calculations have been carried out for the dissolved metal, the FIAM corrected dissolved concentration and the BLM based corrected dissolved concentration (see equations 7 – 9). The BLM model, PNEC Pro, only has BLM's for four of the six metals. Two of the nine sample locations also had conditions which were out of the calibration range for the BLM model for Cu and Ni. Therefore the PNEC model tends to under predict the msPAF.

A possible cross validation of the relation between the calculated chronic msPAF and the real metal exposure in the field is the use of bioaccumulation in sediment bioassays. This has been tried in the Netherlands (Besten, 1995) and has resulted in a second-tier risk assessment called TRIAD (Chapman, 1996). TRIAD has three pillars consisting of chemical, toxicological and ecological measurements. Correlation between the water quality, the sediment quality, the impact on bioassays and the amount of bioaccumulation was often difficult to prove (Swartjes, 1999; Lahr, 2003). Improvements were made by including soil and sediment conditions, and comparing these with msPAF model results (Veltman, 2007; Veltman, 2008). A whole-sediment toxicity bioassay as applied for marine sediments (Forrester, 2003; Schipper, 2010) also correlates bioaccumulation with sediment concentrations, expressing this correlation with biota-sediment accumulation factors (BSAFs) (Botwe, 2017). Unfortunately, the bioassays for Lake Ketelmeer for this period (1999) are based on acute toxicity bioassays and a limited set of chronic exposure in vivo bioassays (on daphnia magna and chironomus riparius) under non-reference test conditions (Lahr, 2003). The Ketelmeer bioassays with positive results (exceeding the Maximum Tolerated Effect

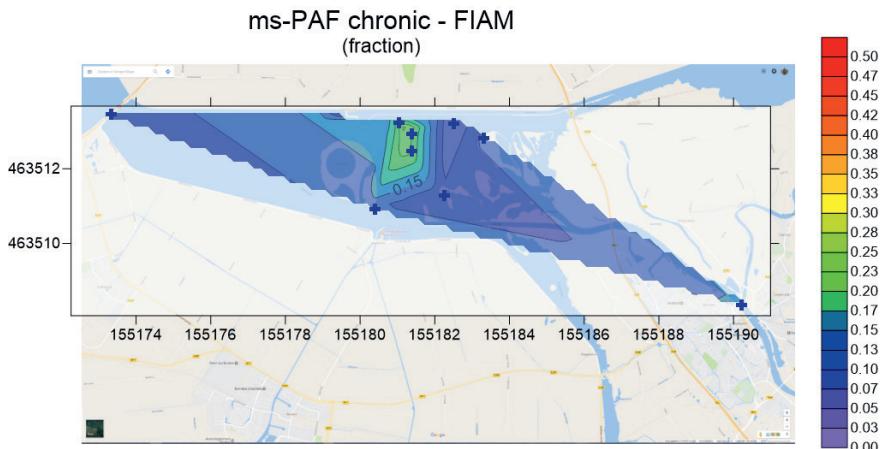
(MTE)) have elevated PAH and PCB sediment concentrations, not elevated metal concentrations. Validation of the calculated msPAF with field observed bioassay MTE values for metals is therefore not possible.

### 3.3.4 Spatial distribution of metals in Lake Ketelmeer

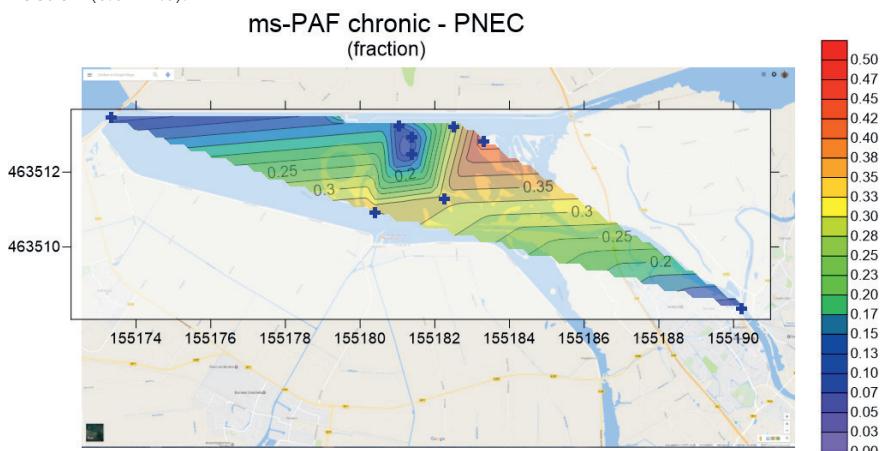
The impact of using the dissolved metal concentration, the FIAM corrected free ion concentration or the BLM based PNEC pro correction on the msPAF can be illustrated when looking at spatial pattern of areas with a high msPAF versus areas with a low msPAF. Figures 5-7 give the spatial distribution for lake Ketelmeer of the calculated chronic exposure msPAF. Figure 5 is based on the measured dissolved metal concentrations. Figure 6 uses the RCRFIAM corrected metal concentrations and Figure 7 the RCRBLM corrected metal concentrations. In case of the RCRFIAM and RCRBLM corrected metal concentration, the input for the msPAF model is based on the calculated bioavailable fraction in natural water compared to the bioavailable fraction at the AA-EQS concentration in DSW, as is explained by equation 7 – 9. By applying the RCRFIAM / RCRBLM correction factor to the dissolved metal concentration in the msPAF model, the ecotoxicological risk prediction has become depended on water quality parameters like pH, alkalinity, salinity and DOC. This is normally not the case when the msPAF is calculated.



**Figure 5** Chronic msPAF distribution across the lake based on dissolved metal concentrations. Measurement locations shown as crosses. The msPAF is expressed as a fraction (0.0 – 1.0).



**Figure 6** Chronic msPAF distribution across the lake based on FIAM corrected metal concentrations . Measurement locations shown as crosses. The msPAF is expressed as a fraction (0.0 – 1.0).



**Figure 7** Chronic msPAF distribution across the lake based on BLM corrected metal concentrations. Measurement locations shown as crosses. The msPAF is expressed as a fraction (0.0 – 1.0).

The chronic msPAF based on the sum of the dissolved metal concentration is low for the whole lake (11%). The FIAM based msPAF shows an increase of up to 27% in the middle north part of the lake, related to a locally lower pH (7.8 versus 8.0 to 8.5 for the rest of the lake). The PNEC (BLM) based msPAF has a maximum of 45% in the north-eastern part, related to a locally low DOC concentration.

### 3.4 Discussion

While water quality standards worldwide are mainly based on dissolved metal concentrations, guidelines have been written on how to incorporate metal speciation and bioavailability for protecting aquatic ecosystems (Scott, 2001). For some metals, like Cd, this has led to different standards for different types of water (EPA, 2001; Lepper, 2004). A broader adaptation of water quality influencing the bioavailable metal fraction and hence the water quality standard has been hampered by the perceived complexity of FIAM modelling. While simpler multiple regression models have been developed (Hattum, 1996; Hendriks, 1997), these models were not adapted by policy makers. In the last ten years BLM models are slowly being adapted within the EU for second tier risk assessment of monitoring data (Rüdel et al., 2014). BLM models are currently available for four metals, although the validated range of water quality parameters variation does not yet cover all natural water bodies (Verschoor, 2012). In this paper we illustrated that the outcome of these more complex models can be simplified by calculating a site-specific Risk Characterization Ratio ( $RCR_{FIAM}$  /  $RCR_{BLM}$ ). These RCR's take into account the measured metal concentration and the local water quality, and compare the outcome with a water quality standard like the AA-EQS (used in this paper).

There are some specific trends in the calculated RCR's. The RCR based on the dissolved metal concentration (the standard method for comparison with the AA-EQS) is low in all parts of the lake, leading to the conclusion that the lake meets the WFD chemical status 'good' or 'not at risk'. The use of the FIAM model results in an exceedance of the RCRFIAM for Cu (1.8) and Pb (1.5) in the north middle part of the lake, an area with a relative low pH (7.9, versus 8.0 – 8.5 for the rest of the lake). Local acidification might lead to an 'at risk' status for Cu and Pb for this part of the lake. The BLM model shows the highest RCR values (RCRBLM 7.5 for Cu, RCRBLM 3.2 for Ni) in the north-eastern corner of the lake. This is due to the low DOC concentration in that part of the lake.

The RCR's for each of the three methods can also be used to calculate the potential ecotoxicological risk, as expressed by the HmsPAF (see Table S.2, supportive information). The msPAF expresses the potential impact of the combined (multi-substances) concentration of contaminants on organisms (Potentially Affected Fraction, as compared to no impact NOEC levels). Using the FIAM/–BLM based RCR's results in the inclusion of the impact of local water quality parameters (like pH, alkalinity, salinity and DOC) on the ecotoxicological risk assessment. This is normally not a part of the msPAF risk assessment. The chronic msPAF shows the same trend as the RCR's based on the different calculation methods. The chronic msPAF is low (11%) based on the total dissolved metal concentration, which is in line with the

WFD chemical status classification ('good'). With the FIAM calculated free metal ion concentration, the chronic msPAF increases to 27% in the north middle part of the lake due to the lower pH in that part of the lake. Locations with a lower pH (<8.0) correspond with locations with a high  $RCR_{FIAM}$  (>1) for Cu and Pb, resulting in a more than twice as high chronic msPAF for these locations. This strong pH dependency based on the  $RCR_{FIAM}$  is not unexpected. The relation with pH and the metal bioavailability and toxicity to fish has been shown to exist for low alkalinity lakes (Spry, 1991). The relatively large impact of a locally twice as high chronic msPAF based on a relative small shift in pH (pH 7.8 versus an average pH of 8.2) in an alkaline lake is not expected (Adhikari, 2006). The BLM calculated bioavailable concentration yields the highest chronic msPAF value (45%), in the north-eastern part of the lake. This corresponds with local low DOC concentrations (3.0 - 3.5 mg/l). The simplified BLM model PNEC Pro is calibrated on a dataset by (Verschoor 2012). This dataset shows DOC as the most discriminating parameter (followed by pH and Ca<sup>2+</sup>). Most data in the dataset used by (Verschoor, 2012) has a DOC concentration of >5.0 mg/l. This might explain why low DOC concentrations often non valid model results. It is recommended to include more datasets based on extensive BLM modelling with low (1.0- 5.0 mg/l) DOC concentrations.

While trends between the  $RCR_{FIAM}$  and  $RCR_{BLM}$  are inconclusive (partly due to out of boundary conditions for the BLM model), it is recommended to look closer at potential ecotoxicological impacts in the north middle to north east part of the lake and monitor the development in pH and DOC concentration in the lake. It is unfortunate that the available bioassays around the same timeframe of the water quality measurements were inconclusive with regard to acute or chronic toxicity. Based on the proceedings in the development of whole sediment bioassays (Botwe, 2017) it is recommended to repeat the lake survey, including these bioassays.

### 3.5 Conclusion

Understanding the relation between contaminant concentrations (like metals) and the local water quality of a water body with regard to the potential ecotoxicity of the contaminants is important to define effective measures to improve the ecological health and therefore the ecological status of the water body (Rebecca, 2006). In the WFD the chemical status of a surface water body is defined by the concentration of individual contaminants in surface water compared to a standard like the AA-EQS. To include the impact of multiple contaminants on the WFD classification, a modification based on the calculation of the msPAF has been proposed (Wijdeveld and Schipper, 2017). In this paper this approach is taken a step further by including

the impact of general water quality parameters (pH, alkalinity, salinity and DOC) on the relative toxicity of metals. To do this in a comprehensive way for water managers and policy makers, the concept of Risk Characterization Ratio's (RCR) for dissolved metals is introduced. The calculation of these RCR's can be based on a more fundamental understanding on what causes the increase or decrease of the ecotoxicity of metals, while still maintaining the link with the accepted and well known standards like the AA-EQS for surface water. In this study both a FIAM and BLM model were used to calculate the impact of local water quality parameters (pH, DOC, salinity and alkalinity) on the RCR. After the calculation of the RCR's, the concept of a water quality dependant ecotoxicity could also be applied to the msPAF model.

An application for a Dutch lake illustrates the usefulness of these RCR's. Calculating the free metal ion concentration with the FIAM model, the north middle part of the lake is highlighted as potentially at risk due to a local lower pH (and hence a  $RCR_{FIAM}$  for Cu and Pb >1). The calculation of the BLM based bioavailable metal fraction shows an area of high risk in the north eastern part of the lake, due to  $RCR_{BLM}$  of >1 for Cu and Ni. This is due to the local low DOC concentration. The calculated RCR factors were also used for the calculation of the local chronic msPAF. Plotting the spatial distribution of the chronic msPAF based on the total dissolved metal, the free metal ion and the BLM bioavailable concentration directly highlights areas with an increased ecotoxicological risk, and links these areas to local differences in water quality parameters such as pH or DOC concentrations. This makes it easier to target these areas and to act appropriately.

Even while the Dutch lake site is one of the best analysed sites in the Netherlands when it comes to metals, much of the variation of the bioavailable fraction of these metals caused by variations in water quality had to be derived by calculations (like bicarbonate linked to carbon dioxide degassing and the observed pH shift), or indirect measurements (like salinity for chloride). Since the local water quality plays such an important role in the RCR of the metal, it is advised to systematically measure all major cations and anions in the water (and include other general water quality parameters like DOC, COD and BOD).

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# 4

## Predicting the impact of seasonal fluctuations on the potential ecotoxicological risk of multiple contaminants in the River Scheldt discharge into the Western Scheldt Estuary

## Abstract

The study site, Land van Saeftinghe, is an area within the Western Scheldt estuary with Special Protection Area (SPA) status for the EU Birds directive. We used a combination of hydrodynamic and water quality monitoring, hydrodynamic and water quality and modelling, ecotoxicity modelling and observations on the ecological status to correlate the water quality to the observed ecological status of the study site.

The monitoring and modelling results show that the copper concentrations are elevated above the Maximum Tolerable Concentration (MTR) during the whole year, while zinc and cadmium show a spring peak ( $>\text{MTR}$ ). Other metals, and all the measured organic contaminants were below the MTR.

The peak in the three metals during springtime translates into an increase in the ecotoxicity, as expressed by the calculated multi-substance Potentially Affected Fraction (msPAF). The msPAF peaked at 25% for all organisms, and 30% for benthic invertebrates. The observed ecological status for the study site at the time of monitoring (2000) was Maximum Ecological Potential (MEP). This result seems to be in contradiction with the exceedance of the MTR for three metals during spring time. However the calculated msPAF during the spring peak of 25% is deemed acceptable based on current policy, therefore potential ecotoxic stress is within acceptable boundaries. The msPAF results therefore do not contradict the MEP status.

The evaluation of the ecological status versus the water quality within the EU Water Framework Directive (WFD) can be improved by using the calculated ecotoxicity (msPAF) instead of the water quality. We propose an additional step for water bodies which are currently 'at risk', based on their chemical status. In this additional step, the msPAF is calculated for all contaminants in the water phase, not discriminating between priority and non-priority substances. The outcome of this calculation defines if the water body is at risk.

## 4.1 Introduction

The Western Scheldt (WS) estuary is an important ecosystem with mudflats, sandbanks and raised saltmarshes, and has a special protected status within the European Union (EU) Habitat Conservation and Protection Guidelines, Birds directive (Directive 2009/147/EC). Protection of the estuary is based on both ecological and chemical status, which refers to a number of specified toxic substances in the context of the Water Framework Directive (EU COM, 2000). The discharge and sedimentation of contaminants by densely populated and industrialized areas of Belgium, the Netherlands and France are major sources of pollution (Ouboter et al., 1998). Since there are still challenges in maintaining the chemical status of the estuary, attempts to restore the ecological status of the estuary might be adversely impacted (Escaravage et al., 2004). We focused on a small part of the Western Scheldt area, the Land van Saeftinghe. The Land van Saeftinghe saltmarsh is considered a Special Protection Area (SPA) and is located close to the harbor of Antwerp and the Scheldt River. The questions addressed in this case study are three folded.

1. Can we use monitoring data, which is limited in time and space, to predict the daily (tidal) and seasonal (river discharge) water quality differences in the estuary.
2. If we can predict the water quality on spatial and time scale for the estuary, can we then correlate the chemical status, as defined by the WFD water quality standards, to a potential ecotoxicological risk?
3. Does the calculated potential ecotoxicological risk give a better match with the observed ecological quality state (as defined by the WFD) of the estuary?
4. By answering these three questions successively, we drafted an addendum to the current WFD chemical status classification by introducing an extra evaluation step; the calculation of the multi-substance Potentially Affected Fraction (msPAF). The msPAF calculates the potential ecotoxicological risk for all contaminants in the water phase.

## 4.2 Material and Methods

### 4.2.1 General description on the approach

To derive the potential ecotoxicological risk for the study site 'Land van Saeftinghe', and compare the potential ecotoxicological risk with the observed ecological status a number of steps were taken:

1. Setting up a hydrodynamic model (SOBEK 1D/2D) for the Western Scheldt (including the suspended sediment transport), based on tidal derived exchange (calibrated on water surface elevation), and varying river discharge (calibrated on the daily discharge).

2. Setting up a water quality model (D-water Quality) based on measurements of the water concentrations of WFD priority substances at different locations within the Western Scheldt estuary. Also, taking into account the suspended sediment concentration and the partitioning of contaminants between the dissolved water phase and suspended matter.
3. Calculations of the potential effected fraction for multiple contaminants (the msPAF) within the study site were based on the resulting water quality predictions using the OMEGA model.
4. Comparison of the msPAF with the ecotope quality status for the study site to determine if toxic stress can be correlated to the observed ecological status.

#### **4.2.2 Hydrodynamic model**

Elskens (2014) has published a 3D model for the WS estuary to carry out environmental simulations based on a flexible resolution model (SLIM) for the hydrodynamics (including the salinity, cohesive suspended sediment and metal partitioning based partially on equilibrium equations and empirical relations). We have chosen to apply a 1D/2D approach for the WS estuary. The hydrodynamic model applied is part of the Deltares model system design and analysis tools (SOBEK Suite, 2014). The SOBEK 1D/2D model is based on the national grid for the Dutch River systems (the South-West Delta model), taking into account the bathymetry and variation in bottom roughness (friction values) of the Western Scheldt, the discharge on the River Scheldt, and the tidal influence at the North Sea Boundary (Western model boundary) (Meijers and Groot, 2007). The eastern model boundary is the joining point of the river Scheldt and the river Rupel (Belgium). The case study site 'Land van Saeftinghe' is 40 km from the eastern river boundary and 60 km from the western North Sea boundary.

A 1D/2D model describes effectively the hydraulic conditions at the case study site Land van Saeftinghe based on a non-stratified water column, and taking into account different flow rates in the central navigation channel (just north of the study site) and the shallow water and intertidal area at the study site.

Water quality is calculated with the D-water quality module within the Deltares systems design and analysis tools (SOBEK Suite. 2014). The SOBEK 1D/2D and D-water Quality models include the transport and sedimentation of suspended matter and the distribution of contaminants between the dissolved phase and suspended matter as expressed by partition coefficients. SOBEK is used for a broad spectrum of water quantity and quality related questions in mainly one dimensional (1D) network systems (e.g., rivers, channels, sewers) and two-dimensional systems (2D) systems based on a horizontal grid (e.g., floodplains and estuaries) [5]. The advantage of using

a 1D based system is that the calibrated national South-West Delta model (Meijers, 2007) can be used. By including the additional 2D layer with a cross section of the bathymetry for the cells, the overall approach can split the 1D model into spatial depended friction maps (outside the main channel) for the bottom roughness. This results in varying flow velocities and therefore spatial differences in water residence time and the sedimentation of suspended matter.

The South West Delta model is a 1D Sobek model with two channels for the Western Scheldt. The total channel flow was therefore divided over the cross section of the Western Scheldt (latitude dependent) with an average water depth of 5 meter (Van Gils, 2005). For the water quantity calculation, the tidal influence (western model boundary) and river discharge (eastern model boundary) of the River Scheldt was calculated using a 2 hour time step based on input from the Sobek model South West Delta for the year 2000 (Meijers and Groot, 2006). For the 2D grid of the Western Scheldt, a size of 1x1 km was used for each cell.

#### 4.2.3 Water quality and suspended sediment modelling

Water quality data was collected by the Dutch Directorate-General of Public Works and Water Management (Rijkswaterstaat/RWS) (Waterbase, 2014). Eastern boundary water quality is based on biweekly monitoring data for Schaar van Ouden Doel for metals and organic contaminants . The coordinates are ((Longitude: 4,2508; Latitude: 51,3503 [WGS84]). For the Western boundary, the biweekly measured contaminant concentrations at buoy SSVH (Longitude: 3,5658; Latitude: 51,412 [WGS84]) near Vlissingen were used. The water quality input was based on total water (dissolved and suspended sediment bound) concentrations. Suspended sediments concentrations are taken from the same eastern and western water quality reference concentrations.

Suspended sediment transport is important since many contaminants are in part bound to the solid phase. The process of partitioning between dissolved and solid phase is well described (Langmuir, 1979; Stumm and Morgan, 1981).

**Equation 1** Partition coefficient

$$K_p = \frac{C_{(\text{suspended solid})}}{C_{(\text{dissolved})}} \left( \frac{l}{kg} \right)$$

K<sub>p</sub> = partition coefficient

(-)

Csuspended solid = concentration contaminant bound to suspended solid

(mg/kg)

Cdissolved = concentration contaminant dissolved in water

(mg/l)

For organic contaminants the partition coefficient was normalized by the organic carbon content of the suspended sediment (POC), resulting in the KOC. The K<sub>p</sub> (metals) and KOC (organic contaminants) partition coefficients are based on the default Dutch values for suspended sediments (Commissie Integraal Waterbeheer, 2000). The contaminants Cd, Cu, Zn, naphthalene, hexachlorobenzene (HCB) and α,β,γ hexachlorocyclohexane (HCH) were selected based on their presence above detection limit in the Dutch on-line water quality database (Waterbase, 2014) for the location 'Schaar van Oude Doel'. Table 1 lists the resulting partition coefficients for the modelled contaminants.

**Table 1** Calculated partition coefficients for modelled pollutants

		<b>log K<sub>p</sub></b> (l/kg)
<b>Metals</b>		
Cadmium		4.93
Copper		4.53
Zinc		4.86
		<b>log K<sub>OC</sub></b> (l/kg)
<b>PAH's</b>		
Naphthalene		2.85
<b>Chlorobenzenes</b>		
Hexachlorobenzene (HCB)		4.61
<b>Hexachlorocyclohexane</b>		
alpha-HCH		3.39
beta-HCH		3.36
gamma-HCH (lindane)		3.37

Sediment transport was modelled with a resuspension - sedimentation approach. The bed shear stress is the primary parameter for resuspension and sedimentation. The bed shear stress is a function of the flow velocity, the roughness of the river bed,

and the water depth. At low bed shear stresses, sedimentation of suspended particles prevails. At intermediate bed shear stresses, sedimentation and resuspension are in a state of equilibrium. When the flow velocity and bed shear stress exceed a threshold level, the sediment erodes. The resuspension of the sediments is controlled by the tangential tension at the bottom caused by the flow. The sediment model has been set up using the processes library D-water Quality and is available as a pre-defined subset. The parameters, after model calibration, defining sedimentation versus erosion of the (suspended) sediment are given in Table 2.

**Table 2** Variables for the suspended sediment

coefficient	Name	Default value	Calibrated value	units
VsedIM3	sedimentation velocity IM3 (clay)	0.01	0.3	m/day
TauScIM3	critical shear stress sedimentation IM3	0.005	0.02	N/m <sup>2</sup>
VResDM	first order resuspension velocity	0.01	0.01	1/day
TauRSiDM	critical shear stress resuspension	0.2	0.2	N/m <sup>2</sup>
RHOIM3	density IM3	1.3 10 <sup>6</sup>	1.3 10 <sup>6</sup>	g/m <sup>3</sup>
PORS1	porosity sediment layer 1	0.50	0.5	-
MinDepth	minimum water depth for sedimentation	0.01	0.01	m

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#### 4.2.4 Potential affected fraction for multiple contaminants (msPAF)

The concept of calculating the Potentially Affected Fraction (PAF) is based on the observed median lethal concentration [LC50] or no-observed-effect concentration [NOEC] for individual toxic components and individual species. The potential toxic risk for multiple substances is then calculated using the distribution of the LC50 or NOEC values (Posthuma et al., 2002; Newman et al., 2000) following the methodologies as proposed by (de Zwart and Posthuma, 2005): by

- (iii) Response Addition (RA), or
- (iv) Concentration Addition (CA).

The type of addition that can be applied depends on the mode of action. Table 3 gives the modes of actions for the modelled contaminants.

**Table 3** Mode of action for each pollutant

Pollutant	CAS	Group	Mode of action
Cadmium	7440439	Metals	Cadmium-specific
Copper	7440508	Metals	Copper-specific
alfa-HCH	319846	Hexachlorocyclohexane	Neurotoxicant: cyclodiene-type
beta-HCH	319857	Hexachlorocyclohexane	Neurotoxicant: cyclodiene-type
lindane (gamma-HCH)	58899	Hexachlorocyclohexane	Neurotoxicant: cyclodiene-type
Hexachlorobenzene	118741	Chlorobenzenes	Nonpolar narcosis
Naphthalene	91203	PAH's	Nonpolar narcosis
Zinc	7440666	Metals	Zinc-specific

The numerical model 'Optimal Modelling for Ecotoxicological Assessment' (OMEGA) incorporates these methodologies to calculate the ecotoxicological risk for multiple contaminants (Hendriks and Van de Guchte, 1997; Hendriks et al., 1998).

The calculation of an msPAF risk level within the OMEGA model is based on the available toxicity data for all organisms; no distinction is made between different groups of organisms. This is due to the lack of sufficient ecotoxicity data to support a more specific clustering of organisms. Based on the combination of different ecotoxicological datasets within Europe and the development of QSAR relationships for contaminants with the same mode of action, the ecotoxicity support database was extended to include more dose effect curves for the WFD priority substances (Wijdeveld, 2007). The extended database could then be split for four different types of organisms (e.g., fish, phytoplankton, benthic invertebrates, macrophytes).

The msPAF was calculated for chronic stress (>72 hours exposure). For the metals, Response Addition (RA) was used and for the organic contaminants, Concentration Addition (CA) was used. The ecotoxicity support database was extended to include more dose effect curves for the WFD priority substances (Wijdeveld, 2007). This created the possibility to establish a PAF for WFD priority substances based on meeting the minimum data required for specific groups of organisms:

- Phytoplankton;
- Macrophytes;
- Benthic Invertebrates;
- Fish.

The PAF can be calculated according to Equation 2 (De Nijs et al., 2008; Sala et al., 2012).

### **Equation 2** Potentially Affected Fraction

$$PAF(C_{diss}, \mu, \sigma) = \int_{-\infty}^{C_{diss}} \frac{1}{\sigma\sqrt{2\pi}} e^{-\left(\frac{(C-\mu)^2}{2\sigma^2}\right)} dC$$

PAF = Potentially Affected Fraction

(-)

$C_{diss}$  = concentration contaminant dissolved in water

(mg/l)

$\mu$  = geometric mean of toxicity concentration data

(mg/l)

$\sigma$  = standard deviation of log transferred toxicity concentration data

(mg/l)

By selecting groups of organisms, instead of all available toxicity data, the geometric mean ( $\mu$ ) and standard deviation ( $\sigma$ ) of the selected groups will vary.

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#### **4.2.5 The ecological quality status for the case study site**

The Western Scheldt is a O2 type waterbody; an estuary with moderate tide (heavily modified). The Western Scheldt is divided in to 13 ecotopes and mapped to define the WFD ecological status. The study area 'Land van Saeftinghe' is part of the mesohaline salinity zone within the Scheldt Estuary (main ecotope ID 1 – Brackish midlow-littoral(hdyn)). Since 2007 the WFD targets for the Western Scheldt are defined by the Prague method for heavily modified water bodies (Programma Rijkswateren 2010-2015, 2009). According to the Prague method (based on the whole estuary, not the specific pilot site location 'Land van Saeftinghe') the Western Scheldt in 2007 scores 'average' for the indicators water flora and macro fauna (Programma Rijkswateren 2010-2015, 2009). In 2012 the ecological quality status for the Western Scheldt area was updated (Brondocument waterlichaam Westerschelde, revised 2012).

For this study, the macro fauna ecological quality status for the study area surveyed in the year 2001 was used (Escaravage et al., 2004). This survey best matched with the water quality data record we used (2000). The WFD ecological quality status in 2001 was derived for both the macroinvertebrates (Escaravage et al., 2004; Wijnhoven et al., 2006; Posthuma et al., 2011) and fish (Breine et al., 2008). More recent publication (after 2007) use an adapted benchmark for macrofauna, the Benthic Ecosystem Quality Index (BEQI) (Twist et al, 2009). This benchmark also takes into account the loss of inter tidal areas and shallow water areas for macrofauna. Therefore the BEQI is not strictly an ecosystem index (based on specie abundance, biomass and variation), but also an area index.

#### 4.2.6 The msPAF versus the ecological quality status

By using the model results for the Land van Saeftinghe location for the water quality, a comparison with the WFD chemical status for this area, as described by (Lepper, 2005), can be made. The calculated msPAF can be compared with the observed overall ecological status, and the ecological status for macro-invertebrates and fish (see paragraph 2.5). A similar approach, comparing the calculated combined ecotoxicity risk (msPAF) with observed ecological quality indices for a study area, was applied by Posthuma and de Zwart (2006 and 2012) for fresh water organisms.

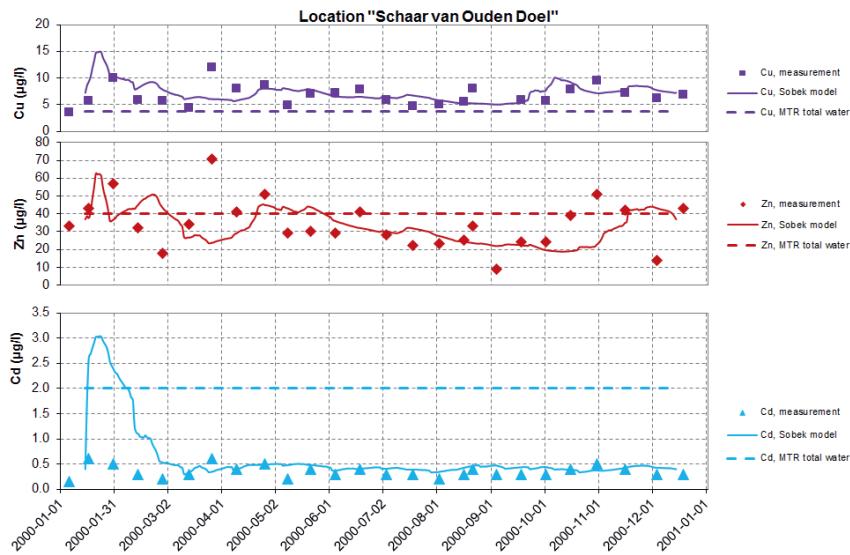
We then incorporated the msPAF model results as an extra step in the WFD water body classification system. This results in a revised WFD chemical classification based on the total contaminants concentration in water, which is non-discriminating between priority and non-priority substances. These results can be compared with the observed ecological status to conclude if a msPAF approach could supplement the WFD water quality standards.

### 4.3 Results

#### 4.3.1 Hydrodynamic and water quality model results

The Sobek model is calibrated for the year 2000 for the contaminants Cd, Cu, Zn, naphthalene, HCB and ( $\alpha$ - $\beta$ - $\gamma$ ) HCH. The model results are compared with the measured contaminants concentration at the monitoring station 'Schaar van Doelen' which is close to the Eastern model border and also close to the study area 'Land van Saeftinghe'. In Figure 1, the results for the location 'Schaar van Doelen' are shown for the metals Cu, Cd and Zn, and compared to the Maximum Tolerable Concentration (MTR) as defined by the Commissie Integraal Waterbeheer (2000). The concentrations for the organic contaminants naphthalene, HCB and ( $\alpha$ - $\beta$ - $\gamma$ ) HCH are not shown. All organic contaminants were below the reporting limit, with the exception of Lindane ( $\gamma$  HCH). The maximum measured Lindane concentration (in April 2000) does not exceed the Annual Average environmental quality standard (AA-EQS).

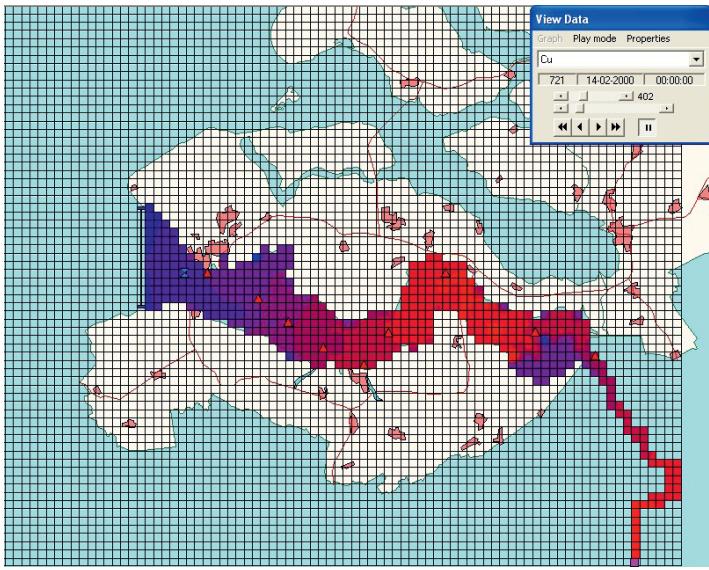
The Sobek 2D model yields the spatial and time dependent concentration of the contaminants with a resolution of 1 x 1 km. Figure 1 illustrates that copper is at or above MTR levels at location 'Schaar van Doelen', and has a seasonal peak concentration early in the year 2000.



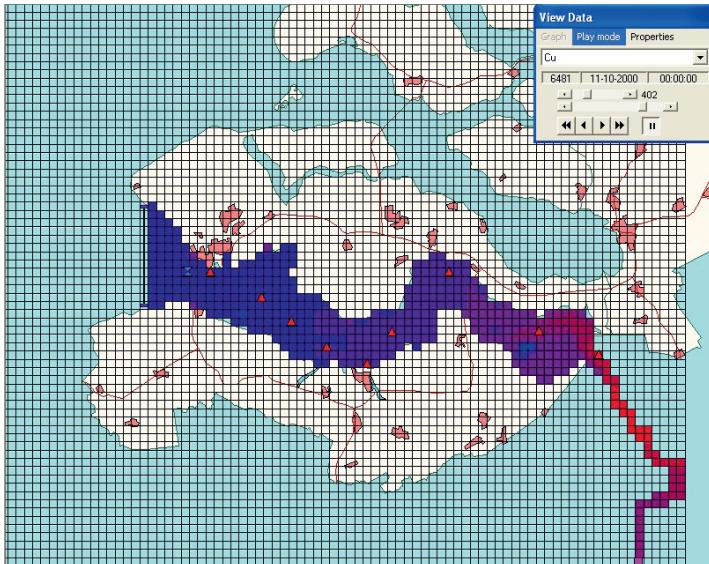
**Figure 1** Location 'Schaar van Ouden Doel', Rijksdriehoeksmeting (RD) coordinates x = 75825, y = 374070. Measured concentration of Copper (square), Zinc (diamond) and Cadmium (triangle) in surface water. Each metal concentration is compared with the Maximum Tolerable Concentration (MTR) (dotted line) and the Sobek model result (solid line).

The discrepancy between measurements and model calculation results for the dissolved metal concentration is due to the input of the total water concentrations (including the suspended sediment bound fraction) in the model. The modelled dissolved concentration is based on the total water concentration and model calculated suspended sediment concentration by use of the  $K_p$  (Equation 1).

Figure 2 shows the copper concentration for the modelled estuary on the 14th of February, during the peak discharge of River Scheldt. Figure 3 shows the copper concentration for the modelled estuary on the 11th October 2000, during a period of low discharge of the river Scheldt



**Figure 2** Modelled concentration dissolved Copper for the Western Scheldt estuary on 14-02-2000, during the peak discharge of the Scheldt river. Boundary conditions (measurements of dissolved Copper) where applied for the western end of the estuary (North Sea) and eastern end (near Antwerpen). In red the high concentrations (above MTR = ) in blue the low concentrations (below MTR). Grid size 1 × 1 km.

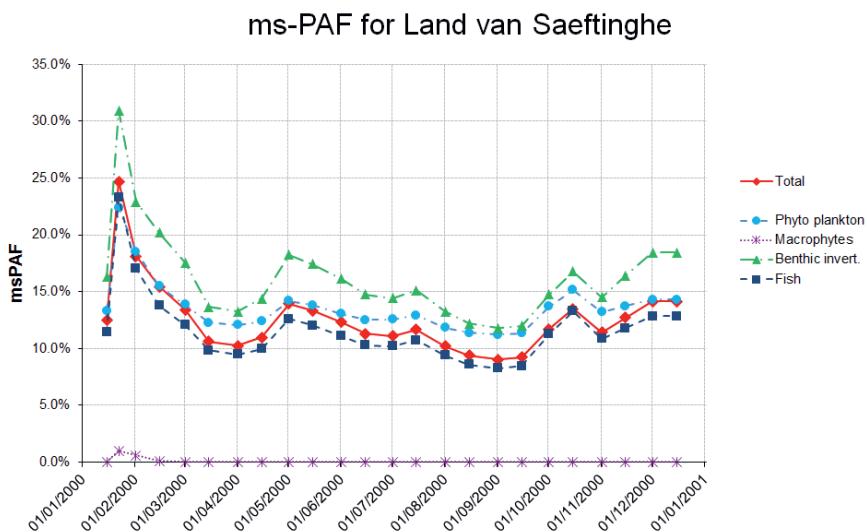


**Figure 3** Modelled concentration dissolved Copper for the Western Scheldt estuary on 10-10-2000, during a period of low discharge of the Scheldt river. Boundary conditions(measurements of dissolved Copper) where applied for the western end of the estuary (North Sea) and eastern end (near Antwerpen). In red the high concentrations (above MTR) in blue the low concentrations (below MTR). Grid size 1 × 1 km.

Figure 1 also shows the cadmium concentration at the location 'Schaar van Doelen'. Cadmium is a WFD priority substance. Exceeding the MTR value for a priority substance leads to 'bad chemical status' according to the WFD. While the water quality samples for the location 'Schaar van Doelen' does not exceed the MTR, the measured concentration on the eastern system boundary (near Antwerpen) leads to a modelled exceeding of the MTR for cadmium during spring. Peak concentrations of Cadmium above the MTR are measured in the Western Scheldt up to 2007. After 2007 due to the adaptation of a water hardness correction for Cadmium, the MTR was no longer exceeded (Programma Rijkswateren 2010-2015, 2009). The modelled Cadmium peak during the spring in 2000 is therefore no exception for this period (up to 2007), and the resulting MTR status classification is 'bad chemical status'.

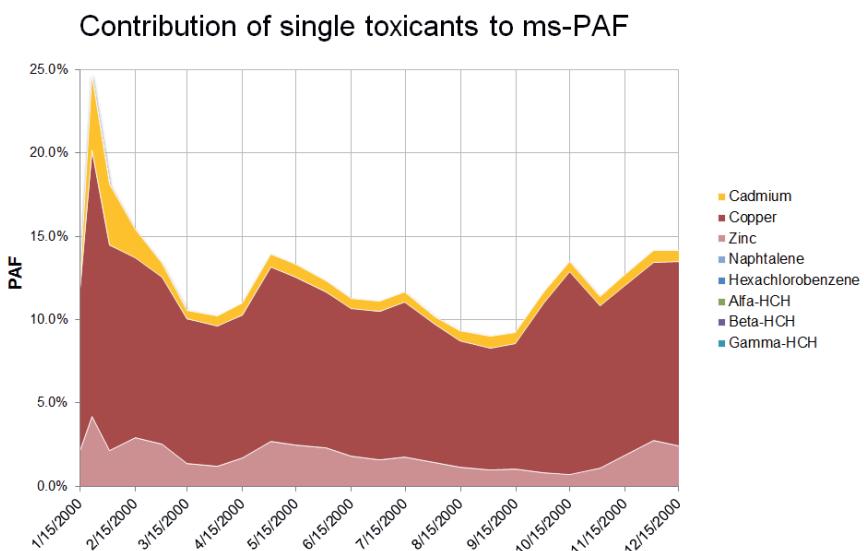
#### 4.3.2 Potential affected fraction for multiple substances and the ecological status

The msPAF for chronic exposure is calculated on a biweekly basis for each group of organisms: Total msPAF, Phytoplankton, Macrophytes, Phytobenthos, Benthic Invertebrates, and Fish. The resulting msPAF is shown in Figure 4.



**Figure 4** Calculated msPAF for the period 01-01-2000 until 31-12-2000 for the location 'Land van Saeftinghe' based on the calculated dissolved concentration for the toxicants Cd, Cu, Zn, naphthalene, HCB and ( $\alpha$ - $\beta$ - $\gamma$ ) HCH. In red (diamonds and solid line) the calculated msPAF for all organisms. In light blue (circle and dotted line) themspAF for phyto plankton. In purple (asterisk and dotted line) the msPAF for macrophytes (no data). In green (triangle and dotted line) for benthic invertebrates. In dark blue (square and dotted line) for fish.

Macrophytes show a relative low toxic stress (the msPAF is close to zero) while benthic invertebrates show a slightly (+5%) higher toxic stress response. Fish and phytoplankton show almost no deviation from the total msPAF. The contribution of each of the single contaminants to the total msPAF is given in Figure 5.



**Figure 5** Contribution of individual toxicants (Cd, Cu, Zn, naphthalene, HCB and ( $\alpha$ - $\beta$ - $\gamma$ ) HCH) to the total msPAF for the period 01-01-2000 until 31-12-2000 for the location 'Land van Saeftinghe'.

The main contribution to the total msPAF at Land van Saeftinghe comes from copper (65% to 90%) followed by zinc (5% to 19%). During the high river discharge in January, cadmium peaks with a 20% contribution to the total msPAF, declining to a 4% contribution for the spring, summer and autumn periods. All organic contaminants with a concentration above the detection limit (naphthalene, HCB and ( $\alpha$ - $\beta$ - $\gamma$ ) HCH) have contributions of <0,1% to the total msPAF and are neglected in the interpretation of the results.

The msPAF levels are compared to the ecological status map for the Western Scheldt for the year 2001 for Land van Saeftinghe (Escaravage et al., 2004). The following two ecotopes are present within the study area:

- Ecotope number 1 : Brackish midlow-littoral(hdyn)
- Ecotope number 2 : Brackish midlow-littoral(ldyn) – muddy

The ecological status for these two ecotopes is at the Maximum Ecological Potential (MEP) relative to the number of species present and macro fauna density indices. For the biomass index, ecotope number 1 also has MEP status, but for ecotope 2 the biomass index is 'Bad'.

## 4.4 Discussion

### 4.4.1 Hydrodynamic and water quality model results

The water quality modelling results provide insight to the spatial and seasonal variation in the concentrations of contaminants within a heterogeneous system like an estuary. Figure 4 illustrates that the long term trend fit between water quality measurements and model results is in good agreement. However, there are measurement points where the modelled and measured concentrations differ by a factor of two to three.

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Part of the reason for this mismatch is that the model is strongly driven by the concentrations on the boundary. If system retention times, based on the hydrodynamic model, are slightly off, the difference in timescale between the biweekly water quality sampling and the daily variance in water quality on the pilot location causes a mismatch. Another error source for an accurate dissolved concentration calculation within the model is the forcing of the model based on total water concentrations. The transport of suspended sediment is calculated by the hydrological model and can therefore differ from the actual suspended sediment concentration. To conserve the total water concentration, the difference in suspended sediment concentration translates to variations on the dissolved contaminant concentration.

For the purpose of this article, the evaluation focused on the seasonal fluctuations in chronic ecotoxicological stress (as expressed by the msPAF) within the natural protection zone of Land van Saeftinghe and the modelling approach provided a chronic exposure level prediction with sufficient accuracy. For an acute toxicity assessment, the current biweekly water quality measurements are too infrequent to predict the impact of a short term event on the ecotoxicological stress in the system.

The model results gives insight in the frequency and duration of the exceedance of water quality standards, like the exceedance of the MTR for cadmium in mid-January to mid-February for Land van Saeftinghe. Since cadmium is a WFD priority substance, this leads to a WFD bad chemical status classification. Looking at the year average water quality, cadmium is close annual average environmental quality standard (AA-EQS). This

would justify a good chemical status classification. Water quality models can contribute to understanding if high peak concentrations in water quality monitoring can be contributed to local conditions (spatial variation) or specific events (time dependent).

Another example of a Dutch water system which shows a strong gradient in the water quality is lake Ketelmeer. (Wijdeveld, 2002). Using a hydrodynamic model combined with a geochemical water quality model, this gradient could be understood. The resulting insight that natural degassing of carbon dioxide, and therefore a shift in the lakes pH, was the cause for an increase in the water concentration of metals lead to the conclusion that part of the planned sediment clean-up operation for the lake was not necessary.

#### **4.4.2 Potential affected fraction for multiple substances versus the ecological status**

The water quality model made it possible to predict the ecotoxicological stress levels for multiple contaminants, as expressed by the msPAF, on spatial and temporal scales. The calculated msPAF can then be used to evaluate the potential threat of contaminants to ecological status. The use of the msPAF approach does not discriminate between WFD priority and non-priority substances. All contaminants are evaluated based on their actual ecotoxicological risk. Having a list of priority substances to check with the obligation to determine water body specific contaminants is useful when screening a water body for potential chemical threats. However, after establishing the key contaminants for a water body, the distinction between priority and non-priority substances becomes arbitrary. The use of water quality standards, like the AA-EQS and MTR, for individual contaminants becomes superfluous. (Posthuma, 2002) explains the relation between the observed ecotoxicological effects on different types of organisms with increasing contaminant dosing and risk assessment (the PAF). The use of the Species Sensitive Distribution (SSD) for setting water quality standards for risk assessment was published in a guideline (EPA, 1985). The use of the multiple contaminant risk assessment (the msPAF) is making use of the same principles which were at the base of the EPA guideline. Calculating the msPAF makes the use of individual water quality standards redundant.

Within the Netherlands, the potential ecotoxicity evaluation limit for sediments applied on land is based on the calculation of the chronic msPAF. The msPAF calculation is based on the input of the (pore) water concentrations by the use of the  $K_p$  (equation 1 in paragraph 2.3). Therefore the potential ecotoxicity evaluation for sediments can be used for water, and vice versa. The msPAF limit is 50% for heavy metals and 20% for organic contaminants (Tuinstra and ten Hove, 2008). Based on the

calculated water quality for the study area Land van Saeftinghe, this policy standard is not exceeded, as is illustrated in Figure 4.

Based on Dutch policy standards, the chronic ecotoxicological stress levels based on the msPAF calculation within the study area are acceptable (the local species are not considered to be at risk). This is in accordance with the observed field indicators for the ecological status for Land van Saeftinghe (Escaravage et al., 2004). With the exception of the biomass index in the muddy parts of ecotope type 2, the study area has the status Maximum Ecological Potential (MEP) in 2001.

More recent studies (2005-2007) use an adapted benchmark for benthic organisms, the BEQI (Twist, 2009). The ecologic quality ratio (eqr) for the Western Scheldt in the period 2005-2007 based on the BEQI was 'moderate'. While the BEQI benchmark principle and the spatial scale (whole Western Scheldt area) is not the same, the underlying sub-benchmark indexes for benthic species abundance, biomass and variation give some indication if the toxic stress on the ecological impact has increased or decreased. These three sub-indices all have the status 'good ecological status'.

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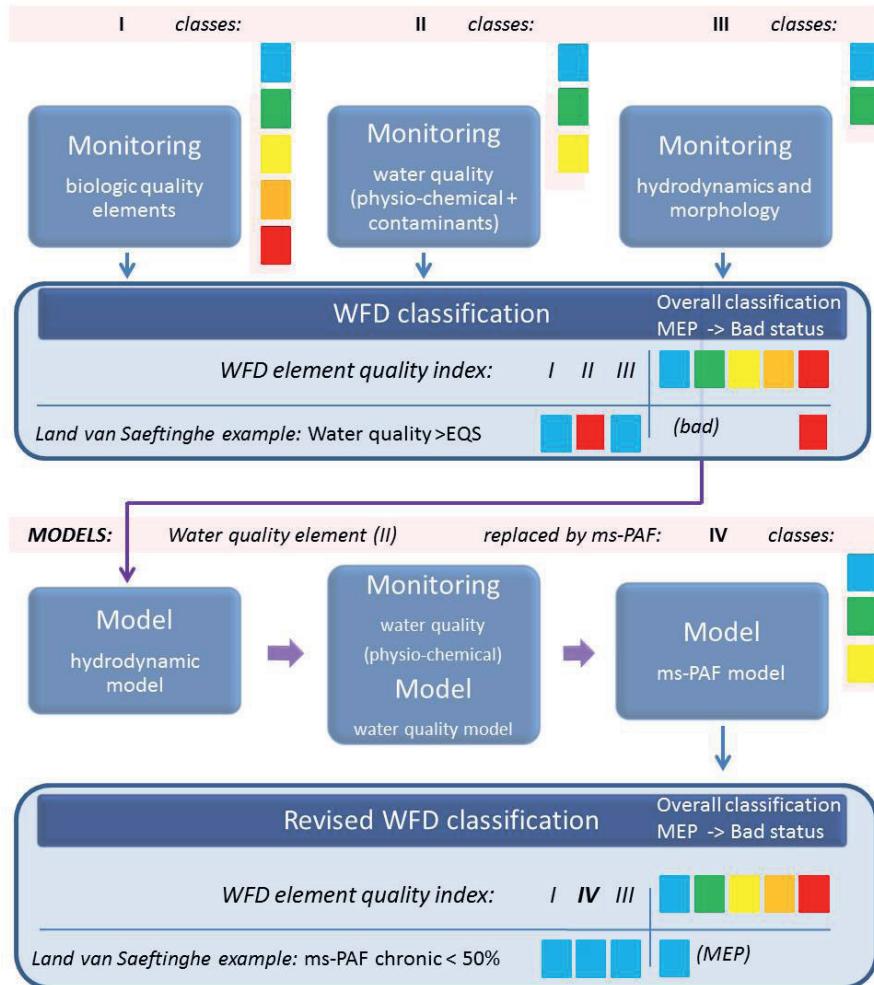
The seemingly good correlation between the msPAF (acceptable risks) and ecological status based on ecological status (MEP (2001), GEP for benthic sub-indices (2007)) looks promising. But evidence from more locations is needed. The current study is speculative with regard to the actual ecotoxicological impact. The msPAF only indicates a potential toxicity, not an actual observed ecotoxicity.

The WFD classifies the ecological status of a water body based on:

- i) The biological quality elements,
- ii) The physico-chemical parameters, and
- iii) The hydromorphology.

The one-out-all-out rule is applied, so that any deviation of the reference conditions or EQS standards results in a lower ecological status. This still leaves the question of what is the relative contribution of each of the three different indices on the ecological status when the criteria are not all met. Attempts to correlate the WFD chemical status based on EQS standards to the WFD ecological status were often inconsistent (Hommen, 2004).

The msPAF method is a powerful tool to predict if exceeding the EQS for multiple contaminants leads to unacceptable toxic stress on the ecosystem as caused by the combined contaminants. The msPAF, as a quality element (iv), can replace or be added to the water quality index as illustrated in Figure 6.



**Figure 6 Top half of Figure:** Water Framework Directive element classification for biological quality elements, water quality (physio-chemical and contaminants) and hydrodynamics/morphology. **Bottom half of Figure.** Replacement of water quality element classification based on contaminant concentration with water quality element classification based on calculated msPAF for all contaminants.

The concept of using msPAF calculations is promising and could also be combined with new evaluations models for metals like the Biotic ligand models (BLM) models (Verschoor et al., 2012). BLM models add water type-specific no effect concentrations to the calculation. For the Western Scheldt this could mean that the impact of salinity

changes due to the mixing of fresh and marine water could impact the exposure. Including BLM models into the msPAF is therefore a logical next step.

## 4.5 Conclusions

The use of numerical models for both hydrological conditions, water quality and ecotoxicological risk has the advantage that spatial and temporal dependent trends can be calculated within the study area with a relatively limited set of measurements. The combined water quality and hydrologic model illustrate a late winter/early spring peak maximum for the exposure to contaminants in the study area 'Land van Saeftinghe'. This is due to the high discharge of the River Scheldt in this period. The use of spatial and seasonal trends in ecotoxicological risk assessment combined with the ability to discriminate the ecotoxicological risk for different groups of organisms can help policy makers to take more efficient measurements to reduce toxic stress by focusing on specific areas, or specific time periods. Knowing which groups of organisms are vulnerable to specific contaminant concentrations also helps to evaluate their role in the specific habitat and food chain.

4

The combined use of water quality monitoring data, water quality modelling, and ecotoxicological risk calculations, based on the msPAF approach, has shown to be a useful tool assisting in the evaluation of the WFD classification for a water body. The msPAF better matches the observed biologic quality index, as compared to using single contaminant water quality criteria. This is illustrated for the case study area Land van Saeftinghe. This area within the Western Scheldt, has a relatively high concentration ( $>\text{EQS}$ ) of metals, especially during spring, due to the high seasonal influx of the River Scheldt. The calculated msPAF shows that copper is the contaminant with the relatively highest contribution to the total potential toxicity, varying between 60% and 90%. The WFD priority substance cadmium only contributes between 4% and 20% to the msPAF. However the WFD chemical status classification 'bad chemical status' is based on the cadmium exceedance of the MTR. These results plead for an added WFD water quality index based on the combined impact of all contaminants, not discriminating between priority and non-priority substances.

The calculated msPAF (for metals, PAHs, HCB and HCHs) is acceptable (according to Dutch legislation), also during the late winter / early spring peak. The WFD classification based on the EQS and one-out-all-out rule would classify the overall status as 'bad chemical status', while the WFD classification based on the msPAF results in a MEP status. This is in accordance with field observations (2001) for the biological quality index (also MEP) and the BEQI sub-indices for benthos (2005-2007).

The use of a numerical hydrological/water quality model helps to understand the system dynamics and system behaviour between water quality measurements. The use of a numerical model is in no way a replacement for long term trend monitoring and the continuous observations if the MEP keeps being realised. The authors realize that the Land van Saeftinghe case study is only one example, although with a relative complete dataset for evaluation (from hydrodynamic conditions, water quality to habitat description and up to date biological quality indexes). If calculating the msPAF can substitute water quality standards is far from proven. Since the method can be applied based on available water quality data, calculation and publishing of the msPAF is recommended to build up a supportive database.

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# 5

## From sediments to soils - changes in pore water metal bioavailability

## Abstract

The application of sediments on land changes the bioavailability of metals in the pore water. In moderate climates the groundwater level in the winter is relative high, while in the summer the groundwater level drops. This fluctuation in groundwater level causes changes in the oxidation/reduction state of soil minerals, and also influences the production and degradation rate of Dissolved Organic Matter (DOM). In this study a Free Ion Activity Model (FIAM) for metals is used in combination with an unsaturated soil groundwater model to evaluate the impact of turning sediment into a soil with a fluctuating groundwater table over a period of ten years. The calculated metal pore water concentrations over depth and time are then used to calculate the Risk Characterization Ratio (RCR) for metals based on a BioLigand model (BLM) and the combined potential ecotoxicity based on the multi substance Potentially Affected Fraction (msPAF).

The results show that the metal pore water concentration is depth dependent and seasonal, with a peak pore water metal concentration in the autumn. At the end of summer there is a high DOM pore water concentration and a relative large oxidized metal fraction in the soil. The rise in the groundwater level in the autumn leads to the reduction of oxidized metal fraction, increasing the dissolved pore water metal concentration. There is also a trend over the 10 year period towards lower average pore water metal concentrations. The BLM model results indicate that the RCR values for metals are high ( $>1$ ) during the first 3 years after the application of the sediment as a soil, dropping to values below 1 after 3 years. The msPAF shows a similar declining trend over time, although it takes longer (5 years) before the msPAF is below 40%.

## 5.1 Introduction

Large scale reallocation of soils in deep under water pits has become common practise in parts of Europe as part of river restoration strategies (Buijse, 2002). The use of soil is seen as a beneficial application according to the EU directive 2000/60/EC (EU COM, 2000), even when the soil contains contaminants. A recent study (Vink, 2017) focusses on the question on what happens to metals when soils become sediments, addressing the impact of large-scale storage of soils in sandpits and lakes and the impact of reduction kinetics on heavy metals and arsenic release to groundwater. (Vink, 2017) takes into account the DOM characterisation, the iron chemistry and the pore water chemistry (including the main anions and cations). In this study the question is reversed, *what happens to the metal availability when sediments become soils?* Sediments are reduced and fully saturated with water, while soils in temperate climate regions have a water shortage in the summer and have a water excess in the winter (Rodriguez-Iturbe, 1999). This yearly cycle exposing the top layer of the soil to air penetration and oxidation during the summer, while in the winter the groundwater level rises causing reduction reactions to dominate.

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The concept that reduced sediments with a sufficient high sulphite content pose no environmental threat with regard to metals is supported by work done on the Simultaneous Extracted Metals (SEM) to Acid Volatile Sulfides (AVS) ratio in soils and sediments (Di Toro et al., 1992; Berry et al., 1996; Van den Hoop et al., 1997). Studies using the SEM/AVS ratio as indicator for the bioavailability of metals in sediments tend to rule out metal ecotoxicity in sediments when the SEM/AVS ratio is low (Van Griethuysen et al., 2004; Vangheluwe et al., 2003; Di Toro et al., 2005).

(Vink, 2017) shows that the underwater storage of soils as sediments can form an environmental risk for groundwater, even when the sulphide concentration in the soil is high.

When large shifts in redox potential occur kinetic oxidation/reduction rates influence the speed at which (im)mobilisation of metals takes place. This can result in the temporal domination of other binding mechanisms or the emission of metals from the sediment, even when SEM/AVS of less than one would suggest that the metals are immobile (Vink et al., 2010).

DOM also plays an important role in the binding of heavy metals, especially the humic and fulvic substances of DOM. A model that incorporated such organic matter specific binding is the Non Ideal Competitive Adsorption (NICA) - Donnan (electrostatic interaction) model (Koopal, 2005).

A third important factor is the iron chemistry (Zhang, 2012). When iron oxyhydroxides minerals in the soil are reduced in the presence of sulphide the mineral iron sulphide ( $\text{FeS}_{(s)}$ ) is formed and precipitates. The formed iron sulphide binds trace metals, lowering the pore water metal concentration. The binding of metals by an excess of sulphites is in short the principle behind the SEM/AVS ratio. However, the loss of iron oxyhydroxides minerals due to  $\text{Fe}^{3+}$  reduction also diminish the cation sorption capacity (Davranche, 2000; Weng, 2008) and therefore increases the trace metal pore water concentration.

Calcite also adsorbs trace metals, showing an initial rapid uptake of trace metals (adsorption) and slow uptake (precipitation) (Comans, 1987).

All these processes have kinetic restraints and often meta-stable reaction products (like the DOM-trace metals ligands).

Sediments and soils under fluctuating redox conditions therefore behave differently as predicted by equilibrium kinetics based risk models. There is relative little literature on soils and sediments with (seasonal) changes in redox potential.

(Salomons, 1985) looks at pore water concentrations of sulphate and iron during the early stage of diagenesis of dredged brackish sediments. (Salomons, 1985) uses large pits (80 (width) x 30 (length) x 6 m (depth)), but the site stayed submerged and therefore did not form a soil.

(Weng, 2001a) looks at a sandy soil profile, and combines a numerical multi surface model with observed pore water trace metals to look at long term (16 years) trends in the soil profile. (Weng, 2001a) shows the dominant (im)mobilisation processes of trace metals as function of soil properties and changes in soil mineralogy over time, but does not give insight in the role of reaction kinetics.

(Pan, 2015a; Pan, 2015b) looks at the mobilisation/immobilisation of trace metals in a flooding/drying cycle of paddy rice soil, using the Donnan membrane method (Weng, 2001b) to collect trace metals from the pore water. The timescale is 100 days with two periods of flooding and two periods of draining. The 5-10 days pore water sampling rate captured most kinetic influences reactions. Reproducing the observed concentrations with a numerical multi surface model leads to an over prediction of the trace metal concentration in the (sub)aerobic ( $\text{Eh} > -100 \text{ mV}$ ) zone.

This study makes use of a location where a 150 cm thick sediment layer is deposited on land. The initial sediment composition and the leachability of metals from the sediment is measured.

By using the metal speciation model CHARON (De Rooij, 1991) in combination with the groundwater model SFYNXZ (De Rooij, 1991) the initial sediment conditions are used to calculate the changes in metal availability in the newly formed soil as function of soil moisture content over a period of 10 years. CHARON stands for the Chemistry Applied to the Research Of Natural systems. CHARON is an extended and modified version of the chemical equilibrium model CHEMEEQ developed by the Rand Corporation (Shapley and Cutler, 1970) and is currently developed and maintained by Deltares. SFYNXZ is a 2D groundwater model based on MODFLOW (Harbaugh, 2005).

During this 10 year period the transition from sediment to soil over a depth of 150 cm is simulated by a yearly fluctuation of the groundwater level over a depth of 100 cm (from the top of the soil), with a minimum pore volume soil moisture content of 50% and a maximum of 100%. During the year cycle the degradation rate of soil Organic Matter (OM) is linked to the soil temperature and soil moisture saturation, resulting in seasonal fluctuating DOM concentrations and soil oxidation/reduction potential. The CHARON/SFYNXZ model simulates the pH, Eh, DOM and metal concentrations as function of soil depth (0 – 150 cm) and in time (0 – 10 years).

The CHARON/SFYNXZ model results are used to calculate the multi-substance Potentially Affected Fraction (msPAF) (Posthuma, 2002) with the OMEGA model (Hendriks and Van de Guchte, 1997).

The model PNEC-Pro (PNEC-Pro, 2016) is used to calculate the pore water specific predicted no-effect concentration for Cu, Ni, Zn, and Pb, based on BLM's.

## 5.2 Material and methods

### 5.2.1 Reference conditions; general sediment/soil parameters and groundwater balance

The reference conditions for sediment application as a soil is based on the STW project 'Lift up of Lowlands - Beneficial use of dredged sediments to reverse land subsidence' (Oliveira, 2017; Tollenaar, 2017). This study is based on the 'Lift up of Lowlands' soil properties, with the exception of the metal concentrations. For the metals the Dutch standard for reallocation of sediments on land without restrictions (Bruin, 1998) is used, including the corresponding standard soil organic matter (OM) and lutum content. The reason to use a risk standard concentration instead of the measured concentration is that the purpose of this study is to look into the impact of the water table variation over a longer period (10 years) on the trend in potential ecotoxicity of the

soil. Therefore a metal concentration is chosen which is deemed safe according to the Dutch soil/sediment risk standard. Table 1 compares the measured concentrations for the Lift up of Lowlands soil with the Dutch standard for reallocation of sediments on land without restrictions.

**Table 1** Measured metal concentrations 'Lift up of Lowlands' soil compared to Dutch standard for reallocation of sediments on land. This study uses the Dutch standard concentrations for metals.

	Lift up Lowlands measured	Dutch Standard reallocation on land	Lift up Lowlands compared to standard
Cd	1.1 mg/kg	4.0 mg/kg	28% pass
Cu	62.2 mg/kg	96 mg/kg	65% pass
Ni	29.0 mg/kg	50 mg/kg	58% pass
Pb	107.8 mg/kg	138 mg/kg	78% pass
Zn	217.3 mg/kg	563 mg/kg	39% pass
Cr	29.8 mg/kg	120 mg/kg	25% pass
As	12.7 mg/kg	14.5 mg/kg	88% pass

Based on the global Dutch soil conditions for Rhine sediments, the initial soil/sediment composition was derived from literature (Table 2). The porosity and bulk density is based on expert judgement on the ripening/consolidation during the of the sediment used for Lift up of Lowlands (the initial bulk density was less than 1.100 gram/dm<sup>3</sup> due to the hydraulic pumping of the sediment slurry). Organic Matter and clay content are in accordance with Dutch standard soil (Van Straalen, 1989). The calcium carbonate content is based on the calcium carbonate for the lutum fraction of Rhine sediment (Salomons, 1975). The total iron content is based on Haringvliet sediment, also Rhine sediment (Canavan, 2007). The initial distribution of iron between iron carbonate, iron sulphite and iron hydroxide minerals is chosen by the author (1/3: 1/3: 1/3). Trace metal concentrations are based on the classification of the Lift Up of Lowlands site as suitable for reallocation of sediments on land without restrictions (Bruin, 1998). All trace metals are assumed to be initially present as sulphide due to the anaerobic sediment conditions before placement on land. Non Ideal Competitive Adsorption (NICA) based on the Donnan potential is included in CHARON. The Nica-Donnan parameters were derived from (Milne, 2003).

**Table 2** Initial soil/sediment composition Lift up Lowlands soil with theoretical metal concentrations (on the left), translated to the FIAM model input (on the right)

Initial composition Lift up of Lowlands soil		->	FIAM model input
<i>soil general parameters</i>			
Organic Matter (OM)	10% (mass % d.s.)	-> OM	5000 (mol/m <sup>3</sup> )
Calciumcarbonate	4% (mass % d.s.)	-> CaCO <sub>3</sub> (s)	1500 (mol/m <sup>3</sup> )
Clay (< 2 µm) content	25% (mass % d.s.)		
Porosity	0.50 φ (= Vv/Vt)		
Bulk density	1500.00 kg/m <sup>3</sup>		
<i>(Trace) metals</i>			
Fe	1.9% (mass % d.s.)		
of which:			
(Fe(CO <sub>3</sub> )(s)	0.63% (mass % d.s.)	-> (Fe(CO <sub>3</sub> )(s)	170 (mol/m <sup>3</sup> )
FeS(s)	0.63% (mass % d.s.)	-> FeS(s)	170 (mol/m <sup>3</sup> )
Fe(OH) <sub>3</sub> (s)	0.63% (mass % d.s.)	-> Fe(OH) <sub>3</sub> (s)	170 (mol/m <sup>3</sup> )
Cd (as CdS(s))	4 (mg/kg)	-> CdS(s)	58 (mol/m <sup>3</sup> )
Cu (as CuS(s))	96 (mg/kg)	-> CuS(s)	2268 (mol/m <sup>3</sup> )
Ni (as NiS(s))	50 (mg/kg)	-> NiS(s)	1278 (mol/m <sup>3</sup> )
Pb (as PbS(s))	138.00% (mg/kg)	-> PbS(s)	999 (mol/m <sup>3</sup> )
Zn (as ZnS(s))	563.00% (mg/kg)	-> ZnS(s)	12913 (mol/m <sup>3</sup> )
Cr (as Cr(OH) <sub>3</sub> (s))	120.00% (mg/kg)	-> Cr(OH) <sub>3</sub> (s)	3461 (mol/m <sup>3</sup> )
As (as As(OH) <sub>3</sub> (s))	14.50% (mg/kg)	-> As(OH) <sub>3</sub> (s)	290 (mol/m <sup>3</sup> )
<i>Pore water (salinity within Dutch drinking water standards)</i>			
Na+	69 mg/l	-> Na+	3.0 (mol/m <sup>3</sup> )
Cl-	106.5 mg/l	-> Cl-	3.0 (mol/m <sup>3</sup> )
<i>Air</i>			
O <sub>2</sub>	21% partial pressure	-> O <sub>2</sub>	2.10E+06 (mol/m <sup>3</sup> )
CO <sub>2</sub>	0.30% partial pressure	-> CO <sub>2</sub>	330 (mol/m <sup>3</sup> )
<i>Model specific sorption parameters based on mineral composition</i>			
CEC	88 (meq/100 gram)	-> CEC	331 eq/m <sup>3</sup>
Fe sorption, only for (OH) <sub>3</sub> (s)	0.63% (mass % d.s.)	-> FEADS	170 (mol/m <sup>3</sup> )
OM sorption, 10% of total OM	1.0% (mass % d.s.)	-> OMSOR	500 (mol/m <sup>3</sup> )
<i>NICA-Donnan parameters (Milne, 2003)</i>			
		P(org1)	0.59 P1 fulvic acid
		P(org2)	0.7 P2 fulvic acid
		Qmax	0.02 number of sites (mol/m <sup>3</sup> )
		a charge	0.002 average bulk charge
		d charge	0.0001 Donnan phase charge

Assuming a minimal horizontal drainage, precipitation and evaporation dictate the yearly groundwater water balance. The results are summarized in Table 3. The Dutch average precipitation and evaporation for the Western Netherlands was used (Sluijter (2011). Rainwater also contains trace metals. Therefore, the average background concentration was added to the precipitation (Van Den Nguyen, 1990).

**Table 3** (Ground)water conditions

<b>(Ground)water conditions</b>		
<i>Precipitation and evaporation</i>		
yearly average precipitation	872 (mm/m2/year)	
yearly average evaporation	572 (mm/m2/year)	
netto groundwater recharge	300 (mm/m2/year)	
<i>Other groundwater parameters</i>		
Year average tempeature	16 (oC)	
Aerobic zone DOM production	30 (mg/l/year)	
Anaerobic zone DOM production	5 (mg/l/year)	
DOM degradation rate	0.0275(fraction per day (both aerobic/anaerobic))	
OM degradation rate	2% (per year)	
DOM retardation pore water	4 (factor)	
<i>Trace metal concentration</i>		
Cadmium	0.07 ( $\mu\text{g/l}$ )	61 ( $\mu\text{g/m}^2$ )
Copper	1.85 ( $\mu\text{g/l}$ )	1613 ( $\mu\text{g/m}^2$ )
Nickle	0.37 ( $\mu\text{g/l}$ )	323 ( $\mu\text{g/m}^2$ )
Lead	2.57 ( $\mu\text{g/l}$ )	2241 ( $\mu\text{g/m}^2$ )
Zinc	8.32 ( $\mu\text{g/l}$ )	7255 ( $\mu\text{g/m}^2$ )
Chroom	0.19 ( $\mu\text{g/l}$ )	166 ( $\mu\text{g/m}^2$ )
Arsenic	0.14 ( $\mu\text{g/l}$ )	122 ( $\mu\text{g/m}^2$ )

The groundwater level was modelled with a 1DV transport model (SFYNXZ) (De Rooij, 1991). The soil was divided in 15 vertical layers of 10 cm (1.5 meter in total). When evaporation exceeds precipitation, air enters into the unsaturated pores. To mimic the heterogeneity of contact with air in soils when the groundwater level drops, the penetration of air is simulated as being in contact with an unsaturated (oxidised) 1DV soil layer. The model also has a saturated 1DV soil layer. Transport between the saturated and unsaturated layers is by molecular diffusion (with a diffusion distance of 1 cm). This way the soil maintains a time dependant reduced fraction, even when unsaturated.

### 5.2.2 FIAM model CHARON, including the NICA-Donnan phase, for trace metals

The FIAM model CHARON (De Rooij, 1991) is used to calculate the free metal ion concentration in the presence of a NICA-Donnan phase (Kinniburgh, 1996). The metals Cd, Cu, Ni, Cr and Zn and As (a metalloid) are selected for the CHARON model. These metals are often present in soils in concentrations above soil standards and can have an anthropogenic origin. Some of these metals (cadmium and nickel) are also a Water Framework Directive (EU COM, 2000) priority substance. The impact

of DOM on the binding of metals in the presence of a NICA-Donnan phase, and hence the formation of metal-organic ligands, is described by (Hiemstra, 2006). Metal complexation constants for a large series of elements have been derived from experimental data published by (Milne, 2003). The FIAM model CHARON also calculates the anaerobic and aerobic formation and degradation rate of DOM based on the soil OM content. Hence, the amount of metal-organic ligand formation (NICA-Donnan phase) is depending on the position in the soil profile and the time of year.

### 5.2.3 BLM model PNEC-PRO

PNEC-pro has been implemented in legal frameworks for EQS-compliance testing and WFD-reporting (Verschoor, 2010). PNEC-pro calculates local, water type specific, predicted no-effect concentrations (PNEC) of Cu, Ni, Zn, and Pb based on BioLigand Models (BLMs) (Verschoor, 2011). Local PNECs are used for compliance checks in higher-tier risk assessments (Rüdel et al., 2015). PNEC-pro (Verschoor, 2012) calculates a Risk Characterization Ratio (RCR) for each metal. The RCR divides the PNEC calculated exposure levels for the measured dissolved metal concentration by the predicted no-effect concentrations based on the local water quality (Muñoz et al., 2009).

### 5.2.4 MsPAF model OMEGA

The concept of calculating the Potentially Affected Fraction (PAF) is based on the observed median lethal concentration [ $LC_{50}$ ] or no-observed-effect concentration [NOEC] for individual components and individual species (single contaminant Species Sensitivity Distribution (SSD)). The potential toxic risk for multiple substances is then calculated using the distribution of the  $LC_{50}$  or NOEC values (Posthuma et al., 2002) following the methodologies as proposed by (De Zwart and Posthuma, 2005):

- (i) Response Addition (RA), or
- (ii) Concentration Addition (CA).

The resulting multi substances Potentially Affected Fraction (msPAF) gives the fraction of the population that is potentially at risk. The characterisation of risk can be by an increase in mortality, degraded reproduction rates or growth deformation (Posthuma, 2002). The definition of risk can be either acute or chronic, depending on the duration of the exposure. Ecotoxicity tests are therefore divided in acute or chronic exposure (Stephen, 1985).

The numerical model 'Optimal Modeling for Ecotoxicological Assessment' (OMEGA) incorporates these methodologies to calculate the ecotoxicological risk for

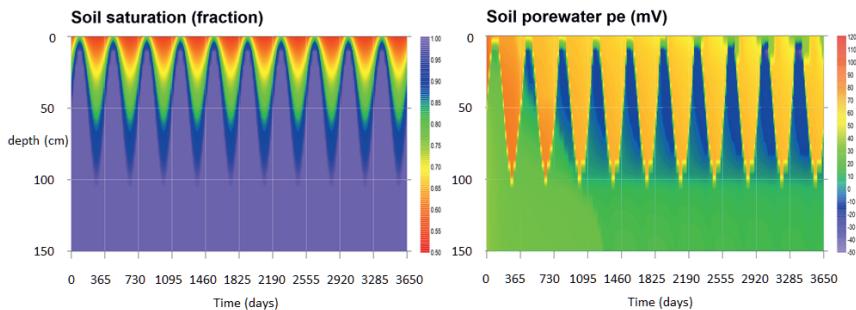
multiple contaminants (Hendriks and Van de Guchte, 1997). The model used the ecotoxicological data for approximately 200 substances (Bruin de, 1998). The data is derived by establishing dose effect relations for a toxicant under standard water conditions defined by DSW (Aldenberg, 2001).

In addition to the metals used for the BLM model PNEC-Pro, cadmium and arsenic were also included. The msPAF was calculated for acute toxicity (less than 24 hours exposure). Response Addition (RA) was used for the metals, concentration addition for the metalloid arsenic.

## 5.3 Results

### 5.3.1 General sediment/soil parameters, model results

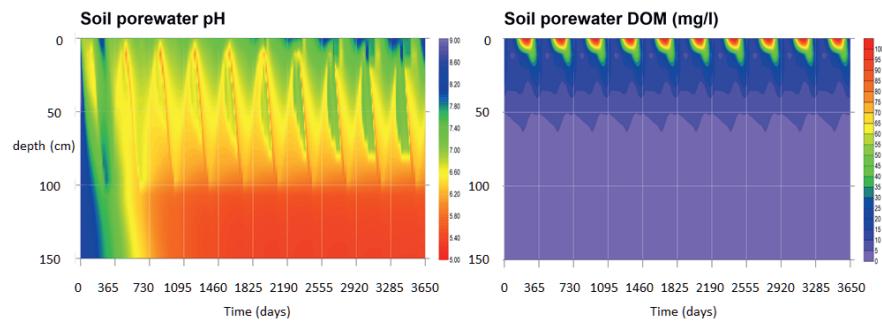
The groundwater level variation is 100 cm. The minimum saturated groundwater level is at 100 cm below surface level. The maximum groundwater level is at 10 cm below the surface level. In Figure 1 the soil profile saturation level (as % of the pore volume) and the soil profile redox potential (mV) is given over a period of 10 years after the sediment has been put on land, illustrating the impact of the groundwater level variation.



**Figure 1** Soil pe during a period of 3650 days (10 year cycles). Time (in days) on the x-axis, the soil depth (in cm) on the y-axis. The redox potential pe (mV) varied between -50 mV and +120 mV. Values >0 mV represent a soil with an unsaturated zone, values <0 mV are representative for a saturated soil.

A dry period (summer) is characterized by a drop in the groundwater level and a rise in the redox potential (above 0 mV, indicating oxidizing conditions). During a wet period the groundwater level rises and the pe declines. Due to the degradation of DOM produces during the summer period (see paragraph 3.1.2.) the pe drops to slightly lower values during multiple year cycles.

The pH and the production and degradation of DOM depends on the saturation level and the correlated aerobic/anaerobic conditions within the soil profile (see the pe fluctuation in Figure 1). Figure 2 shows the calculated pH and DOM concentration over a period of 10 years.



**Figure 2** Soil pH and DOM concentration during a period of 3650 days (10 year cycles). Time (in days) on the x-axis, the soil depth (in cm) on the y-axis. The DOM concentration varied between 110 mg/l during summer in the upper 10 cm of the profile, to <5 mg/l for the intermediate (>50 cm) and deeper (>100 cm) part of the soil profile during the whole year.

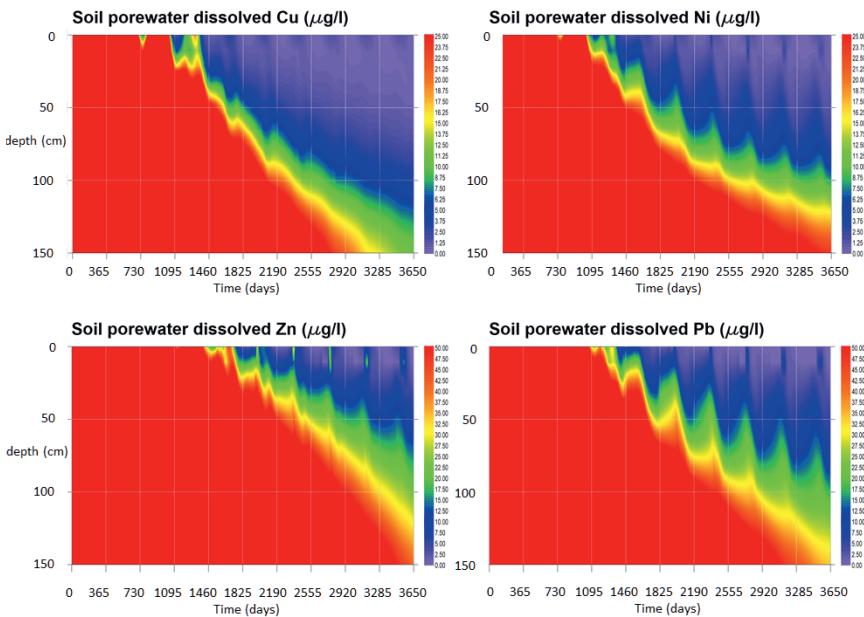
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In the top 100cm of the soil profile, the pH drops to 6.0 during dry period (summer) and rises to 7.6 during the wet period (winter). In the deeper part of the soil profile (>100 cm) the pH varies between 5.3 and 6.1.

The DOM production is highest during the dry period (summer), especially in the top 10 cm of the soil profile. The DOM concentration varies between less than 5 mg/l in the deeper parts of the soil profile (>100 cm), up to 110 mg/l in the top 10 cm of the soil profile during a dry period (summer).

### 5.3.2 FIAM model CHARON, dissolved trace metals in the groundwater during multiple year cycles

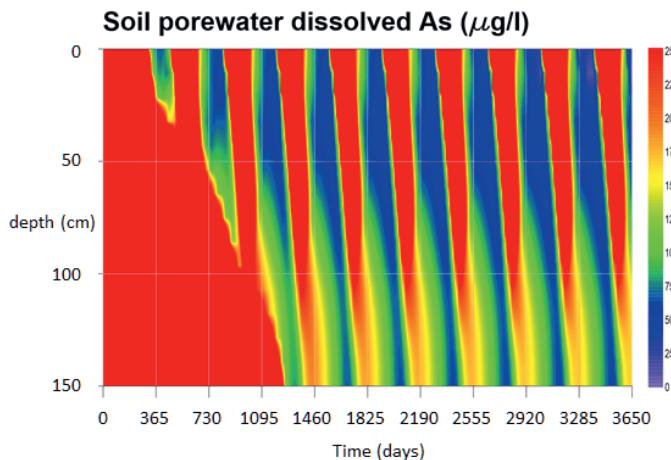
The soil pore water profile for Cu, Ni, Zn, and Pb (the four PNEC-pro metals) over a period of 10 years is given in Figure 3.



**Figure 3** Soil pore water concentration for copper, nickel, zinc and lead during a period of 3650 days (10 year cycles). Time (in days) on the x-axis, the soil depth (in cm) on the y-axis.

All four metals (Cu, Ni, Zn and Pb) follow the same pattern. The first 3-5 years after putting the sediment on land, the concentrations are high over in the whole soil profile, declining after 3-5 years in the top 100 cm of the soil. During dry periods (summer), the concentrations spike, but to a far lesser extent than during the first 3-5 years.

To illustrate that not all metal like elements follow this pattern, the concentration of arsenic (a metalloid) over 10 years is given in Figure 4.



**Figure 4** Soil pore water concentration for arsenic during a period of 3650 days (10 year cycles). Time (in days) on the x-axis, the soil depth (in cm) on the y-axis.

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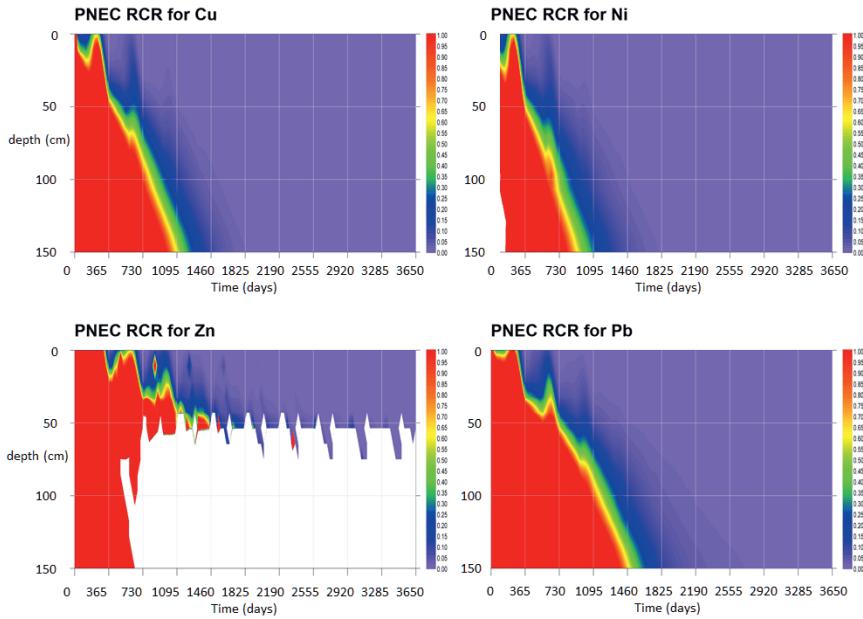
During dry periods (summer) arsenic is mobilized in the unsaturated top part of the soil profile. When the groundwater level rises (during autumn), arsenic is transported to the lower part of the soil profile, where it is bound (mainly to the iron oxides and soil OM). The high arsenic mobility in the summer is mainly due to the DOM production in the top soil layer (upper 10 cm). As-DOM ligands make up for 50% of the dissolved arsenic concentration.

### 5.3.3 BLM model PNEC-PRO in the groundwater during multiple year cycles, model results

The BLM model PNEC-pro uses the local water quality parameters DOM, Ca<sup>2+</sup>, Mg<sup>2+</sup> and Na<sup>+</sup> to calculate the predicted no-effect concentrations (PNEC) for each of the four metals. In the chosen soil schematisation Mg<sup>2+</sup> was not taken into account since calcite and not dolomite is the dominant buffering mineral for the reference location (Lift up of Lowlands). Na<sup>+</sup> was modelled, but not reacting. The Na<sup>+</sup> concentration is constant and defined by the boundary input (rainwater). Mg<sup>2+</sup> and Na<sup>+</sup> are therefore chosen as a constant based on the closest rainwater station (RIVM station 444) (Boschloo, 1999).

$$\begin{aligned} \text{Mg}^{2+} &= 22 \mu\text{mol/l} = 0.53 \text{ mg/l} \\ \text{Na}^+ &= 188 \mu\text{mol/l} = 4.3 \text{ mg/l} \end{aligned}$$

Figure 5 shows the calculated PNEC RCR's up to 1.0 as function of soil profile depth over a period of 10 years on a monthly base.

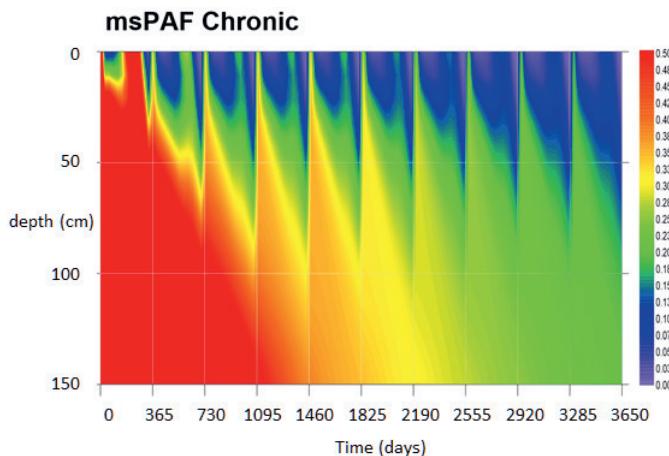


**Figure 5** PNEC RCR's up to 1.0 in the soil pore water for copper, nickel, zinc and lead during a period of 3650 days (10 year cycles). Time (in days) on the x-axis, the soil depth (in cm) on the y-axis. If the PNEC could not be calculated due to the models out of boundary conditions, the graph is white.

The initial (first year) RCR for all four metals is high in the lower part of the soil profile. Due to an increase in pH and the DOM concentration in the top 50 cm of the soil profile, the RCR rapidly (within a year) drops to values below one (below the NOEC concentration).

### 5.3.4 MsPAF model OMEGA in the groundwater during multiple year cycles

The msPAF results indicate how many of the organisms are at risk of experiencing an observable toxicological impact due to the presence of a mixture of metals. The calculations have been carried out for the following contaminants in the soil pore water; arsenic, cadmium, copper, nickel, zinc and lead. The resulting calculated chronic msPAF is given in Figure 6 during a period of 10 years.



**Figure 6** Chronic msPAF (as fraction) in the soil pore water during a period of 3650 days (10 year cycles). Time (in days) on the x-axis, the soil depth (in cm) on the y-axis.

## 5.4 Discussion

While the FIAM model geochemical soil and pore water constants are calibrated for steady state sediments with a similar composition (Wijdeveld, 2018) it is difficult to validate a FIAM model under dynamic conditions. This is especially the case in the presence of an unsaturated zone with a high DOM production rate, and hence a potential large influence of the NICA phase. This study has been done in collaboration with Wageningen University & Research (WUR), The Netherlands, as part of the NWO program 'Lift up of Lowlands' providing the generic NICA-Donnan model parameters (Milne, 2003). More detailed studies on the relation between measured DOM concentration levels and the speciation of dissolved metals in soils with alternating flooding and drainage were carried out by the WUR (Pan, 2015a; Pan, 2015b). The main drawback of these studies in relation to this study is that the soil composition was fundamentally different, and the period of flooding and drainage is shorter (two cycles in 128 days) as compared to the year cycle simulated here. The soil with the best matching properties is the FY soil (from the vicinity of Fuyang City, China) since this soil has clay (25%), organic matter (9.2%) and calcite (21%), resulting in a pH of 7.5 and a DOC content of 189 mg C per litre (equivalent of 473 mg/l DOM). The modelled Lift up of Lowlands soil has more or less similar properties (see Table 2), although a slightly lower organic matter content. The DOC/DOM content is not measured for the Lift up of Lowlands soil, but similar peatlands in Northeastern Germany show DOC release ranged from 4 to 123 mg/l (10 to 308 mg/l DOM). The degree of decomposition

and pH were found to be the major driving factors for DOC release, with the highest DOC concentrations in the most degraded part of the peat (Schwalm, 2015).

We are not aware of more recent similar work on alternating flooded/wetted soils, measuring changes in redox conditions, pH, DOM and dissolved metals in correlation with FIAM modelling which includes the formation of DOM-metal ligands considering non ideal competitive adsorption (NICA) conditions. Earlier work (Jung, 1997) looks at seasonal variation of metals in soils during flooding and drainage, but lacks a predictive modelling element. Du Laing ( 2009) presents a review on processes influencing the change in trace metal behaviour in floodplains, including the influence of kinetic restraints on redox-sensitive processes. We take these processes and kinetic restraints into account in the FIAM model. For the soil composition and direct comparison with measurements we compare our results with the FY soil measurements by (Pan, 2015b).

#### 5.4.1 General soil parameters

The observed seasonal trend that the top soil Eh increases and pH decreases with a lower water table in the summer is observed in flood plains (Du Laing, 2009), seasonal flooded peatlands (Schwalm, 2015) and rice paddies. (Jung, 1997). An increase in DOM concentrations in the top 10 cm of peat soil during summer was also observed by (Clark, 2005). In years with a significant drop in the water table, the pH in the top soil also dropped due to the oxidation of organic/organic sulphur stored in the peat (measured by an increase in the sulphate release). These processes are also present in the FIAM model (sulphate concentrations are not presented in this paper), and the modelled trends for Eh, pH and DOM follow the trends described in literature. Table 4 gives an overview of the measured general soil parameters for the FY soil (Pan, 2015b) versus the outcome of the FIAM calculations for the currently studied Lift op of Lowlands soil.

**Table 4** General soil parameters, measurements (Pan, 2015b) versus FIAM model results

Soil parameter	FY soil (measured)	Lift up of Lowland soil (calculated)
Eh min -max	-250 mV - +400 mV	-50 mV - +120 mV
pH min-max	7.2 - 8.1	6.0 - 7.6 (top 100 cm)
DOM min – max	? - 473 mg/l	5 – 110 mg/l

The trends in Eh, pH and DOM as function of the soil oxidation state (flooded/drained) follow a similar pattern.

### 5.4.2 Dissolved trace metals

A direct comparison with the FY soil (Pan, 2015b) (Table 5) shows that the Lift up of Lowland soil is in general less contaminated with trace metals, with the exception of zinc and lead.

**Table 5** Trace metal pore water concentrations, measurements (Pan, 2015b) versus FIAM model results

Soil parameter	FY soil pore water (measured) ( $\mu\text{mol/l}$ )	Lift up of Lowland soil pore water (calculated) ( $\mu\text{mol/l}$ )
Cadmium	0.0 - 0.18	0.00 - 0.05
Copper	0.0 - 4.1	0.00 - 2.09
Nickel	0.2 - 3.1	0.00 - 1.17
Zink	0.0 - 5.1	0.00 - 13.07
Lead	0.0000 - 0.008	0.00 - 1.01
Arsenic	--	0.00 - 0.59

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More important than the absolute pore water trace metal concentrations are the seasonal trends as function of soil saturation. The FY soil spikes when flooded for the first time (which is the reverse from the Lift up Lowlands soil, which is saturated at the start and drains when applied as a land soil). What is similar on both the FY soil and the Lift up of Lowlands soil is that at low water level (drained state) the pore trace metal concentration normally rises. The exception is that in the last test period for the FY soil (85 to 100 days, drained state) some trace metals seem to be depleted. The Lift up of Lowlands soil shows a similar trend over the years, but needs more time to reach a lower pore water trace metal concentration. The lower DOM concentrations in the Lift up Lowlands soil, and hence a lower leaching of DOM bound trace metals during flooding/saturation might be part of the reason for the difference in timescale. Due to the difference in test time scale (the FY soil experiment lasted 120 days in total, with two flooded and two drained periods), it is difficult to compare the multi cycle trends. The kinetic processes as described by ((Du Laing, 2009) better fit with the timescale of this paper (a decade) as compared to the 128 days for the FY soil.

Looking at multiple year cycles, the initial high dissolved trace metal concentrations in the top soil (upper 50 cm) drop after one to three year (depending on the trace metal). There is some seasonal variation, also due to the continuous yearly DOM production/degradation cycle with strong DOM-metal ligand formation in the dry summer period (high DOM concentrations in the top soil), declining during the wet winter period. The drop in trace metal concentrations is due to leaching of the pore

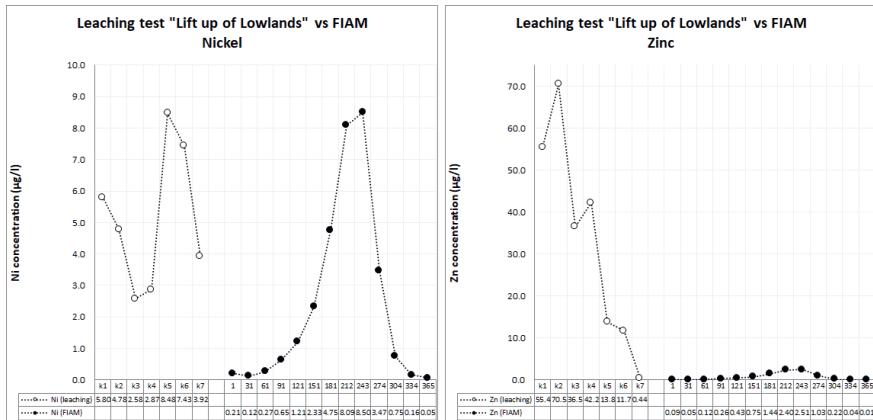
water (flushing out the freely dissolved metals and DOM bound metals), and fixation of trace metals over time of newly formed iron oxides with a high sorption capacity in the top soil. Arsenic is the exception due to continuous changes in the iron sulphide/iron oxide minerals, influencing the release of arsenic.

While there are differences in absolute values for the FY soil (measurements) as compared to the c soil (calculations), the similarities in trends when flooding/draining (FY soil) or wetting/drying (Lift up of Lowlands soil) for both the general soil parameters as also for the trace metal concentrations is striking. The FIAM model is able to reproduce the impact of the dominant soil processes on the main soil parameters and trace metals when a soil is seasonally varying in groundwater level. However, without pore water samples there are no guarantees that the calculated values are 100% representative for real field conditions.

#### **5.4.3 Comparison FIAM model results with leaching experiments**

The 'Lift up of Lowlands' program is part of the EU INTERREG project CEAMaS (2012-2015). The CEAMaS projects focussed on the use of sediments, including the use of sediments for the formation of land soils. Five EU sediment quality guidelines were used for this evaluation (French, Irish, Flemish, Dutch and German). Two of these five sediment standards (the Dutch and Flemish) include a leaching test for metals according to NEN 7373 (2004). While the methodology of a leaching test is different from a natural dry/wetting cycle, the leaching test gives an indication if metals become mobile when the soil is saturated and flushed with oxygen containing water. The NEN 7373 leaching test for the 'Lift up of Lowlands' sample was performed by Deltares. Figure 7 illustrates the results of the leaching tests during seven leaching steps. Each steps represents an increased Liquid/Solid ratio (L/S) ratio between sediment/soil and the added water, up to a 10/1 ratio. The leaching results are compared with the FIAM results for year with a monthly interval. Figure 7 only plots the results for nickel and zinc since the other metals like copper and lead were below the limit of detection (LOD).

The soil sample for the Lift up of Lowlands' leaching test was taken roughly one year after the deposition of the sediment, therefore FIAM calculation for year two is chosen as reference.



**Figure 7** Left figure, the measured nickel eluate and FIAM model concentrations in µg/l (y-axis) versus the eluate fraction (k1 – k7) / time period in year two (days). Right figure, the results for zinc.

When comparing the concentration range, the nickel concentration of the leaching test eluate is in the same range as the FIAM model results in the top 10 cm of the soil during the simulated year cycle (0 – 9 µg/l). However, the measured zinc concentration in the eluate is much higher (range 0 – 70 µg/l) compared to the FIAM model results (0 – 2.5 µg/l). The high zinc concentrations in the eluate samples dilutes over time, dwindling to almost zero for fraction k7. This indicates that the zinc contamination in the leaching experiment might be the result of a flushing of a soil adsorbed zinc fraction instead of the result of an ongoing oxidation and therefore continuous mobilisation.

While there are similarities between the NEN 7373 leaching test and the FIAM model simulated natural year cycle when it comes to introducing oxygen into the soil, the FIAM results in Figure 7 illustrate that there are more processes in natural soils that influence the mobility and leachability of metals. Therefore the NEN 7373 leaching test results are not suitable to validate the FIAM model. The reverse can also be said; the NEN 7373 leaching test are not suitable to evaluate the use of sediments for the formation of soils.

#### 5.4.4 Sensitivity analyses FIAM model

The FIAM model has a great number of parameters that are soil and situation specific, and therefore uncertain. When grouped, the main uncertainties are:

- The equilibrium thermodynamic constants (including the sorption to OM and soil minerals like clays) for redox sensitive elements like metals
- The kinetic exchange rates when changes occur
- The complexation of metals, including the complexation with DOM
- The formation and degradation of DOM
- The water content in different parts of the unsaturated soil profile

This study is therefore does not represent 'the' truth for the impact of wetting/drying on a freshly formed soil like the former sediments used for the 'Lift up of lowlands' project. The FIAM model calculations illustrate the dynamics and timescale of change in pore water concentrations caused by multiple wetting/drying cycles over multiple years.

For the sensitivity analyses, the FIAM model parameters (thermodynamic constants, kinetic rates, DOM production and degradation rates) were kept constant. The focus is on the impact of a period of dry (100 mm per year less rainfall, 100 mm per year more evaporation) and wet (100 mm per year more rainfall, 100 mm per year less evaporation) years on the dynamics of the metals pore water concentration (see Table 6).

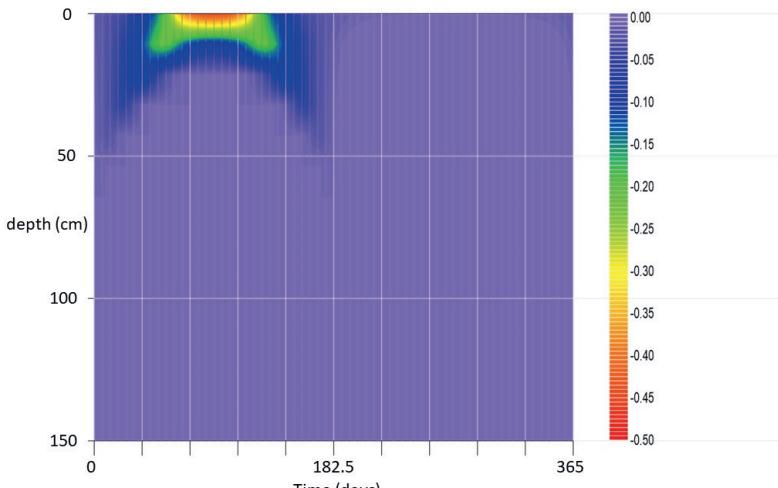
**Table 6** Reference rainfall and evaporation as compared to a period of wet and dry years

	Reference	Dry year	Wet year
Rainfall (mm/year)	872	772	972
Evaporation (mm/year)	572	672	472

The difference between a wet and dry year is most relevant during the spring period (with a relative high water level, see Figure 1), where the water level is lower in the upper 20 cm of the soil (see Figure 8).

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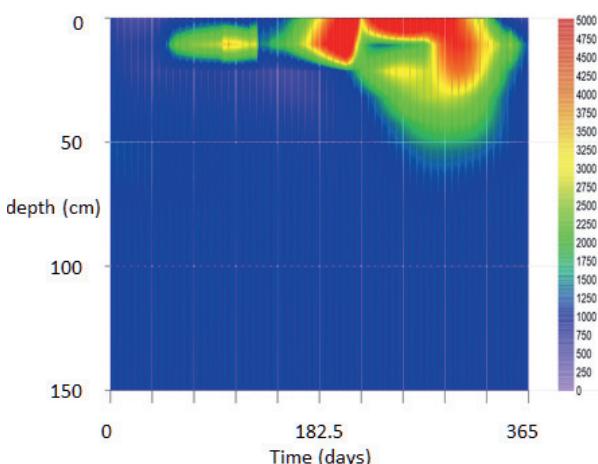
### Difference in soil saturation, dry versus wet year



**Figure 8** Difference in soil moisture content as fraction in a dry versus a wet year during a period of 365 days. Time (in days) on the x-axis, the soil depth (in cm) on the y-axis.

The impact of a dry year is most sever in the summer, when the upper 20 cm of the soil is almost completely dried out, as is shown in Figure 9 for cadmium.

### Difference in dissolved Cd concentration, dry versus wet year



**Figure 9** Difference in dissolved cadmium content (fraction) in a dry versus a wet year during a period of 365 days. Time (in days) on the x-axis, the soil depth (in cm) on the y-axis.

The high concentration factor increase for cadmium (factor 10.000) is due to the drop in the groundwater level in late winter/early spring (see Figure 8), causing an earlier oxygen penetration in the top soil (+/- upper 20 cm), and hence longer period of oxidation of the metal sulphides. The oxidation of sulphides releases cadmium (and other trace metals) to the pore water. The early oxygen penetration also enhances the OM degradation, causing a higher DOM production and higher DOM concentrations in the pore water, as is shown by (Pan, 2015b) for the drainage stage of rice paddy soils. The DOM forms a metal-ligand complex, enhancing the solubility of the trace metals. Evaporation of the pore water in the top soil during the summer and lasting until late autumn (around 180 to 330 days) causes the concentration levels of dissolved cadmium to further increase. In the autumn/winter there is a net water surplus (more rain than evaporation), transporting the dissolved cadmium deeper into the soil profile (+/- 50 cm). At this depth the redox potential is low, the cadmium immobilized as cadmium sulphide (solid).

While the FIAM model might overpredict the summer concentrations for metals like cadmium in the top soil under long term dry conditions, the effect of an enhanced oxidation on an increase of dissolved trace metals in sediments is something which is also observed in natural systems (Förstner, 2006). Studies on the impact of the duration of the drainage stage (with soil oxidation) of paddy soils on cadmium solubility also shown an increased dissolved cadmium concentration with longer drainage periods (De Livera, 2011).

#### **5.4.5 BLM model, PNEC levels**

The trend in dissolved metal concentrations with depth over time is mimicked by the PNEC. After the first year(s) (depending on the trace metal) the PNEC does not rise above 1.0 in the top 50 cm of the soil profile. Based on the individual trace metal concentrations and the water quality conditions in the top 50 cm of the soil, the trace metals are therefore no longer considered a biological risk based according to the BLM model.

For zinc the conditions to calculate the PNEC were outside the PNEC-Pro calibrated boundary conditions for the deeper part (>50 cm) of the soil after the first year. This is mainly due to the pH, which drops below 6.0.

Since the Lift up of Lowlands soil is considered an uncontaminated (class A) soil, the PNEC levels should not exceed 1.0. The fact that the PNEC exceeds 1.0 in the top 50 cm of the soil during the first year(s), and longer form the deeper parts of the soil, illustrates that the transition from sediment to soil introduces a temporal exposure risk. This temporal risk is further explored with the msPAF model.

### 5.4.6 MsPAF

For use of sediments on land, the guiding principle in the Netherlands is that the chronic msPAF for metals should not exceed 50% (Van Noort, 2006; Posthuma, 2006). The chronic msPAF for metals in this study is based on the calculated pore water concentrations for cadmium, copper, nickel, zinc, lead and arsenic. Figure 6 illustrates that the 50% value is exceeded in the complete soil profile during the first year. The chronic msPAF level for metals drops after the first year in the top (upper 50 cm) of the soil during the dry period (summer), shortly spiking in the top soil to values of 42% during the start of the wet period (autumn to winter).

An earlier study on the impact of putting sediments on land (Harmsen, 2012) shows a chronic msPAF value close to 50% (Harmsen, 2012). (Harmsen, 2012) used the total sediment metal concentrations instead of pore water concentrations. The msPAF calculations were based on equilibrium partitioning, not taking into account the seasonal trends in pore water chemistry. In this study we show that the msPAF in the transition phase of sediment to soil can be improved when taking into account the variation in local pore water quality parameters like DOM and pH. The correction of dissolved metal concentrations based on water quality parameters is the base for the BLM concept (see paragraph 4.3).

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The variation in groundwater level not only influences the pore water quality parameters and therefore the BLM PNEC, but also influences the total dissolved pore water metal concentration. The total dissolved concentration is used for the msPAF calculation. While the spatial pattern over soil depth and time for the individual metals according to BLM PNEC calculation (Figure 5) and the combined metals chronic msPAF calculation (Figure 6) is somewhat different, the trend that the potential ecotoxicological impact decreases over multiple dry-wet year cycles is the same. This is especially the case in the top 50 cm of the soil, where the msPAF does not exceed the 50% threshold after the second year. The reason why the msPAF shows a strong repeating short spike in the top 50 cm of the soil over the years is due to the incorporation of the arsenic pore water concentrations (see Figure 4) in the msPAF calculation.

## 5.5 Conclusion

Putting sediments on land to form a new soil is a geochemical dynamic process. Taking a location where a layer of 200 cm of sediment (before consolidation) was put on land (Lift up of Lowlands) and simulating the development of this newly formed

soil over a 10 year period shows that, especially during the first few years, the soil is changing in ecotoxicity. This change is most profound in the top 50 cm of the soil, where there is an unsaturated zone for more than 50% of the year. During the sediment to soil transition time the metals pore water concentrations spike, the BLM RCR values for the metals exceed 1.0 and the chronic msPAF for metals is over 50%. This enhanced ecotoxicological effect is somewhat tempered during wet years, but enhanced during dry years.

The duration of the transition time varies somewhat based on the chosen evaluation criterium (being the dissolved metal concentration, the BLM RCR or the msPAF), but all criteria congregate that uptake risk in the upper 50 cm of the soil has dropped to acceptable levels after 3 years. Legislation on sediment use on land should take this transition time into account, adapting the land use during this period of 3 years on the potential higher exposure for crops and cattle in the top 50 cm of the soil.

## Acknowledgements

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# 6

## Scientific progress in sediment and water quality assessment

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Chapter six describes the trends in scientific progress over the past 25 years (see Chapter 2) in relation to the risk assessment of sediments and water quality from a legislation point of view in the Netherlands.

## Introduction

In this Chapter the period between 1993 and 2018 is described in four episodes

- The first period (1993 – 2000) is characterised by the development of a national integral water management framework.
- The second period (2000 – 2008) covers the introduction of the EU Water Framework Directive.
- The third period (2008 – 2018) is triggered by the thread of a large scale flooding in 1995, leading to the ‘Room for the River’ project and a new Soil Directive.
- The final period (2018 - ...) looks at sediments as part of a circular economy resource.

## 6.1 Water and Sediment standards, the period 1993 - 2000

### 6.1.1 Water and sediment standards in the Netherlands

In 1993 the sediment guideline 'Beleidsstandpunt Verwijdering Baggerspecie' (BVB, 1993) is published. This policy document on sediment quality standards results from the first integral cross sectoral environmental ambition plan 'Nationaal MilieubeleidsPlan' (NMP, 1988). Since water and sediment quality are correlated by the equilibrium partition (Chapter 2.3 – Equation 1 and 2) there is a link with the water quality standards ,as defined by the 'Derde Nota Waterhuishouding' (DNW, 1988), and the sediment quality standards (BVB, 1993). This link is maintained in the 'Vierde Nota Waterhuishouding'(NW4, 1998).

Equilibrium partitioning is based on the soil parameters organic matter and clay content (Chapter 2.3 – Equation 3). By normalizing against a reference soil with 10% organic matter and 25% clay, a soil type independent national Dutch sediment standards could be derived. These standards were published in 'Integrale Normstelling Stoffen – Milieukwaliteitsnormen bodem, water, lucht' (INS, 1997).

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### 6.1.2 Correlation between water and sediment standards

The equilibrium partition coefficient for metals and organic contaminants in soil and sediments (Chapter 2.3 – Equation 1 and 2) and the standard soil correction constants (Chapter 2.3 – Equation 3) are given under Supportive information – Paragraph 1 Table 1 (equilibrium partition coefficient) and Table 2 (standard soil constants). The (BVB, 1993) sediment standards are given under Supportive information – Paragraph 1 Table 3.

An often used reference is the 'streefwaarde' (target value). (BVB, 1993) publishes the target values in groundwater for metals and organic contaminants. The soil standards in (BVB, 1993) also have a target value (the class 0 - 1 boundary). When the equilibrium partitioning coefficients as published in (INS, 1997) and the soil target values (BVB, 1993) are used the groundwater target value can be calculated. When comparing the (BVB, 1993) target values for groundwater with the calculated (BVB, 1993; INS, 1997) target values there are discrepancy's (Table 1).

**Table 1** (BVB, 1993) target values for groundwater compared calculated target values for groundwater

Contaminant	Target values in Groundwater (BVB, 1993)	Calculated target values in groundwater (BVB, 1993; INS, 1997)	Difference between the calculated versus (BVB, 1993) groundwater concentration
<b>Metals</b>	( $\mu\text{g/l}$ )	( $\mu\text{g/l}$ )	
Sb	10		
As	10	2.9	-71%
Ba			
Cd	0.4	0.006	-98%
Cr	1.0	0.34	-66%
Co	20		
Cu	15	0.72	-95%
Hg	0.05	0.0018	-96%
Pb	15	0.013	-100%
Mo	5		
Ni	15	4.375	-71%
Se			
Sn	10		
V			
Zn	65	1.3	-98%
Contaminant	Target values in Groundwater (BVB, 1993)	Calculated target values in groundwater (BVB, 1993; INS, 1997)	Difference between the calculated versus (BVB, 1993) groundwater concentration
<b>PAH's</b>	( $\mu\text{g/l}$ )	( $\mu\text{g/l}$ )	
naftalene	0.1	0.064	-36%
antracene	0.02	0.014	-32%
fenantrene	0.02	0.015	-26%
fluoranthene	0.005	0.001	-82%
benzo(a)anthracene	0.002	0.00028	-86%
chryseen	0.002	0.00032	-84%
benzo(k)fluoranthene	0.001	0.00021	-79%
benzo(a)pyrene	0.001	0.00023	-77%
benzo(ghi)perylene	0.002	0.00004	-98%
indenopyrene	0.0004	0.00008	-79%

In general the calculated target values for groundwater based on the sediment/soil target value and the equilibrium partitioning are lower than the target values for groundwater. This means that the sediment standards are over protective, or that

equilibrium partitioning coefficients between sediment and water is in general too high, underpredicting the groundwater concentration. Another reason is the implicit incorporation of background concentrations in groundwater within the target values, hence the sediment contribution to the groundwater has to be less (INS, 1997).

### **6.1.3 An International perspective on standard soil normalisation**

Normalisation of contaminant concentrations in sediments in the timeframe of 1993 – 2000 is also suggested outside the Netherlands. The element mostly used for sediment normalization is aluminium (Al) since it represents aluminosilicates, the main group of minerals generally found in the fine sediment fractions. Al is supposed to have a negligible anthropogenic input and behave conservatively. Therefore, Al can be used to normalize for grain-size and for mineralogical variability (Din, 1992; Covelli and Fontolan, 1997). An alternative to Al is the use of Lithium (Li) for the normalization of the metal data from sediments derived mainly from glacial erosion of crystalline rocks (Loring, 1991). The United Nations Environmental Programme (UNEP, 1995) also suggest the use of Al and Li (paragraph 15.4 – Normalisation Procedures). Although normalisation on Al and Li has been used in many studies for marine sediments (Herut, 2006) the interaction of metals with organic matter is missing and normalization is site specific due to different background levels in Al and Li.

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The impact of standard soil normalisation in an international context is shown based on the sediment samples analyses for the EU INTERREG project CEAMaS (2012-2015). Table 1 in 'Supportive Information – 6. Chapter 6' gives the uncorrected and standard soil normalized sediment concentrations for metals (based on the standard soil correction parameters for organic matter and lutum as shown in 'Supportive Information – 2. Chapter 2'). Table 4 in 'Supportive Information – 6. Chapter 6' gives the national sediment standards for Ireland, Flanders, France, Germany and The Netherlands. Normally only the Dutch standard soil normalisation.

The impact of standard soil normalisation on the use of five sediment according to the legislation of five different countries is shown in Table 3. Table 2 gives the lutum and organic matter content for each of the five sediment examples needed for the standard soil normalisation. If a sediment does not meet one or more of the metal concentrations levels, the sediment is not applicable for sediment use (one out - all out). Meeting the tier 1 level means an unrestricted use of the sediment. Sediment use between tier 1 and tier2 is often allowed with restrictions. Not meeting tier 2 means the sediment is considered a waste.

**Table 2** Lutum and organic matter content in percentage dry weight for five sediments (example 1 – 5)

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 1	Example 2	Example 3	Example 4	Example 5
lutum (<2 µm) % dry weight	7.0	1.8	1.0	7.1	5.3	7.0	1.8	1.0	7.1	5.3
organic matter % dry weight	22.4	11.5	55.6	16.1	12.6	22.4	11.5	55.6	16.1	12.6

**Table 3.** Five sediments are classified for seven metals according to five national standards with an upper and lower tier level (if applicable). Each time a sediment exceeds a standard this is scored. This is done without soil normalisation (part 1), with standard soil normalisation (part 2) and as difference (part 3). The difference (part 3) illustrates the increase or decrease of sediment use according to the national standards due to the standard soil normalisation (CEAMaS, 2015).

**Part 1**, the scoring of five sediments on the exceedance of five national sediment standards (upper and lower tier) without soil normalisation

National soil legislation system		Scoring results per metal without soil normalisation							
Tier 1		Metal exceeding standard (times)							Number of sediments not allowed to use according to tier 1 level
		As	Cd	Cu	Cr	Pb	Ni	Zn	
Irish	Lower level	5	4	3	4	5	4	5	5
Flemish	free us excavated soil	1	3	3	1	2	0	4	4
French	Level 1 (N1)	2	3	3	4	3	0	3	4
German	Integriertes Schadstoff-/Sedimentmanagement im Elbe-Einzugsgebiet	5	5	2	5	5	5	4	5
Dutch	Bbk, living (class A)	2	1	1	0	1	0	2	2
Number of sediments not meeting the tier 1 criteria for metal x according to 5 national soil standards		5	5	3	5	5	5	5	
Tier 2		Metal exceeding standard (times)							not allowed to use according to tier 2 level
Irish	Upper level b	0	1	1	0	0	0	2	2
Flemish	secondary resource	0	0	0	0	0	0	0	0
French	Level 2 (N2)	0	2	0	0	0	0	2	2
German	No level 2 tier (same as level 1 tier)	5	5	2	5	5	5	4	5
Dutch	Bbk, industry (class B)	0	0	0	0	0	0	0	0
Number of sediments not meeting the tier 2 criteria for metal x according to 5 national soil standards		5	5	2	5	5	5	4	

**Part 2**, the scoring of five sediments on the exceedance of five national soil directives (upper and lower tier) with soil normalisation

National soil legislation system		Scoring results per metal with soil normalisation							
		Metal exceeding standard (times)							Number of sediments not allowed to use according to tier 1 level
Tier 1		A <sub>2</sub>	B <sub>3</sub>	C <sub>5</sub>	D <sub>3</sub>	E <sub>2</sub>	F <sub>2</sub>	G <sub>1</sub>	
Irish	Lower level	4	4	1	3	4	0	4	4
Flemish	free us excavated soil	1	4	1	1	2	0	3	4
French	Level 1 (N1)	1	4	1	3	3	0	2	4
German	Integriertes Schadstoff-/Sedimentmanagement im Elbe-Einzugsgebiet	4	5	1	4	5	5	3	5
Dutch	Bbk, living (class A)	1	1	0	0	1	0	0	1
Number of sediments not meeting the tier 1 criteria for metal x according to 5 national soil standards		4	5	1	4	5	5	4	
Tier 2		A <sub>2</sub>	B <sub>3</sub>	C <sub>5</sub>	D <sub>3</sub>	E <sub>2</sub>	F <sub>2</sub>	G <sub>1</sub>	not allowed to use according to tier 2 level
Irish	Upper level b	0	1	0	0	0	0	1	1
Flemish	secondary resource	0	0	0	0	0	0	0	0
French	Level 2 (N2)	0	3	0	0	0	0	0	3
German	No level 2 tier (same as level 1 tier)	5	5	2	5	5	5	4	5
Dutch	Bbk, industry (class B)	0	0	0	0	0	0	0	0
Number of sediments not meeting the tier 2 criteria for metal x according to 5 national soil standards		5	5	2	5	5	5	4	

**Part 3**, the difference in scoring when using the standard soil normalisation. In blue the increase in the number of sediments that can be used according to the national standards when using soil normalisation. In red the decrease in the number of sediments that can be used according to the national standards when using soil normalisation.

National soil legislation system		impact of soil normalisation		impact of soil normalisation
Tier 1		Increase (blue) or decrease (red) of allowed sediment use	Tier 2	Increase (blue) or decrease (red) of allowed sediment use
Irish	Lower level	1	Upper level b	1
Flemish	free us excavated soil	0	secondary resource	0
French	Level 1 (N1)	0	Level 2 (N2)	-1
German	Integriertes Schadstoff-/Sedimentmanagement im Elbe-Einzugsgebiet	0	No level 2 tier (same as level 1 tier)	0
Dutch	Bbk, living (class A)	1	Bbk, industry (class B)	0

Standard soil normalisation is in most cases beneficial for sediment use. Most legal systems show less rejections when standard soil correction is applied. The exception is Cadmium for Example 3, based on the French level 2 criterium. The rejection is due to the low lutum content for example 3 (1% lutum versus 25% lutum for a standard soil).

Note that standard soil normalisation is only applied in the Dutch legislation , therefore the Table 3 results are only illustrative. The application of the Dutch standard soil normalisation parameters to non-Dutch sediments is not recommended. The parameters are specific for Dutch sediments. Due to differences in clay mineralogy and organic matter structure these parameters differ for different geological and climatological areas. However, standard soil normalisation could be an improvement for the evaluation of sediment use when applied on water body scale.

#### **6.1.4 Policy perspective during the 1993 – 2000 period**

In the period of 1993 – 2000 most of the frameworks to evaluate the ecotoxicological risks as explained in Chapter 2 (PAF based on SSD, FIAM free metal fraction, SEM/AVS for available metal fraction) were already developed and used to set water target values and maximum allowed concentrations for metals and organic contaminants (Crommentuijn, 1997a; Crommentuijn, 1997b; Kalf, 1995; Van de Meent, 1995). A routine determination of parameters like the free metal fraction based on the measured pore water chemistry or acid volatile sulphide content in sediments was deemed impractical. Sediment normalisation parameters were used instead, based on relative simple to detect sediment parameters like the organic matter and lutum content.

Main evaluation criteria during the 1993 – 2000 period:

- Water quality standards for single contaminants based on SSD risk levels are already in use (INS, 1997)
- Equilibrium partitioning between soil/sediment and water connect sediment and water quality standards
- Detailed ecotoxicological risk evaluation frameworks for both water and sediment were already developed, but a somewhat simplified approach based on standard soil correction constants for organic matter and lutum is chosen.

This period is characterized by a relative conservative approach with regard to the acceptance of contaminant risks in sediments (NW4, 1998). The implication of this policy is that much of the sediments cannot be reused when dredged, and that Confined Disposal and Aquatic Disposal Facilities (CDF's/CAD's) had to be developed.

The cost of this large scale contaminated sediment storage policy for both the central government (RWS) and local governments (waterboards) were published in 2001 (AKWA, 2001) and one reason to look differently at acceptable sediment risk criteria for contaminants.

## 6.2 Water Framework Directive, 2000 - 2008

### 6.2.1 Chemical and ecological status description

In 2000 the Water Framework Directive (WFD) (EU COM, 2000) was introduced, identified 41 dangerous chemical substances in water bodies: 33 priority substances and 8 other pollutants (EU COM, 2008b). The concentration for these substances are evaluated based on quality standards, like the Annual Average - Environmental quality standards (AA-EQS) and the Maximum Allowed Concentration (MAC-EQS). The substances for a water bodies are set by risk levels based on observed effects in ecotoxicological risk assessments. The ecotoxicological risk assessments are carried out by establishing the concentration-effect relation for individual chemical components and individual test species (see Chapter 2.1 - Maximum Tolerated Risk (MTR) Levels based on the Potentially Affected Fraction (PAF)). The quality assurance and publication of the WFD priority substances is done by the Fraunhofer-Institute Molecular Biology and Applied Ecology (Lepper, 2005).

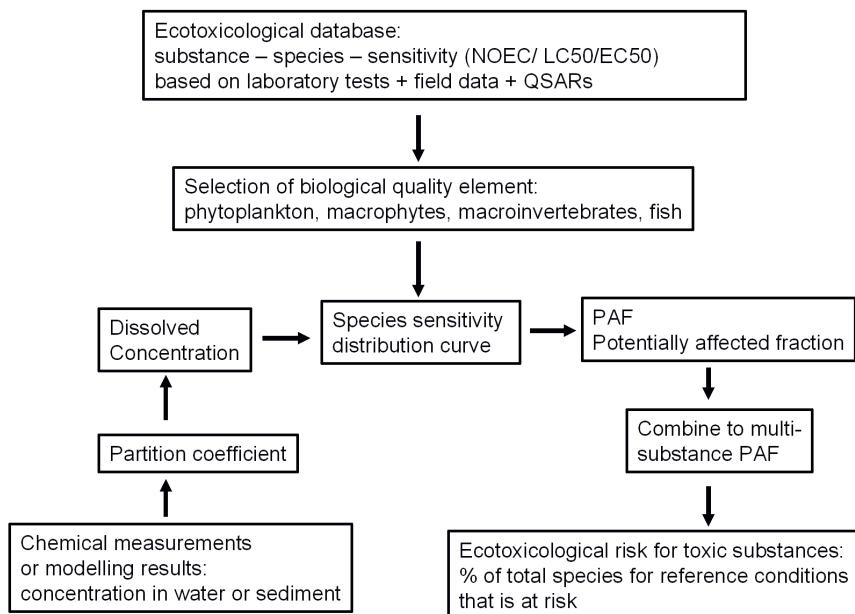
6

The WFD classifies water bodies on both the chemical and ecological status. To assess the ecological quality, the WFD uses an ecotope classification, as an example for the Western Scheldt (Escaravage, 2004; Hoey, 2007) (Supportive information, Chapter 2, Figure 1). The ecological quality status is based on species diversity, species density and species biomass; the biological quality elements ( Supportive information, Chapter 2, Figure 2).

### 6.2.2 Linking the chemical and ecological status

The WFD is based on preserving or improving the ecological status of the whole water body. On the water body scale, 'simple' dose effect relations between individual toxicants and individual species have to be aggregated to an evaluation of the toxic effect of chemical components for the whole water body. To resolve this incongruity between individual-based data and the complex biological entities addressed in ecological risk assessment, a model framework was introduced to link individual species-sensitivity distributions to risk levels for multiple contaminants on the water body scale (see Chapter 2.2 – msPAF). This ecotoxicity model OMEGA was developed

by (Hendriks 2001a; Hendriks 2001b; Hendriks 2005). In an efforts to link the chemical and biological quality of surface waters the EU project (REBECCA, 2006) published an overview on the current knowledge on indicators and methods for Water Framework Directive Ecological Status Assessment (Figure 1).



**Figure 1** Framework for modelling biological response to toxic pressures (REBECCA, 2006)

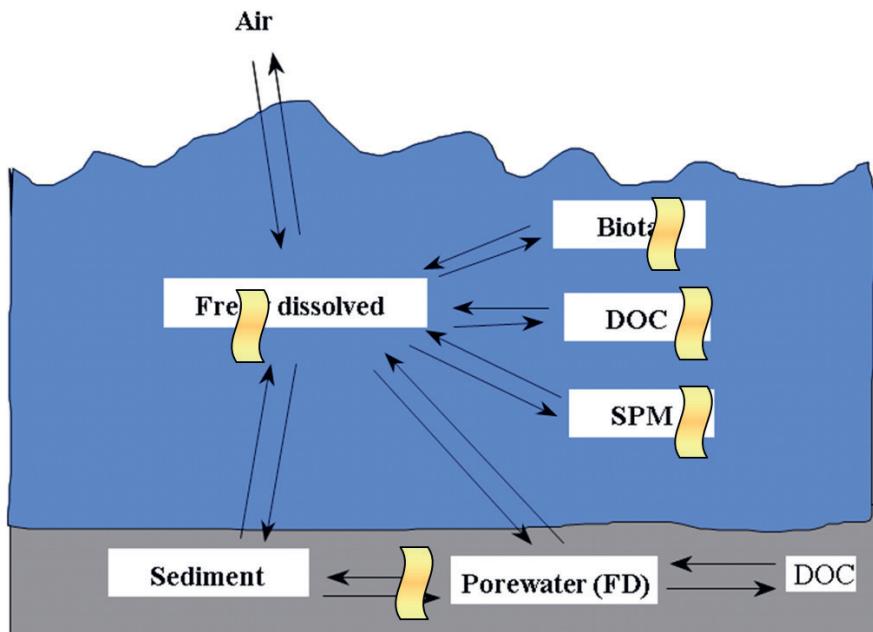
### 6.2.3 Implications of the WFD for the Netherlands

The requirement to have both a good chemical and good ecological status in a waterbody strengthened the research on the bioavailable fraction of contaminants. For organic contaminants the sorption to organic matter became an important topic, while for metals improvements to FIAM, BLM and SEM/AVS models were made (see Chapter 2.4 – FIAM, Chapter 2.5 – BLM and Chapter 2.6 – SEM/AVS) (Cornelisse, 1999; Hulscher, 2005; Schröder, 2005; Griethuisen, 2006; Groenenberg, 2011). Most studies was done on sediments and the interaction of sediments with biota, also with respect to bioaccumulation of contaminants (Vijver, 2005). Ironically the WFD does not include sediments or soils as part of the waterbody.

Meeting the chemical quality targets in a waterbody is no guarantee for a good ecological status. Since the WFD requires measures to be effective to meet the ecological criteria,

the focus shifted to non-priority and non-hazardous contaminants, nutrients. Nutrient load reduction and understanding pathways for nutrient emissions (Rozemeijer, 2010) became critical. This thesis does not cover the nutrient impact on the water quality.

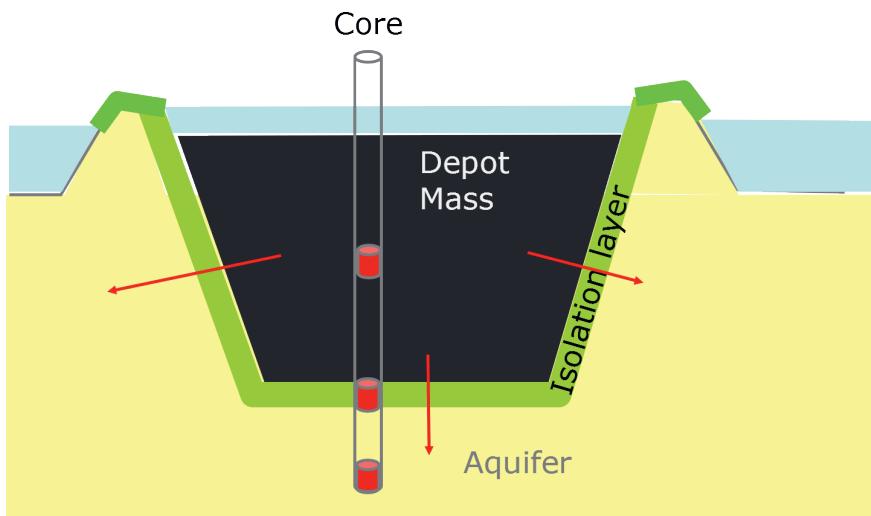
For sediment and soil quality standards, the period between 2000 and 2008 (Bbk, 2008) is an interbellum due to the lack of sediments as part of the WFD. In this interbellum the impact of CDF's/CAD's (constructed to store contaminated sediments, as part of the 1993 – 2000 sediment policy) is evaluated, as an example in the (UVD, 2006) project. The UVD project co-developed the Passive Sampling technique to detect the dissolved pore water concentration of organic contaminants in sediment (Smedes, 2013). Figure 2 illustrates the principle of a multi-phase equilibrium for the distribution of contaminants.



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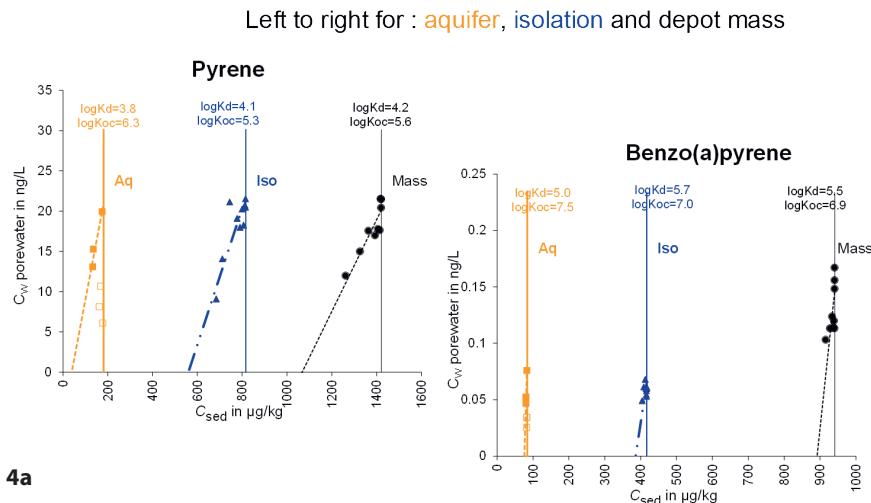
**Figure 2** Multi-phase equilibrium for the distribution of contaminants. SPM is the passive sample material, as is presented by the yellow punched tape (Smedes, 2015).

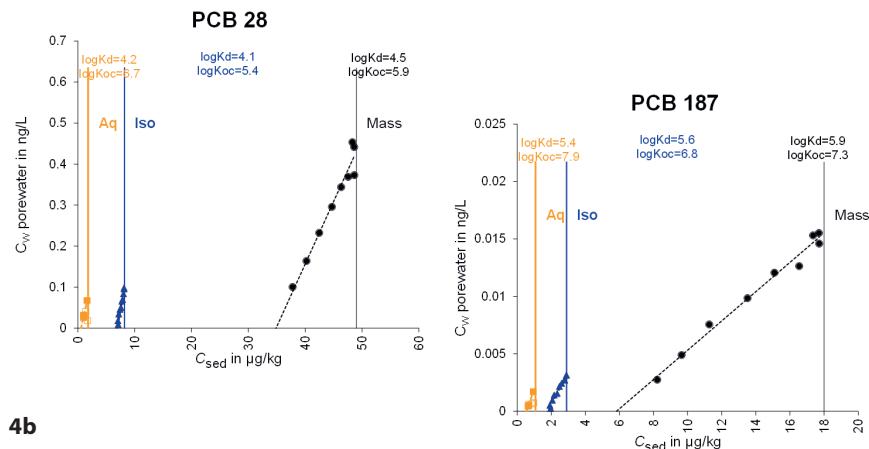
By varying the ratio between the amount of sediment and the amount of passive sampler, the technique can not only measure the actual pore water concentration, but also the potential available fraction of the contaminant for desorption. For CDF IJsseloog a core same is taken with material from the CDF (depot mass), the isolation layer and the aquifer (see Figure 3 for a schematic view).



**Figure 3** Schematic view of core samples taken from the CDF (Smedes, 2015).

Figure 4 gives the resulting pore water concentrations, partition coefficient (expressed as  $K_d$  and  $K_{oc}$ ) and inaccessible fraction for two PAH's (pyrene and benzo(a)pyrene) and two PCB's (PCB-28 and PCB-187).

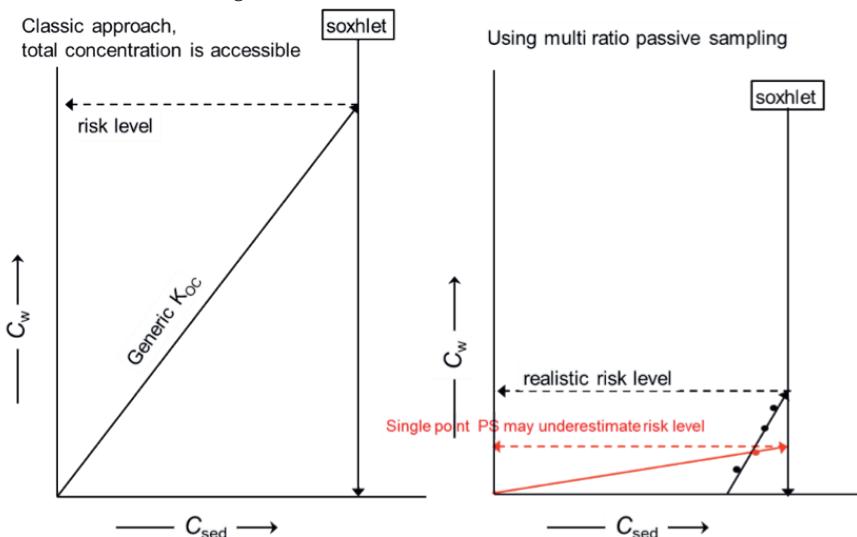




**Figure 4** Passive sampling results for CDF 'IJsseloog', measuring the pore water concentration and inaccessible fraction for two PAH's (pyrene and benzo(a)pyrene) and two PCB's (PCB-28 and PCB-187) (Smedes, 2015).

The results in Figure 4 illustrate that the availability of organic contaminants varies as function of the type of subsurface material. The  $K_{oc}$  for the depot mass is not the same as for the aquifer, the difference is on average  $\frac{1}{2}$  log unit. Also the realistic risk level based on an  $C_w$  concentration not only depends on the  $K_{oc}$ , but also on the size of the inaccessible fraction (Figure 5) (Smedes, 2015).

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**Figure 5** Difference between classic risk level determination (on the left) based on total concentrations (Soxlet extraction) and the multi-ratio passive sampling determined realistic risk level (on the right) (Smedes, 2015).

#### **6.2.4 Policy perspective during the 2000 – 2008 period**

The introduction of the WFD strengthened the approach to focus on the relation between risk levels based on observed effects in ecotoxicological risk assessments for setting water quality standards (AA-EQS and MAC-EQS), as was done before 2000. The introduction of the WFD did not drastically change the Dutch policy with regard to water quality or sediment quality.

Main evaluation criteria during the 2000 – 2008 period:

- Introduction of the WFD does not fundamentally change the way water quality standards are derived, although some changes are made on EU level.
- Sediment standards are not part of the WFD, no change in policy.
- The period between 2000 and 2008 is used to validate methods to derive the bioavailable fraction of contaminants in sediments and soils, preparing the way for a new soil directive in 2008.

### **6.3 ‘Room for the River’ - introducing a new Soil Directive, 2008 - 2018**

#### **6.3.1 The urgency for change, an almost flooding of the rivers and limited budgets for sediment remediation**

In 1993 and 1995 the rivers Meuse and Rhine almost flooded large parts of the Netherlands. In 1995 a total of 250.000 people were evacuated to prevent casualties in case the dike would breach. Therefore the project ‘Room for the River’ (2007 – 2018) was planned by the Dutch Ministry of Infrastructure and the Environment, and decided to be implemented by the government (PKB, 2006).

For the Room for the River program roughly 30 mln. m<sup>3</sup> soils and sediments had to be reallocated. Of these soils and sediments 90% (27 mln. m<sup>3</sup>) was used within the project, of which 2 mln. m<sup>3</sup> of soils and sediments was used to create shallow lakes. To enable the use of so much of the soil and sediments from the floodplain and the riverbed, a new evaluation framework to assess the risk of soil and sediments was needed. A new soil directive was introduced in 2008. The soil directive consists of two parts ‘Besluit bodemkwaliteit’ (Bbk, 2008) and ‘Regeling bodemkwaliteit’ (Rbk, 2008). The (Bbk, 2008) gives the context for sediment use, the (Rbk, 2008) the sediment criteria for use on neighbouring land.

In the new soil directive, the sediment and soil risk evaluation shifted from a ecotoxicological impact based standard for each location towards a ‘stand still’

principle on system scale. Use within the same system (or water body) is allowed as long as the current function of the system (or water body) can be maintained and the overall sediment/soil and (ground)water quality remains the same. Sediment standards can therefore be system specific (see Chapter 1.1 - Figure 4).

The system specific evaluation of the impact of the use of sediments and soils is the reason that the Room for the River project could be carried out with a social acceptable budget and within a realistic timeframe. The total project budget for Room for the River was 2.219 mln. euro (PKB, 2006). The total amount of sediment and soil reallocated was 30 mln. m<sup>3</sup>, of which 90% could be reallocated within the project. If the (BVB, 1993) based scenario for sediments was followed (AKWA, 2001), on average 30% of the sediments (9 mln. m<sup>3</sup>) would be considered too contaminated for use without clean-up. Even when using CDF's the cost for storing 9 mln. m<sup>3</sup> soil/sediment would be around 207 mln. euro (price indexed with 2.5% for the period 2003 – 2018) (AKWA, 2003). This excludes the cost for transport and taxes.

### **6.3.2 New evaluation methods for water and sediment quality assessment**

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During the 2008 – 2018 timeframe insights in the availability of contaminants in sediments and soils increased. The research done during the interbellum (Cornelisse, 1999; Hulscher, 2005; Schröder, 2005; Griethuyzen, 2006; Groenenberg, 2011; Vijver, 2005) can be applied to evaluate if contaminant risks are acceptable based on water body specific conditions.

#### **6.3.2.1 BLM**

The BLM method (Chapter 2.5) is accepted for the WFD evaluation of the water quality for the metals copper, nickel and zinc (Vink, 2010; Verschoor, 2012; Verschoor, 2013; Rüdel, 2015) and recently lead (Van Sprang, 2016). Further development of BLM's takes place within Registration Evaluation and Authorization of Chemicals (REACH). Chapter 3.4 gives an example of the use of a BLM model for lake Ketelmeer. In Chapter 5.5 the BLM model is used to calculate the Risk Characterization Ratio for pore water in a sediment to soil transition. A critical note with the BLM model is that predictions of the bioavailable contaminant fraction are only valid within the calibrated water quality conditions. A deviation of these conditions, like a low DOC concentration (lake Ketelmeer), makes the results unpredictable.

#### **6.3.2.2 msPAF**

The concept is explained in Chapter 2.2. In Chapter 4.6 (Western Scheldt surface water) and Chapter 5.6 (pore water in a sediment to soil transition) the msPAF is

calculated based on dissolved contaminant concentrations and the OMEGA model (version OMEGA 6.0; Durand-Huiting, 2006).

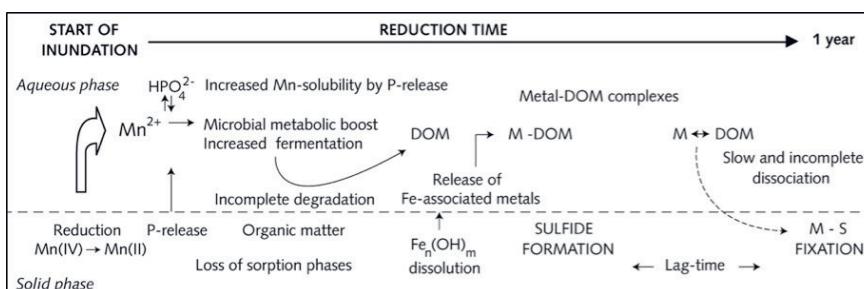
#### 6.3.2.3 SEM/AVS with $f_{oc}$

The SEM/AVS model has been improved by inclusion of the organic matter fraction ( $f_{oc}$ ). (Di Toro, 2005) demonstrates that the SEM/AVS model with the inclusion of the organ matter bound metal fraction closely relates to metal BLM's calibrated to water column organisms and freshwater chemistry.

#### 6.3.3 Shallow lakes

One application of soils and sediments which were removed for increase the hydrological discharge capacity of the river in the 'Room for the River' project is the creation of shallow lakes from old sand and gravel mining pits. These pits are deep (over 20 meter water depth) and hence temperature stratified during the summer period. Light penetration to the bottom is absent, limiting the biological activity. In theory filling the pit with soil and sediments makes the water depth more shallow and in potential leads to light penetration towards the lake bottom. Water plants can grow and the water quality and ecological quality improves.

In practice the impact was not always positive. For the (UVD, 2006) project the pore water metal concentrations were measurements. This showed that it is incorrect to use a  $K_d$  (Chapter 2. 3 - Equation 1) to describe the equilibrium between sediment and pore water. Also the SEM/AVS ratio (Chapter 2.6 – Equation 7) insufficiently takes into account the impact of reaction kinetics. In the presence of Dissolved Organic Matter (DOM) a semi stable Metal-DOM complex is formed, even when sufficient sulphides are present (Figure 6).



**Figure 6** Delayed immobilisation of heavy metals in soils and sediments under reducing and anaerobic conditions. Consequences for flooding and storage (Vink, 2010).

The impact of the formation of a relative mobile semi-stable metal-DOM ligands is especially important when creating shallow lakes with sediment or soil. Figure 7 illustrates the pore water trends for five shallow lakes created with contaminated sediments or soils, with contamination levels above class 'wonen' (living) or 'industrie' (industry) (Table 4).

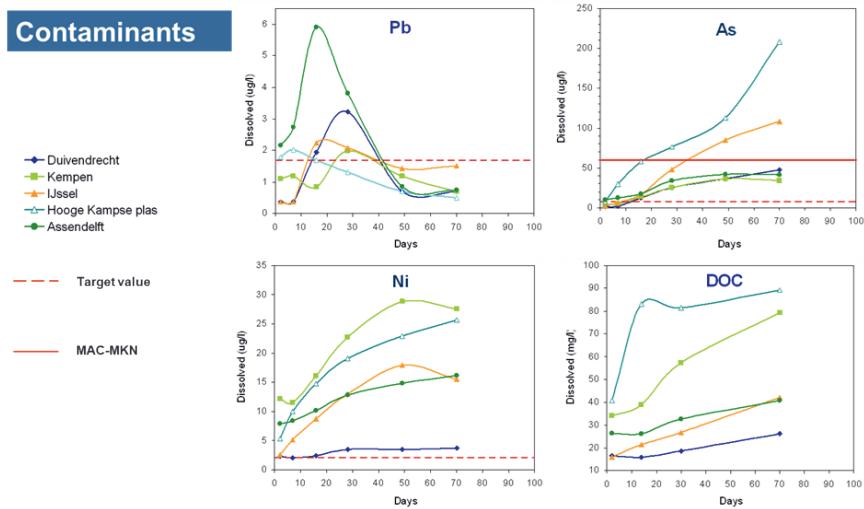
**Table 4** Sediment/soil quality used for creating five shallow lakes, metal concentrations in the sediment mg/kg (Vink, 2012). Metals presented in white meet the target value in sediment/soil, metals presented in orange are applicable for living, metals presented in red are applicable for industrial use.

	1 Dulvendrecht	2 De Kempen	3 IJssel-Wijhe	4 Hooge Kampse plas	5 Assendelft
Element (mg/kg)					
As	20	8,5	18,3	22,2	22,1
Ba	200	98,6	345	236	2287
Be	1,21	0,6	2,1	1,0	1,7
Cd	0,46	0,97	1,3	0,24	2,5
Co	8,8	6,8	18,4	6,22	20,6
Cr	34,2	31,8	69,5	21,8	127
Cu	31,5	80,5	40,1	23,7	309
Hg	0,26	0,06	0,54	0,15	5,9
Ni	31,1	25,1	54,8	21,4	73,7
Pb	211	73,1	66,1	74,5	696
Sn	6,4	7,9	3,3	3,8	49,4
V	48,1	42,2	71,9	34,7	82,4
Zn	195	1324	308	80,8	1919
Lutum (%)	10	3,8	9	4,1	5,6
Org. matter (%)	5	1,9	4,9	4,5	7,2

*Na bodemtypecorrectie en toetsing Bbk*

Klasse wonen

Klasse Industrie



**Figure 7** Trends in lead, arsenic, nickel and doc concentration during the first 100 days after the deposition of soils to create a shallow lake, five locations in the Netherlands (Vink, 2012). The solid red line represents the Maximum Allowed Concentration quality standard (MAC-MKN) for groundwater, the dashed red line is the target value in groundwater.

Figure 7 plots the measured pore water metal concentrations during the first 70 days of this transition. The five soils locations and the local specific soil quality is shown in Table 4. Lead pore water concentrations for all five locations spike above the target value during the first 40 days, after this period the pore water concentrations drop below the target value. Nickel and arsenic pore water concentrations are dependent on the location, but in general they increase over time and exceed the target value (nickel) or MAC-MKN (arsenic). DOC concentrations also increase over time, but at a different rate for the different locations.

Focusing on arsenic, the two locations with the highest arsenic concentration in the soil, 'Hooge Kampse Plas' and 'Assendelft' show a different pattern in the pore water concentration over time. The location 'Hooge Kampse Plas' has a higher DOC concentration and a high (above MAC-MKN) pore water arsenic concentration. The DOC concentration at 'Assendelft' is lower, the pore water arsenic concentration does not exceed the MAC-MKN.

The measured pore water concentrations for some of the metals exceed the target or even MAC-MKN value for groundwater (Figure 7). This is due to the transition of an aerobic soil to an anaerobic sediment. Metals are co-mobilized due to the reduction and dissolution of the soil (hydr)oxide minerals. When in equilibrium these metals are immobilized due sulphite fixation. During the transition from soil to sediment there

is no equilibrium. The kinetic reaction rate of the dissolved metals to bind with DOC dominates over the sulphite fixation, forming a semi stable and mobile metal-DOC ligand (Figure 8). Therefore both the soil/sediment standards based on equilibrium partitioning (Chapter 2.3 - Equation 1) and the SEM/AVS ratio (Chapter 2.6 – Equation 7) do not correctly predict the metal availability in groundwater.

#### **6.3.4 Policy perspective during the 2008 – 2018 period**

Main evaluation criteria during the 2008 – 2018 period:

- Water and sediment quality standards are more system specific due to the adaptation of risk assessment models (BLM, and SEM/AVS)
- A new soil directive is introduced, with the focus on the stand still principle.
- Less strict (related to total contaminant concentrations) sediment and soil quality standards made the large scale reallocation of soils and sediments possible, but sometimes with unforeseen and unwanted consequences (shallow lakes).

### **6.4 Sediment in a circular economy, 2018 - ...**

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#### **6.4.1 Sediment in a circular economy, the waste versus building directive**

'Room for the River' illustrates that use of sediments in the Netherlands is considered as use of building materials. This is made possible due to the 'stand still' principle for application of soil and sediments on a water body level. In most other EU member states sediment standards strictly bound to target levels. Not meeting the reference criteria means that sediments are considered a waste material according to the EU Waste Framework Directive (EU COM, 2008a). To be in line with (EU COM, 2008a), it is important to:

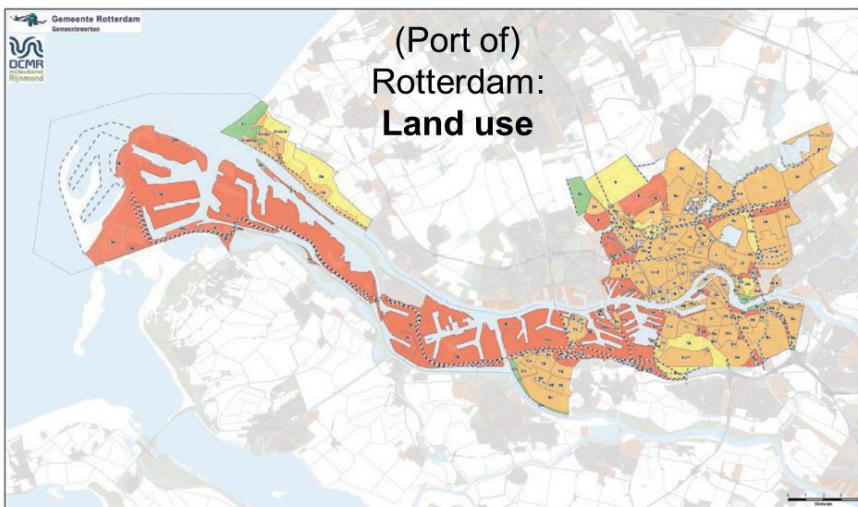
- (1) Characterise the sediment as useful material,
- (2) Define sediment concentration standards which do not degrade the local system (stand still principle), and
- (3) Meet with the emission criteria for building materials.

**(1) Characterise the sediment as useful material**

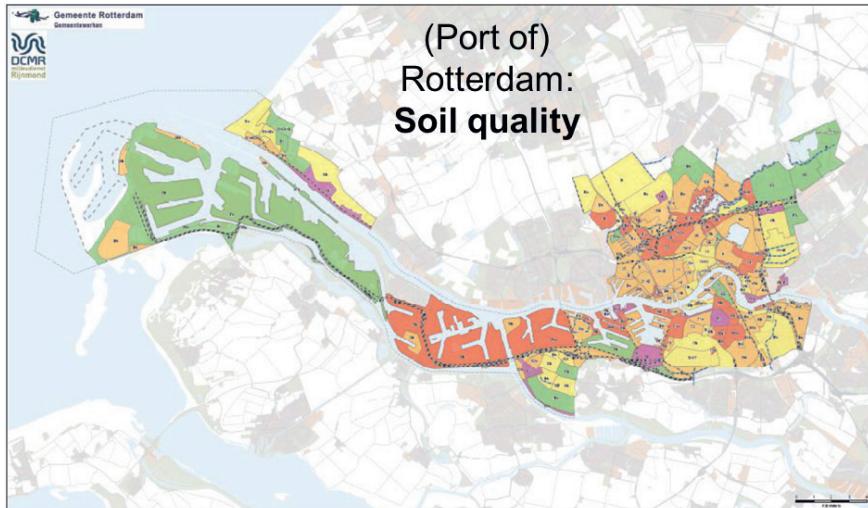
The use of sediment as a resource (beneficial use of sediment) is described in the Dutch waste policy document LAP3 (LAP3, 2017), sector plan 40 (sediment). LAP3 refers to the Dutch soil directive (Bbk, 2008) for the evaluation of the stand still principle within the same system (river basin). LAP3 gives examples of what is seen as beneficial use of sediment.

**(2) Define sediment concentration standards which do not degrade the local system**

The (Bbk, 2008) defines the stand still principle based on the current land use, the current sediment or soil quality versus the applied sediment or soil quality. This is illustrated in Figure 8 (land use) and Figure 9 (current soil quality). As an example, areas with an industrial land use (Figure 8, in red) but with clean soil (Figure 9, in green) can only accept clean soils or sediments. While the same industrial land use with moderately contaminated soil can accept soils or sediments with a moderate contaminant concentration.



**Figure 8** Land use Port of Rotterdam. Red is industry, orange is living area, yellow is agriculture, green is nature (Roeloffzen, 2013)



**Figure 9** Soil quality Port of Rotterdam. Purple is strongly contaminated, red is moderately contaminated, orange is slightly contaminated, yellow is very slightly contaminated, green is clean (Roeloffzen, 2013)

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### (3) Meet with the emission criteria for building materials

For determination of the emission of building materials there are different test protocols . For inorganic components in sediments (mostly metals) the most used are the (NEN 7373, 2004) (column leaching test) and NEN 7375 (diffusion test). Figure 10 illustrates for five sediments the msPAF based on the seven eluate fractions for the column leaching test (NEN 7373, 2004) (CEAMaS, 2015).

#### 6.4.2 The use of sediments in five EU member states, differences in legislation

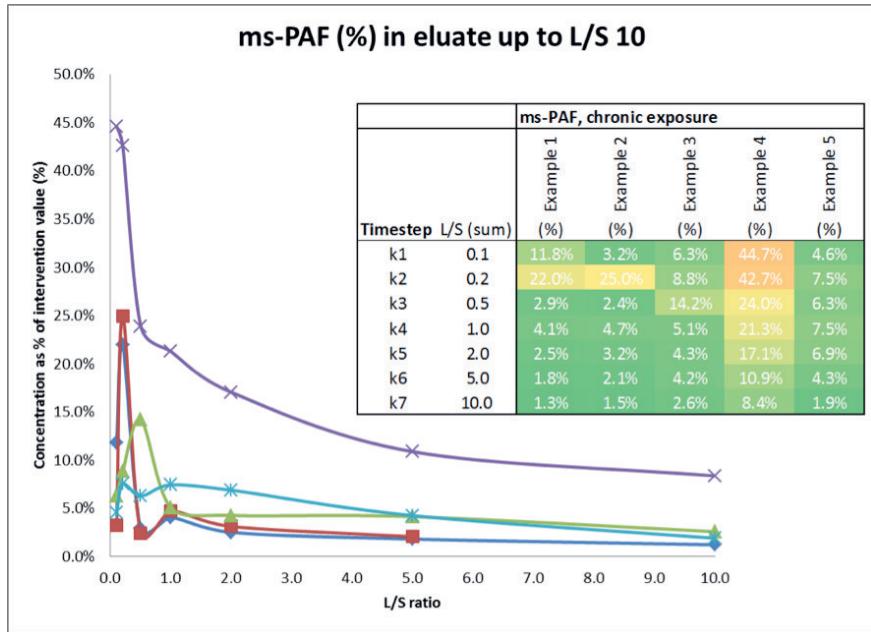
In (CEAMaS, 2015) characterisation and leaching tests were carried out on five contaminated sediments (Supportive Information – Chapter 6, Table 1 – 3). Based on the total concentration in the sediment the French, Irish, Flemish, German and Dutch sediment directives are used to classify the sediment (Supportive Information – Chapter 6, Table 4). The results of the classification are given in Table 5 (see also Chapter 6.2 – Table 3 for the scoring on individual metals).

**Table 5** Results of sediment classification for five contaminated sediments according to five national sediment directives. The classification is done according to an lower and upper concentration limit (if applicable). For each sediment (Example 1 – 5) the percentage of the highest scoring metal is given. In red the sediments clearly not meeting the sediment class limit (>150%). In orange the sediments close to the sediment class limit (50% – 150%). In green and yellow the sediments well below the sediment class limit (<50%). (CEAMaS, 2015).

		<b>Sediment concentration as function of soil standard concentration</b>				
		Example 1	Example 2	Example 3	Example 4	Example 5
Legislation system						
Irish	Lower level	497%	133%	180%	908%	539%
	Upper level b	194%	46%	57%	151%	96%
Flemish	free us excavated soil	397%	80%	109%	530%	315%
	secondary resource	64%	13%	17%	64%	38%
French	Level 1 (N1)	288%	87%	138%	530%	315%
	Level 2 (N2)	144%	43%	69%	265%	157%
German	Integriertes Schadstoff-/Sedimentma	938%	911%	965%	2889%	1717%
Dutch	Bbk, living (class A)	458%	379%	357%	217%	376%
	Bbk, industry (class B)	48%	67%	37%	52%	39%
	ZBT (Marine criteria (**))	218%	70%	104%	159%	104%
<i>Total times sample meeting standard</i>		2	7	4	2	3
<i>Total times sample exceeding standard</i>		8	3	6	8	7

Table 5 shows that only in Flanders and The Netherlands five out of the five sediments can be used, although under restrictions (Figure 10 and 11 illustrate the application according to the stand still principle). In Ireland, France and Germany at least two of the five sediments would be considered waste.

In the Netherlands the use of sediments is evaluated according to the NEN 7373 leaching test for building material (Supportive Information – Chapter 6, Table 5 – 7). The leaching test results are used to calculate the msPAF with the OMEGA 6.0 model (Durand-Huiting, 2006). The results are plotted in Figure 10.



**Figure 10** (chronic exposure) results for five sediments for the (NEN 7373, 2004) leaching tests for the seven collected fractions. The x axis gives the liquid to solid (L/S) ratio, the y-axis the msPAF (chronic). The Table summarizes the msPAF results for each of the five sediments for each of the seven fractions (CEAMaS, 2015).

For metals a of 50% for sediments allocated on neighbouring land is deemed acceptable (Bbk, 2008; SenterNovem, 2008). Note that in the past water quality standards for single contaminants were based on a  $HC_{5\%}$  with an additional safety factor of 10 (INS, 1997). The msPAF of 50% for metals therefore seems high, even when the potential toxic impact is not for a single metal but for all metals combined.

#### 6.4.3 Policy perspective during the 2018 - ... period

Main evaluation criteria during the 2018 – .... period:

- The Dutch soil directive (Bbk, 2008) and the EU Waste Directive (EU COM, 2008a) have been harmonized by definition of specific beneficial use criteria and the implementation of the stand still principle on system scale as guidance.
- The Netherlands form an exception with this implementation of contaminated sediment within the soil directive within Europe.
- The use of contaminated sediments is evaluation with a second tier risk assessment, the leaching test. However the conditions of these leaching tests differ from the natural conditions in soils and sediments.

- While there is still a role for the more advanced sediment risk assessment models (BLM, and SEM/AVS) to set local standards for sediments and soils, the current practice is to use the soil directive criteria (stand still principle and leaching tests) for the application of contaminated sediments.

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# 7

Conclusions with  
regard to the  
scientific progression  
in sediment and  
water quality  
standards

Chapter 2.9 formulates the hypotheses and research questions. In this chapter the research questions are discussed by looking at the scientific progress versus changes in water and sediment legislation in the Netherlands in the period 1993 and 2018. This timeframe is divided in four periods (as described in Chapter 6). Conclusions are drawn if legislation matches with the scientific insights during the specified time period.

Whether the hypotheses of this thesis are proven, and how the hypotheses can be implemented in water and sediment legislation, is discussed.

Based on scientific knowledge in 2018 on sediment and ecological risk assessment, recommendations are given on how to improve the sediment and water quality standards.

## **7.1 1993 - 2000: The development of a national integral water management framework.**

By using sediment specific characteristics to normalize sediment contaminant concentrations (based on the sediment organic matter and lutum content, see Chapter 2.3) the Dutch legislation in this time period is ahead of legislation as compared to other countries. The United Nations Environmental Programme (UNEP, 1995) recommends normalisation on aluminium and lithium, but does not include a recommendation for organic matter.

The period from 1993 up to 2000 is characterized by a linked approach between sediment and water quality standards. The water quality standards are based on ecotoxicity tests with a relatively large safety margin (the Maximum Tolerated Risk is a factor 10 lower than the HC<sub>5</sub> value, see Chapter 2.1). The water quality standards are based on the total dissolved contaminant concentration. Chapter 3 illustrates that using the total dissolved water concentration is not always a conservative method to predict ecotoxicological risks. Both the FIAM and BLM model predict areas which have a higher risk due to differences in the water composition.

The translation of water quality standards towards sediment standards in the 1993 – 2000 period is based on equilibrium partitioning (Chapter 2.3), and therefore assumes that contaminants in sediments are potentially available for biological uptake. In view of model concepts that take into account non-equilibrium behaviour, like the SEM/AVS model (Chapter 2.6), the assumption of equilibrium partitioning leads to the overprediction of potential ecotoxicological risks in sediments and therefore relative conservative (protective) sediment quality standards.

However, the use of equilibrium partitioning in sediments undergoing change, like the use of sediment on land, can underpredict the contaminant risks during the change. Chapter 5 shows that even with the relative conservative sediment quality standards (sediment meets the Dutch standard for reallocation of sediments on land in 1998), the multi substances Potentially Affected Fraction can be high due to changes in the mineral sediment matrix (see the 2008 – 2018 timeframe).

## **7.2 2000 – 2008: The introduction of the Water Framework Directive.**

The period around the introduction of the Water Framework Directive (WFD) is exciting from a scientific point of view. Advanced models to describe the bioavailable contaminant fraction are developed and validated, made possible by the improvement in measuring techniques like the NICA-Donnan membrane ( Weng, 2001b) for metals and the passive sampler for organic contaminants (Smedes, 2013). BioLigand models are developed and validated for several metals (Verschoor, 2010) and the SEM/AVS model for describing the non-equilibrium behaviour of metals in sediments is extended with the interaction of metals with the sediment organic matter. The improved SEM/AVS  $f_{oc}$  model seems to be a feasible alternative for a sediment BLM models (Di Toro, 2005), forming a bridge between the water phase based BLM's and the sediment quality.

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However, the introduction of the WFD in 2000 does not fundamentally change the way water and sediment quality standards are derived in the Netherlands. For sediment and soil quality standards, the period between 2000 and 2008 (Bbk, 2008) is less relevant due to the lack of sediments as part of the WFD.

## **7.3 2008 – 2018: And a new Soil Directive**

The largest change with regard sediment quality standards came in 2008 with the introduction of a new soil directive. With the need to reallocate large volumes of contaminated sediments the stand still principle for water and sediment quality became the guideline for the period 2008 - 2018. While there is still a general sediment/soil standard classification system (see Chapter 1 – Figure 4) there is more room for location specific sediment/soil standards. The location specific standards are based on the current land use, the current sediment or soil quality versus the applied sediment quality (see Chapter 6.4 – Figure 8 and 9). The stand still principle is fundamentally different from the earlier 1993 – 2008 approach, in which sediment standards are based on observed ecotoxicological impacts in water and equilibrium partitioning.

The advantage of the stand still principle for sediments and soils is that more advanced ecotoxicological risk evaluation methods, as derived in the 2000 – 2008 period (improvements of the SEM/AVS method with organic matter binding, the developed BLM's, FIAM model with NICA-Donnan based organic matter interaction, use of combined contaminant concentrations by use of the msPAF), can be applied to local conditions.

The result is less strict legislation for contaminants in sediments and an easier use of contaminated sediments. The benefit for society is that a project like 'Room for the river' (2007 – 2018) could be carried out within societal acceptable cost, improving safety against flooding and nature development. The drawback was that scientifically foreseen degradation of local water bodies, like the release of contaminants when using soils for filling pit lakes (see Chapter 6.3.3 – Shallow Lakes), took place. This occurred despite the stand still principle.

## 7.4 2018 – ...: Sediment in a circular economy

With the current challenge to create a more circular economy, sediment use is essential as a replacement of raw materials to compensate for land subsidence and nature-based flood protection. In many cases contaminated sediments have to be and can be used, as long as the stand still principle is maintained. Concepts like Life Cycle Assessment and ecosystem services (see also Appendix A) can help policy makers to look over sectoral boundary's to find sustainable sediment use solutions.

However, these solutions do not lessen the value of a scientifically based framework to derive water and sediment/soil standards. Policy makers tend to push toward the limits of what is allowed. For example in the case for the use of sediment on land, the policy criterium is a msPAF of 50% for metals (SenterNovem, 2008). Chapter 6.4 - Figure 10 illustrates how close to this policy criterium some of the beneficially usable sediments are. Chapter 5.6 illustrates that under changing conditions the 50% msPAF threshold can be exceeded. It is also questionable why a msPAF of 50% for sediment on land is deemed acceptable when the basis risk assessment in 1993 was based on a HC<sub>5</sub> (5% of the species are potentially at risk) with a safety margin of a factor 10 for a single contaminant (INS, 1997).

## 7.5 Conclusions with regard to the hypotheses

### 7.5.1 Local water and sediment conditions influence the potential ecotoxicity

This thesis offers no experimental proof on how to determine the bio-availability of a contaminant concentration, nor does it validate the actual biological uptake or the bioaccumulation based on the calculated potential ecotoxicological risk.

However, there is no doubt in literature that local water and sediment conditions influence the potential ecotoxicity of contaminants by influencing the bio-available concentration in water and sediment (see Chapter 3 – 5). This thesis shows how the bio-available concentration can be calculated based on different model concepts predicting the bio available concentration (FIAM, BLM, SEM/AVS), and how to combine multiple contaminant concentrations in a single potential ecotoxicological risk assessment (ms-PAF).

This thesis applies the different model concepts to predict the impact of local water and sediment conditions and translate these impacts into water and sediment correction factors, based on Risk Characterization Ratio's (RCR's). These RCR's can be used with relative minor changes to the sediment or water quality standards, and hence can be adapted within the current national and EU legislation.

### 7.5.2 Slow reaction kinetics under changing sediment conditions influence the potential ecotoxicity

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A change in redox conditions in sediments influence the partition between sediment and pore water and hence the bio-available fraction, as is illustrated in Chapter 6. The experimental proof of this change in mobilisation and immobilization of metals is based on the flooding/drying cycle of paddy rice soil (Pan, 2015a; Pan, 2015b), but not further experimentally researched in this thesis. Therefore, this thesis gives no direct proof to validate the hypothesis.

However, this thesis combines models to evaluate the kinetically restrained transformation of sediments to soil when sediments are used on land. The models simulate the impact of fluctuation of the redox potential on the bio-available fraction. The model input is based on realistic reference soil conditions in the Netherlands and supported by sensitivity analyses. The results indicate a strong seasonal dependency of the potential ecotoxicity.

While the hypothesis remains unproven it is recommended to further validate the impact of slow reaction kinetics under changing sediment conditions, especially when sediments are used on land or soils are used under water.

## 7.6 Recommendations

It is a challenge for the future to find ways to combine sediment (or soil) use with in-situ evaluation methods in order to give insight into the potential long-term ecotoxicological risks. Scientific concepts and methods are well developed, especially now that the BLM and SEM/AVS models are combined with more detailed metal - organic matter interaction studies (partly with the help of FIAM NICA-Donnan models).

Scientists can help policy makers and water managers to find practical ways for the implementation of these methods. The use of Risk Characterization Ratio's (RCR) for metals based on local water quality parameters would improve the correlation between the local water quality and the dissolved metal concentration to assess the local ecotoxicological risk. For copper, nickel, lead and zinc for water bodies, within the water quality validation range of the Biotic Ligand Models, the  $RCR_{BLM}$  is best suited. For other metals and for water bodies outside the BLM water quality validation range, the Free Ion Activity Model (FIAM)  $RCR_{FIAM}$  works best to improve upon non-site specific water quality standards.

The introduction of the stand still principle for the overall quality of a system (Bbk, 2008) when it comes to the application sediment and soil has been (and is) a game changer. For some applications of sediments or soils under changing conditions the stand still principle does not hold true, and the use of a more advanced risk approach is advised. For soils applied under water, the Simultaneous Extracted Metals (SEM) to Acid Volatile Sulphides (AVS) ratio (SEM/AVS) with the addition of the organic matter sorption ( $f_{oc}$ ) can improve the risk assessment. But more research is needed, since the role of slow reaction kinetics when it comes to the fixation of metals in soils/ sediments can temporally increase the concentration and mobility of metals.

The impact of reaction kinetics on the lack of fixation of metals in redox sensitive applications of sediments is a warning to critically look at the legislation that allows a Multi substances Potentially Affected Fraction (msPAF) of 50% for metals in sediments to be used on land. It is questionable if legislation should allow that 50% of all organisms can be exposed to a lethal dissolved metal concentration. The basis risk assessment in 1993 was based on a hazardous concentration for a single contaminant for five percent of the species ( $HC_5$ ), with a factor of 10 safety margin (INS, 1997). Taking into account the redox dependant changes in sediments placed on land, the msPAF can increase during certain periods of the year and therefore a msPAF of 50% can be exceeded. Validation of models describing the impact of reaction kinetics under field conditions is advisable to further improve the ecotoxicological risk assessment of sediments.

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## Glossary

Annual Average Environmental Quality Standard (AA-EQS)	In the WFD Daughter Directive, Annual Average Environmental Quality Standard are set for surface waters for all 33 priority substances. The guideline is to take a water quality sample every four weeks, resulting in 13 samples to determine the annual average surface water concentration.
Benthic Ecosystem Quality Index (BEQI)	The term benthic refers to anything associated with or occurring on the bottom of a body of water. The animals and plants that live on or in the bottom are known as the benthos. The BEQI is the WFD marine benthos metric for transitional and coastal waters and the salt lakes.
Biotic Ligand Models (BLM)	Biotic Ligand Models are developed to describe the toxicity of metals for organisms, especially fish. Toxicity is not simply related to total aqueous metal concentration, but depends on both metal-ligand complexation and metal interaction with competing cations at the site of action, the fish gill. Therefore the BLM model takes into account the impact of the general water quality (as does the FIAM model) and also the gill specific passage of ions.
Cation Exchange Capacity (CEC)	Cation-exchange capacity is a measure of how many cations can be retained on soil particle surfaces. Negative charges on the surfaces of soil particles (mainly on OM and clay's) bind positively-charged molecules (cations).
Chronic exposure	The ecotoxicity of a chemical can usually be described in terms of the length of exposure to the hazard. The timescale for testing chronic exposure varies (often from 6 to 21 days in bioassays), but is always more than 24 hours (the maximum time for acute toxicity).
Confined Disposal Facilities (CDF)	A Confined Disposal Facility is an area designed for the containment of contaminated dredged material that provides control of potential releases of contaminants to the environment. Dikes or other structures may be used to isolate dredged material both in upland and aquatic CDF's. The main, basic objective for a CDF is to retain dredge material solids and allow the discharge of clean process water from the confined area.
Ecotope	Ecotopes are the smallest ecologically distinct landscape features in a landscape mapping and classification system. As such, they represent relatively homogeneous, spatially explicit landscape functional units that are useful for stratifying landscapes into ecologically distinct features for the measurement and mapping of landscape structure, function and change.

Free Ion Activity Models (FIAM)	The Free Ion Activity Model calculates the free metal ion concentration in water based on the water quality. Metals can form ligands, as an example with anions or dissolved organic matter. These metal ligands are considered no longer to be bioavailable for uptake in organisms. The FIAM model therefore 'corrects' the ecotoxicity of metals based on the local water quality. The FIAM model does not take into account the actual interaction with organisms, as does the BLM model.
Good chemical status	A WFD classification for a water body (like a river, lake or estuary), based on meeting all AA-EQS contaminants standards (for the 33 priority substances and if applicable for all water body specific contaminants). The WFD used the 'one out – all out' principle, exceeding one AA-EQS standard means that the water body is not in a good ecological status.
Good ecological status	A WFD classification for a water body (like a river, lake or estuary). The status is basis on specific criteria and boundaries for the biological, physico-chemical and hydromorphological elements. Biological assessment uses numeric measures of communities of plants and animals (for example, fish and rooted plants). Physico-chemical assessment looks at elements such as temperature and the level of nutrients, which support the biology. Hydromorphological quality looks at water flow, sediment composition and movement, continuity (in rivers) and the structure of physical habitat.
Maximum Ecological Potential (MEP)	The Maximum ecological potential (MEP) is a WFD definition to describe the reference conditions for the best approximation to a natural aquatic ecosystem that could be achieved given the hydromorphological characteristics that cannot be changed without significant adverse effects on the specified use or the wider environment.
Maximum Tolerable Concentration (MTR)	The maximum tolerable concentration is a slightly older (2000) Dutch water quality standard. In the WFD this upper allowable limit is replaced by the Maximum Acceptable Concentration (MAC-QS).
Multi substances Potentially Affected Fraction (msPAF)	A methodology to calculate the accumulative ecotoxicological risk for multiple contaminants in water by using the mode of action of the contaminant. For contaminants with a similar mode of action and a similar end point (like a NOEC), a hazard unit (HU) can be calculated, using the relative toxicity of each contaminant. The sum of the HU's gives the combined ecotoxicological risk. For contaminants with a different mode of action, the individual ecotoxicological risk is calculated and added to the total risk.

Non Ideal Competitive Adsorption (NICA) – Donnan model	A FIAM model to describe the equilibrium adsorption between water and solid phases, using non-ideal competitive adsorption (NICA). To describe the non-ideal behavior the Donnan potential based on the electrostatic interactions between ions and solid particles calculated. The NICA-Donnan model is mainly used to describe the adoption of metals to dissolved organic matter and clay particles.
No Observed Effect Concentration (NOEC)	The no observed effect concentration is a risk assessment parameter that represents the concentration of a pollutant that will not harm the species involved, with respect to the effect that is studied.
Priority substance	A set of 33 contaminants defined by the WFD as priority substances, which could threaten human health or ecosystems.
Standard Dutch soil (SDS)	Standard Dutch soil is a normalization standard to recalculate contaminant concentrations to a soil with 10% organic matter and 25% lutum (clay). Dutch soil standards refer to the SDS normalized concentration.
Water Framework Directive (WFD)	The Water Framework Directive 2000/60/EC is an EU directive which commits European Union member states to achieve good qualitative and quantitative status of all water bodies. It is a framework in the sense that it prescribes steps to reach the common goal rather than adopting the more traditional limit value approach.





# A

Appendix:  
CEDA position  
paper, Beneficial Use  
of Contaminated  
Sediments

## CENTRAL DREDGING ASSOCIATION



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## Position Paper Thesis

Using a wide range of case studies, this paper demonstrates that contaminated sediments can be used beneficially. The driving principles are:

- (1) Sediments should be viewed as a resource
- (2) Potential risks can be managed or avoided, and
- (3) The social - economic value is positive

The key objectives of this paper is to demonstrate that it is technical suitability to beneficially use contaminated sediment for a range of end-use applications and that no dredging project should be avoided on the basis that 'no action' is preferable to a risk management approach when all benefits are considered.

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## Introduction

The beneficial use of contaminated sediments is generally no different than the use of uncontaminated sediments. Both types of sediment can be beneficially applied, yet there are restrictions imposed on contaminated sediments regarding the potential environmental impacts from contaminant exposure; as such, this sediment must be managed appropriately. Approaches to managing the risks associated with this sediment includes treatment, which has led to the development of innovative construction techniques over the last two decades.

This paper provides several case studies regarding the beneficial use of contaminated sediments, an overview of effective treatment techniques and examples of relevant risk evaluation and decision-making frameworks. Within this context, this paper demonstrates that the beneficial use of sediment with varying degrees of contaminations is feasible when decision makers focus on value-added solutions and risk management, as opposed to 'no action' and risk avoidance approaches.

While this paper does not include a detailed comparison of country-specific legislation (e.g., sediment quality standards or disposal regulations), the case studies and situations described herein illustrate the importance of flexible regulations that facilitate beneficial use of (contaminated) sediments, considering the specific origin, properties and application opportunities..

## Perception of risk

The definitions of 'contaminated' and 'uncontaminated' sediment are generally based on regional screening levels or sediment quality standards, compared to the sediment concentration. These standards are only an indication for the potential (eco) toxicological risks and are not directly linked to the actual, location-specific impact that contaminated sediments have on the environment. There is also a large geographical variation in the natural occurrence of contaminants in sediment. This variation is often discounted when using local standards, yet it illustrates that the definition and interpretation of 'contaminated' is subjective.

This paper does not present a case for disregarding the presence of contaminants in the sediment. Instead, it illustrates the importance of revisiting the original purpose of why sediment standards were derived, which is to prevent the degradation of the ecosystem by exposure to contaminants. As the beneficial use of contaminated sediments avoids this exposure and eliminates the risk, it can be as beneficial as the

use of 'clean' sediments. As such, the perception and regulatory barriers regarding contaminated sediments need to be re-assessed.

By focusing on the perception of risk in a broader context, we intend to avoid discussing the different directives and legal definitions of contamination or waste and the different sediment quality standards, which are typically country specific. The purpose of this paper is to illustrate what can technically be done to mitigate environmental risks when beneficially using contaminated sediments, as opposed to 'doing nothing' on a watershed system scale, which leads to environmental management paralysis.

This paper provides an overview of the different sediment treatment techniques that can be used to mitigate the environmental risks. The selection of a treatment technique is often guided by both the legal/regulatory system and the applicability of the treatment process and characteristics of the project location itself. In countries with a well-defined soil/sediment assessment system, each contaminant that has impacted water or the sediments is traceable to their legal owners (e.g., United States [US] Superfund sites); the policy is implemented to reduce the contaminant levels through source control. These remedial actions may include dredging and treatment, capping, natural attenuation or a hybrid of these approaches that encompasses adaptive management. Under the US Superfund, clean-ups are financially governed by the 'Polluter Pays Principle', who will then support 100% of the clean-up. When ownership is less clear and/or if funds are lacking, this situation often leads to the 'do nothing' scenarios. Some countries choose to implement a 'stand still principle' with regard to the emission of contaminants to surface and groundwaters. In that scenario, the focus shifts from total concentration standards (like in the EU Waste Directive) to a (bio) available fraction approach (as in the Dutch Soil Directive).

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## Tools for Decision Making

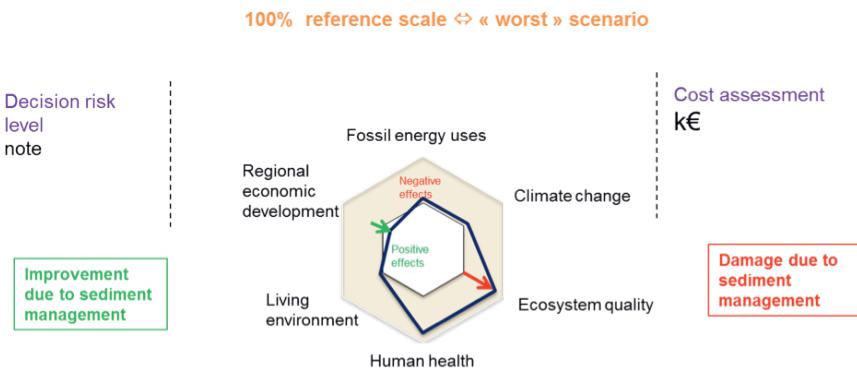
Sediment use, including the use of contaminated sediments, can and should be evaluated in a broader multi-criteria evaluation of long-term cost and benefits of sediment use, rather than a short-term economic analysis. There are several tools that can be used to incorporate the different aspects of sediment use.

One such tool is the Life-Cycle Assessment (LCA), also called the 'cradle-to-grave' analysis. While this assessment normally targets production as well as the use and disposal cycle of a product, the method can be adapted to both avoid use and reuse primary and/or unrenewable resources. The LCA approach can also score

and rank different sediment solutions (disposal, treatment, beneficial use) against multiple criteria. One particularly popular criterium is the carbon footprint; however, environmental impacts are also evaluated and as such, an adapted Social Life Cycle Assessment (UNEP, 2013) can be used to look at social cost/benefits. Sustainable practices are also encouraged in LCA evaluations.

Another method to balance the cost/benefits of sediment use is to look at the 'services' that the sediment provides. More information on types of criteria regarding the definition of services provided by the sediment, including setting up an assessment framework, can be found at the Millennium Ecosystem Assessment website<sup>2</sup>.

An example of a project evaluation within this broader context is illustrated in Figure 1.



**Figure 1** Example of a relative ranking method for the management and material recovery of waterways sediments (Lemiere, 2010), <https://hal-brgm.archives-ouvertes.fr/hal-00691510>.

## From 'No Action' to Beneficial Use

Sediments from urban and port environments may be contaminated by point or non-point sources. They are also subject to complex sediment transport regimes, which may disperse contamination away from the original source. These sediments pose unique challenges for dredging and remediation/restoration programs. Sediment contamination is usually associated with fine-grain size fractions, which has fewer beneficial opportunities for coastal restoration and construction applications when compared to sand. Conversely, fine-grained sediments provide suitable raw material

<sup>2</sup> Millennium Ecosystem Assessment, 2005, <http://www.millenniumassessment.org>

for several treatment options (reducing/binding or destroying the contaminant load) with high value and beneficial applications. Global regulatory programs often deem these contaminated sediments as waste, but in the 21st century they should be viewed as a global resource.

There is a negative public perception of using contaminated sediments. However, the 'no action' alternative or delay of dredging results in economic, environmental (remedial) and societal losses. The 'no action' response eventually can lead to a variety of adverse effects on navigation, water storage capacity and ecological services, as sediments accumulate in waterways. In the near future, these effects are likely to be enhanced by climate change. Therefore 'no-action' dredging alternatives have the potential to shift of costs from an individual project to a societal problem, which may ultimately require additional flood protection measures or alternative infrastructure. The costs not only shift between projects but also in time, thus contributing to conditions that can make dredging not only unavoidable, but likely even more expensive. The 'no action' response can lead to regulatory and decision-making paralysis; it also reduces the incentive for continuing innovative technology development to create a better outcome for the beneficial use of contaminated sediments.

Conversely, the applications of amended and/or treated contaminated dredged materials provide multiple options for beneficial use. From a sustainability perspective, dredged material may, for example, replace non-renewable resources (from quarries) in the creation of manufactured soils. With the stabilization of dredged materials with cements, blast furnace slags, lime and fly ash, it is possible to provide structural and non-structural fill material for Brownfield economic and community development projects. Physical treatment processes such as sediment washing result in manufactured soil production and high temperature applications using rotary kilns to produce light weight aggregates or construction grade cement; both have been used to repurpose contaminated sediments. The use of amended/treated dredged materials as a raw material replaces primary soil material, which is a limited and increasingly expensive resource. The beneficial use of contaminated sediments also minimizes the disposal of contaminated dredged material in upland landfills, thus increasing the landfill service life.

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There has been significant programmatic progress regarding the efficient use of contaminated sediments as a resource. Programs focused on the beneficial use of sediments focus on upland ex-situ materials science (structural) and include EU

projects<sup>3</sup> and the US Environmental Protection Programs<sup>4</sup> (EPA, 2011). These programs have been at the forefront of changing the perception of contaminated sediments from a waste to a sustainable resource. There is increasing global acceptance of applying innovative sediment treatment processes as part of the Regional Sediment Manufacturing Facility (RSMF) programs (Stern, 2017) that use back-end integration to incorporate beneficial uses of contaminated sediments in upland Brownfield and Greenfield development. This RSMF approach can drive policy and legislative changes that will encourage economic development and revitalize the impacted urban landscapes. These strategies should reduce processing costs (and encourage manufacturing) through a Life Cycle Approach that combines treatment with end user applications.

Many countries are working cooperatively on market drivers for the beneficial use of contaminated sediments in soils, biosolids and structural amendment-fill areas. This collaboration creates economic incentives and good technical knowledge for development of future business, i.e. entrepreneurial incubators. Ultimately, large-scale operations focused on the beneficial use of contaminated sediments could be integrated with other alternative approaches for using contaminated sediments.

## Case study examples

The beneficial use of contaminated sediments can be categorized into five different applications, known as the Five R's (see the CEDA Information Paper (CEDA, 2019)).

1. **Raw Material:** Substitution for virgin manufactured soil or building materials, such as tiles or aggregates
2. **Remediation:** Clean up of contaminated sites or closure of landfills or mines
3. **Reclamation:** Creating new or expanding existing land, primarily for human/commercial development activities
4. **Restoration:** Creation of habitat to support aquatic organisms and wetlands to improve the natural value of the environment
5. **Resiliency:** Shoreline nourishment and (dike) reinforcement for defence against floods and extreme climatic events

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3 European examples include: SEDI.PORT.SIL (LIFE+ Environment Policy and Governance, 2010-2013), CEAMas (North-West European Interreg IVB, 2012-2013), SETARMS (North-West European Interreg IVB, 2007-2013), SEDILAB (supported by CD2E, France ), SMOCs (Huxley College of the Environment, 2012), CIRIA (Construction Industry Research and Information Association), EcoSed (Industrial Research Chair in Sediment, Mines Douai, France), GeDSET (Interreg France-Wallonie-Vlaanderen, 2008-2013) and the Sedimateriaux Approach (supported by CD2E, France).

4 New Jersey Department of Transportation/New York and New Jersey Harbor Sediment Decontamination Program in the United States (part of US Superfund Innovative Technology Evaluation Program, 2005-2009)

These Five R's are ordered in increasing use of nature and decreasing human intervention. The case studies which illustrate the beneficial use of contaminated sediments cover all of these areas, but mostly concentrate on the solutions that are influenced more greatly by human activity and high socioeconomic value. This bias is because handling contaminants always increases project costs, thus requiring a solution with a combined benefit of cost avoidance and additional economic and social benefits.

Table 1 categorizes all case studies for the Information Paper and Position Paper in relation to the Five R's and their areas of application. Case studies for contaminated sediments are highlighted with an underline, and treatment with an italic font. The treatment techniques used for the contaminated sediment case studies are briefly described in the next section of this paper.

The contaminated sediment case studies show that higher cost solutions typically involve on-land construction applications in urban environments. These applications are spatially constrained by distance to the source material site. Transport costs hamper long distance applications, often rendering the solution site-specific. We note that there are still no large-scale solutions for contaminated sediments on a fully integrated watershed or on a regional scale. Pollution prevention, regional assessments and public education continue to be important to identify and drive solutions on a large watershed scale.

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## Treatment Techniques with Beneficial Applications

The choice of the treatment technique is site-specific. It depends on the site configuration, nature of the contaminants (chemical vs. physical), treatment goals and local governance. Here we focus mainly on techniques. The methods outlined below illustrate the main principles of the more commonly used methods for treating contaminated sediments. The differentiator is that some of these treatment options can produce a beneficial use that is in line with the Five R's.

### Chemical Immobilization

Chemical immobilization uses binders to physically strengthen the sediment for structural or non-structural engineering use (such as infill for land reclamation) while also reducing the mobility and solubility of the contaminant. This process achieves both the beneficial use of contaminated sediments and contaminant immobilization.

Suitable materials include hydraulic cements, GGBS (ground granulated blast furnace slag), fly-ash, lime, bentonite, calcium aluminate, super-sulphated cement, magnesium and iron oxides and activated carbon. Chemical immobilization is frequently used not only because of the relatively low cost and high availability of these materials, but also because of its demonstrated ability to immobilize heavy metals, TBT (tri-butyl tin) and inorganic compounds. These binders can be mixed with the sediments both in-situ and ex-situ; mixing ex-situ has the advantage of producing a more homogenous mix.

See the case studies '*R1A\_2012\_FR*' (*Freyernet 12 Road Construction*), '*R1A\_2015\_US*' (*Stabilization through Pneumatic Flow Tube Mixing*), '*R3B\_2010\_NO*' (*Stabilization with hydraulic binders*), and '*R3B\_2018\_SE*' (*Stabilization with hydraulic binders*).

### **Bioremediation**

Bioremediation is the addition of microbial agents to the sediments (either in situ or after dredging) to break down contaminants to non-toxic by-products. It is relatively inexpensive to carry out and is particularly suitable for the treatment of organic contaminants and many heavy metals. Bioremediation requires very specific environmental and physical conditions to be most effective for contaminated sediments.

See the case study '*R2A\_1995\_NL*' (*Bioremediation by landfarming*).

### **Phytoremediation**

Phytoremediation is the use of plants such as hemp, pigweed and mustard to bioaccumulate and degrade heavy metals and organic pollutants. It is a relatively low-cost solution and has the added value of potential recovery of valuable metals from the plants. It is suited to shallow contamination such as spills and discharges and requires a commitment to long-term monitoring to ensure plants continue to thrive. Like bioremediation, it returns the sediment to a natural and environmentally stable state.

See the case study '*R2A\_1995\_NL*' (*Bioremediation by landfarming*).

### **Thermal Desorption**

Thermal desorption is a specialized ex-situ process in which the sediment is heated indirectly in a rotary kiln to volatilize the contaminants. The off-gas is then treated

separately and either discharged, collected or thermally destroyed.

For more information see (EPA, 1994).

### **Sediment Washing and Sand Separation**

Ex-situ sediment washing separates the coarse, non-contaminated fraction from silts and clays, which have the greatest contaminant absorption capacities. This separation produces sands and gravels that can be beneficially re-used. The finer fractions can also be further treated by organic destruction using strong oxidants, liquid-solid separation and subsequent back-end dewatering to produce a sediment filter cake end-product, which can also be beneficially used. The creation of a beneficial use product, such as a blended manufactured soil that meets residential or non-residential standards, has been demonstrated in the Palermo (Italy) case study.

See the case study '*R1A\_2017\_IT*' (*Sediment Washing*).

### **Ex-situ High Temperature Processing**

High temperature rotary kilns or plasma systems operating at 1400 °C can be used for commercial-scale treatment and beneficial use of sediments. When heated at high temperatures sufficient to melt sediments, the addition of modifiers/minerals creates a pozzolan. The organics are dissociated or destroyed and the metals are immobilized in a glassy slag and pulverized to produce a construction grade/stabilized cement. Rotary kilns are also used to produce light weight aggregates from pelletized sediments. Both construction grade cement and light weigh aggregates comprise the beneficial outputs of this process, replacing the use of virgin natural resources.

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See the case study '*R1A\_2018\_US*' (*Cement-lock Technology*)

### **Confined Disposal Facility (CDF)**

Strictly speaking, a CDF is not considered a sediment treatment option; however, it can be classified as beneficial when used for land reclamation or a continuous source to substitute a raw material.

A CDF is often used to create a long-term viable storage solution for contaminated sediments, provided that there is adequate space and engineering/ecological feasibility to show that the CDF option can be supported with long-term management and monitoring protocols (also see the chapter 'Examples of Beneficial

Use Techniques'). Alternatively, CDFs can be integrated with sediment treatment as part of a 'renewable' CDF strategy. For example, consider a situation when a CDF is filled to capacity and the re-siting of a new CDF is not feasible. Through 'mining' the CDF with subsequent sediment treatment options, such as sediment stabilization, the CDF could then be 'renewed' to create a potentially infinite capacity when the sediments are mined, treated, and beneficially used.

Creating a CDF can often be combined with the local mining of clay, sand or gravel. CDF's create the needed upland land reclamation for construction activities that become economic drivers (mostly in ports). CDF's can be part of an overall sediment strategy solution through combining economic benefit with a safe long-term storage solution for contaminants. As such, CDF's contribute to the overall ecological value of the project by creating high value habitats like wetlands and shallow lakes.

See the case study '*R5B\_2006\_NL*' (*Room for the River Project*).

## Associated Activities

### Dewatering

Dewatering is used to prepare the sediment for treatment, enabling more effective mixing of the immobilizing agent if applicable. Dewatering can be carried out by lagooning and draining in settling ponds or barges, mechanical dewatering, geotubes, electro-dewatering and as a pre-cursor to thermo-chemical treatment. Dewatering can also be used as a sediment volume reducing measure, as part of a storage solution (landfill).

See the case studies '*R1A\_1985\_DE*' (*Moorburg Dewatering Fields*), '*R1A\_1993\_DE*' (*METHA-Plant - Large Scale Sediment Treatment*), '*R1A\_2006\_NL*' (*Slufter Sand Separation Project*), and '*R2A\_1998\_DE*' (*Alternative Disposal Site Capping Material*).

### Secondary Mining

Secondary mining is the removal of the contaminant for further use. This can be carried out as part of the immobilization technique, as in the cases of phytoremediation (burning the plants to extract metal compounds - 'phytomining') or liquefied gas solvent extraction (when solvents are vaporized to isolate organic materials for recycling). This has the benefit that the treated sediment can then beneficially be used elsewhere.

See the case study '*R1A\_1993\_DE*' (*METHA-Plant - Large Scale Sediment Treatment*).

## Field trials

Field trials are an important way of demonstrating the full-scale performance of a treatment process including immobilization techniques. The information derived from both the engineering and process effectiveness, coupled with a beneficial use application, is particularly valuable information to support public education about the process, especially with high temperature and physical separation technologies. Field trials are also particularly relevant to chemical immobilization where binders are mixed into the dredged sediments. A field trial is carried out to confirm the efficacy of binders that have been selected from laboratory-scale bench testing and then are used for full-scale verification testing (e.g., in-situ strength and permeability testing, leaching tests).

## Conclusions

In this paper we show how sediments are a resource, even when contaminated. Sediment management and therefore use of sediments is necessary, as ‘no action’ simply transfers, often increasing, risk and cost to future generations.

The tools to assess the impact of using contaminated sediments versus ‘no action’ are well established and are applicable to a wide range of conditions/project scenarios. In addition to assessing the environmental risks associated with contaminants, these tools evaluate and rank the sediment use solutions based on conventional metrics (e.g., economics, LCA) and their overall contribution to sustainability.

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The case studies illustrate that most of the current applications that include contaminated sediments fall within the raw material and remediation categories. These categories are relatively capital intensive and therefore may be predominantly small scale and ad-hoc (point source) solutions. To avoid the long-term financial and ecological losses of ‘no action’ scenarios, and to use contaminated sediment as a solution for climate change and circular economy challenges, we need a more integrated view on sediment management and a shift to more field- and full-scale applications in restoration and resiliency categories.

There are several available well-demonstrated treatment techniques that can reduce the risk of contaminant exposure. If an application is chosen and the sediment is characterized, field trials will help to validate the effectiveness of the treatment options. These field tests can also help to assess any additional benefits (like secondary mining).

The main conclusion is that the presence of contaminants is only one factor in the evaluation of how sediments can be beneficially used. It is evident that sediments must be used beneficially, as 'no action' often leads to unacceptable risks and/or decision-making paralysis. There are many scenarios in which the use of contaminated sediments is beneficial; these scenarios are both economical, ecological and in view of the Sustainable Development Goals (see the case studies). Legislation should therefore follow the approaches used in the case studies as much as possible to implement the beneficial use of contaminated sediments

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**Table 1.** Case studies classified after Function (rows) and Technique (Columns). Rows 1 through 5 refer to Function and columns A through D refer to Technique. Case study nomenclature includes a reference to Function, Technique, year at project start and location of the project..

Technique → ↓Function	A. On Land Natural or enhanced treatment	B. In Water Reallocation at final location	C. In Water Reallocation at strategic location	D. In Water Enhanced Trapping
1. <b>Raw Material</b>	R1A_1985_DE R1A_1993_DE R1A_1996_DE R1A_2006_DE R1A_2006_NL R1A_2012_FR R1A_2015_US R1A_2017_IT R1A_2018_US			
2. <b>Remediation</b>	R2A_1988_DE R2A_1995_NL R2A_2015_DE			
3. <b>Reclamation</b>	R3A_2016_US R3A_2018_NL	R3B_2006_NZ R3B_2010_NO R3B_2018_SE		
4. <b>Restoration</b>	R4A_2010_NL	R4B_2002_US R4B_2005_US R4B_2008_US R4B_2016_NL R4B_2016_UK(a) R4B_2016_UK(b)	R4C_1999_NL R4C_2002_US R4C_2007_US R4C_2016_NL	
5. <b>Resiliency</b>	R5A_2004_DE R5A_2005_BE R5A_2013_FR R5A_2018_NL R5A_2019_BE	R5B_1990_UK R5B_2006_NL R5B_2010_US	R5C_2008_US	R5D_2015_ID



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# B

## Appendix (in Dutch): ‘Variatie door speciatie, een case studie in het Ketelmeer: Verandering in de (vrij) opgeloste concentratie’

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## Samenvatting

(Zware) metalen in het oppervlaktewater komen in diverse vormen voor. Een deel van de zware metalen zijn geabsorbeerd aan het zwevend slib, een deel is 'vrij' opgelost en een deel van de zware metalen vormen met organische of anorganische verbindingen complexen. Voor opname in organismen is de vrij opgeloste fractie van groot belang. Deze vrij opgeloste concentratie bedraagt echter slechts enkele tientallen procenten tot soms enkele procenten (of nog minder) van de totale hoeveelheid zware metalen in het oppervlaktewater.

Als casestudie voor een speciatiestudie is het Ketelmeer gekozen. Speciatiemodellering geeft inzicht in het belang van de in het Ketelmeer optredende processen op de ontwikkeling van de totaal opgeloste en vrij opgeloste concentratie op het traject Kampen–/-Ketelbrug.

De in het Ketelmeer optredende processen hebben tot gevolg dat de berekende vrij opgeloste concentratie op het traject Kampen/Ketelbrug met circa 20% (koper) tot circa 30-35% (cadmium-zink) afneemt.

## Inleiding

De Nederlandse wateren worden intensief bemonsterd op waterkwaliteit. Hierbij wordt (mede om analytisch/technische redenen) de totaal concentratie in het oppervlaktewater gemeten. Opgeloste stoffen in het water zoals b.v. zware metalen kunnen echter in diverse type verbindingen voorkomen. Dit proces, waarbij stoffen onderling interactie vertonen, heet speciatie. Hoe bepaalde interacties verlopen wordt beschreven door de wetten van de thermodynamica. Omdat het proces van speciatie in principe wiskundig te beschrijven is kan een numeriek model toegepast worden om de speciatie te berekenen. WL | Delft Hydraulics heeft voor het berekenen van de speciatie in water het model CHARON (Rooij, 1991) ontwikkeld.

Aan de hand van een case studie voor het Ketelmeer wordt gedemonstreerd wat het belang is van speciatiemodellering om veranderingen in een systeem te begrijpen en te verklaren.

## Het principe van speciatie

Speciatie is de eigenschap van onder andere zware metalen om zich met diverse stoffen te binden en daarmee een complex te vormen. Speciatie wordt beïnvloed door een breed scala aan factoren in het oppervlaktewater, waarvan de belangrijkste zijn:

- de hoeveelheid metaal & ligand (ook organische liganden zoals DOC),
- de pH,
- het zuurstofgehalte,
- de macro chemie ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}/\text{Mn}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{S}^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , pH, alkaliteit),
- de hoeveelheid en aard van de vaste stof in de waterfase (voor ad- en desorptie wordt veelal de Cation Exchange Capacity als maat voor de mate van interactie aangehouden).

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Om de vrij opgeloste metaal concentratie te bepalen kan gebruik gemaakt worden van specialistische meettechnieken waarbij uitsluitend de vrij opgeloste metaal concentratie gemeten wordt (Helmke, 1995). Een andere optie is om gebruik te maken van een numeriek speciatiemodel. WL | Delft Hydraulics heeft voor dit doel CHARON (Rooij, 1991) ontwikkeld en ingezet in diverse studies (Wijdeveld, 1998). Deze aanpak is ook voor het Ketelmeer gevuld.

## Stofkeuze en condities in het Ketelmeer

Het oppervlaktewater in het Ketelmeer bevat een scala aan verontreinigde stoffen, waaronder zware metalen. Deze stoffen komen in opgeloste en zwevend slib gebonden vorm het Ketelmeer binnen via de IJssel te Kampen en verlaten (deels) het Ketelmeer via de Ketelbrug. Als gidsstoffen zal het speciatiegedrag van de zware metalen cadmium, koper en zink op het traject van Kampen naar de Ketelbrug beschouwd worden. Er is gekozen voor deze gidsstoffen wegens hun verschillend systeem- en/of speciatiegedrag:

- Cadmium: gevoelig voor chloride variatie en de totale massa in het oppervlaktewater massa is ruwweg evenredig verdeeld over de opgeloste en zwevend slib gebonden fractie.
- Koper: zeer gevoelig voor veranderingen in het (opgelost) organisch stofgehalte en van de totale massa in het oppervlaktewater is meer dan 75% in opgeloste vorm aanwezig.
- Zink: lijkt op koper maar minder gevoelig voor (opgelost) organisch stofgehalte, kent meer invloeden van andere liganden en heeft een grotere bijdrage van de zwevend slib gebonden fractie aan de totale massa in het oppervlaktewater.

In het traject Kampen/Ketelmeer vinden een aantal veranderingen plaats (zie tabel 1):

- De pH neemt toe.
- De zweven slib concentratie neemt af.
- De jaargemiddelde DOC concentratie neemt toe, evenals het OC gehalte van het sediment.

**Tabel 1** Veranderingen in het traject Kampen/Ketelbrug (Jaarboek, 1999)

parameter	Kampen gemeten (1999)	Ketelbrug gemeten (1999)	verschil
pH -log(H <sup>+</sup> )	8.0	8.3	0.3
DOC (mg/l)	3.6	4.6	1.0
zwevend slib (mg/l)	22.9	17.1	-5.8
OC gehalte zw. slib (%)	4.8	4.9	0.1

De relatief lage pH in het Ketelmeer bij Kampen is het gevolg van kooldioxide oververzadiging in het Rijn/IJssel water. Deze oververzadiging wordt veroorzaakt door de hoge belasting van de Rijn met afbreekbaar organisch materiaal (lozingen, afspoeling landbouwgronden), waarbij bij afbraak kooldioxide gevormd wordt. Bovendien is het Rijnwater van oorsprong oververzadigd aan kooldioxide (grondwater

Rijnslenk). In het Ketelmeer vindt nalevering van kooldioxide plaats en daarmee een pH stijging.

Het afnemend zwevend slibgehalte is het gevolg van netto sedimentatie in het Ketelmeer. De toename van het (D)OC gehalte kan worden toegeschreven aan de hoge primaire productie in het Ketelmeer.

## Initialisatie

Voordat het effect van de veranderende condities kan worden geëvalueerd dient het model geïnitieerd te worden op basis van de macrochemie. Uitgangspunt bij deze initialisatie is 'standaard' Rijnwater. Na macro chemische initialisatie worden de zware metalen in het model opgenomen. Hiertoe worden de gemeten concentraties in 1999 bij Kampen en de Ketelbrug (jaarboek, 1999) aangehouden (tabel 2). Voor de totale massa berekening is het in tabel 1 weergegeven gemeten zwevend slib gehalte toegepast.

**Tabel 2** Zware metaal concentraties voorbeeldstoffen

parameter		Kampen gemeten (1999)	Ketelbrug gemeten (1999)	Verschil (%)
<b>cadmium</b>				
opgeloste concentratie	(ug/l)	0.085	0.063	-26%
zwevend slib concentratie	(mg/kg)	1.52	2.15	41%
totale massa aan zwevend slib	(ug/l)	0.035	0.037	
totale massa in oppervlaktewater	(ug/l)	0.120	0.100	<b>-17%</b>
<b>koper</b>				
1)	opgeloste concentratie	<b>11.0</b>	3.2	-71%
	zwevend slib concentratie	62.0	62.0	0%
	totale massa aan zwevend slib	1.4	1.1	
	totale massa in oppervlaktewater	12.4	4.3	<b>-65%</b>
1.1)	opgeloste concentratie, <b>gecorrigeerd</b>	<b>3.7</b>	3.2	-12%
	totale massa in oppervlaktewater	5.1	4.3	<b>-15%</b>
<b>zink</b>				
	opgeloste concentratie	21.0	12.7	-40%
	zwevend slib concentratie	430	488	13%
	totale massa aan zwevend slib	9.8	8.3	
	totale massa in oppervlaktewater	30.9	21.0	<b>-32%</b>

1) De in 1999 gemeten koper concentratie te Kampen (zeer hoog) werkt sterk af van de gemeten koper concentratie in andere jaren te Kampen. Vermoedelijk is er sprake van een notatiefout. Correctie van deze fout levert de onder 1.1) vermelde koperconcentratie.

De na kalibratie op de meetwaarden berekende verdeling over de verschillende complexen is weergegeven in tabel 3.

**Tabel 3** Initiële speciatie in het oppervlaktewater bij Kampen

parameter	Kampen totaal opgelost	Speciatie (als % van opgeloste concentratie) (1)								
		vrij metaal	met-DOC	met-Cl+	met-Cl <sup>2-</sup>	met-OH+	met-OH <sup>2-</sup>	met-CO <sub>3</sub>	met-(CO <sub>3</sub> ) <sub>2</sub>	met-HCO <sub>3</sub>
cadmium	0.085 (ug/l)	24.6%	20.0%	50.7%	0.9%	1.0%		2.2%		
koper	11.0 (ug/l)	1.0%	98.7%							
zink	21.0 (ug/l)	20.6%	50.7%			2.3%	2.6%	16.6%	1.4%	2.2%
										3.5%

1) In tabel 3 zijn alleen complexen opgenomen welke voor meer dan 0,5% aan de opgeloste concentratie bijdragen.

Zoals uit tabel 3 blijkt is slechts 1 tot 25% van de totaal opgeloste concentratie als vrij opgelost metaal aanwezig. Tabel 3 illustreert ook het verschil in de belangrijke liganden voor de beschouwde zware metalen. Voor cadmium is chloride van belang, terwijl dit voor geen van de andere metalen een rol speelt. Opgelost organisch materiaal (DOC) is voor alle beschouwde metalen van belang, al varieert de mate van binding met het opgelost metaal tussen de 20 en 99%. Tot slot is de sterke (bi)carbonaat afhankelijkheid van de zink opmerkelijk.

## Variatie in speciatie, het traject van Kampen naar de Ketelbrug

In Tabel 2 is al de gemeten verschuiving in de water en zwevend slib kwaliteit op het traject van Kampen naar de Ketelbrug weergegeven. Kan speciatiemodellering de optredende verschuiving verklaren?

Om antwoord te geven op deze vraag wordt de invloed van in het Ketelmeer optredende processen geëvalueerd:

- Ontgassing van kooldioxide,
- Primaire productie,
- Netto sedimentatie van zwevend slib (integraal beschouwd met het effect van ontgassing en primaire productie).

## Ontgassing van kooldioxide

Doordat de mate van oververzadiging met kooldioxide afneemt richting Ketelbrug neemt de pH in het oppervlaktewater toe (van een pH van 8,0 naar een pH van 8,3). Deze pH verschuiving (en de in het Ketelmeer optredende netto sedimentatie) heeft de in Tabel 4 weergeven gevolgen voor de (vrij) opgeloste concentratie:

**Tabel 4:** Effect pH verschuiving en sedimentatie op de (vrij) opgeloste en zwevend slib concentratie

parameter	Berekende concentratie			Gemeten concentratie		Verschil gemeten versus berekend locatie Ketelbrug
	Kampen pH = 8,0	Ketelbrug pH = 8,3	afname (%)	Kampen pH = 8,0	Ketelbrug pH = 8,3	
<b>cadmium</b>						
totale op geloste concentratie (ug/l)	0.085	0.062	27%	0.085	0.063	1%
vrij op geloste concentratie (ug/l)	0.021	0.015	30%			
zwevend slib gebonden concentratie (mg/kg)	1.51	2.20	-46%	1.52	2.15	-2%
totale massa aan zwevend slib 1) (ug/l)	0.034	0.038				
totale massa in oppervlaktewater (ug/l)	0.120	0.100	17%	0.120	0.100	0%
<b>koper, gecorrigeerd</b>						
totale op geloste concentratie (ug/l)	3.7	3.2	12%	3.7	3.2	1%
vrij op geloste concentratie (ug/l)	0.037	0.029	20%			
zwevend slib gebonden concentratie (mg/kg)	61	101	-66%	62.0	62.0	-63%
totale massa aan zwevend slib 1) (ug/l)	1.4	1.7				
totale massa in oppervlaktewater (ug/l)	5.1	4.9	2%	5.1	4.3	-15%
<b>zink</b>						
totale op geloste concentratie (ug/l)	21.2	16.2	24%	21.0	12.7	-28%
vrij op geloste concentratie (ug/l)	4.36	2.85	35%			
zwevend slib gebonden concentratie (mg/kg)	424	575	-36%	430.0	488.0	-18%
totale massa in oppervlaktewater (ug/l)	9.7	9.8				
totale massa in oppervlaktewater (ug/l)	30.9	26.0	16%	30.9	21.0	-24%

B

Het verloop van de (totaal) opgeloste cadmium concentratie kan verklaart worden door het pH effect op de adsorptie aan zwevend slib (en de optredende netto sedimentatie). Voor koper en zink kan het pH effect en de sedimentatie de waargenomen massa-afname in het oppervlaktewater niet volledig verklaren.

## Primaire productie

Het Ketelmeer kent een hoge primaire productie. Deze hoge primaire productie komt onder meer naar voren in het toenemend DOC gehalte in het oppervlaktewater en een toenemend OC gehalte van het zwevend slib (zie Tabel 1). Het speciatiemodel CHARON is opnieuw gekalibreerd op basis van de totale massa in het oppervlaktewater bij Ketelbrug en de daar heersende condities (hogere pH, hoger DOC gehalte en een hogere bindingssterkte aan het zwevend slib vanwege het hogere OC gehalte).

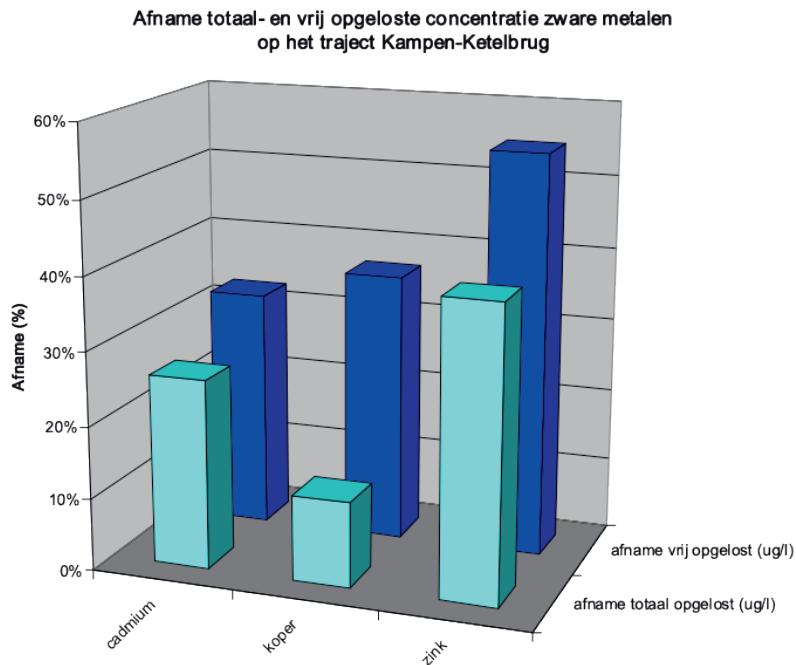
De voor- en na herkalibratie berekende (vrij) opgeloste en zwevend slib gebonden concentraties staan weergegeven in Tabel 5.

**Tabel 5:** Effect herkalibratie voor Ketelbrug op de (vrij) opgeloste en zwevend slib concentratie

parameter	Kampen calibratie Kampen	Ketelbrug alleen pH en sed. effect	herkalibratie Ketelbrug met DIOC toevoeging	Gemeten concentratie Ketelbrug pH = 8.3
<b>cadmium</b>				
total opgeloste concentratie (ug/l)	0.085	0.062	0.063	0.063
vrij opgeloste concentratie (ug/l)	0.021	0.015	0.014	
zwevend slib gebonden concentratie (mg/kg)	1.51	2.20	2.15	2.15
totale massa aan zwevend slib 1) (ug/l)	0.034	0.038	0.037	
totale massa in oppervlaktewater (ug/l)	0.120	0.100	<b>0.100</b>	<b>0.100</b>
<b>koper, gescreigd</b>				
total opgeloste concentratie (ug/l)	3.7	3.2	3.2	3.2
vrij opgeloste concentratie (ug/l)	0.037	0.029	0.023	
zwevend slib gebonden concentratie (mg/kg)	61	101	62	62
totale massa aan zwevend slib 1) (ug/l)	1.4	1.7	1.1	
totale massa in oppervlaktewater (ug/l)	5.1	4.9	<b>4.3</b>	<b>4.3</b>
<b>zink</b>				
total opgeloste concentratie (ug/l)	21.2	16.2	12.7	12.7
vrij opgeloste concentratie (ug/l)	4.36	2.85	1.97	
zwevend slib gebonden concentratie (mg/kg)	424	575	488	488
totale massa aan zwevend slib 1) (ug/l)	9.7	9.8	8.3	
totale massa in oppervlaktewater (ug/l)	30.9	26.0	<b>21.1</b>	<b>21.0</b>

## Conclusies

De voor opname in organismen beschikbare zware metaal concentratie in oppervlaktewater (de vrij opgeloste metaal concentratie) is slechts een fractie van de totaal opgeloste zware metaal concentratie. Voor de beschouwde zware metalen cadmium, koper en zink varieert de vrij opgeloste concentratie tussen de 1% (koper) en 20-25% (cadmium, zink) van de totaal opgeloste fractie. Bovendien neemt de vrij opgeloste concentratie op het traject Kampen-Ketelbrug sterker af dan de totaal opgeloste concentratie (zie Figuur 1).



**Figuur 1** Afname van totaal- en vrij opgeloste concentratie zware metalen op het traject Kampen-Ketelbrug

B

In het Ketelmeer treden diverse processen op welke van invloed zijn op de verandering in de (vrij) opgeloste concentratie op het traject Kampen/Ketelbrug. Niet alle processen zijn voor alle zware metalen van even groot belang:

- Cadmium kent uitsluitend een pH effect op de adsorptie aan zwevend slib (in combinatie met netto sedimentatie). Dit komt doordat de voor cadmium belangrijkste ligand, chloride, op het traject van Kampen naar de Ketelbrug niet wezenlijk in concentratie veranderd.
- Koper is zeer gevoelig voor veranderingen in de (D)OC concentratie.
- Zink is gevoelig voor veranderingen in de (D)OC concentratie. Zink kent echter nog een aantal anorganische complexen. Deze anorganische complexen zijn sterk pH afhankelijk. Dit verklaart dat de vrij opgeloste zink concentratie op het traject Kampen/Ketelbrug een afwijkend beeld laat zien van de totaal opgeloste zink concentratie.

Speciatiemodellering is een instrument dat kan helpen bij het beoordelen van risico-veranderingen in een watersysteem in afwezigheid van (of in aanvulling op) geschikte meettechnieken voor de vrij opgeloste metaal concentratie. Als zodanig is de tool zinvol om het effect van veranderingen in een systeem te beoordeeld of om een nadere risico-evaluatie uit te voeren bij normoverschrijding. Behalve de beschouwde case studie voor het Ketelmeer, waar de nadruk lag op pH effecten, sedimentatie en primaire (D)OC productie, geeft speciatiemodellering ook inzicht in processen zoals bijvoorbeeld veranderingen in de zuurstofhuishouding, de invloed van gebiedsvreemd water, zoute kwel, stratificatie in de waterkolom en de gevolgen van de inundatie van polders en uiterwaarden (bodem/water uitwisseling).

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B



# Supportive information

## 2. Chapter 2 'Ecotoxicological risk evaluation models over the past 25 years'

**Table 1** Partition coefficient  $K_d$  and  $K_{oc}$  for soil and sediments (INS, 1997)

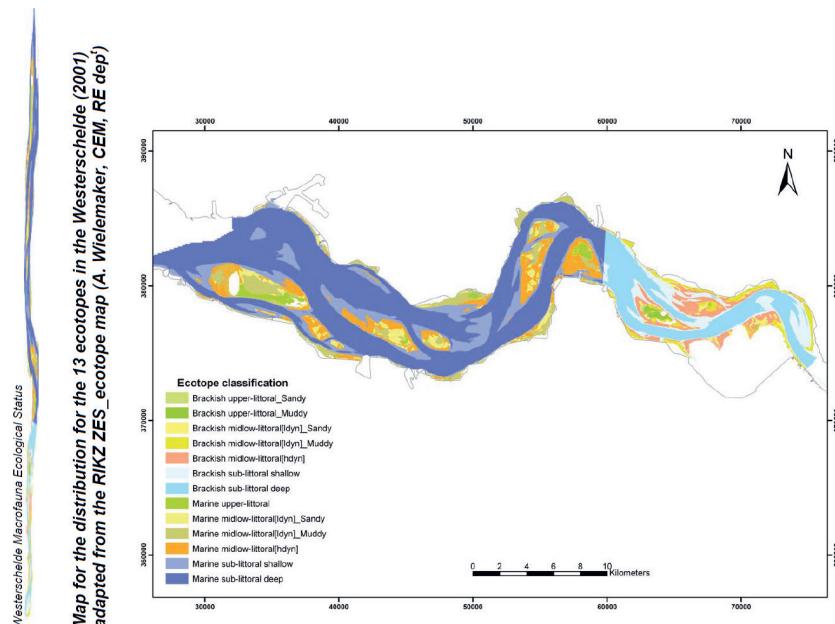
Contaminant		Contaminant	$\log K_d$ (l/kg)	$\log K_{oc}$ (l/kg)
<b>Metals</b>	<b><math>K_d</math> (l/kg)</b>	<b>PAH's</b>		
Sb	3700	naftalene	2.37	3.37
As	10000	antracene	3.52	4.52
Ba	1350	fenantrene	3.53	4.53
Cd	130000	fluorantene	4.23	5.23
Cr	290000	benzo(a)anthracene	4.86	5.86
Co	3900	chryseen	4.8	5.8
Cu	50000	benzo(k)fluoranthene	5.07	6.07
Hg	170000	benzo(a)pyrene	5.04	6.04
Pb	6400000	benzo(ghi)perylene	5.7	6.7
Mo	1120	indenopyrene	5.47	6.47
Ni	8000			
Se	590			
Sn	371500			
V	5500			
Zn	110000			

**Table 2** Standard soil/sediment constants for metals (INS, 1997)

<b>Contaminant</b>	<b>A</b>	<b>B</b>	<b>C</b>
Sb	1	0	0
As	15	0.4	0.4
Ba	30	5	0
Cd	0.4	0.007	0.021
Cr	50	2	0
Co	2	0.28	0
Cu	15	0.6	0.6
Hg	0.2	0.003	0.0017
Pb	50	1	1
Mo	1	0	0
Ni	10	1	0
Se	1	0	0
Sn	4	0.6	0
V	12	1.2	0
Zn	50	3	1

**Table 3** Sediment standards (BVB, 1993 – Appendix 4)

Contaminant	'Streefwaarde' Class 1 (mg/kg dry weight)	'Grens-waarde' Class 2 (mg/kg dry weight)	'Toetsings-waarde' Class 3 (mg/kg dry weight)	'Interventie-waarde' Class 4 (mg/kg dry weight)
<b>Metals</b>				
Sb				
As	29	55	55	55
Ba				
Cd	0.8	2	7.5	12
Cr	100	380	380	380
Co				
Cu	36	35	90	190
Hg	0.3	0.5	1.6	10
Pb	85	530	530	530
Mo				
Ni	35	35	45	210
Se				
Sn				
V				
Zn	140	480	720	720
<b>PAH's</b>	(µg/kg dry weight)	(µg/kg dry weight)	(µg/kg dry weight)	(µg/kg dry weight)
naftalene	15	50		
antracene	45	50		
fenantrene	50	50		
fluoranthene	15	300		
benzo(a)anthracene	20	50		
chryseen	20	50		
benzo(k)fluoranthene	25	200		
benzo(a)pyrene	25	50		
benzo(ghi)perylene	20	50		
indenopyrene	25	50		
<b>sum 10 PAH's (VROM)</b>	<b>1000</b>		<b>10000</b>	<b>40000</b>



**Figure 1** Ecotopes for the Western Scheldt (from MEP/GEP WESTERSCHELDE)

Overview of the indicators and sub-indicators with their classification scaling. The weighing factor is applied by the highest intergration step from the three Scales to the scale of the whole water-body.  $S_{MEP}$  represents the MEP standard estimated for the required number of species and individual species as defined in Table 10 and Figure 11.

SCALES	Ecosystem Scale	Ecotope Scale				Within Ecotope Scale			Ecological Quality Ratio
		1		2		2			
Weighing factor									
Eco-logical status	$B_{macro \cdot P_{prim}}$ gAFDW m <sup>2</sup> /gCyr <sup>-1</sup>	Mud-flats %	Shallow areas %	Sand flats %	Mussel banks ha	Macro. diversity	Macro. density	Macro. biomass	
MEP	>1/15 <2/15	>15	>15	>12	>200	$S_{MEP}^*$	$t_{calc} < t_{table}$	$t_{calc} < t_{table}$	1.00
GEP	>2/15 <1/5	<15 >12	<15 >12	<12 >9	<200 >150	$>S_{MEP} \times 0.75$			<1.00 <0.75
MODE-RATE	>1/15 <1/2.5	<12 >9	<12 >9	<9 >6	<150 >100	$>S_{MEP} \times 0.50$			<0.75 >0.50
POOR	>1/2.5 <1/1	<140 >1/100	<9 >6	<9 >3	<100 >50	$>S_{MEP} \times 0.30$			<0.50 >0.30
BAD	>1/1	<1/100	<6	<6	<3	$<S_{MEP} \times 0.30$	$t_{calc} > t_{table}$	$t_{calc} > t_{table}$	<0.30

**Figure 2** Establishing the ecological quality ratio based on ecosystem scale, ecotope scale and within ecotope scale (NIOO-CEMO)

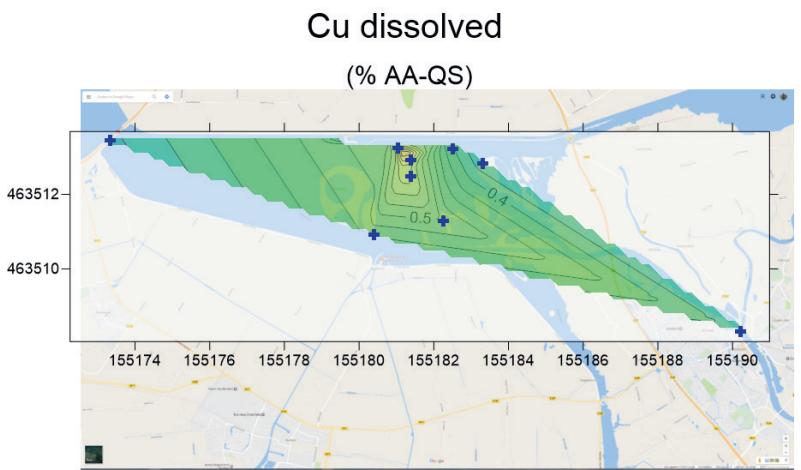
### 3. Chapter 3 'Variation in the availability of metals in surface water, an evaluation based on the dissolved, the freely dissolved and Biotic Ligand Model bioavailable concentration'

**Table S.1** Measured and calculated (FIAM and PNEC) concentrations in µg/l for Cd, Cr, Cu, Ni, Pb and Zn in Lake Ketelmeer surface water. All concentrations are compared to the reference (DSW) AA-EQS to calculate the RCR. In case the measured values where below the reporting limit, 70% of the reporting limit is used.

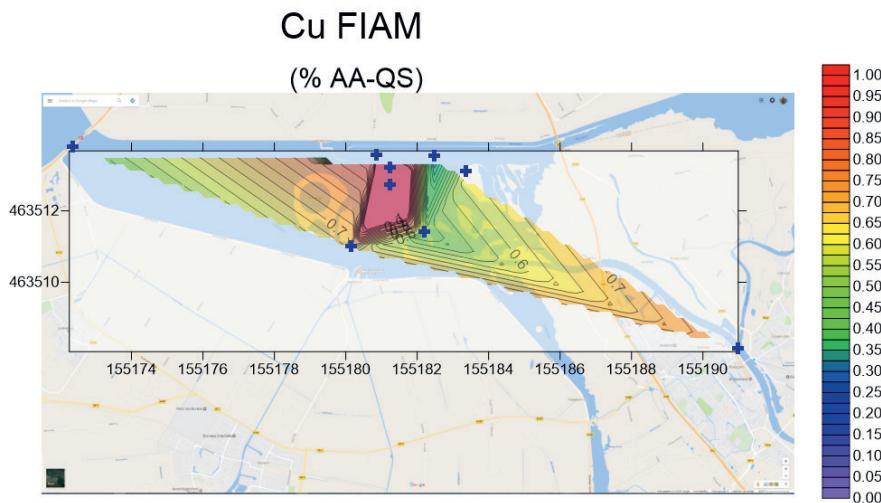
Location	pH	Cd measured	FIAM free diss µg/L	RCR Factor	PNEC conc. at risk µg/L	RCR Factor	Cr measured µg/L	FIAM free diss µg/L	PNEC conc. at risk µg/L	RCR Factor	RCR	RCR factor
AA-EQS in DSW	8.5	0.15	<b>1.00</b>	<b>1.00</b>	n.a.	<b>0.30</b>	<b>1.00</b>	<b>0.30</b>	<b>1.00</b>	<b>1.00</b>	n.a.	
Ketelmeer E2	8.5	0.070 (*)	0.47	0.015	0.34	0.70	(*)	2.33	0.70	2.33		
Ketelmeer E3	8.3	0.070 (*)	0.47	0.017	0.37	0.70	(*)	2.33	0.70	2.33		
Ketelmeer Ost 2	8.2	0.070 (*)	0.47	0.017	0.38	0.70	(*)	2.33	0.70	2.33		
Ketelmeer Ost 3	8.6	0.070 (*)	0.47	0.015	0.32	0.70	(*)	2.33	0.70	2.33		
Ketelmeer Ost 6	8.2	0.070 (*)	0.47	0.017	0.36	0.70	(*)	2.33	0.70	2.33		
Ketelmeer Ost 8	7.9	0.070 (*)	0.47	0.019	0.41	0.70	10.00	10.00	3.00	10.00		
Ketelmeer IJm-BRT	7.8	0.070 (*)	0.47	0.019	0.42	0.70	(*)	2.33	0.70	2.33		
Kaapen	8.0	0.069	0.46	0.018	0.39	0.70	(*)	2.33	0.70	2.33		
Ketelmeer West 1	8.3	0.063	0.42	0.015	0.39	1.64	5.48	1.64	5.48	1.64		
						1.68	5.41	1.68	5.41	1.68		
(*) Data below reporting limit, 70% of reporting limit has been used												
Location	pH	Cu measured	FIAM free diss µg/L	RCR Factor	PNEC conc. at risk µg/L	RCR Factor	Ni measured µg/L	FIAM free diss µg/L	PNEC conc. at risk µg/L	RCR Factor	RCR	RCR factor
AA-EQS in DSW	8.5	<b>10.0</b>	<b>1.00</b>	<b>0.10</b>	<b>0.0</b>	<b>1.00</b>	<b>2.10</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>OD</b>	
Ketelmeer E2	8.5	5.0	0.50	0.09	0.50	1.41	3.54	2.0	0.10	1.61	0.10	OD
Ketelmeer E3	8.3	4.5	0.45	0.13	0.67	1.05	4.27	2.0	0.10	1.71	0.11	0.62
Ketelmeer Ost 2	8.2	5.0	0.50	0.16	0.88	7.58	0.66	2.5	0.13	2.19	0.14	5.41
Ketelmeer Ost 3	8.6	4.0	0.40	0.06	0.31	1.45	2.75	2.0	0.10	1.55	0.10	OD
Ketelmeer Ost 6	8.2	3.5	0.35	0.11	0.61	0.47	7.53	2.0	0.10	1.75	0.11	1.77
Ketelmeer Ost 8	7.9	7.0	0.70	0.34	1.81	OD	2.5	0.13	2.29	0.14	5.77	0.43
Ketelmeer IJm-BRT	7.8	6.0	0.60	0.32	1.72	OD	0.7	(*)	0.04	0.65	0.04	6.78
Kaapen	8.0	3.5	0.35	0.15	0.79	OD	2.0	0.10	1.77	0.11	3.73	0.61
Ketelmeer West 1	8.3	3.2	0.32	0.09	0.49	OD	2.0	0.10	1.67	0.10	OD	
(*) Data below reporting limit, 70% of reporting limit has been used												
Location	pH	Pb measured	FIAM free diss µg/L	RCR Factor	PNEC conc. at risk µg/L	RCR Factor	Zn measured µg/L	FIAM free diss µg/L	PNEC conc. at risk µg/L	RCR Factor	RCR	RCR factor
AA-EQS in DSW	8.5	<b>7.2</b>	<b>1.00</b>	<b>0.75</b>	<b>1.00</b>	<b>1.21</b>	<b>75.0</b>	<b>1.00</b>	<b>26.44</b>	<b>1.00</b>	<b>22.18</b>	<b>3.38</b>
Ketelmeer E2	8.5	3.5 (*)	0.49	0.36	0.49	7.27	0.48	15.0	0.20	6.02	0.23	22.63
Ketelmeer E3	8.3	3.5 (*)	0.49	0.57	0.76	6.44	0.54	9.0	0.12	4.65	0.18	0.66
Ketelmeer Ost 2	8.2	3.5 (*)	0.49	0.68	0.90	12.03	0.29	23.0	0.27	11.35	0.43	20.92
Ketelmeer Ost 3	8.6	3.5 (*)	0.49	0.27	0.37	7.57	0.46	13.0	0.17	4.37	0.17	23.77
Ketelmeer Ost 6	8.2	3.5 (*)	0.49	0.68	0.90	5.65	0.62	7.0	0.09	3.97	0.15	19.84
Ketelmeer Ost 8	7.9	3.5 (*)	0.49	1.03	1.37	4.28	0.82	2.0	0.28	14.59	0.55	17.20
Ketelmeer IJm-BRT	7.8	3.5 (*)	0.49	1.15	1.53	3.25	1.08	7.0	0.09	5.10	0.19	15.97
Kaapen	8.0	2.5	0.34	0.62	0.82	3.32	0.74	15.4	0.21	9.97	0.38	17.36
Ketelmeer West 1	8.3	1.8	0.25	0.30	0.39	3.01	0.60	12.7	0.17	6.60	0.25	18.77
(*) Data below reporting limit, 70% of reporting limit has been used												

**Table S.2** msPAF for the measured dissolved concentration, the FIAM calculated concentration and the PNEC calculated conc.

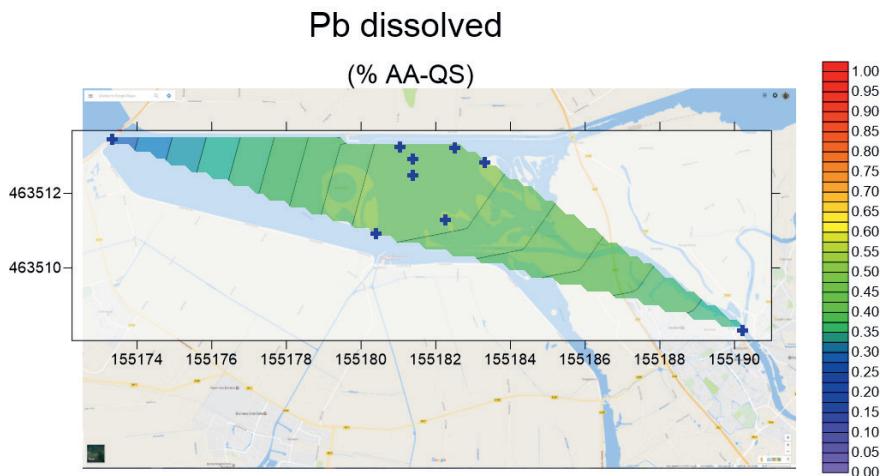
ms-PAF		Acute			Chronic			
x	y	dissolved (%)	FIAM (%)	PNEC (%)	dissolved (%)	FIAM (%)	PNEC (%)	
AA-QS in DSW		<b>9.1%</b>	<b>9.1%</b>	<b>9.1%</b>	<b>21.9%</b>	<b>21.9%</b>	<b>21.9%</b>	
Monitoring stations lake		dissolved (%)	FIAM (%)	PNEC (%)	dissolved (%)	FIAM (%)	PNEC (%)	
Ketelmeer K2	182.160	511.300	3.5%	6.4%	9.0%	8.3%	10.3%	33.5%
Ketelmeer K3	180.100	510.900	3.4%	7.6%	9.7%	7.4%	13.2%	36.1%
Ketelmeer Oost 2	180.800	513.440	3.8%	8.4%	5.7%	8.8%	17.1%	14.8%
Ketelmeer Oost 3	182.440	513.420	3.4%	5.6%	8.2%	6.9%	6.9%	29.2%
Ketelmeer Oost 6	183.325	512.980	3.3%	8.0%	12.1%	5.9%	13.0%	45.1%
Ketelmeer Oost 8	181.200	513.100	4.0%	10.4%	8.0%	11.2%	26.6%	10.9%
Ketelmeer IJm BRT	181.200	512.600	2.3%	10.5%	8.3%	8.9%	24.8%	6.8%
Monitoring stations boundaries								
Kampen	190.990	508.060	3.3%	8.0%	7.5%	6.4%	15.6%	8.4%
Ketelmeer West 1	172.260	513.680	3.3%	5.9%	6.9%	5.8%	9.8%	6.4%



**Figure S.1** Dissolved Cu concentration as % of AA-EQS.  
Measurement locations shown as crosses.



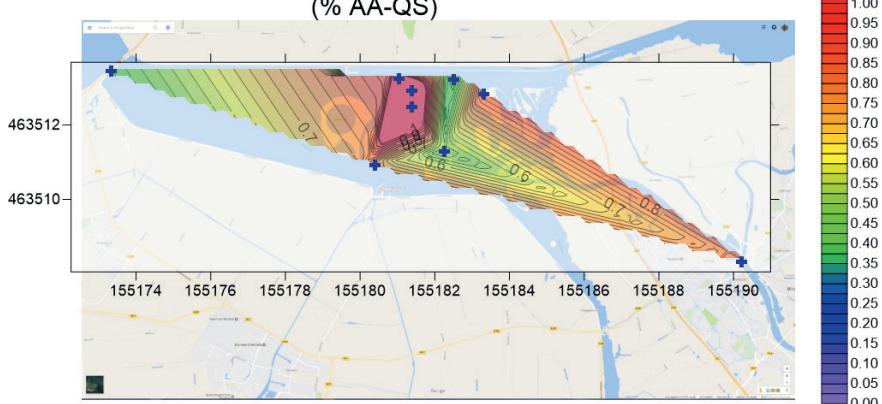
**Figure S.2** RCR<sub>FIAM</sub> corrected Cu concentration as % of AA-EQS.  
Measurement locations shown as crosses.



**Figure S.3** Dissolved Pb concentration as % of AA-EQS.  
Measurement locations shown as crosses.

## Pb FIAM

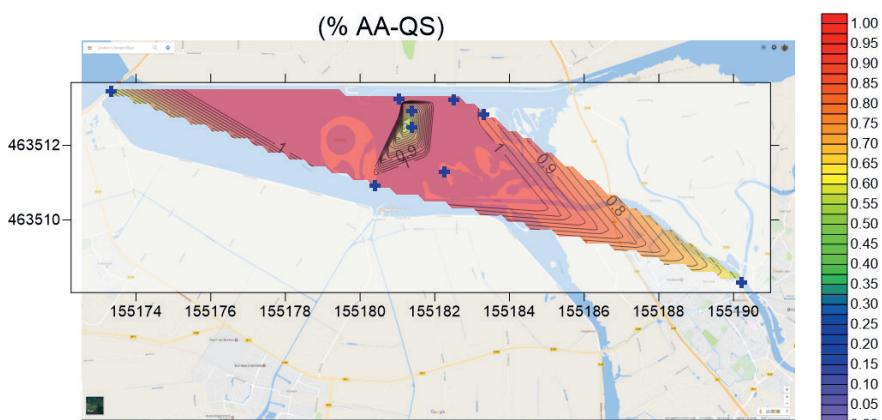
(% AA-QS)



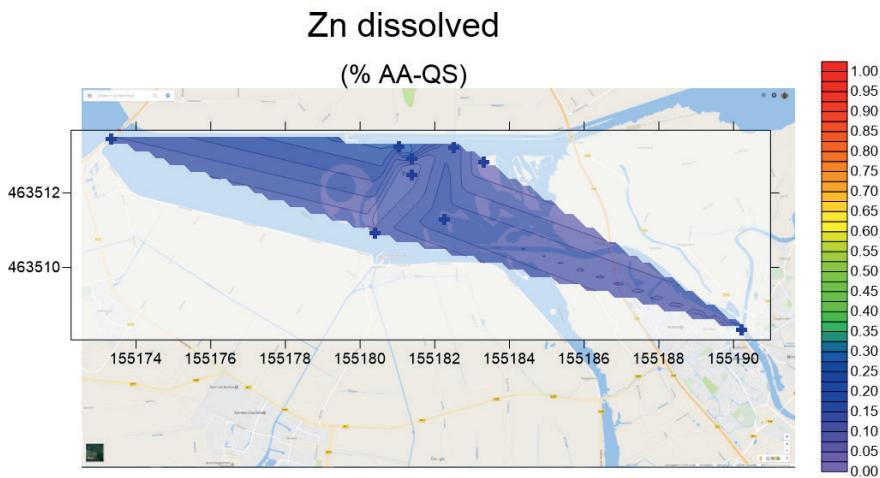
**Figure S.4**  $\text{RCR}_{\text{FIAM}}$  corrected Pb concentration as % of AA-EQS.  
Measurement locations shown as crosses.

## Pb PNEC

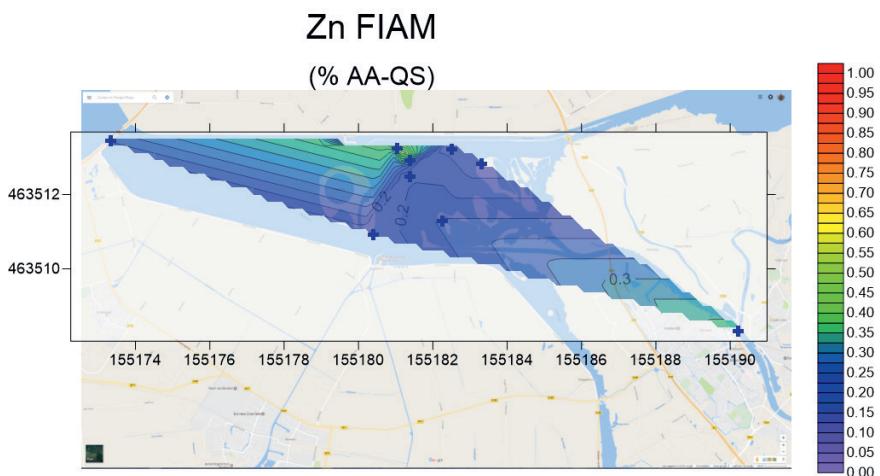
(% AA-QS)



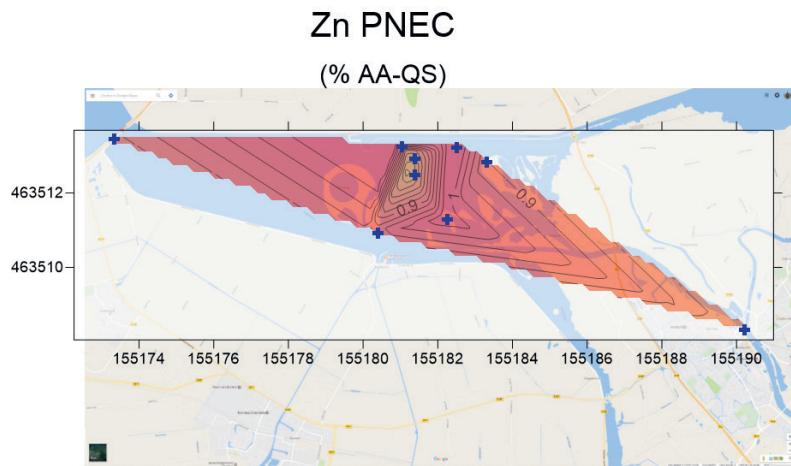
**Figure S.5**  $\text{RCR}_{\text{BLM}}$  corrected Pb concentration as % of AA-EQS  
Measurement locations shown as crosses.



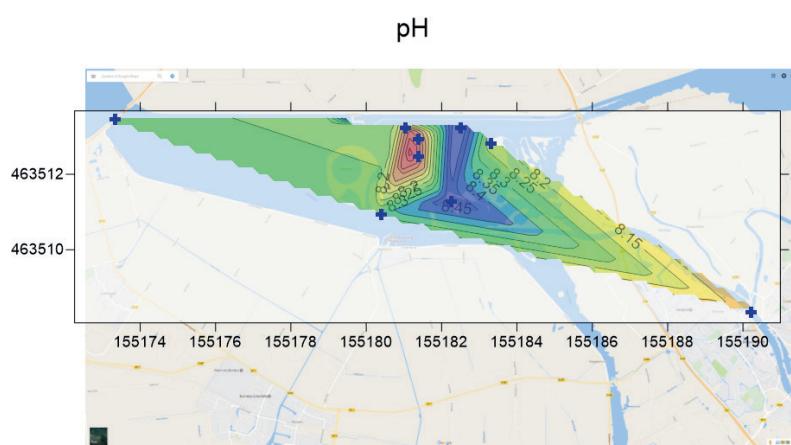
**Figure S.6** Dissolved Zn concentration as % of AA-EQS.  
Measurement locations shown as crosses



**Figure S.7** RCRFIAM corrected Zn concentration as % of AA-EQS.  
Measurement locations shown as crosses.



**Figure S.8** RCRBLM corrected Zn concentration as % of AA-EQS  
Measurement locations shown as crosses.

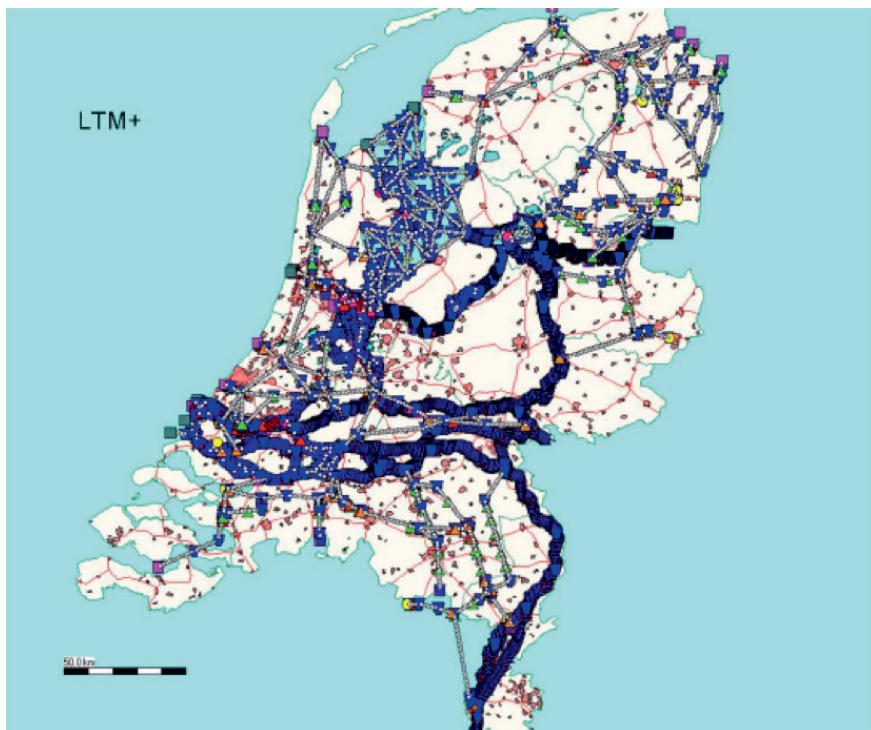


**Figure S.9** pH distribution within the lake  
Measurement locations shown as crosses.

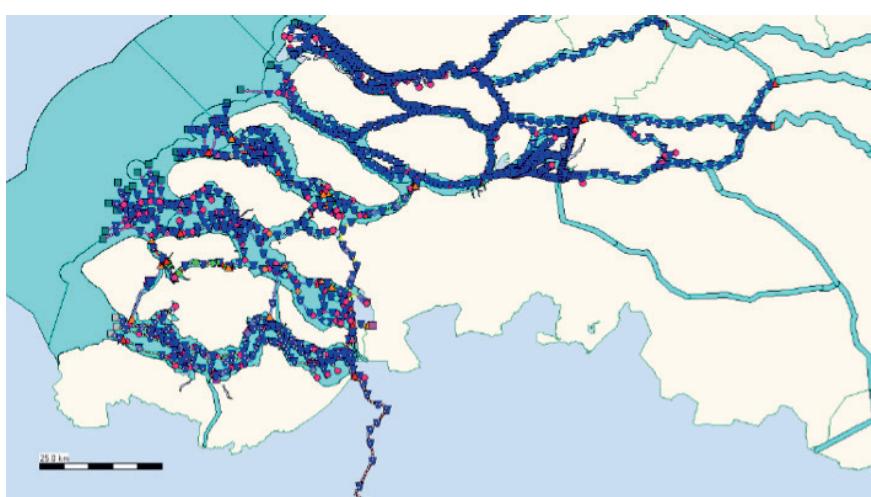
#### 4. Chapter 4 'Predicting the impact of seasonal fluctuations on the potential ecotoxicological risk of multiple contaminants in the River Scheldt discharge into the Western Scheldt Estuary'



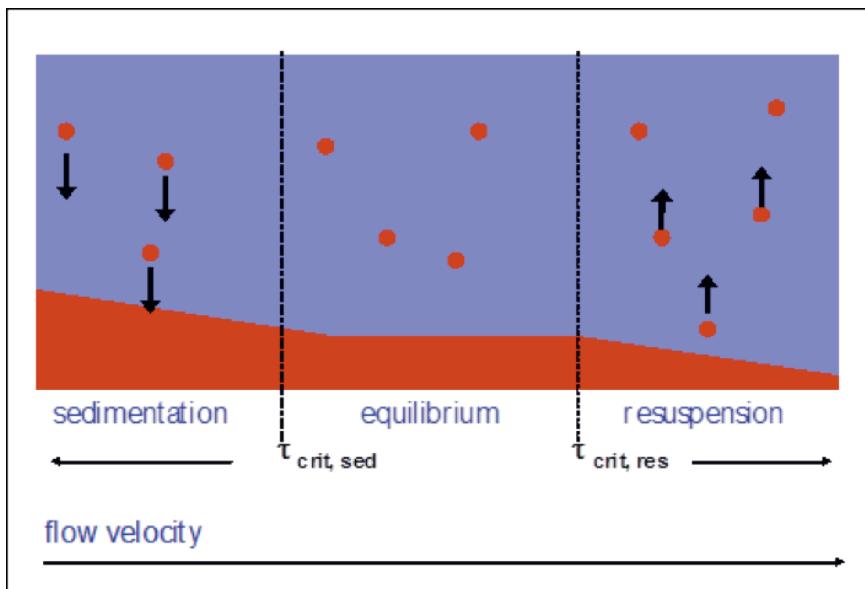
**Figure i** Location of Land van Saeftinge and Schaar van Ouden Doel in the eastern model boundary of the River Scheldt (Google Earth)



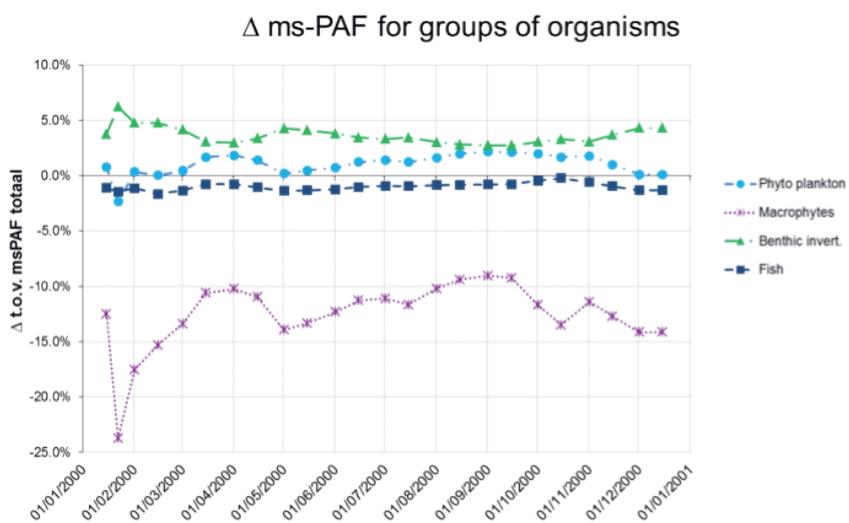
**Figure ii** Sobek 1D land covering model



**Figure iii** Sobek 1D detailed model for South Western part of the Netherlands



**Figure iv** Bed shear stress and flow velocity dependent sedimentation and erosion



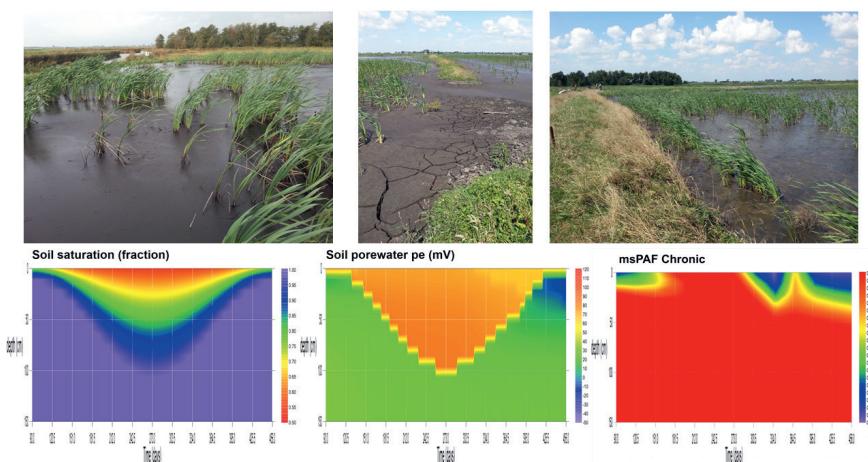
**Figure v** Differences in ms-PAF between different groups of organisms

**Table i** Calculated ms-PAF (total) for Land van Saeftinghe at different times in the year, split by contribution per contaminant

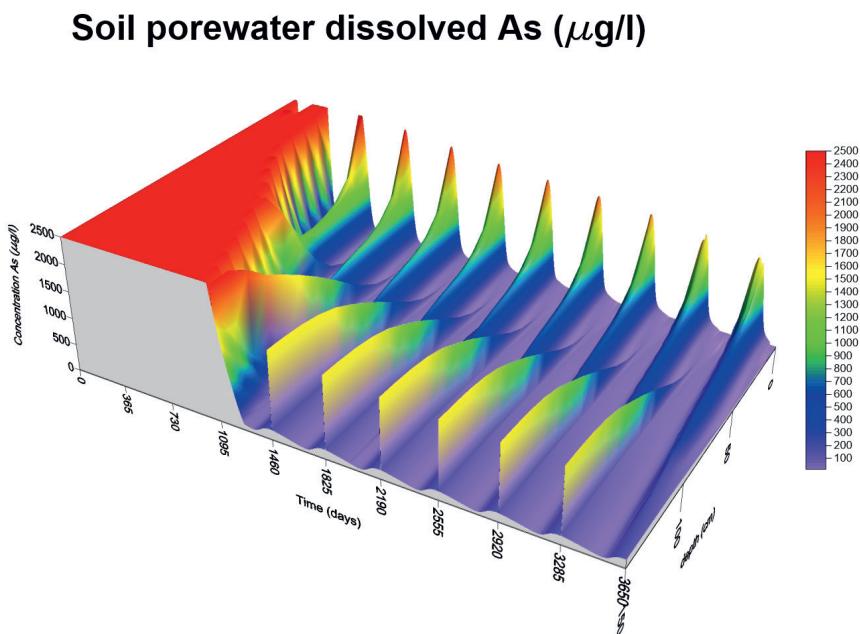
Date	Cadmium	Copper	Ars-HCH	BaP-HCH	Gemma-HCH	Tetrachlorobenzene	Naphthalene	Lindane	ms-PAF
15/01/2000	0.61%	10.03%	0.00%	0.00%	0.00%	0.00%	0.00%	2.17%	12.5%
22/01/2000	4.84%	17.16%	0.00%	0.00%	0.00%	0.00%	0.00%	4.50%	24.7%
01/02/2000	3.82%	12.96%	0.00%	0.00%	0.00%	0.00%	0.00%	2.21%	18.1%
15/02/2000	1.76%	11.24%	0.00%	0.00%	0.00%	0.00%	0.00%	3.00%	15.4%
01/03/2000	0.85%	10.38%	0.00%	0.00%	0.00%	0.00%	0.00%	2.56%	13.4%
15/03/2000	0.54%	8.89%	0.00%	0.00%	0.00%	0.00%	0.00%	1.34%	10.6%
01/04/2000	0.62%	8.57%	0.00%	0.00%	0.00%	0.00%	0.00%	1.22%	10.2%
15/04/2000	0.73%	8.77%	0.00%	0.00%	0.00%	0.00%	0.00%	1.71%	11.0%
01/05/2000	0.79%	10.80%	0.00%	0.00%	0.01%	0.00%	0.00%	2.76%	14.0%
15/05/2000	0.80%	10.38%	0.00%	0.00%	0.01%	0.00%	0.00%	2.51%	13.3%
01/06/2000	0.67%	9.63%	0.00%	0.00%	0.01%	0.00%	0.00%	2.32%	12.3%
15/06/2000	0.63%	9.07%	0.00%	0.00%	0.00%	0.00%	0.00%	1.82%	11.3%
01/07/2000	0.62%	9.09%	0.00%	0.00%	0.00%	0.00%	0.00%	1.61%	11.1%
15/07/2000	0.59%	9.56%	0.00%	0.00%	0.00%	0.00%	0.00%	1.74%	11.7%
01/08/2000	0.50%	8.46%	0.00%	0.00%	0.00%	0.00%	0.00%	1.42%	10.2%
15/08/2000	0.63%	7.75%	0.00%	0.00%	0.00%	0.00%	0.00%	1.15%	9.4%
01/09/2000	0.74%	7.44%	0.00%	0.00%	0.00%	0.00%	0.00%	1.00%	9.0%
15/09/2000	0.66%	7.69%	0.00%	0.00%	0.00%	0.00%	0.00%	1.01%	9.2%
01/10/2000	0.69%	10.36%	0.00%	0.00%	0.00%	0.00%	0.00%	0.82%	11.7%
15/10/2000	0.59%	12.31%	0.00%	0.00%	0.00%	0.00%	0.00%	0.75%	13.5%
01/11/2000	0.56%	9.94%	0.00%	0.00%	0.00%	0.00%	0.00%	1.08%	11.4%
15/11/2000	0.64%	10.45%	0.00%	0.00%	0.00%	0.00%	0.00%	1.89%	12.7%
01/12/2000	0.70%	11.06%	0.00%	0.00%	0.00%	0.00%	0.00%	2.79%	14.2%
15/12/2000	0.61%	10.03%	0.00%	0.00%	0.00%	0.00%	0.00%	2.17%	14.2%

## 5. Chapter 5 'From sediments to soils - changes in pore water metal bioavailability'

From sediment to soil, from wet to dry to wet during a 1 year period. Impact on soil moisture, redox and msPAF profile



**Figure S.1** Graphical abstract, including seasonal pictures of the case study location



**Figure S.2** 3D presentation of the soil pore water concentration for arsenic during a period of 3650 days (10 year cycles). Time (in days) on the x-axis, the soil depth (in cm) on the y-axis.

## 6. Chapter 6 'Scientific progress in sediment and water quality assessment'

**Table 1** Metal concentration in sediments for five EU sediments. (\*) after normalisation for Dutch standard soil

metals		Example 1	Example 2	Example 3	Example 4	Example 5	Example 1	Example 2	Example 3	Example 4	Example 5
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	(*) standard soil corrected (mg/kg)				
Antimone	Sb	1.0	1.0	0.8	1.3	1.1	1.0	1.0	0.8	1.3	1.1
Arsenic	As	17.3	11.9	12.7	44.1	29.5	16.0	8.4	16.5	36.9	22.6
Barium	Ba	57.5	418.4	105.6	109.6	90.3	24.2	104.6	23.9	46.4	32.9
Cadmium	Cd	2.1	0.6	1.1	6.4	3.8	2.4	0.5	2.2	6.4	3.4
Chromium	Cr	96.7	20.5	29.8	160.8	114.8	62.0	11.0	15.5	103.3	69.5
Cobalt	Co	114.5	94.7	89.4	54.1	93.9	50.5	26.2	22.7	24.0	36.3
Copper	Cu	52.6	39.1	62.2	76.1	53.2	47.7	24.9	84.5	61.2	38.0
Mercury	Hg	4.7	6.9	10.3	4.4	7.2	4.1	5.1	10.1	3.6	5.7
Lead	Pb	162.2	77.0	107.8	123.2	88.0	151.6	57.3	135.1	106.1	70.3
Molybdenum	Mo	2.2	2.7	1.6	1.3	0.9	2.2	2.7	1.6	1.3	0.9
Nickel	Ni	20.9	27.3	29.0	34.2	25.0	10.2	9.2	9.1	16.7	10.9
Selenium	Se	2.0	2.5	1.7	4.2	3.8	2.0	2.5	1.7	4.2	3.8
Tin	Sn	6.2	5.2	3.5	7.2	2.4	2.7	1.4	0.9	3.1	0.9
Vanadium	V	73.6	23.1	34.6	95.9	77.8	35.9	7.8	10.9	46.9	34.0
Zinc	Zn	795.0	160.6	217.3	571.6	378.2	550.9	79.5	174.8	370.4	219.8
					% lutum (< 2 µm)		7.04	1.75	1.01	7.12	5.29
					% organic matter		22.44	11.55	55.56	16.10	12.59

$$(*) S_{soil} = S_{default\ soil} \times \frac{A + [B .(\% lutum)] + [C .(\% OM)]}{A + [B .25] + [C .10]}$$

- $S_{soil}$  = standard for soil or sediment to be evaluated (mg/l)
- $S_{default\ soil}$  = standard for default soil (mg/kg)
- %lutum = measured lutum content of soil or sediment (%)
- % OM = measured organic matter content of soil or sediment (%)
- A, B, C = constant dependant of contaminant

S

**Table 2** Standard soil parameters for each metal

(*)	A	B	C	Example 1	Example 2	Example 3	Example 4	Example 5
Sb	1	0	0	1.0	1.0	1.0	1.0	1.0
As	15	0.4	0.4	1.1	1.4	0.8	1.2	1.3
Ba	30	5	0	2.4	4.0	4.4	2.4	2.7
Cd	0.4	0.007	0.021	0.9	1.2	0.5	1.0	1.1
Cr	50	2	0	1.6	1.9	1.9	1.6	1.7
Co	2	0.28	0	2.3	3.6	3.9	2.3	2.6
Cu	15	0.6	0.6	1.1	1.6	0.7	1.2	1.4
Hg	0.2	0.003	0.0017	1.2	1.3	1.0	1.2	1.3
Pb	50	1	1	1.1	1.3	0.8	1.2	1.3
Mo	1	0	0	1.0	1.0	1.0	1.0	1.0
Ni	10	1	0	2.1	3.0	3.2	2.0	2.3
Se	1	0	0	1.0	1.0	1.0	1.0	1.0
Sn	4	0.6	0	2.3	3.8	4.1	2.3	2.6
V	12	1.2	0	2.1	3.0	3.2	2.0	2.3
Zn	50	3	1	1.4	2.0	1.2	1.5	1.7

**Table 3** Organic contaminant concentration in sediments for five EU sediments.

	Example 1 mg/kg	Example 2 mg/kg	Example 3 mg/kg	Example 4 mg/kg	Example 5 mg/kg
<b>4. Poly Aromatic Hydrocarbons (PAH's)</b> sum 10 PAH	5.7	20.9	2.5	3.3	
<b>d. polychlorinated biphenyls (PCB's)</b> sum 7 PCB	0.113	0.016	0.018	0.113	
<b>6. Pesticides</b> <b>a. organochloro pesticides</b> sum DDT/DDE/DDD	0.001	0.005	0.010	0.005	
sum drins	0.005	0.000	0.000	0.009	
sum HCHs	0.000	0.000	0.000	0.001	

**Table 4** Sediment standards for Ireland, Flanders, France, Germany and The Netherlands

	Irish		Flemish		French		German (+)	Dutch (*)		
metals	Lower level	Upper level b	fresh excavated soil	secondary resource	Level 1 (N1)	Level 2 (N2)	Integriertes Schadstoff-/Sedimentmanagement Elbe-Einzugsgebiet	Bbk, living (class A)	Bbk, industry (class B)	ZBT (Marine criteria (**))
Antimone	Sb								15	
Arsenic	As	9	70	35	250	25	50	10	29	29
Barium	Ba								395	625
Cadmium	Cd	0.7	4.2	1.2	10	1.2	2.4	0.22	4	4
Chromium	Cr	120	70	91	1250	90	180	100	120	380
Cobalt	Co								25	240
Copper	Cu	40	110	72	375	45	90	30	96	190
Mercury	Hg	0.2	0.7	1.7	5	0.4	0.8	0.15	1.2	1.2
Lead	Pb	60	218	120	1250	100	200	47	138	580
Molybdenum	Mo								5.0	200
Nickel	Ni	21	60	56	250	37	74	3	50	210
Selenium	Se								100	
Tin	Sn								900	
Vanadium	V								250	
Zinc	Zn	160	410	200	1250	276	552	200.0	563	2000
										365

Irish classification of marine sediment: Cronin, M, et al. 2006. Guidelines for the Assessment of Dredge Material for Disposal in Irish Waters, Marine Environment and Health Series, No. 24

Flemish classification of marine sediment: VLAREMA. 2012. Implementatie van de Europese kaderrichtlijn (EG) 2008/98 voor het beheer van afvalstoffen in Vlaanderen.

French classification of marine sediment: The Paris Convention of 22 September 1992, replacing the Oslo Convention on the protection of the marine environment of the North-East Atlantic (OSPAR Convention 92).

(+)Germany has no chemical marine quality standard, the fresh water sediment standard according to the ARGE Elbe classification is used. Source: 'Status of ecotoxicological assessment of sediment and dredged material in Germany and The Netherlands', Dutch-German Exchange (DGE) on Dredged Material - Part 5 - March 2007. Federal Institute of Hydrology, Germany

(\*\*)The Netherlands use a normalisation system for sediment concentrations based on organic matter and lutum content. Sediment standards are described in the soil directive (Bbk, 2008): Bbk, 2008, Besluit bodemkwaliteit, Staatsblad, 2007-12-03, publicatie 469

(\*\*\*)The ZBT (disposal of sediment at sea) has no sediment normalisation

**Table 5** Results of NEN 7363 (2004) leaching test with a Liquid to Solid ratio of 10. Concentration in each of the seven fractions and the total leached volume versus the Liquid to Solid (L/S) ratio.

		Example 1	Example 2	Example 3	Example 4	Example 5
k1	ml	27.8	29.8	2.0	30.2	15.6
k2	ml	26.9	29.8	2.1	29.9	16.4
k3	ml	81.0	87.0	5.9	90.0	52.1
k4	ml	135.0	145.0	9.7	150.6	87.0
k5	ml	270.9	291.0	19.4	300.1	173.1
k6	ml	812.0	872.1	58.4	901.1	519.1
k7	ml	1354.1	1453.1	97.0	1502.3	866.1
total (ml)		2707.7	2907.8	194.5	3004.2	1729.5
final L/S		10.00	10.01	10.01	10.00	9.99
correction factor L/S 10		1.00	1.00	1.00	1.00	1.00

**Table 6** Results of NEN 7363 (2004) leaching test with a Liquid to Solid ratio of 10. The total leached amount based on seven fractions is divided by the allowed leaching amount according to (VLAREA, 2012) and the (Bbk, 2008) for NV (non-formed building materials) and IBC (isolated) building material.

L/S 10 Legislation	Flemish	VLAREA				Dutch	NV building material					Dutch	IBC building material				
		Example 1	Example 2	Example 3	Example 4		Example 1	Example 2	Example 3	Example 4	Example 5		Example 1	Example 2	Example 3	Example 4	Example 5
<b>metals</b>																	
Antimone	Sb						1.2%	0.9%	0.9%	11.4%	1.8%	0.5%	0.4%	0.4%	5.2%	0.8%	
Arsenic	As	3.3%	2.2%	2.3%	73.9%	25.6%	3.0%	2.0%	2.0%	65.7%	22.8%	1.3%	0.9%	0.9%	29.6%	10.3%	
Barium	Ba						1.0%	0.9%	2.1%	0.9%	0.7%	0.2%	0.2%	0.5%	0.2%	0.1%	
Cadmium	Cd	1.2%	2.9%	4.1%	5.5%	5.4%	0.9%	2.2%	3.0%	4.1%	4.0%	0.6%	1.5%	2.0%	2.7%	2.7%	
Chromium	Cr	7.1%	7.0%	7.5%	9.0%	9.9%	5.6%	5.6%	5.9%	7.2%	7.8%	0.5%	0.5%	0.5%	0.6%	0.7%	
Cobalt	Co						1.4%	2.7%	5.1%	6.8%	3.2%	0.3%	0.6%	1.1%	1.5%	0.7%	
Copper	Cu	1.5%	1.5%	1.6%	2.1%	1.1%	0.8%	0.8%	0.9%	1.2%	0.6%	0.1%	0.1%	0.1%	0.1%	0.1%	
Mercury	Hg						3.6%	1.9%	1.5%	10.4%	2.1%	0.9%	0.5%	0.4%	2.6%	0.5%	
Lead	Pb	0.1%	0.1%	0.1%	0.1%	0.1%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Molybdenum	Mo						1.7%	1.9%	0.6%	24.6%	1.0%	0.1%	0.1%	0.0%	1.6%	0.1%	
Nickel	Ni	1.0%	2.7%	7.2%	53.0%	6.5%	1.7%	4.7%	12.2%	90.3%	11.1%	0.4%	1.0%	2.6%	18.9%	2.3%	
Selenium	Se						0.1%	0.1%	0.1%	2.7%	0.1%	0.0%	0.0%	0.0%	0.1%	0.0%	
Tin	Sn						0.3%	0.0%	0.1%	0.1%	0.2%	0.1%	0.0%	0.0%	0.0%	0.0%	
Vanadium	V						9.8%	7.4%	4.2%	14.7%	6.9%	0.9%	0.7%	0.4%	1.3%	0.6%	
Zinc	Zn	4.3%	3.5%	3.5%	3.1%	4.1%	2.6%	2.2%	2.2%	1.9%	2.6%	0.9%	0.7%	0.7%	0.6%	0.8%	

**Table 7** Bbk, 2008 Bijlage A. behorende bij paragraaf 3.3 van de Regeling bodemkwaliteit  
- Maximale samenstellings- en emissawaarden bouwstoffen.

Parameter	Vormgegeven (E <sub>64d</sub> in mg/m <sup>2</sup> )	Niet-vormgegeven (mg/kg d.s.)	IBC-bouwstoffen (mg/kg d.s.)
antimoon (Sb)	8,7	0,32	0,7
arseen (As)	260	0,9	2
barium (Ba)	1.500	22	100
cadmium (Cd)	3,8	0,04	0,06
chroom (Cr)	120	0,63	7
kobalt (Co)	60	0,54	2,4
koper (Cu)	98	0,9	10
kwik (Hg)	1,4	0,02	0,08
lood (Pb)	400	2,3	8,3
molybdeen (Mo)	144	1	15
nikkel (Ni)	81	0,44	2,1
seleen (Se)	4,8	0,15	3
tin (Sn)	50	0,4	2,3
vanadium (V)	320 <sup>1</sup>	1,8 <sup>1</sup>	20
zink (Zn)	800	4,5	14
bromide (Br)	670 <sup>2</sup>	20 <sup>2</sup>	34
chloride (Cl)	110.000 <sup>2</sup>	616 <sup>1,2</sup>	8.800
fluoride (F)	2.500 <sup>2</sup>	55 <sup>2</sup>	1.500
sulfaat (SO <sub>4</sub> )	165.000 <sup>2</sup>	1.730 <sup>2,3</sup>	20.000



# C

Appendix: Case studies  
CEDA position paper  
'Beneficial Use of  
Contaminated Sediments'

**Project****Construction of the road: 'Freycinet 12'**

Classification	R1A_2012_F-Freycinet12
Location	GPMD, Dunkirk, France
Volume	1800 m <sup>3</sup> of sediments reused
Technique	Immobilisation-stabilisation / building material
Contaminants	TPH, PCB, heavy metals, PAH's
Granulometry	Silty
Scale	full scale
Client	GPMD: Grand Port Maritime de Dunkerque
Consultant	n.a.
Contractor	ENVISAN, COLAS
Research institute	Ecole des mines de Douai
Research program	n.a.
Contact	Envisan France, alain.pieters@envisan.com, sofie.herman@envisan.com, +32-477 727 839)
Status	Commercial
Year Start – End	2012

**Description of the project**

The re-use of contaminated sediments from the Port of Dunkirk in road structures was initiated as early as 2002. On that date, the Port started cooperation with the Ecole des Mines de Douai and various industrial partners in order to design alternative materials for stabilised sub base road layers.

After a first project phase of lab scale tests, in 2005, a pilot test was carried out on a 300 m<sup>2</sup> plot where a 50 meter long road was constructed using treated sediments. The objective was to verify the industrial feasibility of the entire process.

The 2005 experiment has demonstrated that the formulation of alternative road materials is possible with sediment. The road has to meet the requirements of the French standard dimension criteria for roads constructed with the usual road materials. Following these results the Port of Dunkirk decided to continue in this way with industrial partners: ENVISAN for dredging and lagooning, and COLAS for the formulation of road materials using this resource.

In 2012, the Port of Dunkirk decided to reconstruct 850 meter long road 'Route du Quai Freycinet 12'. The road structure is designed for 15 years of traffic with an average of 100 heavy good vehicles per day.

The usual road structure drawn by the technical services of the Port for the tender requirements consists of 6 cm of hot mix asphalt on 40 cm of slag bound mixture on the sand platform.

Taking into account the results of its studies on the sediments dredged in October 2011,

COLAS Nord Picardie proposed the following mechanically equivalent alternative road structure: 5 cm of high modulus bituminous concrete on 6 cm of EME (Asphalt concrete with high modulus) / 30 cm of material containing the contaminated sediment dredged and lagooned by Envisan on the sediments treatment platform.

This solution consumes 1 m<sup>3</sup> of sediment per 10 m<sup>2</sup> of roads. Thus, 450 m<sup>3</sup> of dry sediment representing 1800 m<sup>3</sup> of dredged sediments were used.

#### ***Geotechnical results.***

The lab study of 2012 gave results which were less optimistic than the ones of the 2005 study. The road mixture reached however a level of mechanical class T2 which was taken into account in the design of the road structure. The short term compressive strength reaches 1.3 MPa after 7 days and allows a correct trafficability for the normal operations on site. The stiffness modulus reaches in the long term more than 9000 MPa and the tensile strength becomes higher than 0.6 Mpa.

Cores extracted at 180 days show a very good cohesion of the material and the level of tensile strength is equal to the one obtained in the laboratory study.

Deflection measured at 60 days after implementing (average < 10 / 100th mm) is correct and shows the proper efficiency of the treated sediment-based layer.

#### ***Environmental monitoring results***

The sediments used for the road were analysed according to the methodological guide for the acceptability of alternative materials in road construction (Setra, 2011)

The analysis confirmed the effectiveness of the treatment by bio remediation revealing no problems in organic pollutants level (BTEX, PCBs, TPH, TOC, PAH) and heavy metals.

In accordance with this guide and the regulation applicable in France, leaching results according to NF EN 12457-2 tests reveal some problems for soluble fraction, sulphate and chloride in the sediment which find their origin in the marine environment.

Tests in partnership with Holcim were conducted on the treated mixture laboratory specimens that show a significant reduction in the soluble fraction by adaptation of the hydraulic binder.

Analysis of the percolated water on a 30 meter long plot helped to verify the efficiency of blocking the soluble fractions by treatment with specific hydraulic binder with close analyses of the A 1 threshold of the law of water.

After finalising the works, analyses of the percolated water in the groundwater, in the nearby dock along the Route du Quai Freycinet 12 and in the piezometer are conducted every month during the first year and six-monthly the following 2 years. One year after the works, no remarkable changes have been detected in the three monitoring points.



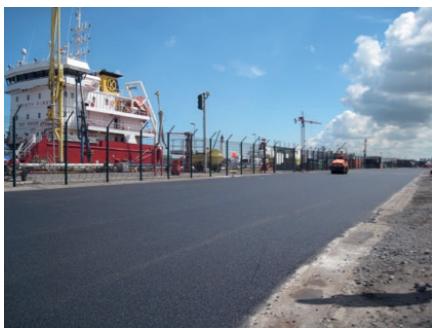
## Graphical information



Pre-treated sediments used in sub base road layers (left) and application of hydraulic binders (right)



Leveling and compaction of the sub base road layer



Final road 'Route du Quai Freycinet 12 »

## References/web links

1. Sofie Herman, Alain Pieters, Daphné Glaser, Pascal Gregoire, Christophe Priez, Didier Desmoulin, David Guglielmetti. A lustrum of valorisation of contaminated sediments from the Port of Dunkirk (France). Dredge dikes conference, Rostock 2014. [http://www.dredgdikes.eu/wp-content/uploads/15\\_Herman\\_WEB.pdf](http://www.dredgdikes.eu/wp-content/uploads/15_Herman_WEB.pdf)
2. Sofie HERMAN , Daphné GLASER, Alain PIETERS, Pascal GREGOIRE, Christophe PRIEZ, Didier DESMOULIN, David GUGLIELMETTI , 2014. Cinq ans de valorisation des sédiments contaminés extraits du Port de Dunkerque (France). XIIIèmes Journées Nationales Génie Côtier – Génie Civil. Dunkerque, 2-4 juillet 2014. [http://www.paralia.fr/jngcgc/13\\_109\\_herman.pdf](http://www.paralia.fr/jngcgc/13_109_herman.pdf)
3. <http://www.envisan.com/fr/activites/travaux-environnementaux/traitemet-des-sediments-et-dragage-environnemental>

**Project****Pneumatic Flow Tube Mixing / Stabilization of Soft Sediments**

Classification	R1A_2015_NJ-Kearny
Location	Kearny, New Jersey, USA
Volume	3928 m <sup>3</sup>
Technique	Stabilization via Pneumatic Flow Tube Mixing (PFTM)
Contaminants	PAHs, Metals
Granulometry	Silty sediment with approximately 3-8% organic content
Scale	Pilot Scale
Client	New Jersey Department of Transportation
Consultant	Jafec USA, Clean Earth, Inc
Contractor	Rutgers University, Center for Advanced Infrastructure and Transportation
Research institute	Beneficial Use of Stabilized Dredged Material
Research program	Robert Miskewitz, Ph.D. Research Associate Professor, Rutgers University, rmiskewitz@envsci.rutgers.edu
Contact	

**Description of the project**

A pilot study was conducted to evaluate the use of the Pneumatic Flow Tube Mixing (PFTM) method for stabilization and solidification of soft sediments dredged from the New York/ New Jersey Harbor (NY/NJ). The PFTM apparatus was assembled and tested on 7/24/2015. Production began on 8/4/2015 and ran through 9/4/2015. The total amount of material process during the deployment was 3928 m<sup>3</sup>.

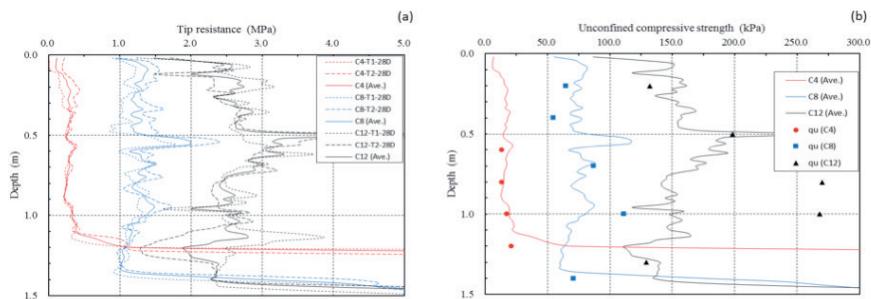
The average strength of amended sediments with 8% cement content (by wet weight), after 28 days, prepared and cured in the laboratory is approximately 200 kPa. The stabilized material was found to be acceptable by the site contractors using their standard plate test. Analysis of leachability of the contaminants from the amended sediment samples indicate no detectable mass of SVOCs, PCBs, or Pesticides. The only metal detected in the leaching tests was arsenic and comparison of stabilized material to raw sediment indicate that approximately 75% of the leachable arsenic was bound by the 8% Portland cement mix and approximately 80% was bound by the 12% Portland cement mix.

This project successfully demonstrated that the PFTM process could be used for sediments dredged from the NY/NJ Harbor and the resulting amended material possessed the required strength and chemical characteristics for upland placement and beneficial reuse. The results of the laboratory and field experimental program demonstrate that the process yields an amended material that possesses the appropriate structural and chemical characteristics.

## Graphical information



Pneumatic Flow Tube Mixing Tool



In-situ Strength Characteristics of Stabilized Sediment

C

## References/web links

Maher, A., Kitazume, M., Janbaz, M., Miskewitz, R., Douglas, S., and Yang, D., (2016) Utilization of Pneumatic Flow Tube Mixing Technique (PFTM) for Processing and Stabilization of Contaminated Harbor Sediment. *Marine Georesources & Geotechnology*, <http://dx.doi.org/10.1080/1064119X.2016.1257668>.

**Project****Sandvika Marina Harbour**

Classification	R3B_2010_N-Sandvika
Location	Oslo, Norway
Volume	4,000 m <sup>3</sup>
Technique	Mass stabilisation of contaminated sediments with hydraulic binders
Contaminants	Tri-butyl tin, As, Ni, Cu, Hg, Pb, Cr, Zn, Cd, PAH
Granulometry	Silty clay
Scale	Full scale
Client	Sandvika Municipality, Oslo, Norway
Consultant	
Contractor	Ramboll
Research institute	Norwegian Institute for Water Research, NIVA.
Research program	
Contact	Norwegian Institute for Water Research, NIVA.
Status	Commercial
Year start - end	2010

**Description of the project**

Contaminated sediment from the seabed at Sandvikselva in the Oslo fjord was removed by dredging and stabilized by mixing with a GGBS plus cement-based binder, and used in the construction of a new quay wall. Approximately 4,000m<sup>3</sup> of sediments were dredged by a mobile crane and grab, and placed behind a concrete sheet pile wall, where mass stabilisation was carried out by injecting and mixing the GGBS/cement binder with the dredged sediments.

The stabilised sediments were used for construction of a new quay wall, providing an additional 3,000m<sup>2</sup> of new amenity land. The binder was a 50:50 mix of GGBS and cement, mixed at a binder content of 140 – 180 kg/m<sup>3</sup> of dredged sediment. The contaminants in the sediment comprised TBT, PAH, mercury and other heavy metals. Compressive strength tests on the stabilised sediments gave strengths in the order of 600–1,000 kPa at 260 days.

A follow up laboratory study on the potential impact of the stabilised sediments on leaching of contaminants concluded that this beneficial use of dredged sediments generally reduces the leaching of heavy metals due to (a) the reduced exposed surface area of contaminated sediments, and (b) immobilization effects of the binders used in the stabilisation.

## Graphical information



Mass stabilisation of dredged contaminated sediment behind concrete quay wall



Completed project – stabilized sediments form new quay wall and walkway

C

## References/web links

Miljøeffekter av stabilisering og solidifisering (STSO) av forurensede sedimenter i utløpet av Sandvikselva. Norsk Institutt for Vannforskning (NIVA) Rapport L.NR. 5972-2010. (Environmental Effects of Stabilization and Solidification (STSO) of Contaminated sediments in the outlet of Sandvikselva. Norwegian Institute of Water Research (NIVA) Report No. L.NR. 5972-2010). [[https://brage.bibsys.no/xmlui/bitstream/handle/11250/214966/5972-2010\\_200dpi.pdf?sequence=1](https://brage.bibsys.no/xmlui/bitstream/handle/11250/214966/5972-2010_200dpi.pdf?sequence=1)]

**Project****Landfarming (bioremediation)  
Oostwaardhoeve**

Classification	R2B_1995_NL-Oostwaardhoeve
Major Function	Remdiation
Other Functions	Restoration
Location	Netherlands
Volume	1.000.000 m <sup>3</sup> (100 ha)
Technique	Bioremediation
Contaminants	PAH and mineral oil
Granulometry	Silty clay
Scale	Pilot scale
Client	Experimental farm Oostwaardhoeve
Executor	Consultant and research institute: Wageningen University; Contractor: De Vries and van de Wiel
Research program	PhD. Project J. Harmsen
Contact	Joop Harmsen, Wageningen University, The Netherlands, Joop.Harmsen@wur.nl
Year start – end	1995 – 2003

**Description of the project**

In the late seventies, early eighties of the 20<sup>th</sup> century The Netherlands realized they had to deal with large volumes (over 250 mln. m<sup>3</sup>) of contaminated sediments. Therefore, large volume, low cost solutions were needed. For sediments contaminated with organic pollutants pilot sites were allocated to evaluate the effectiveness of passive landfarming.

For research purposes, dredged sediments from different harbors and sluices in the Netherlands (Petroleum Harbour, Wemeldinge, Geul Harbour and Zierikzee) where taken and put on fields of 5 x 5 m to study the leaching, drying/shrinking and bioremediation. The main pollutants were PAH's and mineral oil. The treatment was passive (no mechanical dewatering or addition of heat).

The research fields were upscaled to 100 hectares, suitable to dewater, ripen and bioremediate 1 mln. m<sup>3</sup> sediment. The fields were planted with Short Rotation Coppice (SRC) crops to accelerate the dewatering and have a secondary beneficial use of the land. The biomass was farmed and used as biofuel. The profit on the biomass grown was low. After 7 years the PAH and mineral oil levels in the soil were mostly below the Dutch soil directive standard, and the leachability of the metals was low due to the fixation of the metals in the formed soil (especially when treated with lime). There was no recognizable transfer of heavy metals to lower soil layers in the monitoring period (1995 – 2001).

Passive landfarming with crop growth is a relative cheap (around 20 euro/m<sup>3</sup> minus benefits from biomass) solution to treat biodegradable organic pollutants. However, the solution requires space, time and does not solve the problem of the removal of heavy metals. While the heavy metal concentrations in the SRC crops were below the maximum concentration allowed in food for cattle, the presence of heavy metals is seen as the limiting factor for treatment of sediments with landfarming.

### Graphical information

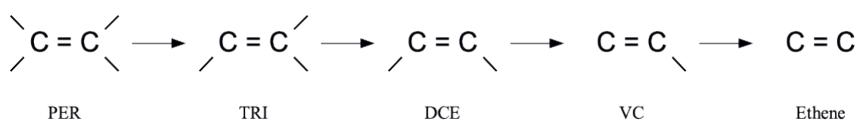


Figure 1: Degradation of micro pollutants by bacteria, example for chlorinated aliphatics



Figure 2: Pilot site Oostwaardhoeve

## References/web links

Sediment and Dredged Material Treatment: [https://play.google.com/store/books/details?id=DkzgkxS99IkC&rdid=book-DkzgkxS99IkC&rdot=1&source=gbs\\_atb&pcampaignid=books\\_booksearch\\_atb](https://play.google.com/store/books/details?id=DkzgkxS99IkC&rdid=book-DkzgkxS99IkC&rdot=1&source=gbs_atb&pcampaignid=books_booksearch_atb)

Soil and Sediment Remediation [https://books.google.nl/books/about/Soil\\_and\\_Sediment\\_Remediation.html?id=T2e09Dn45U8C&redir\\_esc�](https://books.google.nl/books/about/Soil_and_Sediment_Remediation.html?id=T2e09Dn45U8C&redir_esc�)

Landfarming of polycyclic aromatic hydrocarbons and mineral oil contaminated sediments. Author(s), Harmsen, ISBN 9085041120

**Project****Re-cycling of contaminated sediment  
from an old dry dock in Fincantieri Area  
– Port of Palermo / Sediment Washing**

Classification	R1A_TBDD_I-Palermo
Location	Palermo, Italy
Volume	76.000 m <sup>3</sup>
Technique	Recovery of material - R5 'Recycling/recovery of other inorganic substances' – from the waste's sandy and gravelly fraction ( $\Phi > 0.063$ mm), according to previously designed specific purposes
Contaminants	Slightly contaminated with heavy metals and with HC>12 up to 8300 ppm
Granulometry	Sand/gravel with 15% of silt and clay, mixed with waste and organic matter
Scale	full scale
Client	Palermo Port Authority
Consultant	N/A
Contractor	Trevi Spa
Research institute	N/A
Research program	N/A
Contact	Giovanni Preda, Trevi Spa, gpreda@trevispa.com, +39 0547319579

**Description of the project**

At the end of the 80s Palermo Port Authority started works to construct the 150.000 DWT Dry Dock, within Palermo Industrial Port. Works were stopped due to a dispute arisen with the Subcontractor.

Up to now the following works – which are included in the original project – were carried out.

- Construction of the foundation bench after remediation with removal and replacement of recent seabed deposits;
- Installation of cellular caissons with the exception of the basic gate-caisson;
- Construction of the diaphragm wall on the caissons' external perimeter to extend the seepage paths during the construction phases up to realization of the foundation slab;
- Completion of grouting to improve imperviousness of the diaphragm wall single panels' joints;
- Installation of the foundation piles of the dock's slab, with insertion of tie rods to be stressed later on.

At the beginning of the 2000s Palermo Port Authority, after terminating the Contract, started to plan the completion works. In order to assess the state of works already

carried out, it was necessary to perform consolidation and static safety works before emptying the dock basin. Works specified in the Contract included dredging of approximately 76.000 m<sup>3</sup> of sediments and waste, for a total of about 117.000 tons of mainly sandy material, contaminated by hydrocarbons C>12, heavy metals and mixed waste, mostly conveyed by 2 sewage pipes (about 500.000 El) which, until 2014, would discharge next to the Dock. Trevi Spa, after being awarded the Contract, drew up the executive design required to perform works, proposing a washing treatment of the waste to be dredged known as Sediment Washing.

### The plant

Trevi Plant is made up of five technological units which were specifically devised to carry out the whole waste management process. The plant consists of different treatment Units:

- Unit A - feeding: it receives the accumulated shovable waste (at the bay) and properly conveys it to the plant, eliminating what may impair the plant's proper functioning by means of a feed hopper equipped with protections, harrows and sensors for detection and removal of magnetic and non-magnetic ferrous materials.
- Unit B - washing and granulometric separation. Through this unit contaminants are transferred from the waste's solid matrix to the washing fluid (sea water) and contaminated fractions are separated from the recoverable ones. The first washing phase is carried out in the drum washing barrel, followed by the wet sieving of coarse materials and a sand refinement process by means of 6 attrition chambers.
- Unit C - chemical-physical treatment of the residual suspension. This unit carries out coagulation and flocculation of suspended solids and their subsequent sedimentation, as well as separation of soluted contaminants through chemical conditioning.
- Unit D - Densification of the fine fraction. Muds concentrated in the chemical-physical treatment, collecting most of contaminants, are further dehydrated through solid/liquid separation devices. The main objective of mud treatment is to minimize the costs for final disposal. The plant, according to specific site needs, is equipped with two different systems of mechanical dehydration: decanter centrifuge and/or filter press. Only in some specific cases, i.e. when the suspension flow is quite high, both units are used simultaneously.
- Unit E - filtration and water cleaning finishing. Waste slurry is conditioned with acid to adjust the pH value. Eventually, filtration is carried out; first on sand beds (corindone/quarzite) to remove any possible soilds and suspended pollutants and, finally, on an active coal bed to remove any dissolved pollutants. At last, wastewater is disinfected and discharged.

The plant has a variable output, mainly according to the granulometric features of the waste to be treated, especially in terms of fine fraction percentages ( $\Phi < 0.063$  mm). In this specific case, the features of sediments to be treated allow a maximum productivity equal to 60 tons/hour.

## The works

The objective of the Sediment Washing treatment is the recycling of materials and subsequent reduction of waste to be disposed of. This technology, if properly applied, always reduces the amount of waste to be recycled/disposed of in external plants; for that reason it can be considered environmentally sustainable and developed in compliance with waste management regulations.

The plant is recovering material - R5 'Recycling/recovery of other inorganic substances' – from the waste's sandy and gravelly fraction ( $\Phi > 0.063$  mm), according to previously designed specific purposes.

After undergoing a compliance audit at the jobsite, the sand achieves CE certification as recycled aggregate satisfying the technical requirements for the specific purposes, regulations and existing standards applied to products (EN12620, EN13242). The separated and densified fine fraction and the other waste are recycled or disposed of in specifically authorized external plants, while waste slurry is cleaned up in a specific section of the Sediment Washing plant and is eventually discharged into surface waters (according to Tab.3 Part 3, Attachment 5 of D.Lgs. 152/2006).

Once the works were finished, approximately 111.000 tons of waste were treated, recovering 41.400 tons of sand, 15.200 tons of gravel, while 25.400 tons of contaminated fine fraction were disposed of in an external plant.

## Graphical information

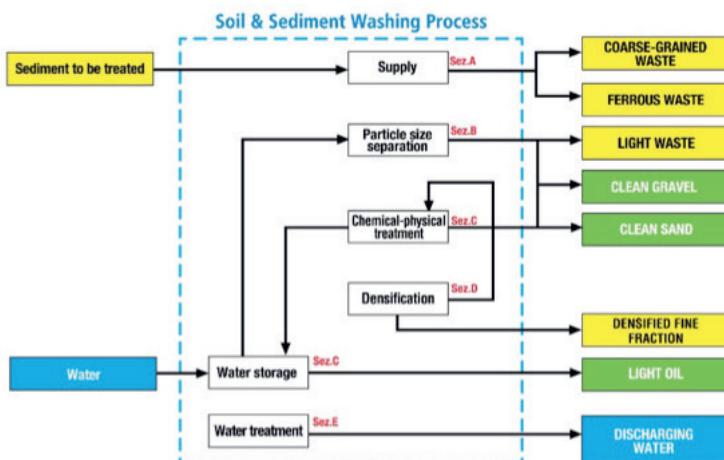


Figure 1: Soil & Sediment washing process



Figure 2: Main outputs



Figure 3: The plant during the night shift

**Project****Cement-Lock Thermo-Chemical Contaminated Sediment Processing**

Classification	R1A_2018_Cement-lock
Location	Bayonne, New Jersey USA
Volume	500 m <sup>3</sup> demonstrated on a 7600 m <sup>3</sup> /year demonstration rotary kiln
Technique	Thermo-chemical high temperature treatment followed by immobilization to make a construction grade cement (30-40% replacement for Portland cement)
Contaminants	Dioxins/Furans, PAHs, Heavy metals, Pesticides
Granulometry	Silty/clayey
Scale	Full scale demonstration
Client	US Environmental Protection Agency Region 2 (USEPA), and New Jersey Department of Transportation (NJDOT)
Consultant	None
Contractor	US Depart of Energy Brookhaven National Laboratory (BNL), 2018 - AMEC-Foster Wheeler (Wood)
Research institute	Gas Technology Institute (GTI) & Gas Research Institute (GRI) / Des Plaines, Illinois USA
Research program	US Environmental Protection Agency Region 2 / New Jersey Department of Transportation - New York/New Jersey Harbor Sediment Decontamination Program
Contact	Al Hendricks, Volcano Partners, LLC, al.hendricks@cement-lock.com, <a href="https://www.cement-lock.com/">https://www.cement-lock.com/</a>
Status	Commercial
Year start-end	2005 - 2018

**Description of the project**

Cement-Lock® (engineered process) is a patented, thermo-chemical manufacturing technology that uses contaminated sediments as a feedstock to produce a remediated pozzolanic glass-like material with marketable value called Ecomelt®. Ecomelt® is a beneficial use product that may be used as a 40% replacement for Portland cement in the production of concrete, at a lower cost than Portland cement alone. The Cement-Lock® process was developed by the Gas Technology Institute under a contract with Brookhaven National Laboratory (BNL), funded by the US Federal Water Resources Development Act and the US Environmental Protection Agency Region 2 Superfund Program. Additional funding and project management support was provided by the New Jersey Department of Transportation Office of Maritime Resources and the Gas Research Institute. A 7600 m<sup>3</sup>/year demonstration plant was constructed at the International Matex Tank Terminal,



Bayonne, New Jersey. Demonstration tests were conducted in 2005 through 2007 and successfully created Ecomelt® from sediment from the Lower Passaic River Superfund site.

The technology consists of feeding a mixture of dewatered contaminated sediment and modifiers (calcium, aluminum and silica to control the texture and properties of the Ecomelt) to a natural gas fired rotary kiln melter that operates at temperatures of 1315° to 1426° C. During processing, the sediment-modifier mixture is thermo-chemically transformed to a homogeneous, lava-like melt that encapsulates inorganic contaminants (heavy metals) – Figure 1.

Organic contaminants are disassociated and destroyed at these elevated temperatures. Inorganic contaminants present in the sediment are immobilized or 'locked' within the pozzolanic glassy product matrix. Organic contaminants in the feedstock are destroyed by the high temperature, to Destruction Removal Efficiencies' of 99.9999+% for compounds such as polychlorinated biphenyls (PCBs), Dioxin/Furans, and pesticides/herbicides. Mercury, lead and other volatilized metals are captured in the air pollution control system. Remaining metals are contained and immobilized in the Ecomelt® which is the primary beneficial use - glassy, pozzolanic material product, which when dried and finely ground, can be used as a partial replacement for Portland cement in the production of concrete.

A demonstration of the beneficial use component was performed in 2008. Ecomelt® product from the Passaic River, New Jersey sediment was ground to cement fineness (<50 µm). The ground product was used as a partial replacement for Portland cement in a batch of concrete for a length of sidewalk situated on the campus of Montclair State University (MSU), New Jersey USA. The concrete has been monitored for evidence of wear, cracking, and spalling. Figure 4 shows a sample of the Ecomelt® (glassy product before grinding) that was used in the demonstration test. Figure 5 shows the pulverized Ecomelt® after grinding to make a construction grade cement, Figure 6 laying of the concrete sidewalk at MSU for the demonstration test and Figure 7 shows the cured sidewalk at MSU.

Since the 2008 demonstration there has been significant re-design and improvements to the Cement-Lock process by Volcano Partners, LLC and AMEC Foster Wheeler (Wood). The uniqueness of this innovative environmental remediation and manufacturing technology lies in the modifiers and the mixture ratios and residence times used in the process, rather than in the thermo-chemical processing equipment itself. All mechanical equipment items are available and in widespread use globally. Consequently, the ability to enlarge the facility from the nominal 7600 m<sup>3</sup>/year demonstration facility to a full commercial 190,000 - 380,000 m<sup>3</sup>/year facility is not limited by mechanical considerations.

### Cement-Lock Process Flow / System pictures:

Figures 1-3.

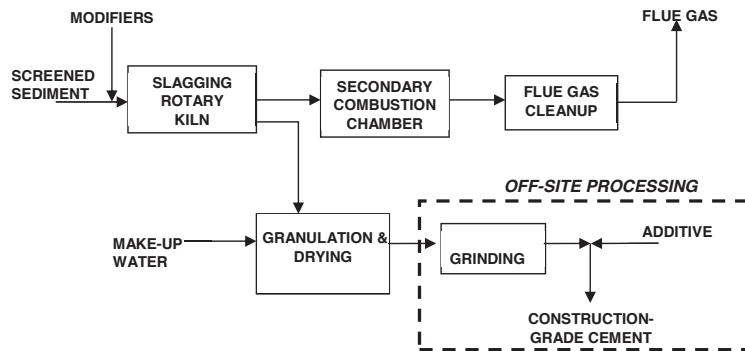


Figure 2. Cement-Lock Demonstration Plant , Bayonne, New Jersey



Figure 3. Rotary Kiln close-up. Dewatered sediment with modifiers are charged into the rotating rotary kiln and exit as a melted sediment followed by a water quench to produce a pozzolan beneficial use product called Ecomelt© which is pulverized to make a 30-40% replacement for Portland cement.

## Graphical information



Figure 4 – Ecomelt© (sediment melt)



Figure 5 – Pulverized Ecomelt©



Figure 6 – Concrete pour



Figure 7 – Concrete cured

## References/web links

1. <https://semspub.epa.gov/work/02/213389.pdf>
2. <http://www.nj.gov/dep/passaicdocs/docs/NJDOTSupportingCosts/DECON-CEMLOCK-ENDESCO-FINALREPORT-PILOT-PHI.pdf>
3. <https://www.slideshare.net/EricAStern1/cement-lock-battelle-poster-final-stern-43668563>
4. <http://sednet.org/download/2%20Eric%20Stern.pdf>
5. [https://www.researchgate.net/publication/281350583\\_Thermal\\_Treatment\\_for\\_Reclamation\\_and\\_Beneficial\\_Use\\_of\\_Contaminated\\_Sediments](https://www.researchgate.net/publication/281350583_Thermal_Treatment_for_Reclamation_and_Beneficial_Use_of_Contaminated_Sediments) (Presented at the 33rd International Conference on Thermal Treatment Technologies & Hazardous Waste Combustors, At Baltimore, Maryland USA, 2014)

**Project****Room for the River**

Classification	R1B_2006_NL-Room for the river
Location	Rhine, Waal, IJssel and Meuse rivers, The Netherlands
Volume	Total sediment/soil volume 35 - 40 mln. m <sup>3</sup> (including flood plain soils), (excess sediment/soil volume 5 mln. m <sup>3</sup> )
Technique	Excavation, segregation and reallocation of the different fractions
Contaminants	Present, but acceptable for use within the Dutch Soil Directive (criteria: no unacceptable ecotoxicological risk and no degradation of the overall quality of the waterbody )
Granulometry	Mix of gravel, sand, silt and clay, both wet (sediment) and dry (floodplain soil)
Scale	Real project scale
Client	Ministry of Infrastructure and the Environment, Rijkswaterstaat
Consultant	Multiple (on different subprojects)
Contractor	Multiple (on different subprojects)
Research institute	STOWA, KNMI, Deltares, Alterra and universities
Research program	National Water and Climate Knowledge and Innovation Programme (covering topics like ecological impact, climate adaptation, resilience, adaptive delta planning, cyclic rejuvenation, flood probability, etc.)
Contact	Deltares (Arjan Wijdeveld)
Status	Implemented (total project budget 2,2 bln. €) – finished in 2015
Year Start – End	2006 – 2015

**Description of the project**

The goal of the Dutch Room for the River Program is to give the river more room to be able to manage higher water levels. For 30 locations measures were taken to give the river space to flood safely. This as an alternative to further increase the height of the dikes. To make this possible, ~ 40 mln. m<sup>3</sup> of soils and sediments had to be reallocated. Most of the soils/sediments could be used to within the project, but for some of the sediments an under water storage site (much like a Confined Deposition Facility or CDF) had to be constructed. By using old (or sometimes newly constructed) quarry sites (gravel, sand or clay) these quarry sites could be partially filled. The end result is an increase in wetland and shallow lake habitat.

Constructing a CDF type of solution (the stored sediments have contamination levels in line with the soil use specific standards, hence they are not seen as contaminated) in former pit lakes is one example of beneficial sediment us within room for the river. There are more examples. See the provided web links for information on the 30 locations.





Figure 1 Room for the River

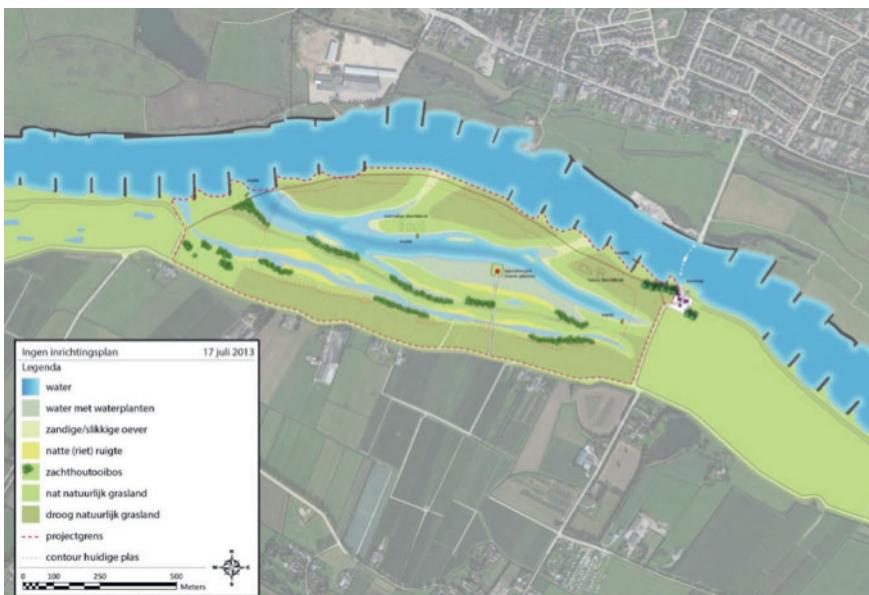


Figure 2 Reallocation site for sediments

## References/web links

- <https://www.ruimtevoorderivier.nl/english>
- <https://www.rijkswaterstaat.nl/english/water-systems/protection-against-water/room-for-the-river.aspx>
- [https://en.wikipedia.org/wiki/Room\\_for\\_the\\_River\\_\(Netherlands\)](https://en.wikipedia.org/wiki/Room_for_the_River_(Netherlands))

**Project****Renovation of a controlled flood area using dredged material from the Durme river**

Classification	R5A_2019_B-Durme River
Major Function	Resilience
Other Functions	Remediation
Location	Durme river, Lokeren - Waasmunster, BE
Volume	Volume reused (~260,000 m <sup>3</sup> )
Technique	Reuse of dredged sediments in new dyke bodies
Contaminants	Heavy metals (Arsenic, Cadmium, Zinc), PCB, PAH, TPH, PFAS
Granulometry	Silty clay and sand
Scale	Project scale
Client	De Vlaamse Waterweg
Executor	Consultant: Witteveen+Bos Belgium NV, Antwerp, Contractor: TBD in 2018
Research program	2 Seas Interreg European initiative USAR - Using Sediments as a Resource
Contact	Client: De Vlaamse Waterweg, Antwerp, Mr. Hans Quaeyhaegens
Consultant:	Witteveen+Bos Belgium NV, Antwerp, Mr. Peter Van den bossche
Year start – end	2019 – 2021

**Description of the project**

Within the framework of the Flemish flood protection program Sigmaplan for the river Scheldt estuary, De Vlaamse Waterweg (The Flemish Waterways, the Flemish agency responsible for the control of around 1000 km navigable waterways in Flanders) plans to renovate the Controlled Flood Area „Potpolder IV“. The renovation of the historical Potpolder IV along the Durme river, a Scheldt tributary, involves the construction of a new ring dyke, length 3600 m and the reprofiling of the existing dyke along the river into an overflow dyke over 2260 m. Dredged material from the Durme river will be used as building material for the construction of new embankments. The project is a pilot within the Interreg 2 Seas program, „Using Sediments as A Resource‘, USAR (Using Sediment as A Resource, Interreg 2 Seas Mers Zeeën).



Based on the investigation report (2018), the sediments in the Durme river contain increased levels of heavy metals, TPH, PFAS, PAH and PCB (exceed the levels for free use VLAREBO Annex V). The concentrations of some heavy metals and TPH exceed the levels of non-moulded building materials (VLAREMA). Furthermore the granulometry of the sediments (silty clay to sand) gives a geotechnical challenge for reuse in the dykes. The dredged material will be treated before use in the new dyke bodies. The dredging strategy

and mobile treatment plant setup will be organized in order to obtain the VLAREMA certificate, to fulfil the requirements of minimal transport and to fulfil the geotechnical stability requirements of the new dyke bodies. The reuse are evaluated based on environmental and geotechnical criteria.

In March 2018 the tender documents for the dredging works will be published. De Vlaamse Waterweg already have prepared for dredging works and dyke concentration the EIA, the archeological investigation and the environmental and building permit. Maximum reuse of dredged sediments into the dyke bodies is requested. The selected contractor will be obligated to first start with a feasibility study for the geotechnical, environmental and juridical aspects. The dredging works at the Durme will start in 2019 and have a duration of approximately three years. As a result the river profile will be reinstalled, nature restoration at the river banks is carried out and no dredged material has to be removed from the area.

### Graphical information



Figure 1. Project area seen from the south



Figure 2. Detail river Durme

### References/web links

1. USAR webpage: <https://www.vlaamsewaterweg.be/usar>
2. VLAREMA - 17 FEBRUARY 2012. - Order of the Government of Flanders adopting the Flemish regulation on the sustainable management of material cycles and waste
3. VLAREBO - Decree on soil remediation and soil protection. DECREE of 27 octobre 2006 on soil remediation and soil protection
4. Flemish flood protection programme SIGMAPLAN <http://sigmaplan.be/nl/projecten/durmevallei/>
5. Investigation report Beneden-Durme. Witteveen+Bos (2018)

**Project****Moorburg Dewatering Fields**

Classification	R1A_1985_D-Moorburg
Location	Hamburg, Germany
Volume	Up to 300,000 (m <sup>3</sup> /year)
Technique	Treatment of silty sediment for further beneficial use options or disposal
Contaminants	Main contaminants present
Granulometry	Silty/sandy/clayey
Scale	full scale
Client	Hamburg Port Authority
Consultant	N/A
Contractor	Hamburg Port Authority
Research institute	N/A
Research program	N/A
Contact	Heinz-Dieter Detzner, Hamburg Port Authority, Heinz-Dieter.Detzner@hpa.hamburg.de, +49 160 8893969; +49 40 428472387
Status	Commercial
Year start – end	1985 –

**Description of the project**

A long-established practice of handling dredged material in Hamburg is the dewatering of the silty dredged material in dewatering fields. The technical facilities were built in Moorburg and have been in operation since the mid-80s.

The individual fields exhibit sizes ranging from 2 – 4 ha and encompass a total area of about 100 ha. They were built on former flushing fields. After profiling the old flushing fields, a 90 cm thick 3-layer mineral silt seal with 2% inclination was installed as abasis for the dewatering fields. Above the base seal there is a 60 - 90 cm thick sand drainage layer into which drainage pipes are installed at approx. 15 m to improve the drainage behavior. This ensures that no polluted wastewater enters the environment in an uncontrolled manner. The dams of the individual dewatering fields were built from sandy mixed soil and are also sealed. The annual treatment capacity of the treatment facility in Moorburg is up to a 300,000 m<sup>3</sup> profile volume.

Basically, the treatment process consists of 4 steps (see also Fig. 1):

1. A hopper dredger pumps the dredged material into the dewatering fields by means of a pipeline up to a height of 1.3 m.
2. After a few weeks the silt has settled to the extent that the supernatant transport water can be drained off and the actual drying process begins.

3. Once the first drying cracks occur a process of putting the dredged material on heaps starts for acceleration of the subsequent dewatering. This process is repeated until the material requirements for beneficial use or disposal have been met.
4. At the end of the dewatering process, the material is removed and trucked to the place of beneficial use or the final disposal sites.

The total dewatering of the silty dredged material takes from 9 to 12 months depending on the weather conditions. The treatment technique does not require complex technologies. However, a major disadvantage is the enormous space consumption associated with the construction of dewatering fields.

### Graphical information

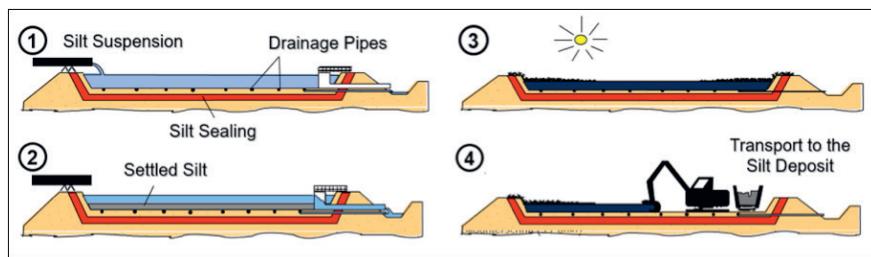


Figure 1: Operation Principle of the Dewatering Fields in Hamburg



Figure 2: Aerial photograph of Dewatering Fields Moorburg-Mitte

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**Project****Dredged material as sealing material on disposal sites**

Classification	R2A_1988_D-HamburgSealing
Location	Hamburg, Germany
Volume	Up to 150,000 m <sup>3</sup> /a
Technique	Use of treated silty-clayey sediment as sealing material instead of clay or silt
Contaminants	Contains heavymetals and organic contaminants
Granulometry	Silty/clayey
Scale	full scale
Client	Hamburg Port Authority
Consultant	N/A
Contractor	Hamburg Port Authority
Research institute	N/A
Research program	N/A
Contact	Marcus Heilmann, Hamburg Port Authority, Marcus.Heilmann@hpa.hamburg.de, +49 151 58482550; +49 40 428472724
Status	Commercial
Year start – end	1988 –

**Description of the project**

Right from the start, the mineral sealing layers of the Hamburg dredged material disposal sites in Francop and Feldhöfe consist of treated, clayey-silty sediment (METHA-Material produced in the METHA-plant). To encourage further beneficial use possibilities the Hamburg Port Authority (HPA) has also applied for a suitability assessment procedure for the use of METHA-Material as secondary raw material for a surface sealing system on disposal sites at the LAGA (Working Group of the Federal States on Waste). In 2008 the evaluation procedure was successfully completed.

In Germany, according to the Landfill Directive, disposal site construction materials must comply with the state of the art. LAGA has set up the Ad Hoc Working Group 'Landfill Technology' for suitability assessments carried out by the Länder. For the use of secondary raw materials, the working group has set the required test criteria and the requirements for proper installation as well as the issues of the quality management as a national standard.

The suitability assessment was based on many individual assessments with detailed technical and organizational specifications. In particular, the focus was on the evaluation of the soil-mechanical and waste-chemical characteristics of the METHA Material. The technical suitability and the environmental harmlessness of the utilization had been demonstrated in the assessment procedure carried out considering established legal German standards.

The requirements for the accredited sealing system are described in more detail in the documents 'Suitability assessment of METHA-Material for the construction of mineral

sealing' and 'Quality management manual – Surface sealing system made of METHA material' (see below in the references).

The following objectives were achieved by using the METHA-Material as a sealing material:

- The consequent beneficial use of waste during the construction of the disposal sites
- Protection of natural resources
- Efficient and cost-saving while using a secondary raw material

### Graphical information

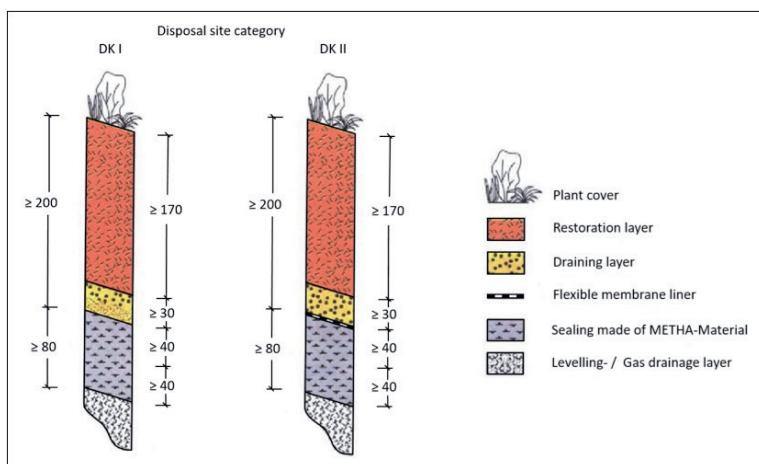


Figure 1: Schematic diagram of the accredited surface sealing system

### References/web links

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**Project****Dredged sediment as dike construction material**

Classification	R1A_2004_D-Hamburg_Dike
Location	Hamburg, Germany
Volume	Large volume – from case to case
Technique	Use of treated silty-clayey sediment as dike construction material
Contaminants	Contains heavy metals and organic contaminants
Granulometry	Silty/clayey
Scale	Pilot scale
Client	Hamburg Port Authority
Consultant	Gesellschaft für Grundbau und Umwelttechnik mbH (GGU), BWS GmbH
Contractor	Hamburg Port Authority
Research institute	TUHH - Hamburg University of Technology and UHH - University of Hamburg
Research program	N/A
Contact	Ulrich Schmekel, Hamburg Port Authority, Ulrich.Schmekel@hpa.hamburg.de, +49 151 11531159; +49 40 428472759
Year start – end	2004 –

**Description of the project**

Following the positive assessment of METHA material as secondary raw material for landfill surface sealing systems, Hamburg Port Authority (HPA) currently investigates its suitability as dike construction material. The objectives were

- To further the consequent beneficial use of mineral waste materials
- To spare natural resources (clay-rich natural marsh soils)
- To enhance cost-effectiveness of depth maintenance in the port of Hamburg.

The design envisages replacement of the lower part of the dike cover with METHA material, while for the top layer the traditional, natural clayey material from the tidal marsh area in Northwestern Germany continues to be employed. Investigations are carried out in two phases: (1) Geotechnical suitability and (2) environmental suitability, the latter focusing on the potential mobilization and release of contaminants. Both aspects were investigated by research projects for which the Hamburg University of Technology and the University of Hamburg were contracted and thereafter assessed by a third independent expert opinion. The assessment is based on laboratory and field investigations. The latter comprise two long-term field pilot dikes which are in



operation since 2004 (Ellerholzkanalbrücken) and 2006 (Drewer Hauptdeich).

Results so far indicate that from a geotechnical point of view the material is suitable for dike construction, given certain boundary conditions. The assessment included modelling of hydraulic stress propagation in different dike designs constructed with METHA material. The field pilot at Ellerholzkanalbrücken, regularly exposed to storm water tides, in 13 years of operation never gave reasons for concern of failure. Laboratory experiments on compactibility show that enhanced drying prior to construction minimizes in situ crack formation and maximizes the achievable extent of compaction and therefore represents a possible optimization step in material production.

From an environmental point of view it appears that the release of contaminants to the groundwater or surface waters is minimal and is judged irrelevant based on comparison with the current environmental legislation regarding groundwater, surface water and soil protection. Both the leachate analyses from the long-term field test as well as the leachate composition following vigorous worst-case treatment in the laboratory indicate that the inorganic as well as the organic contaminant inventory is firmly occluded in stable mineral and organic compounds; both under the initial anaerobic as well as under the later aerobic conditions observed in situ. Following the experts' assessment, HPA currently is in the process of approval by the Hamburg Ministry for Environmental Protection and Energy (BUE) and includes METHA material as an alternative design variant in the planning process for current dike strengthening projects.

## Graphical information



Figure 1: Photo of pilot dike construction using METHA Material below a layer of natural marsh sediment in 2004. Photo by J.Gebert.

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**Project****Dredged material as clay substitute in the ceramic industry**

Classification	R1A_1996_D-Hamburg_Raw
Location	Hamburg, Germany
Volume	30,000 m <sup>3</sup> (brick production) & > 50,000 m <sup>3</sup> (LWA)
Technique	Use of treated, silty-clayey sediment as raw material instead of clay
Contaminants	Slightly contaminated with heavy metals and organic contaminants
Granulometry	Silty/clayey
Scale	Pilot scale / full scale
Client	Hamburg Port Authority
Consultant	N/A
Contractor	Hanseaten Stein Ziegelei GmbH & Fibo Exclay Deutschland GmbH
Research institute	N/A
Research program	N/A
Contact	Heinz-Dieter Detzner, Hamburg Port Authority, Heinz-Dieter.Detzner@hpa.hamburg.de, +49 160 8893969; +49 40 428472387
Year start – end	1996 – 2016

**Description of the project**

The beneficial use of treated, silty-clayey sediment, especially the METHA-Material produced in the METHA plant, is feasible in the manufacturing of ceramic products, e.g. bricks und light weight aggregates (LWA). In this field, the Hamburg Port Authority has extensive, in parts also long-term, experiences.

The Hanseaten-Stein Ziegelei GmbH (HZG) had operated a pilot brickyard from 1996 until 2000. As part of the brick production process, natural clay was subsidized by the use of METHA-Material in an extend of up to 70%. Approximately 7 million bricks had been produced during the 4 years of operation using 40,000 t of METHA-silt demonstrating the technical capability of the METHA-Material for this purpose. All operational and environmental requirements had been achieved safely at any time throughout the process. In the past, however, it was not possible to establish a large-scale brickyard at the market, especially due to economic conditions.

METHA-material had been also used in the production of LWAs. During the period from 2004 to 2016, more than 65,000 t of METHA material were delivered to FIBO ExClay Deutschland GmbH, to use the material as a substitute for clay in their LWA production. While using 10 % - 15 % of METHA-Material as part of the raw material composition, no difficulties in the operation of the kiln were recognised. All LWA quality parameters according to the standard production had been fulfilled and, moreover, no essential

technical process adjustments were necessary to meet the environmental requirements. Unfortunately, the good cooperation, which lasted for more than 10 years, ended with the closedown of the clay pit in 2016.

The following objectives were achieved by using the METHA-Material as a secondary raw material in the ceramic industry:

- Establishing technical processes for the beneficial use of treated, silty-clayey dredged material
- Protection of natural resources
- Efficient and cost-saving while using a secondary raw material

### Graphical information



Figure 1: Kiln car with bricks leaving the HZG brick kiln (1997)



Figure 2: Flue gas cleaning of the HZG brickyard (1997)



Figure 3: LWA's leaving the Fibo ExClay rotary kiln



Figure 4: LWA raw product

C

### References/web links

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## Acknowledgement

It has been a privilege to be able to work on these scientific insights and incorporate them into national and international sediment guidelines, laws and policy frameworks. This thesis is the result of many national and international research programs; the EC 6th Framework programmes REBECCA (contract SSPI-CT-2003-502158) and FLOODSITE (contract GOCE-CT-2004-505420), the EC INTERREG IVB NWE programmes CEAMAS (project 360K) and SURICATES (project NWE 462) and the Dutch NWO program 'Lift up Lowlands' (project 11344). From the applied research side there are over 50 projects on sediment management, commissioned by the Dutch Government the Department of Waterways and Public Works (RWS).

The topic of sediment and water quality standards attracted much attention, also in an international context. As an example the Dutch Prime minister Jan Peter Balkenende and Her Majesty Queen of Netherlands, His Highness Prince of Orange and Princess Maxima were at the opening of the Aquatic Science Centre (ASC) in Singapore in 2011. Preparing the building and opening of the ASC as part of the National University of Singapore (NUS) team members was one of my highlights.

A special thanks to the management organisation of the Dutch Confined Disposal Facilities 'Ijsseloog', 'Slufter' and 'Ingen' (Gert Kamerling, Douwe van 't Zet, Janco Portijk, Gijs Berger, Ronald Rutgers, Dick van Wanig and sons and many others) for their years of support to combine scientific research with on-site fieldwork and the practical implementation in their management strategies for contaminated sediments.

I wish to thank my colleagues at the Delft University of Technology (my promotor Prof. Timo Heimovaara and co-promotor Claire Chassagne), at the Cork Institute of Technology (Joe Harrington), at the Radboud University (Prof. Jan Hendriks) and at Deltares (especially Dr. Cor Schipper). I am grateful for all the collegial support through the years and the small pushes to write down this thesis.

I am extremely grateful for my wife Mariëlle Frankhuisen and my children Jaël and Maarten, for keeping faith that someday this thesis would be finished. The same is true for my parents and my parents in law.

## About the author

Arjan Jeroen Wijdeveld was born on 15 February 1971 in Eindhoven, The Netherlands. After completing Athenaeum at the Jacob-Roelandslyceum in Boxtel in 1989 he started with a study Chemistry at the University of Utrecht. Finishing his propaedeutic in Chemistry, he switched to the Earth Science faculty at the University of Utrecht, doing his masters in Geochemistry with extra subjects in Environmental Law at the Faculty of Law, Economics and Governance. He participated in the Indian ocean expedition, doing research on the diageneses of iodide and iodate in pore waters from the Indian Ocean (1993- 1994). His master thesis was on the measurement and modelling of the long term PAH desorption from sediment from the Petrol harbour (Amsterdam), at the Netherlands Organisation for applied scientific research TNO (1995).

In 1995 Mr. Wijdeveld joined WL | Delft Hydraulics, now Deltares. At Deltares Mr. Wijdeveld is and has been responsible for a number of large Dutch research programs focusing on emission of contaminants from Confined Disposal Facilities (CDF's) for sediments and the gas production and escape routes of gas from these deposits. This has led to the development and deployment of new measurement techniques for monitoring contaminant transport and gas emission in and from sediments (like the use of passive samplers for pore water concentrations and the determination of the bio-available contaminant fraction , the development of an automated gas emission setup to determine the in-situ gas production in sediments under different conditions, the development of a gas traps to determine the gas flux from the sediment towards the surface water and from the surface water towards the atmosphere). Combined with lab scale experiments, this data has been used to develop and validate numerical models for the evaluation of the impact of CDF's with regard to contaminant leaching and greenhouse gas emissions. Much of this research has been used for the Dutch legislation on CDF's.

Mr Wijdeveld participates in the development of complex chemical numeric models, including the speciation of heavy metals, the kinetically hindered desorption of organic pollutants and the ecotoxicological impact of pollutants. With these models, a wide variety of studies for groundwater, sediment and surface water has been performed, mainly with regard to chemical pollutant behaviour. His knowledge has contributed to the successful participation of Deltares in a variety of EU 6<sup>th</sup> and 7<sup>th</sup> Framework programs on ecotoxicological stress (REBECCA, FLOODSITE and MODELKEY). Mr Wijdeveld has worked for the Technical University of Delft (2013-2015) on the EU INTERREG IV-b program CEAMaS, now continued by the EU INTERREG NWE program SURICATEs (2017-2021). Both INTERREG programs focus on the use of sediments in a North Europe perspective.

In 2007 Mr. Wijdeveld became co-pi for a large research program in Singapore, the Aquatic Science Centre Pandan (a joint venture between Deltares and the National University of Singapore). His role was to set up new research proposals for disciplinary cross cutting problems with regard to tropical urban water management. The project resulted in a unique outdoor flume test facility in Singapore.

From 2016 on Mr. Wijdeveld became the department head of the Experimental Facility Support group. He and his group are responsible for the operation and accurate measurements in the large scale flumes and basins of Deltares. As an example, for the Delta flume (<https://www.deltares.nl/en/facilities/delta-flume>). He and his group also improve and develop measuring devices (<https://tinyurl.com/y8xjsvjo>, <https://tinyurl.com/y6vfg2j8>).

The PhD. thesis started in 2007, with the SDWA research program in Singapore. This resulted in an outdoor flume test facility and co-authorship on papers with a very fundamental approach on the interaction between contaminants, biofilms and macrophytes. The practical application of this knowledge for water managers was lacking. Therefore in 2011 Mr. Wijdeveld decided to focus his thesis on strengthening the link between geoscience and governance, working on the transition of seeing sediments as a problem (BVB, 1993) towards the acceptance of sediments as a part of a system solution (Bbk, 2008). Sediments, also when contaminated, became a resource for many water system related challenges.





