
REMOBILIZATION OF HISTORICALLY CONTAMINATED SEDIMENTS
DURING HIGH DISCHARGES IN THE RIVER RHINE

Author: M.F.A. Scholten

Supervisors: Utrecht University: S.M. Hassanizadeh

Deltares: J.P.M. Vink

J.A.G. van Gils

MASTER THESIS

Abstract

During the post-war period industrial activity increased resulting in higher emission rates, which caused an overall degradation of biological conditions in the Rhine over the period 1960-1970 (Wolff, W.J., 1978). Thereafter, the concentrations of most heavy metals in the water considerably decreased. But, high discharge events, associated with climate change can cause resuspension of old contaminated sediments. Data analysis of the River Rhine at Lobith shows a decreasing contaminant concentration with increasing discharge in the lower regimes. This may be caused by dilution. During higher discharges, however, contaminant concentrations appear to increase slightly. Distinct relations are hard to establish due to a significant decrease in the amount of data points with increasing discharge. In addition, higher discharges cause a dilution effect and suspension of bigger grains, these have a lower sorption capacity for contaminants. These processes cover up actual effects. Therefore, a model is used to examine high discharge events. Using Delft3D-WAQ, two numerical experiments are performed, one with a constant emission pattern and the other with a variable emission pattern with emission peaks between 1968 and 1975. Model results demonstrate that the scenario with the variable emission pattern shows a deterioration of suspended particulate matter quality with increasing discharge, indicating a mobilization of historically contaminated sediment layers.

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1 Introduction

1.1 Scope

Sediments are important in water resource management. During the post-war period, contaminants were discharged in large quantities into water bodies, due to municipal and industrial wastewater effluents and several diffusive sources. Subsequently, contaminants accumulated in sediments throughout these water bodies.

They are mainly deposited in slow flowing waters like old oxbow lakes, harbors and flood plains, and are covered by cleaner sediments, which are deposited in the last decades. However, during extreme discharge events, these contaminated sediments may become resuspended.

Förstner and Owens (2007) showed that the River Rhine has a huge erosion capacity. During the flood event of 1999, contaminated sediments were mobilized, transported and deposited in tidal harbors, estuaries and coastal areas.

Different scientists agree that higher discharges lead to higher concentration of suspended particulate matter, hereafter referred to as SPM. However, the quality of SPM is often not considered.

The scope of this study is to find a relationship between high discharges and SPM quality and endeavor to model this process.

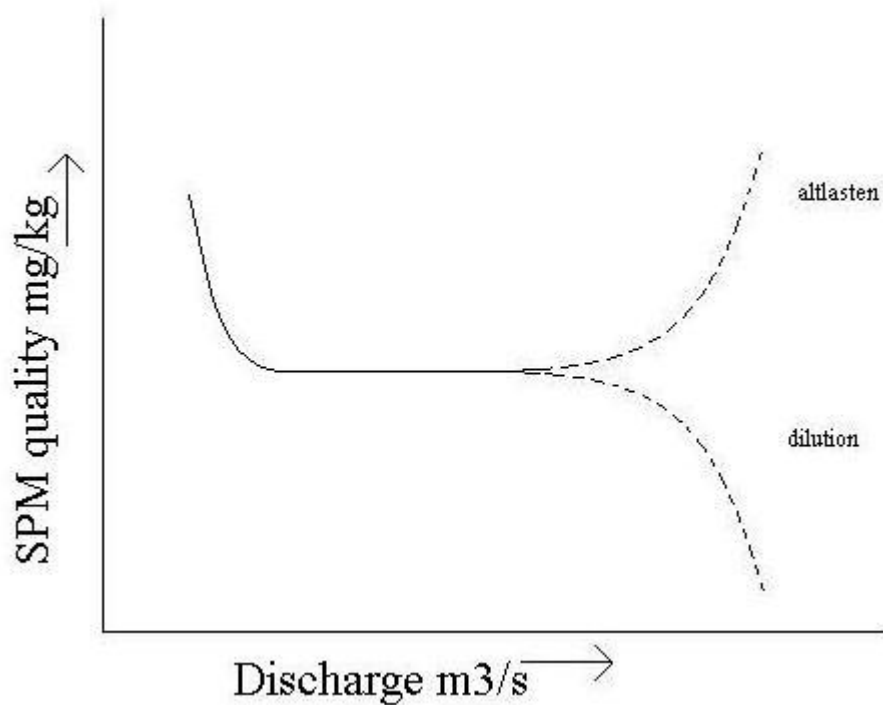


Figure 1.1: Schematic representation of the relation between discharge and SPM quality.

The figure above shows a schematic representation of SPM quality with increasing discharge. SPM quality may deteriorate by resuspension of historically polluted sediments. Dilution, due to high discharges, may show the opposite effect.

1.2 Problem definition

Discharge regimes are dynamic processes that fluctuate over time. Although these events are naturally occurring they have an impact on the condition of a river system. Increasing floods, associated with climate change might increase the risk of transportation of contaminated sediments. Due to high discharges old contaminated sediments, Altlasten, can get resuspended and deposited downstream.

1.3 Hypothesis

Our hypothesis is that SPM quality deteriorates due to the resuspension of historically polluted sediments, further referred to as Altlasten, during high discharges of the River Rhine.

1.4 Goals

The main goal of this study is to determine whether Altlasten get resuspended during high discharges. Special attention is given to the following research questions:

- Does SPM quality deteriorates when discharge increases?
- Is it possible to model and predict contaminated fluxes, and if so, predict critical values for this to occur?

2 Theoretical background

2.1 The River Rhine

The river Rhine is the primary artery of one of the most important economic regions of Europe. The river has a total length of about 1,250 km, a drainage area of circa 185,260 km² and an average discharge of about 2,300 m³ s⁻¹ (Tockner et al. 2009). Its catchment is located in nine different countries (Austria, Belgium, France, Italy, Germany, Liechtenstein, Luxembourg, Netherlands and Switzerland). The pressure on the river is high due to the fact that it serves multiple purposes. It provides services for transportation, power generation, industrial production, urban sanitation, drinking water, agriculture and tourism (Van der Velde and Van den Brink 1994).

During the post-war period, industrial activity increased significantly. This development added a massive load of toxic material, chemical components, culminating in an overall degradation of biological conditions in the Rhine over the period 1960-1970 (Wolff, W.J., 1978). Hereafter, the concentrations of most heavy metals considerably decreased. In the last decades the water quality of the river Rhine has improved due to reduced introduction of contaminants (Aarts et al. 2004).

2.2 Sediment quality

To demonstrate the presence of Allasten, Vink and Winkels (1991), investigated the sediment quality of Lake IJsselmeer, one of the branches of the River Rhine in the Netherlands. This was an erosive tidal gully before a barrier dam was built in 1932 to separate Lake IJsselmeer from the North Sea. Hereafter, rapid sedimentation occurred. Vink and Winkels (1991) discovered a relation between thickness of sediment layers and time periods in which they were deposited, based on former water depths, dry matter contents, net sedimentation rate and consolidation. During their study, thickness profiles of contaminated layers over time were constructed.

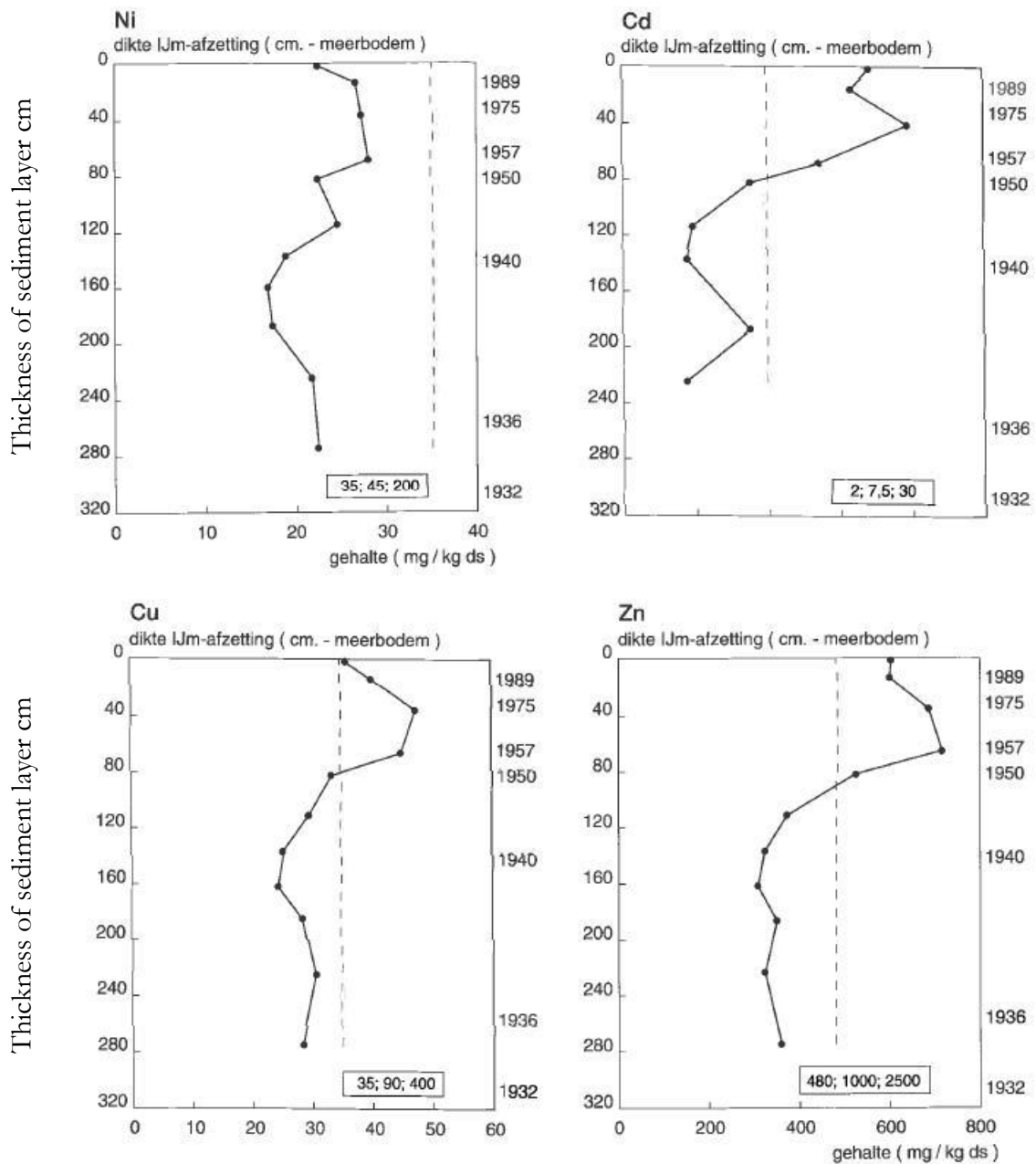


Figure 2.1: Corrected values for the contaminants Nickel, Cadmium, Copper and Zinc. Measurements have been done in the fairway in Lake IJsselmeer (Vink and Winkels, 1999)

From the figures above it can be stated that quality of deposited matter showed a maximum during the 1960's, the period of increased industrial activity. In the early 1970's, the quality improved due to European actions to decrease contaminant loads. Vink and Winkels also took measurements in other areas in Lake IJsselmeer and found out that trends, like stated above, are found throughout the entire lake IJsselmeer. These figures show the presence of Altlasten in Lake IJsselmeer. Since Lake IJsselmeer receives sediment from the River Rhine, patterns like this probably can be found upstream in tributaries or other areas where deposition of sediment takes place. However, thickness of layers can vary over different locations.

2.3 Problems with contaminated sediments

Sources of contaminants can be divided in point and diffusive sources. Point sources are fairly stable sources and do not depend on meteorological factors. Major point sources are for example wastewater plants.

Diffusive sources are dynamic in place and time. The magnitude of emission is related to meteorological factors. Major sources are for example surface runoff, erosion, and groundwater.

According to Stigliani and Anderberg (1992), point sources have become less significant in total amount of waste in the Rhine catchment since the 1970s. Nowadays, diffusive processes are the main contributor of pollutants.

During high discharges, storm water can access forelands and deposit a contaminant layer. As can be seen in figure 2.1, cross sections of foreland sediments show an increasing concentration of contaminants with depth, indicating a deposition of contaminants in the past with relative cleaner sediment layers on top of them. Erosion of these layers contributes to increasing contaminant concentration during high discharges.

2.3.1 Financial issues; dredging

Due to the fact that the slope of rivers in the Netherlands is relatively small, flow velocities tend to decrease and sedimentation rates increase. The port of Rotterdam is such an area where discharge and flow velocity are low. This results in high sedimentation rates of small-sized suspended matter. Because of shipping traffic it is important that a certain water depth is maintained. Every year large amounts of sludge is dredged from the port of Rotterdam. This sludge contains metals, organic chemicals and other contaminants, causing a threat to the environment.

Dredging of sediments can have two goals:

- Creating minimal water depth for nautical activity.
- Sanitation of contaminated sediments.

In general, dredged material from coastal areas like harbors is dumped into the North Sea. However, concerning contaminated sediments, other strategies have to be addressed.

- Storage of contaminated dredging material in depots.
- Process dredged sediment to raw materials for building industry, after cleaning of the sediment.

Both storage of contaminated sediments and cleaning of dredged material are expensive activities. In addition, dredging of contaminated sediment is more expensive than dredging of uncontaminated sediments.

Dredging prices of uncontaminated sediments vary from €1 to €5 per m³ and €3 to €15 per m³ of contaminated sediments (Van der Kooij et al 2010).

Costs of storage depots in the Netherlands are estimated at €160 million (Municipality of Rotterdam 1986), prices of the storage itself not included.

In addition, cleaning prices are even higher. In table 2.1, an overview is given of the dredging costs in the Netherlands in 2004.

Estimated backlog in amounts of sediments to be dredged and estimated total costs in 2004.

	Backlog, millions m ³ of sediment	Total costs in millions of €
Maintenance dredging	57	900
Remediation	50	1.400
Total	107	2.300

Table 2.1 from Van der Kooij et al 2010. Contaminated sediments.

It may be clear that dredging is an expensive undertaking but it is necessary to maintain shipping trade in the Netherlands. However, cleaner sediments could seriously reduce dredging and storage costs.

2.3.2 Environmental issues

Organisms that live in and around the sediment can easily take up and store contaminants in organs and fat. Smaller organisms are eaten by larger animals and contaminants are introduced in our food chain, imposing a threat to humans. Both organic and inorganic particles adsorb better to smaller particles. In calm waters, fractions of SPM will be low so quality can be poor. Because of this, after a flood event, tributaries and connected oxbow lakes can get a huge input of contamination (Heimann et al. 2011).

2.4 Contaminants

Sediments can contain a wide range of chemical components such as nutrients, metals, Polychlorinated Biphenyls (PCBs) and Polycyclic Aromatic Hydrocarbons (PAHs), which have been deposited earlier in significant concentrations (Beurskens et al., 1993). Sediments can act as a sink for contaminants, meaning a greater flux in than flux out. However, during erosion events, contaminants get resuspended and the sediment will become a source of pollutants (Westrich B. Förstner U., 2007). Especially during high discharges massive amounts of sediment will be eroded and contaminants can be released.

Since flood events will happen more frequently and more severe due to climate changes (Scheurer et al. 2009), this imposes a serious threat for the environment. Erosion of old contaminated sediments can have a major contribution to total amount of contaminants in the River Rhine since the emission of point sources is reduced.

In general, three types of contaminants are identified.

- Nutrients
- Heavy metals
- Organic micro pollutants

2.4.1 Nutrients

Contamination of nutrients consists mostly of nitrogen compounds on the one hand, including nitrate, nitrite, and ammonium and of phosphorous components on the other hand, including phosphate and ortho-phosphate. Nutrients can cause ecological

problems like eutrophication and an unbalance in ecological diversity. Main sources are agriculture, wastewater treatment plants and due to natural sources like erosion.

2.4.2 Organic micro pollutants

Organic micro pollutants are substances that do not occur in open water by nature, with some exceptions (e.g. Polycyclic Aromatic Hydrocarbons). Commonly they are introduced to the river system by runoff from industrialized and urban areas. Because of chemical characteristics, high $\log P_{ow}$ (meaning that the ratio adsorbed/dissolved is high, in chapter 3 this process will be explained more carefully), many organic contaminants tend to bind to sediment and organic matter and dissolve very badly. Organic pollutants can easily be taken up by organisms that live up and around the sediment. Degradation rates are in general very low. PCBs, HCBs and pesticides degrade aerobically into mono-chloro-benzenes and mono-chloro-phenols with a half life time of some decades (Beurkens 1995). These components have an increased mobility compared to the original contaminants which causes a threat for groundwater pollution.

Polycyclic Aromatic Hydrocarbons (PAHs) naturally occur due to forest fires and volcanic eruptions, however the anthropogenic contribution is significant.

2.4.3 Heavy metals

Heavy metals are very common pollutants in aquatic environments and biota. Both natural and anthropogenic sources add metals to the environment. Heavy metals of anthropogenic origin are released to the river system as inorganic complexes or hydrated ions. They are easily adsorbed on the surfaces of sediment particles through relatively weak physical or chemical bonds. Therefore, heavy metals of anthropogenic origin are found predominantly as a labile extractable fraction in sediments (Singh et al, 2007). Heavy metals are soluble in water with normal pH and oxygen concentrations. However, they get very insoluble when they bind to hydroxides, carbonates, phosphates and especially sulfides (Van der Kooij et al. 2010). This occurs due to a shortage in oxygen and increased levels of organic materials, this causes a reduction of sulfates to sulfides and an increasing pH value. Components like hydroxides and sulfides can solidify to larger structures with oxides like iron and aluminum and with organic matter. When flow velocities are reduced they sink and accumulate into sediments. Summarizing above: reduction changes the sorption behavior of metals.

Metals can be transported when adsorbed to suspended particulate matter (SPM). In addition, when anaerobic sediment layers get in contact with the aerobic water column, metals are released due to oxidation processes and can be transported in solution (Morse 1994, Vink et al. 2010).

In contrast to organic pollutants, heavy metals are not removed by natural processes like decomposition. When heavy metals enter natural waters they become part of the water sediment system. (Jain, C.K. 2004).

2.5 Water quality

As mentioned before, due to climate change, river discharges will become more extreme, both floods and drought will happen more frequently. These events pose serious problems to water quality and quantity. All IPCC models show a rise of temperature in the future, indicating more extreme discharges. Whether this results in floods or droughts depends on different regions.

Van Vliet and Zwolsman (2008) showed that a decrease in discharge resulted in a significant deterioration of water quality, with respect to water temperature, eutrophication, major elements and some heavy metals and metalloids. This reduction in water quality is mainly caused by algae blooms, which production is increased by higher temperatures, longer residence times and a reduction in dilution capacity.

However, in this study, the focus is on contamination, especially contaminants adsorbed to SPM, during high discharges.

It is difficult to give a general description for water quality that describes every situation. Since water bodies are used for multiple purposes, different qualities are required. As already mentioned above, a water body like the river Rhine is used as drinking water supply at the one hand and it has to discharge treated wastewater on the other hand. In addition it may be used for fishing, boating, swimming and provides a habitat for several ecosystems. One of the problems in defining water quality is to find a standard that reflects the water quality in a sense that is useful for all purposes.

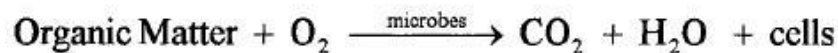
Concerning water quality, a distinction can be made between chemical and biological quality. Chemical quality can be tested by means of in situ measurements and to test collected samples in the laboratory. This is a time consuming process. Another possibility is to check water on certain forms of life and biota which will reveal biological quality. The amount of organisms, and some specific organisms in particular, is a representation of river quality. Based on the organisms and plants an estimation of water quality can be assessed. On the other hand, when certain species are absent on places where they are expected, water quality is probably poor. This technique gives a good dynamic view of river quality while measurements and lab results provide information for only that exact time and location. On the contrary, missing species indicate poor water quality but the problem, is it for example temperature or presence or absence of certain components, remains in some cases unrevealed.

According to Davis and McCuen (2005) there are 12 parameters that give an identification of the quality potential.

- Dissolved oxygen (DO)
 - Water in streaming rivers mixes with oxygen from the air above. Shallow, turbulent river absorb oxygen faster than deep, slow flowing waters do. Fish need oxygen for respiration, when concentration oxygen concentrations drop, fish become stressed and even die.
- pH
 - pH is a measure of the acidity of the water. Lower pH values indicate higher acidity of the water. A drop of pH in river water is devastating for fish populations. Acids are usually introduced in the river system by atmospheric deposition as a result of the combustion of fossil fuels.
- Temperature
 - Water temperature has an indirect affect on water quality since water temperature and concentrations of DO are strongly related to each other. High temperature waters can contain less DO. Sunlight is an important contributor to water temperature but also industrial activity plays a major

role. Power plants use river water for cooling, this water is discharged back to the river with higher temperatures. Natural higher temperature in summer periods combined with increasing cooling water demand can result in lower concentrations of DO.

- Suspended solids
 - Suspended solids are primarily small particles like silt and clay. High concentration of suspended solids cause of blockage of sunlight which is harmful for plants that need light for photosynthesis. In addition, suspended solids transport other materials that are harmful like heavy metals, pesticides, biodegradable organic matter and bacteria.
- Oxygen demanding substances
 - Many organic compounds biodegrade when exposed to oxygen. Reactions can be represented as follows:



Organic matter can be of natural origin but also anthropogenic sources contribute to biodegradable material.

- Nitrogen compounds
 - Nitrogen can be present in water in several forms depending on pH and redox characteristics. Ammonium is a common compound in the environment that contains nitrogen in a reduced state. In aerobic water systems ammonium can transform to nitrite and nitrate. This process consumes DO and is known as nitrification. Nitrate is utilized by algae, promoting their growth.
- Phosphorus
 - Phosphorus is required for growth and like nitrogen it is a primary nutrient and is found in several forms. High levels of phosphorous can lead to eutrophication.
- Microbial pathogens
 - Pathogens are organisms that bring diseases and include bacteria and viruses.
- Heavy metals
 - Heavy metals are toxic, in high concentrations, depending on the different metals and organisms. These metals include cadmium, chromium, copper, lead, mercury, nickel and zinc. They usually get adsorbed to suspended solids. Heavy metals do not degrade with time in the environment which is the reason that older contaminated sediments can still be a source of pollution.
- Oils and grease
 - Oils cause several problems for the environment. The degradation of oil consumes BO and they contain organic and inorganic contaminants.
- Organic compounds
 - Organic compounds that are toxic at low dissolved concentration include pesticides and Polycyclic Aromatic Hydrocarbons (PAHs).
- Trash
 - Trash is one of the most visible polluters. It is mostly plastic materials and degrades very slowly in the environment.

2.6 Masking effects

This study focusses on transport of contaminants, adsorbed to SPM, during high discharges. When discharge is plotted against adsorbed contaminants, this can lead to distorted relations, since many processes cover up the actual effects. These processes are addressed in the following paragraphs.

2.6.1 Increasing grain sizes

It is known that contaminants adsorb better to smaller fractions like clay and silt than to coarser grains like sand and gravel. When discharge increases, flow velocity tend to increase as well and transport capacity of the river rises. Consequently, bigger particles get in suspension.

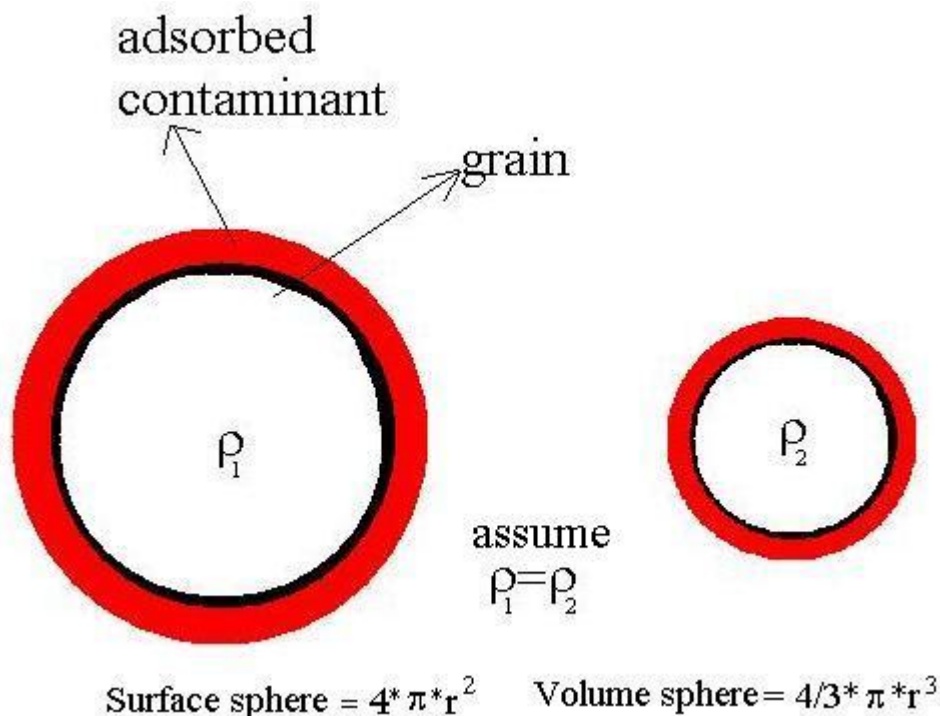


Figure 2.2 : Schematic representation of the relation between size of particles and the surface available for sorption of contaminants.

Figure 2.2 gives a schematic representation of a small and bigger particle which has a contaminant adsorbed to its surface. When we assume a grain size of 2 and 6 micrometers respectively, the mass adsorbed to the bigger grain is 9 times the mass adsorbed to the small grain since adsorption takes place on the surface. The mass of the big grain itself however is 27 times the mass of the small grain.

Summarizing above: the relation volume to surface is 1:3.

Therefore, increasing discharges can lead to a reduction of contaminants adsorbed to SPM in [mg/kg], however this does not implicitly indicate improvement of SPM quality.

2.6.2 Clean sediment

Historically contaminated sediments are covered by relative clean sediments, which are deposited, in the last few decades. Subsequently, erosion events and resuspension due to higher discharges will, in the first place, lead to resuspension of relative clean sediments. This causes a dilution effect with increasing discharge.

2.6.3 Partitioning coefficient

In an aquatic system, distribution of contaminants occurs over 3 compartments:

- Water (dissolved contaminants < 0.45 μm)
- SPM (adsorbed contaminants to particles: in solution/suspension)
- Sediment (solid phase)

The way in which an ion exchanges between mobile and solid phase is characterized by its partitioning coefficient, K_d .

$$K_d = \frac{\text{amount adsorbed to solid phase [mg / kg]}}{\text{amount dissolved [\mu g / l]}} \quad [l/g]$$

The binding of contaminants to SPM is by means of adsorption. Adsorption is a force between ions, atoms or molecules from a gas, liquid or dissolved solid and a surface. Adsorption is a surface-cased process.

When adsorption takes place, the solute is, by definition, not conservative.

In general it is assumed that the component in the liquid and the component in the solid are in equilibrium with each other, in other words, equilibrium adsorption takes place. In this case the mass fraction of adsorbed solute corresponds uniquely to the solute mass concentration in the fluid.

$$s = K_D C$$

Where s = adsorbed mass of dry soil

K_D = distribution coefficient

C = concentration in the fluid

To determine the relationship between adsorbed mass and concentration in the fluid, batch experiments are performed. During such experiments a solute is added to a suspension that consists of soil in water. When the suspension reaches equilibrium, solute concentration can be measured. With this result adsorbed mass fraction is calculated as follows:

$$\frac{M_0 - C_{eq} V_w}{M_s} = S_{eq}$$

Where:

M_0 = mass of solute added to suspension

C_{eq} = equilibrium concentration in fluid

S_{eq} = mass adsorbed

V_w = volume of water

M_s = mass of solid grains

Several factors affect the value of K_D .

Increasing pH gives lower values of K_D , or in other words, more solute tends to go in solution.

Increasing temperature gives also lower values of K_D .

In general, negatively charged soil had higher K_D .

With organic solutes, the main adsorption mechanism is driven by hydrophobic interaction between solutes and organic carbon in the soil. Organic solutes are for example light non aqueous phase liquids (LNAPLs) and dense non aqueous phase liquids (DNAPLs). In the case of organic solutes, higher carbon content in the soil means larger K_D . In these cases the relation between K_D and the amount of organic matter is considered to be linear.

$$K_D = f_{OC}K_{OC}$$

Where f_{OC} is the mass fraction of organic carbon in the soil and K_{OC} is the organic carbon partitioning coefficient.

The partitioning coefficient is supposed to be constant, however, K_D values strongly depend on composition and reactivity of both water and sediment (Vink and de Weert, 2009). The partitioning coefficient will be discussed elaborately further in this paper.

2.6.4. Redox reactions

When anoxic sediment gets in contact with the oxic water column, oxidation processes occur. Sulfides get oxidized to sulfates.

Usually, metals in anoxic sediments occur as metal sulfides like Pyrite, they form an important sink for contaminants. However, during resuspension metals can be released into the water column via oxidation (Sullivan, L.A., Bush, R.T., 2002).

This reaction of sulfide to sulfate produces protons and causes an acidification. The amount of metals bound to the sediment also strongly depends on pH. When pH increases, more metals get bound to the sediment or suspended matter. So due to acidification even more metals are released to the water column.

Variations of pH and O_2 are the most important parameters that influence the mobility of trace metals (Wen, X., Allen, H.E., 1999).

So reduced sediment layers get in contact with the oxic water column due to erosion, as a consequence, sulfides get oxidized to sulfate and metals can be released in the water column. Therefore, desorption processes can occur.

3 Materials and methods.

3.1 Monitoring databases

For this study datasets of the River Rhine are used. Data originates from live.waterbase.nl, which is the monitoring program of Rijkswaterstaat, from the BfG, the German federal Institute of Hydrology, and MWTL (Monitoring Waterstaatkundige Toestand des Lands) data is used.

Databases contain monitoring data from the River Rhine at Lobith. Measured components include nutrients, heavy metals and organic micro pollutants. They are administrated both in dissolved and adsorbed phase and total concentrations.

3.1.1 Contaminated loads

During flood events, more water is transported along the Rhine River. This process can cause a dilution effect on contaminants. Therefore, it is interesting to look at loads.

The datasets that are used contain information about SPM concentration, discharge, and for some chemical components dissolved concentration and concentration adsorbed to SPM. Loads per time unit are found by means of some simple calculations.

$$\begin{aligned} Q[\text{m}^3/\text{s}] * \text{SPM}[\text{mg}/\text{day}] &= \text{SPM}[\text{g}/\text{s}] \\ \frac{\text{SPM}[\text{g}/\text{s}]}{1000} &= \text{SPM}[\text{kg}/\text{s}] \\ \text{SPM}[\text{kg}/\text{s}] * \text{contaminant}[\text{mg}/\text{kg}] &= \text{contaminant}[\text{mg}/\text{s}] \\ \text{Contaminant}[\text{mg}/\text{s}] * 3600 * 24 &= \text{contaminant}[\text{mg}/\text{day}] \end{aligned}$$

By means of these calculations concentrations can be converted to loads. Since relations between adsorbed contaminants and discharge may not be convincing due to masking effects discussed in chapter 1 it may be elucidated to examine the relation between loads over discharge.

3.1.2 Compounds of interest

For this study we are interested in the remobilization of historically contaminated sediments. Therefore we mainly focus on metals since they do not degrade in time and because they are widely deposited during the post-war period.

In addition copper, nickel and zinc are interesting because of the fact that environmental quality standards are formulated, and as a consequence it is possible to determine in which cases these standards are exceeded.

3.1.3 Partitioning coefficient

For this study the relation between discharge and partitioning coefficient is examined. To investigate whether there is a relation or not, K_d values of high discharges are compared with K_d values of low discharges.

3.2 Model simulation

3.2.1 Introduction

A model is by definition a simplified representation of, a part of, the real world. Models can be used to help understanding complex phenomena, occurring in real water systems. Once it is proven that they correctly represent certain aspects of reality, they can be used to simulate real situations and to predict outcomes of certain events.

As already mentioned this study focusses on SPM quality in during high discharge events. By using a model we want to answer the following research question: assuming that older sediments are indeed released during high discharge events, can we estimate the associated contaminant fluxes and the resulting concentrations in SPM during high discharge events?

We use the following overall strategy to achieve this goal:

- We simulate a longer period (about 10 years) with an interannually and seasonally variable hydrology, including a flood event);
- We create a SPM model that behaves realistically: (a) it shows a realistic variation of SPM with time; (b) it shows a realistic variation of SPM with river discharge; and (c) it shows realistic residence times of SPM in the Rhine River network;
- We carry out numerical experiments (“scenarios”) where we attach a metal to the SPM: by reconstructing the period from the 1960s to today, we try to answer our research question.

Section 3.2.2 below discusses some general aspects of Delft3D-WAQ. Section 3.2.3 discusses the specific model used in this study.

3.3.2 Delft3D-WAQ

This study uses Delft3D-WAQ (e.g. WL Delft Hydraulics, 2007) to model transport of contaminants in the river Rhine. Delft3D-WAQ is a state-of-the-art and flexible water quality model applied in > 1000 studies over the past 30 years by > 100 research institutes, government bodies and consultants. It is an open source product, which means it can be inspected, used and if necessary adapted without restrictions. Delft3D-WAQ can be used for a wide range of model substances and allows great flexibility in the processes to be modelled. Note that Delft3D-WAQ is not a hydrodynamic model, so the flow of water itself can be derived from a whole range of other models. Below, we provide a general description of Delft3D-WAQ. The specific application to the Rhine will be discussed in section 3.2.3.

Mass balances

Delft3D-WAQ uses mass balances to administrate state variables, such as SPM, nickel or zinc. The system is divided in computational cells. Mass is transported by water flowing from one cell to another with a negative term in the mass balance for the cell where water is flowing out and a positive term for the cell that receives water. This method is mass conserving.

Computational cells are combined in one, two or three dimensions so that every water system can be represented, and substances can be transported through the whole system. Within a computational cell substances can convert to other substances, so physical processes like resuspension add settling, chemical processes like adsorption and nitrification and biological processes like production of algae can be included. In addition, mass can be added to a cell from outside the modelled water system, to simulate waste loads from point and diffuse sources.

In Delft3D-WAQ the following equation is solved for every cell, state variable and time step.

$$M_i^{t+\Delta t} = M_i^t + \Delta t \times \left(\frac{\Delta M}{\Delta t} \right)_{Tr} + \Delta t \times \left(\frac{\Delta M}{\Delta t} \right)_P + \Delta t \times \left(\frac{\Delta M}{\Delta t} \right)_S$$

Where:

- Δt is the time step
- M_i^t is the mass at the beginning of a time step.
- $M_i^{t+\Delta t}$ is the mass at the end of a time step
- $\left(\frac{\Delta M}{\Delta t} \right)_{Tr}$ is the change in mass due to transport
- $\left(\frac{\Delta M}{\Delta t} \right)_P$ is the change in mass due processes
- $\left(\frac{\Delta M}{\Delta t} \right)_S$ is the change in mass due to sources (e.g. waste loads, river discharges)

This equation is a simplified representation of the well known mathematical advection-diffusion equation.

It should be noticed that the basic principles of Delft3D-WAQ are the same whether you have one state variable and only two computational cells, or you have several tens of state variables and thousands of computational cells. The only difference is the number of times that Delft3D-WAQ has to solve above equation.

Schematic representation

In the model, the water system is divided in computational cells, as shown in figure 3.1. Each cell is defined by its volume and dimension. Note that Δx , Δy and Δz can all have different values so computational cells does not have to be cubical shapes. Each cell can share surface with another cell, the atmosphere and sediment and has a number ranging from 1 to N, where N is the total number of cells. In addition, each surface area that is shared with another cell has a number ranging from 1 to Q where Q is the total number of shared surface areas. Between these surface areas mass exchange can occur from one cell to the other.

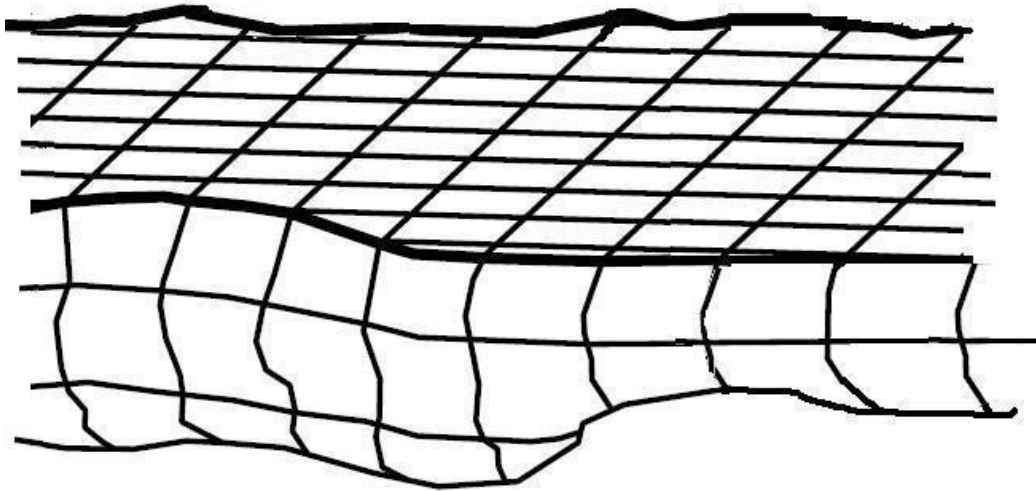


Figure 3.1 : Schematic representation of a river divided in computational cells.

So for each cell these characteristics are defined:

- Volume
- Surface area
- Dimension
- Shared surface area with another computational cell

Thus, in Delft3D-WAQ a water system is described as a network of computational cells. These cells are interconnected and water flows from one to the other. Both substances in the water and water quality processes are taken into account, which forms the basic for water quality modelling.

This is a succinct summary of how Delft3D-WAQ works, additional information can be found in e.g. *Delft3D-WAQ Versatile water quality in 1D, 2D or 3D systems including physical, (bio) chemical and biological processes*, by WL Delft Hydraulics and Delft3D-WAQ. Documentation of the input file. User manual. Part of input file. 2008. and *Technical Reference Manual Delft3D-WAQ*, by WL Delft Hydraulics, 2005.

3.2.3 Model for the River Rhine

Study area, schematisation and hydrology

In the model for the River Rhine the Rhine catchment, as showed in figure 3.2, is simulated.

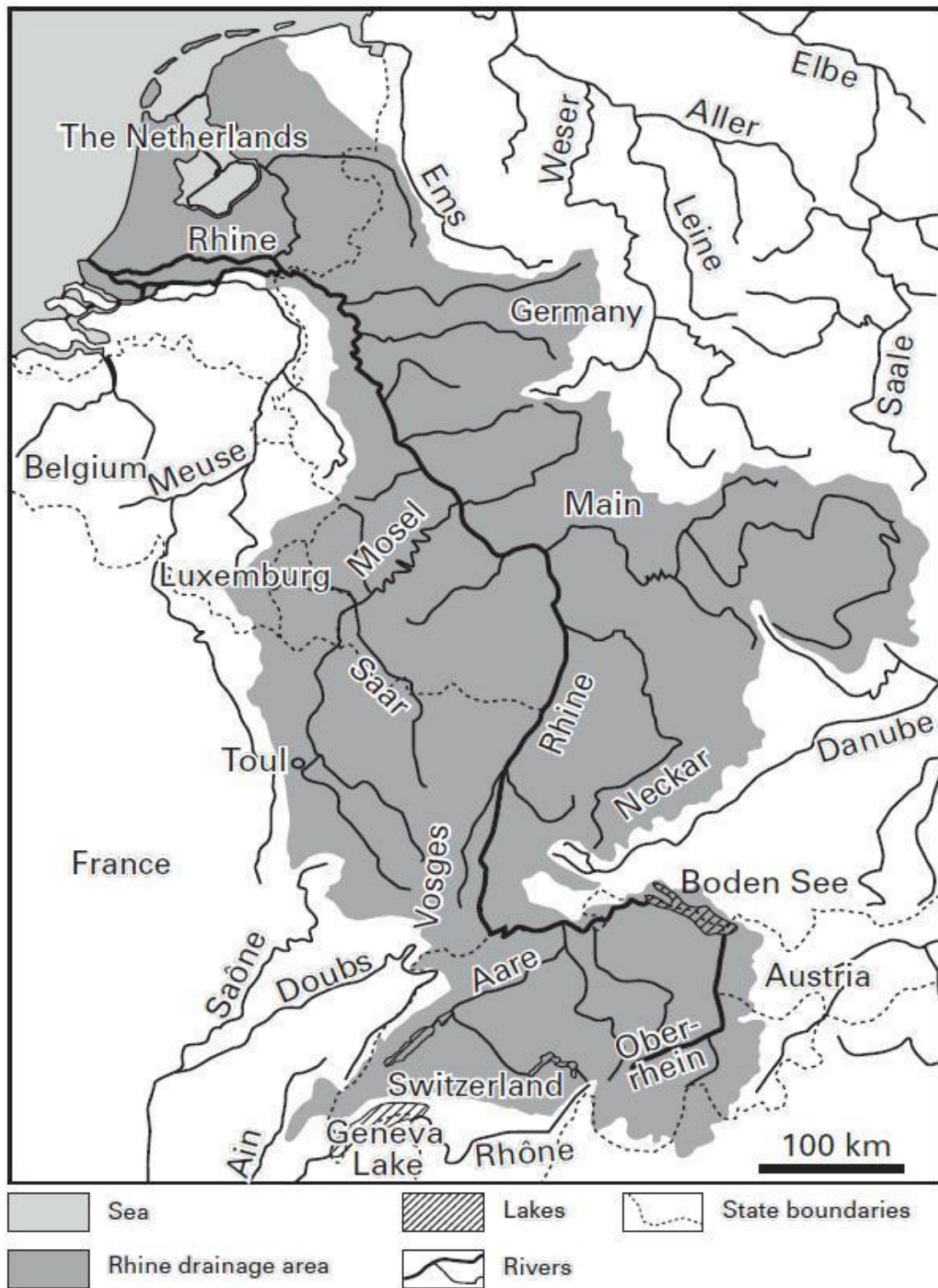


Figure 3.2: The Rhine catchment (Berendsen, 2005).

The schematisation and the hydrology of the River Rhine have been derived from an application of the hydrological model WFLOW, set up in the framework of the Deltares OpenStreams initiative (www.openstreams.nl). WFLOW is an integrated hydrological model that calculates the water flows in the surface water and the groundwater driven by meteorological conditions, soil and subsoil properties and land use. It has a rectangular grid with 1000x1000m grid cells.

In Delft3D-WAQ we simulate only the surface waters, and only those water courses that have an average water flow that exceeds $1 \text{ m}^3/\text{s}$. This leads to a schematisation of 15289 segments. The segments represent a river section from bank to bank and from bottom to surface: though Delft3D-WAQ has the ability to model 3-dimensionally, we use a 1-dimensional approach.

In WFLOW and Delft3D-WAQ this catchment is distinguished in 14 different areas as showed in figure 3.3.

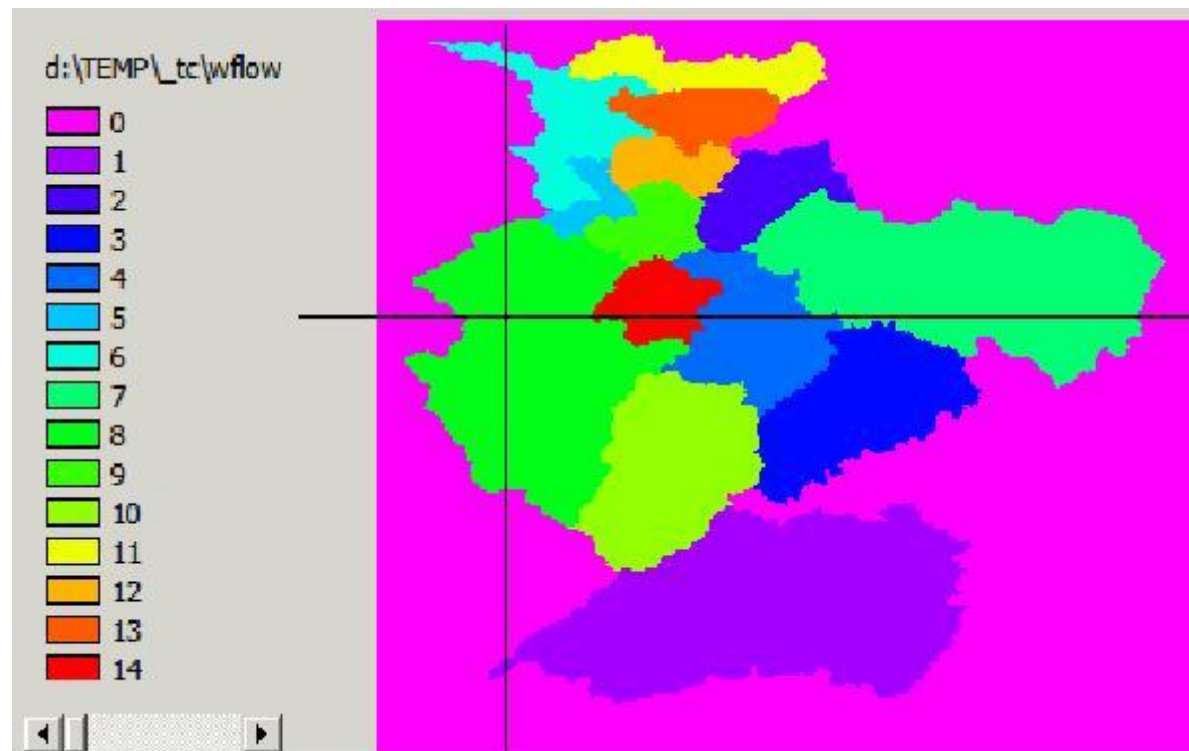


Figure 3.3: The Rhine catchment as represented in Delft3D-WAQ.

Areas represent the following places near the River Rhine.

1. Basel
2. Kalkhoven
3. Rockenau
4. Kaub
5. Köln
6. Lobith
7. Raunheim
8. Cochem
9. Andernach
10. Maxau
11. Schermbeck
12. Menden
13. Hattingen
14. Grolsheim

Every one of the 15289 segments has two inflows defined: one representing “fast” runoff processes (direct runoff via the soil surface) and one representing “slow” runoff processes (via groundwater). In the model, both contaminants as SPM that are introduced to the river system can originate from surface runoff or from groundwater flows schematically presented in figure 3.4.

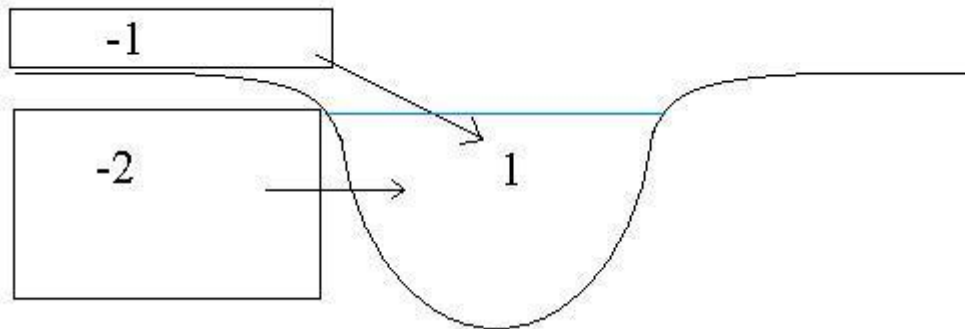


Figure 3.4: Schematic representation of inputs to the river in the model. Box -1 represents surface runoff, box -2 represents groundwater flow and box 1 represents the river.

The amount of SPM and contaminants flowing in with the runoff can be define either cell-by-cell or for the 14 different areas (shown above).

The hydrology of the model provides 4000 days of hydrology data, representing the period from 1 January 1985 up to 14 December 1995. This period includes three significant floods with a discharge exceeding $10.000 \text{ m}^3/\text{s}$ at Lobith (1988, 1993, 1995). For our water quality simulations, we can repeat this hydrological period to realise simulations over longer time spans.

Water quality model definition

Delft3d-WAQ distinguishes two fractions of silt, IM1 and IM2, and one metal. By varying the values of these parameters, characteristics of IM1, IM2 and the metal can be controlled. All the parameters that are included in the model are described below.

The model distinguishes 11 different parameters described below.

VSedIM1 and VSedIM2: Settling velocity [m/d]. The velocities of the two fractions by witch particles sink to the bottom.

TaucSIM1 and TaucSIM2: Critical shear stress for sedimentation [Pa]. These parameters determine when sedimentation takes place. When this parameter is low, no sedimentation occurs.

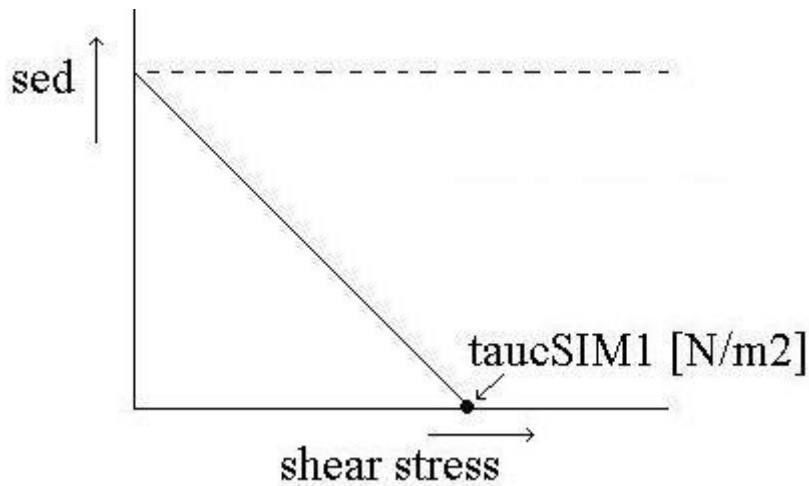


Figure 3.5: The behaviour of sedimentation with shear stress and the influence of τ_{cSIM1} .

'KdCuIM1': Partitioning coefficient [m³/kg]. Partitioning coefficient of Copper, this shows the way how adsorbed and dissolved Copper relate. In this case it shows in what way Copper is adsorbed to IM1.

'KdCuIM2': Partitioning coefficient [m³/kg]. Partitioning coefficient of Copper, this shows the way how adsorbed and dissolved Copper relate. In this case it shows in what way Copper is adsorbed to IM2.

'KdCuIM1S1': Partitioning coefficient between Cu and M1 in layer 1.

'KdCuIM2S1': Partitioning coefficient between Cu and M1 in layer 2.

'SWPoreChS1': This parameters shows whether the system is reduced or oxic.

'ZResDM': Suspension flux [g/m²/d]. When critical shear stress for resuspension is exceeded, this parameter determines how fast particles are suspended.

'TaucRS1DM': Critical shear stress for resuspension in layer 1 [Pa]. This parameters determines when resuspension occurs. When this parameter decreases, resuspension events increase.

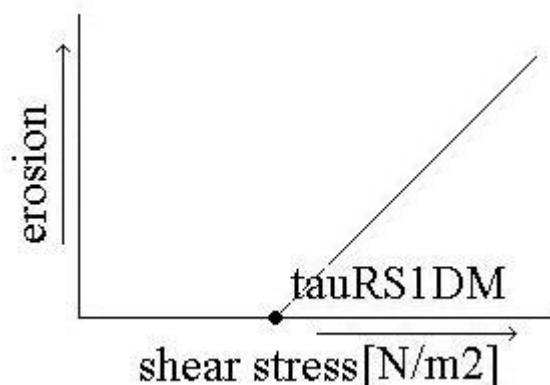


Figure 3.6: The behaviour of erosion with shear stress and the influence of τ_{RS1DM} .

In appendix 1, all parameters that result from the model are listed with a short description.

3.3 Water quality simulations

3.3.1 Single cell model simulation

When the model was tested, processes between shear stress, erosion and deposition did in the first place not react as expected. In general it was expected that resuspension increased with increasing shear stress and sedimentation increased with decreasing shear stress. To investigate relations between shear stress, sedimentation and resuspension, a simplified version of the model is developed.

Deposition and erosion rates are derived from empirical relationships in accordance with local values of the bed shear stresses (Soltanpour and Jazayeri, 2009). Mass deposition is based on the proposed concept of Krone (1962).

$$\frac{dm_D}{dt} = \left(1 - \frac{\tau_b}{\tau_D}\right) w_{sb} C_b \quad \tau_b \geq \tau_D \quad (1.1)$$

$$\frac{dm_D}{dt} = 0 \quad \tau_b < \tau_D \quad (1.2)$$

Where $\frac{dm_D}{dt}$ represents the rate of mass deposition per unit area, τ_b is shear stress at the bed-fluid interface, τ_D is critical shear stress for deposition, w_{sb} is settling velocity near the bed and C_b is the sediment concentration near the bed.

From the applied shear stress the rate of erosion can be calculated (Partheniades and Kennedy, 1966).

$$\frac{dm_E}{dt} = E \left(\frac{\tau_b}{\tau_E} - 1 \right) \quad \tau_b \geq \tau_E \quad (1.3)$$

$$\frac{dm_E}{dt} = 0 \quad \tau_b < \tau_E \quad (1.4)$$

Where $\frac{dm_E}{dt}$ is the rate of mass eroded per unit area, τ_E is critical shear stress for erosion and E is the erosion constant based on mineral components of mud, salinity, etc (Soltanpour and Jazayeri, 2009).

Above formulas determine erosion and deposition flux. To get a better understanding of these fluxes and the relations between fluxes and shear stresses, some simple exercises are performed with this simplified model. In Delft3D-WAQ, as mentioned above, multiple boxes are linked and data is transported from one box to the other. In this case just one box is present. All the other parameters remain the same. Purpose of this example is to investigate sensitivity of sedimentation and resuspension fluxes.

The box that is created has such a volume and flow that residence time of water is about 20 days. Therefore, time consuming processes like sedimentation and resuspension can occur.

Most important difference of this example with respect to the real model is that shear stress can be controlled, in the previous situation shear stress follows out of a calculation. Now, shear stress can be varied over time and relations between resuspension, sedimentation fluxes and shear stresses are investigated.

SPM model simulation

Main field of interest is the relation between SPM quality and discharge. Therefore, the setup is to compare SPM quality and discharge relations in three scenarios, which are described further in the chapter. First zinc will be examined hereafter, the same scenarios with different substances, for instance nickel and copper, can be calculated.

3.3.2 Tracer/residence time

In a river system, SPM gets suspended during high flow velocities, but when discharge decreases and flow velocities drop, SPM settles down and accumulates until the next flood. Therefore, residence times of SPM are higher than residence times of water. To investigate whether this principle holds for the model a sediment tracer is added.

To track SPM that flows to the system a metal is added with an infinite high partitioning coefficient. By doing this, the metal is adsorbed to SPM and does not dissolve in water. In the first three months this metal is introduced in the system from every area with the same concentration as SPM, for every gram of SPM there is one gram of metal. After three months, metal injection stops and only clean sediment gets introduced. Due to deposition and resuspension the metal stays in the system for a longer period.

To compare the behaviour of the metal with the behaviour of water another tracer is introduced. In this case the tracer is a metal with a very low partitioning coefficient. As a result of that the metal does not adsorb to SPM, instead it dissolves in water and therefore traces the water flowing through the system.

When the two tracers are compared, we basically compare the residence time of SPM with water in the system.

3.3.3 Scenarios

When the model is tested and provides suitable results it can be used as a prognostic tool. In that case, three different scenarios should be calculated.

1. First, a constant injection of a contaminant is injected, in order to get a year load that corresponds to the loads that can be found in the literature. In the model this is accomplished by a constant emission of a contaminant in time and in all areas. The model administrates in and out fluxes. Because of that, it is possible to monitor the total amount of contaminants that flows through the system. Therefore, the value can be adjusted in order to get a realistic number for the contaminant transported by the model and values found in the literature. In this case we keep the partitioning coefficient constant.
2. The second scenario is a variable emission pattern. As described in the literature the River Rhine has become cleaner in the last decades, peak emissions were

between 1960 and 1970. In the model emission can be changed in time, schematically a pattern like displayed below is simulated.

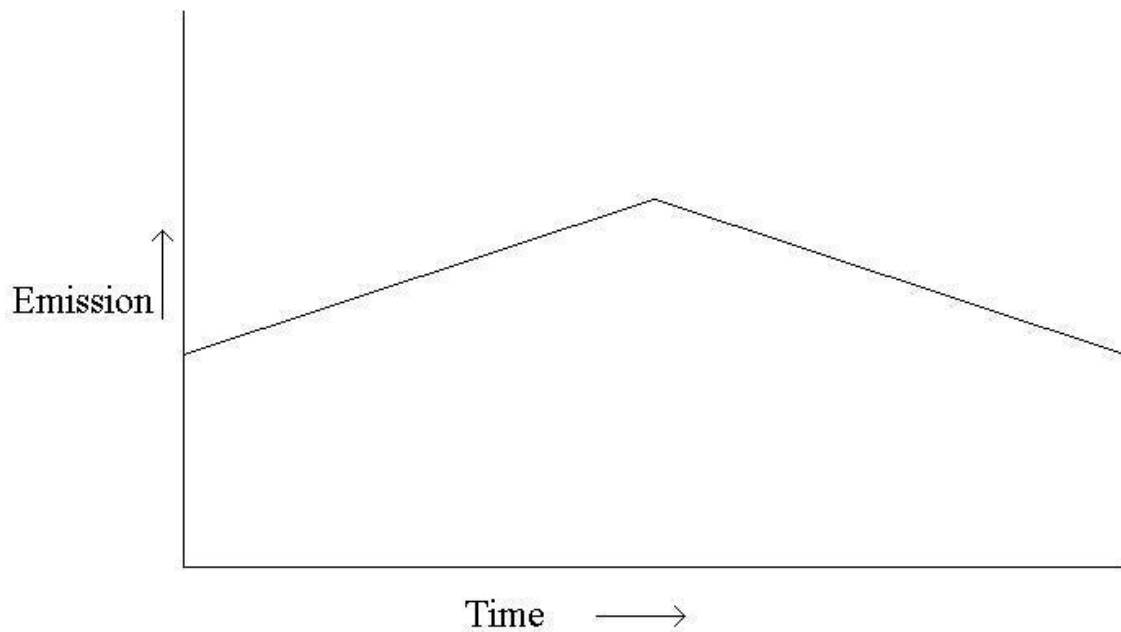


Figure 3.7: Schematic representation of emission pattern in the River Rhine. Peak lies between 1960 and 1970.

In the River Rhine, contaminant loads are administrated since 1990. For this study we are especially interested in the period somewhere between 1960 and 1970. Rijkswaterstaat monitores total concentrations of copper, nickel and zinc on waterbase since 1968. Due to the fact that discharges are not available for this period it is not possible to calculate total loads. Therefore, an estimation is made, based on total concentrations since 1968.

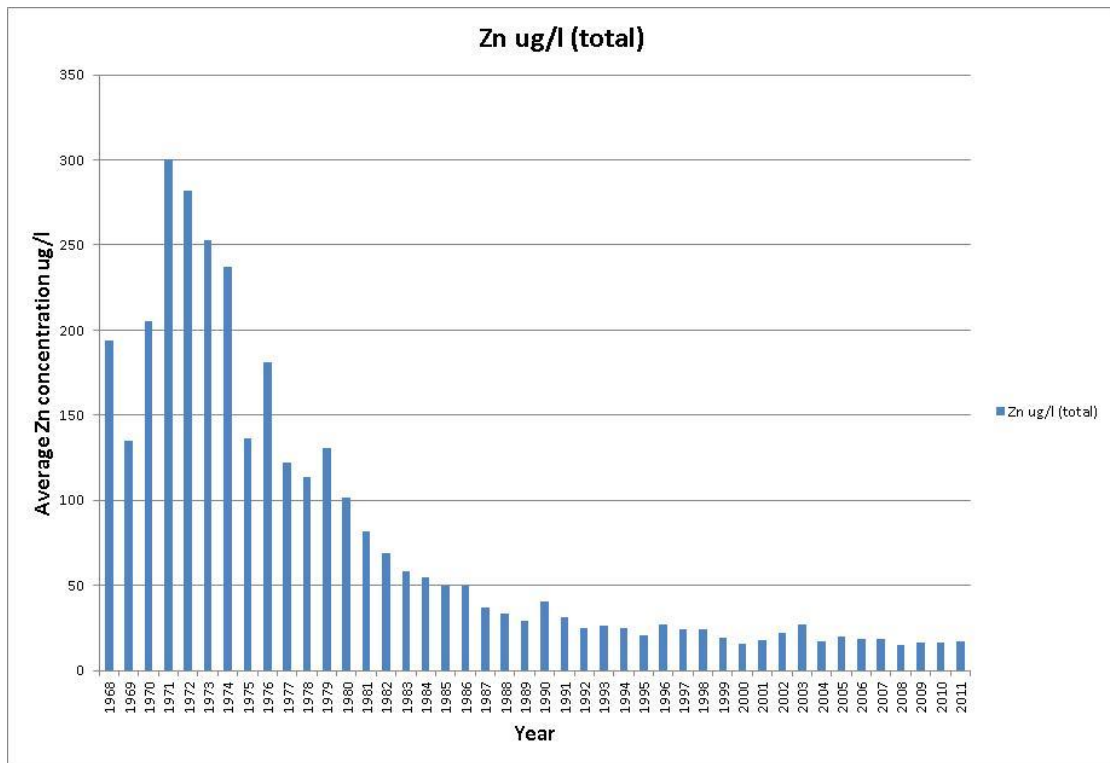


Figure 3.8: Average zinc concentration in ug/l (unfiltered) per year in the period from 1968 till 2011. It is clear that concentrations were highest in the beginning of the 70s.

During the modelling, an emission pattern as showed in the figure above needs to be reproduced.

3. During the analyses of the dataset from Lobith, it was found that the Kd of Zinc slightly decreases with increasing discharge. The model needs to be adjusted in order to reproduce this behaviour. Two different fractions are known by the model. At first, both fractions had the same Kd value. However, as mentioned before, smaller particles have a larger sorption capacity, therefore it is realistic to assign different Kd values to the two fractions. So the third scenario is a variable contaminant injection and a variable Kd.

4 Results and discussion

4.1 Measurements

4.1.1 Suspended Particulate Matter (SPM)

Lots of studies about the effects of climate change indicate an increasing discharge for the River Rhine in winter as a result of intensified snow-melt and increased winter precipitation. Therefore, the risk of resuspension of historically contaminated sediments grows. In the past the River Rhine has shown a huge erosion capacity during flood events, associated with remobilization of accumulated contaminants. Contaminants are transported both dissolved in water and adsorbed to SPM. Transport of contaminants by adsorption strongly relates to the availability of SPM.

Discharge and amount of SPM, transported along the river, are closely related. In general it can be said that increasing discharges causes an increase in concentrations of SPM, however, SPM concentrations remain constant during lower discharges, as shown in figure 4.1 and 4.2.

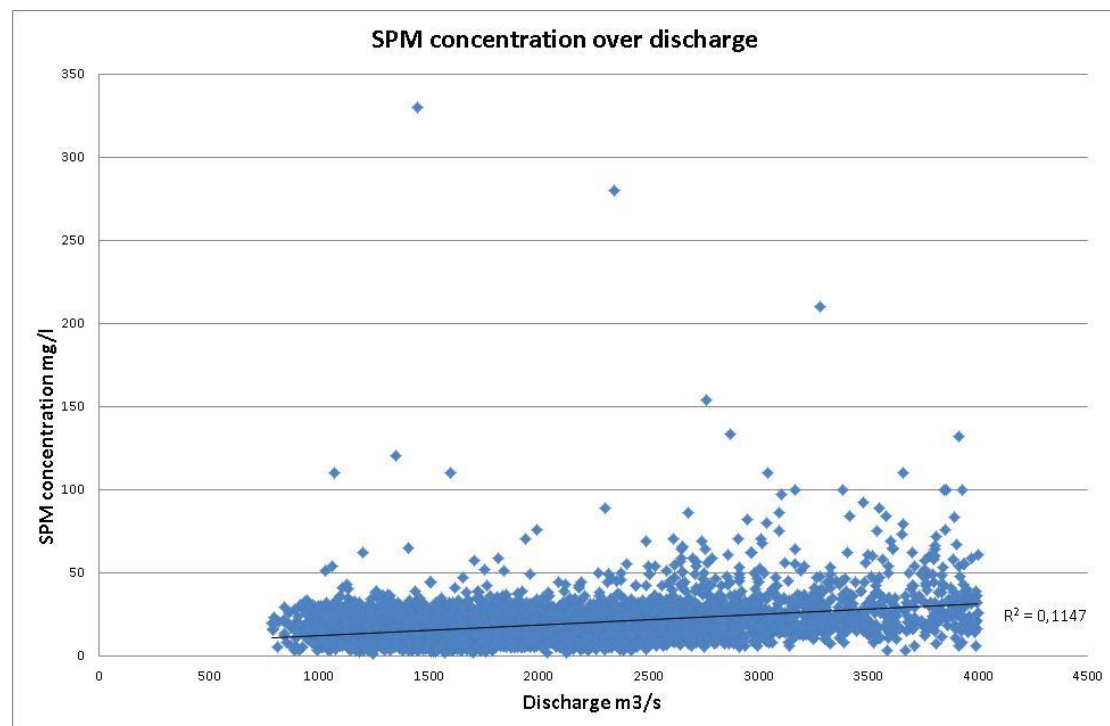


Figure 4.1: Concentration of SPM over low discharge in the river Rhine at Lobith in the period 1995-2009.

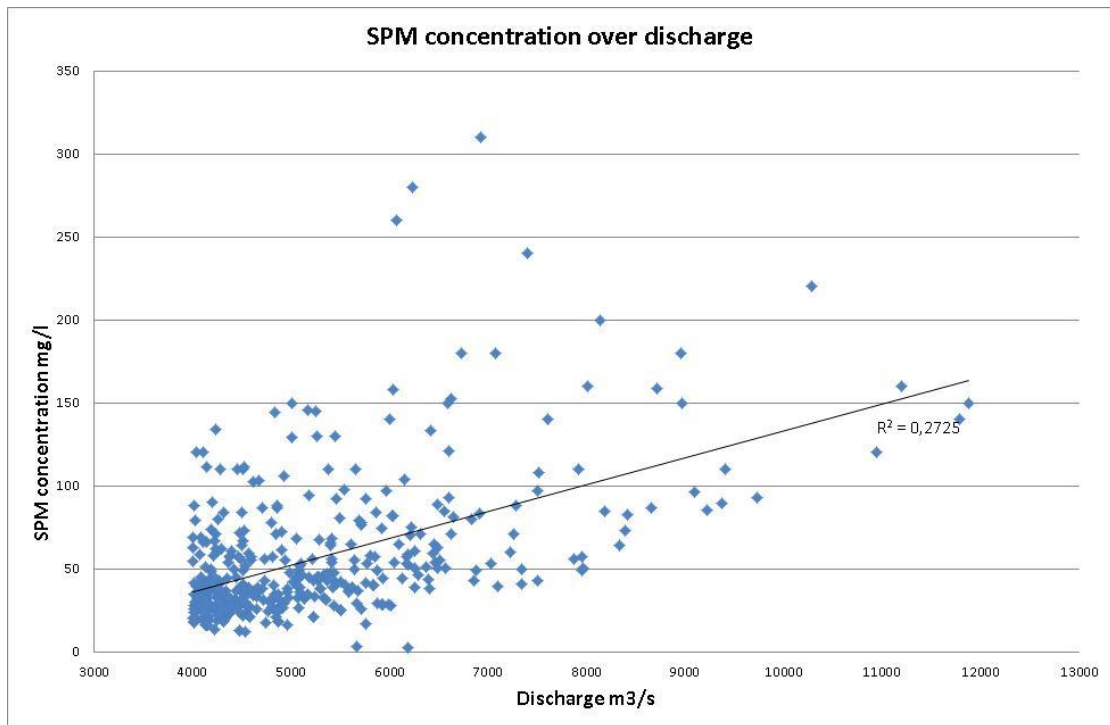


Figure 4.2: Concentration of SPM over high discharge in the River Rhine at Lobith in the period 1995-2009.

For pragmatic reasons, 4000 m³/s has been chosen as a critical value. Concentration of SPM tends to increase from 3000 m³/s, however, concentration of contaminants indicate a change around 4000 m³/s. Concentrations of both SPM and contaminants during periods above and below this critical discharge are examined. As becomes clear from figure 4.2, a strong relation exists between discharge and SPM concentrations, especially above this critical value.

In addition, figure 4.4 shows a typical result of a discharge peak together with a peak in SPM concentration indicating the correlation between them.

In the river Rhine the relation between discharge and SPM concentration is limited by the amount of available sediment (e.g. Asselman 1997). When discharge increases, SPM concentration will increase initially, but from the moment easily available sediment supply has run out, SPM concentrations drop. Usually, SPM reaches peak concentration before the discharge peak. This phenomenon is called ‘clockwise hysteresis’ (Burgos et al, 2008).

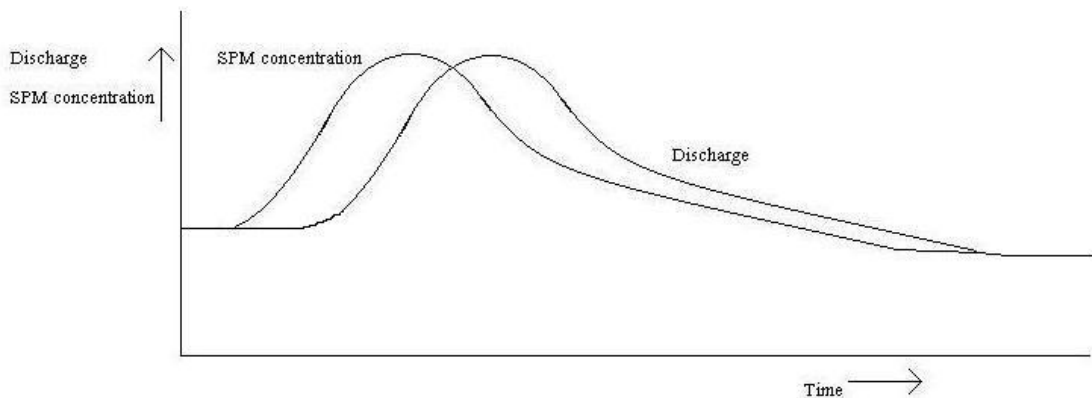


Figure 4.3 : schematic representation of peak SPM concentration and peak discharge events.

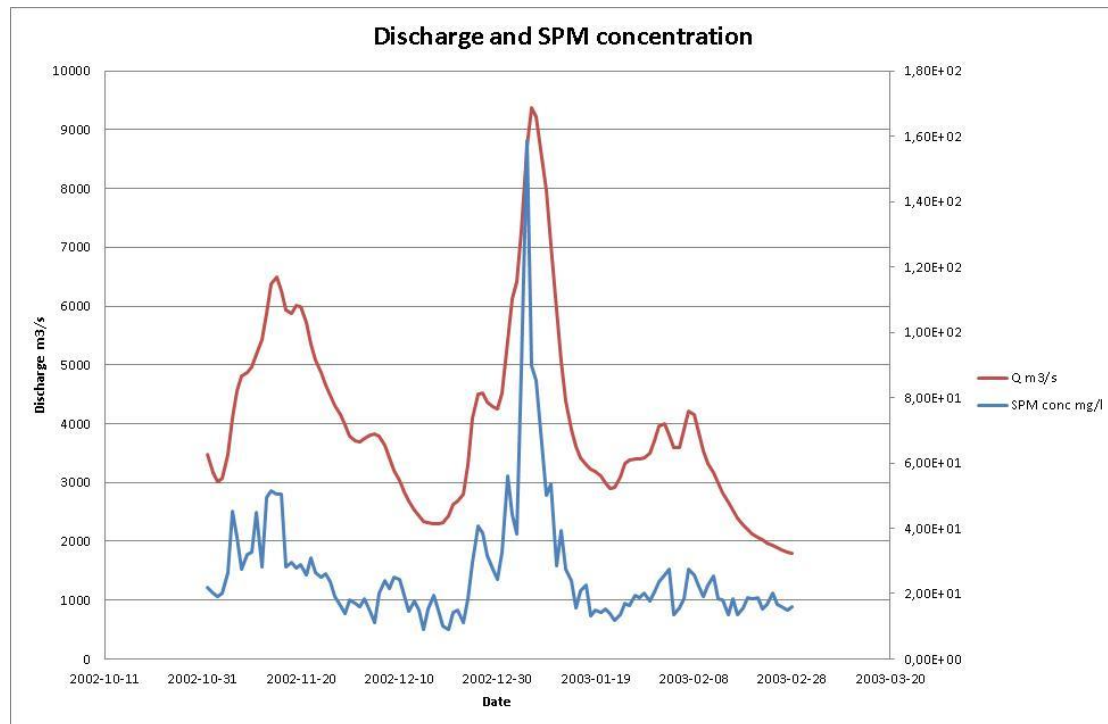


Figure 4.4: SPM and discharge peaks with time during an event in 2002..

Since SPM concentration depends on the availability of sediment, the amount of erosion is an important factor in the transport of particles. Erosion can be described with the Krone-Partheniades formula, already discussed in the 'bakje' model as well.

$$\frac{dm_E}{dt} = E \left(\frac{\tau_b}{\tau_E} - 1 \right)$$

Where $\frac{dm_E}{dt}$ is the rate of mass eroded per unit area, τ_E is critical shear stress for erosion

and E is the erosion constant. In addition τ_b is described by: $\rho g \frac{u^2}{C^2}$

- A: erosion flux [kg/m²/s]
- M: erosion parameter [kg/m²/s]
- τ_b : bottom shear stress [N/m²]
- τ_c : critical shear stress for erosion [N/m²]
- ρ : fluid density [kg/m³]
- g: gravitational acceleration [m/s²]
- u: flow velocity [m/s]
- C: Chézy roughness parameter [-]

As becomes clear from above formula, erosion flux increases with increasing bottom shear stress and bottom shear stress increases with increasing flow velocity. Since $Q=A*u$, where Q = Discharge [m³/s], A = cross sectional area of the channel [m²] and u

= the flow velocity [m/s], it is evident that increasing discharge causes an increased erosion flux.

4.1.2 Adsorbed contaminants

Contaminants are transported along the river in various states, dissolved in water or adsorbed to SPM. During low discharges SPM concentrations are low, however, contaminants are still introduced to the river system. Therefore, quality of SPM can be poor. Van der Heijdt & Zwolsman (1997) showed that SPM quality can seriously improve during higher discharges due to dilution of SPM with relative clean sediment. Asselman (2003) also showed an improvement of SPM quality with discharge.

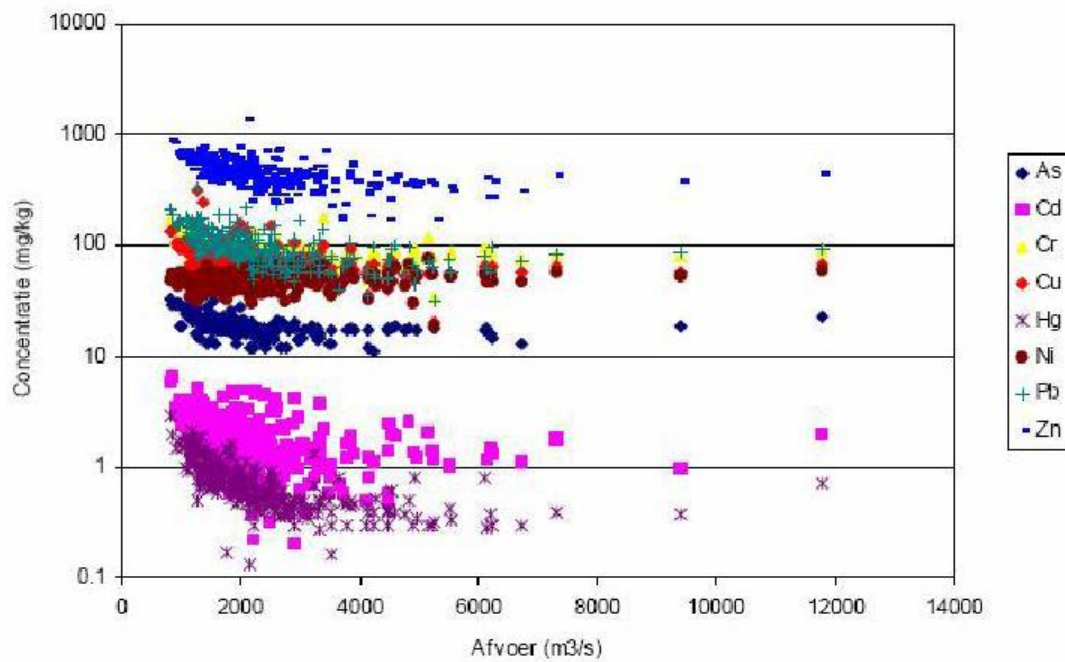


Figure 4.5: SPM-associated heavy metal concentrations ('concentratie') versus Rhine discharge ('afvoer') at Lobith (Asselman, 2003)

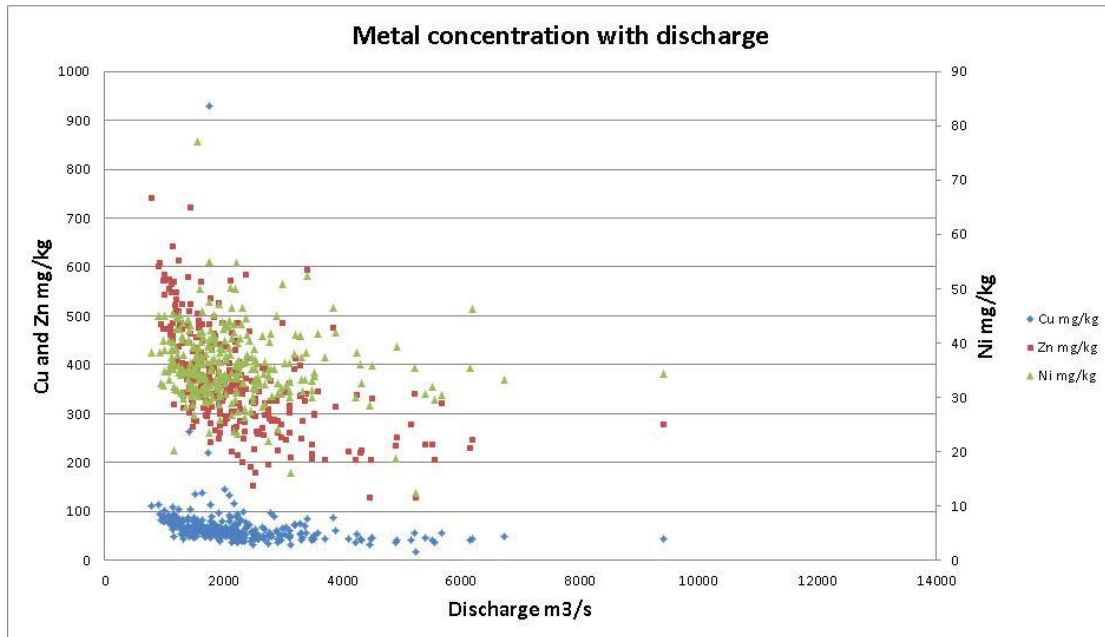


Figure 4.6: Relation between discharge and copper, nickel and zinc, following from database analysis during this study (Period 1995-2009).

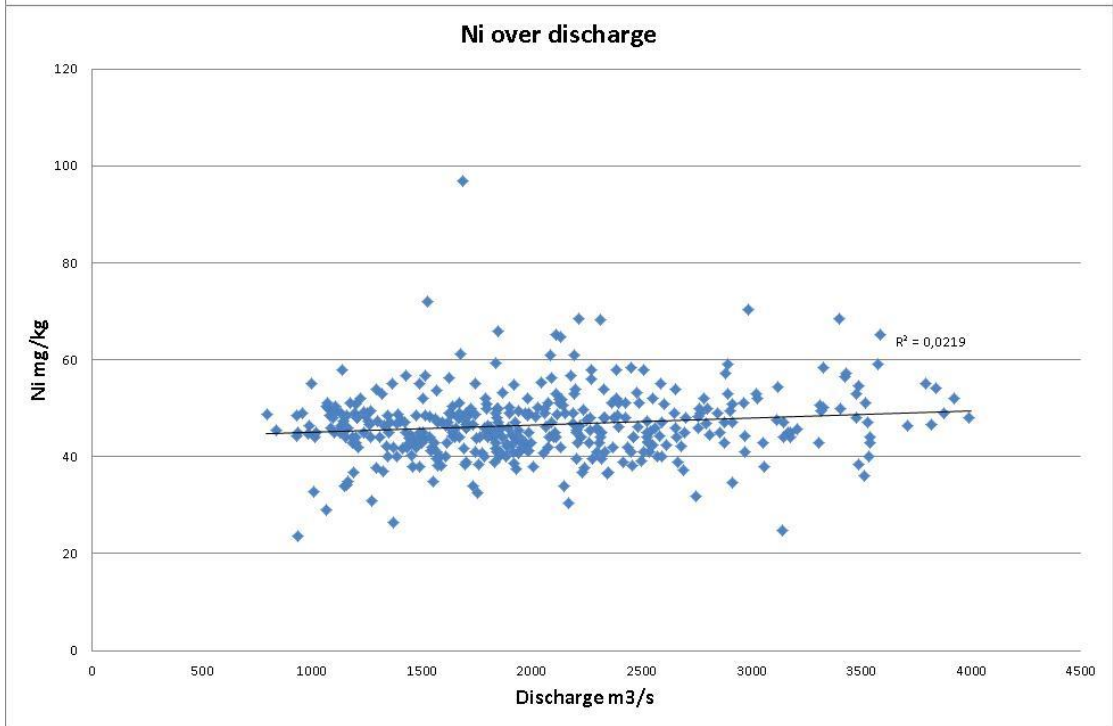
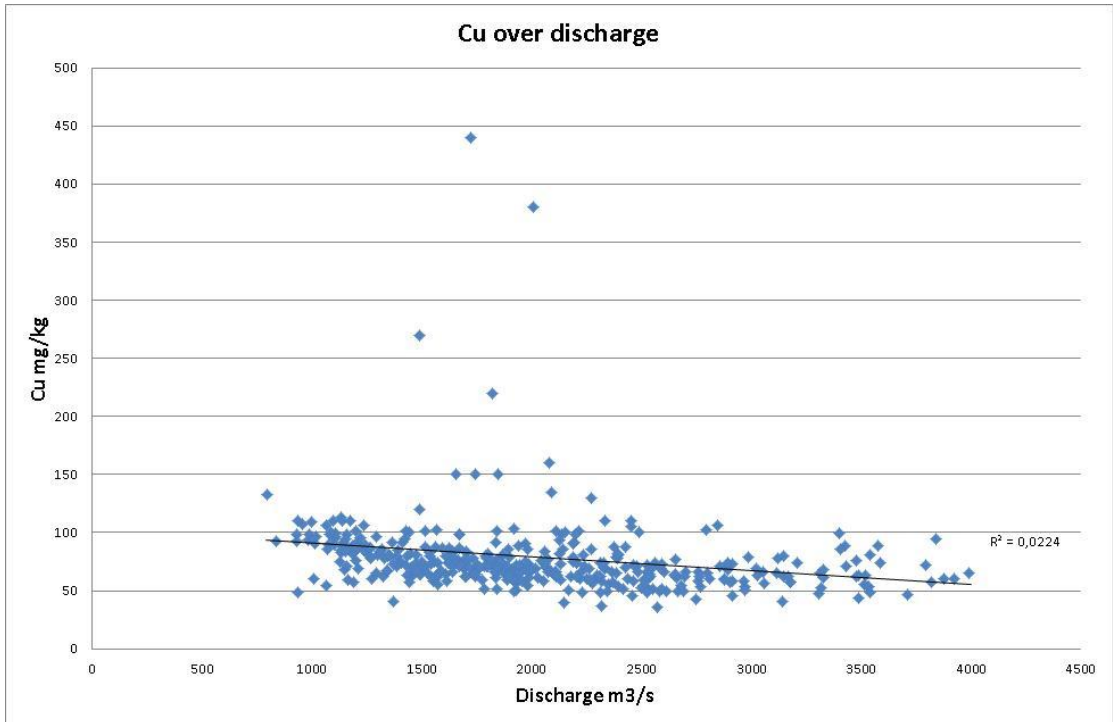
Figure 4.5 and 4.6 basically show the same relation, a dilution effect when discharge increases and during higher discharges, the amount of data decreases.

Mean reason why this research is because most studies are confined to literature or data analysis while during this study model simulations are performed as well.

As can be seen in figure 4.5 and 4.6, improvement of SPM quality is especially established in the lower discharge regimes, e.g. from 2000 m³/s to 4000 m³/s.

Reasons for this improvement are probably a dilution effect due to erosion of relative clean sediment. Historically contaminated sediments are deposited during the 70s. In the last 4-5 decades they are covered with cleaner sediments, so during erosion events these clearer sediments will get resuspended first. Hence the improvement of SPM quality during higher discharges. In addition, masking effects as discussed in chapter 2.6 may also create a decreasing trend with increasing discharge.

The focus for this study is on resuspension of Altlasten during high discharges, therefore, concentrations of contaminants are examined above and below the critical value of 4000 m³/s, in order to investigate a potential difference between high and low discharges.



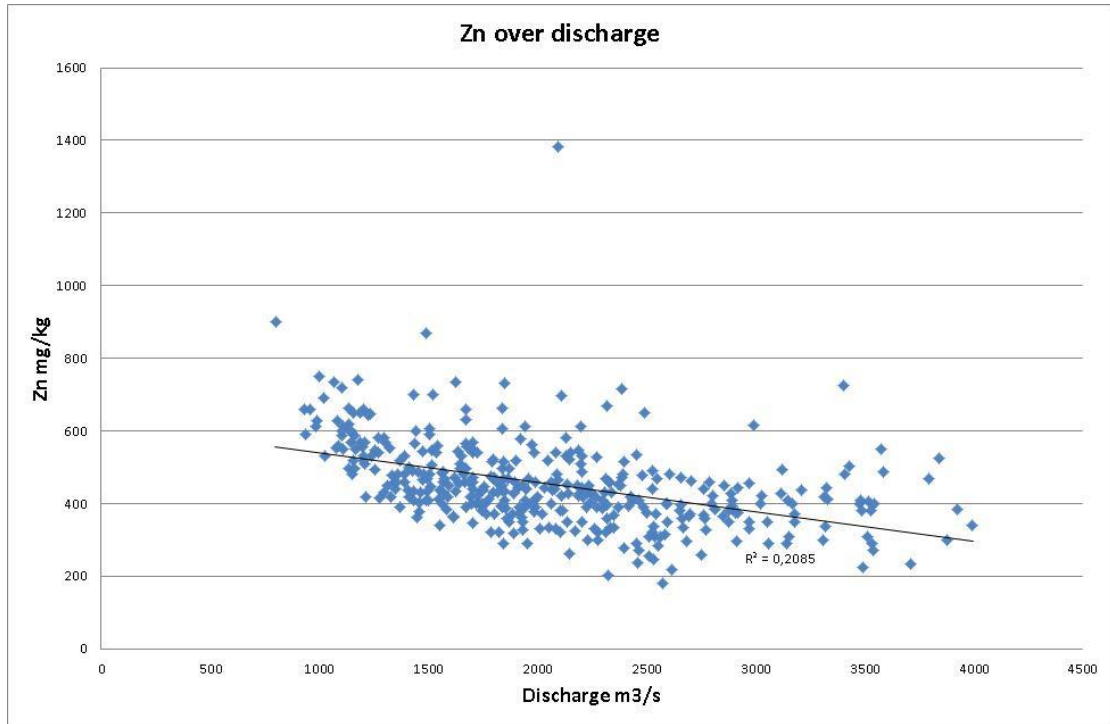
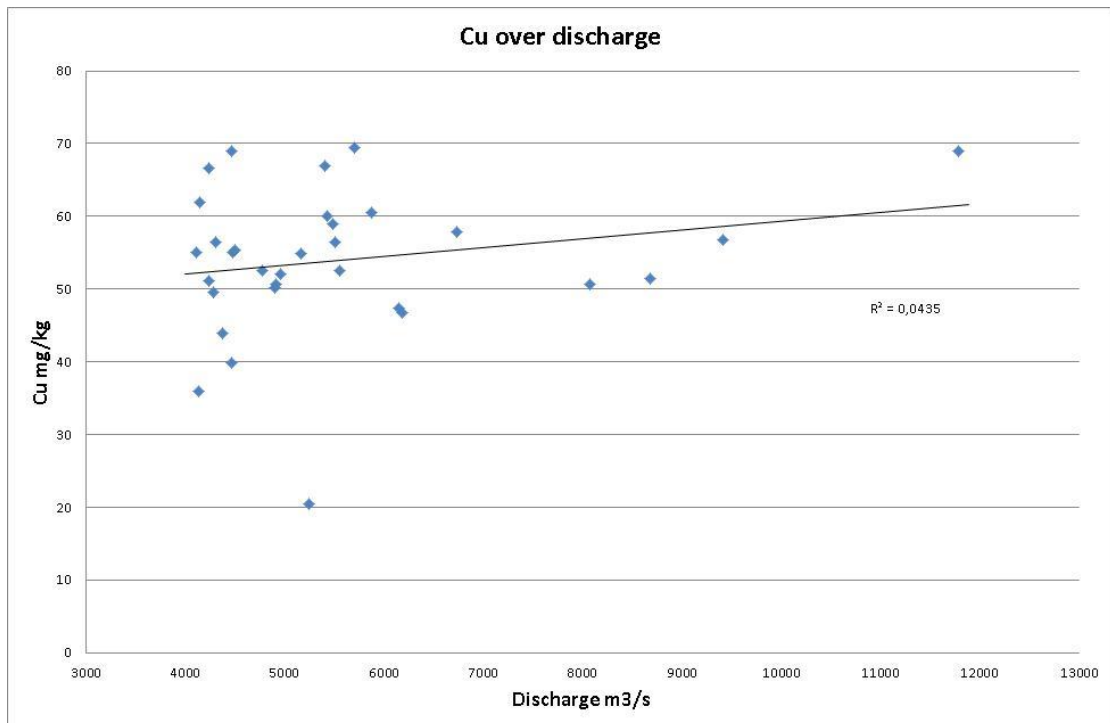


Figure 4.7: Relation between discharge below critical value and adsorbed metals (Period 1995-2009).

Figure 4.7 shows the relation between discharge and adsorbed metals, below critical value. Although R^2 is not very strong, a general decreasing trend is observed. This same relation is examined for discharges above the critical value, as showed in figure 4.8.



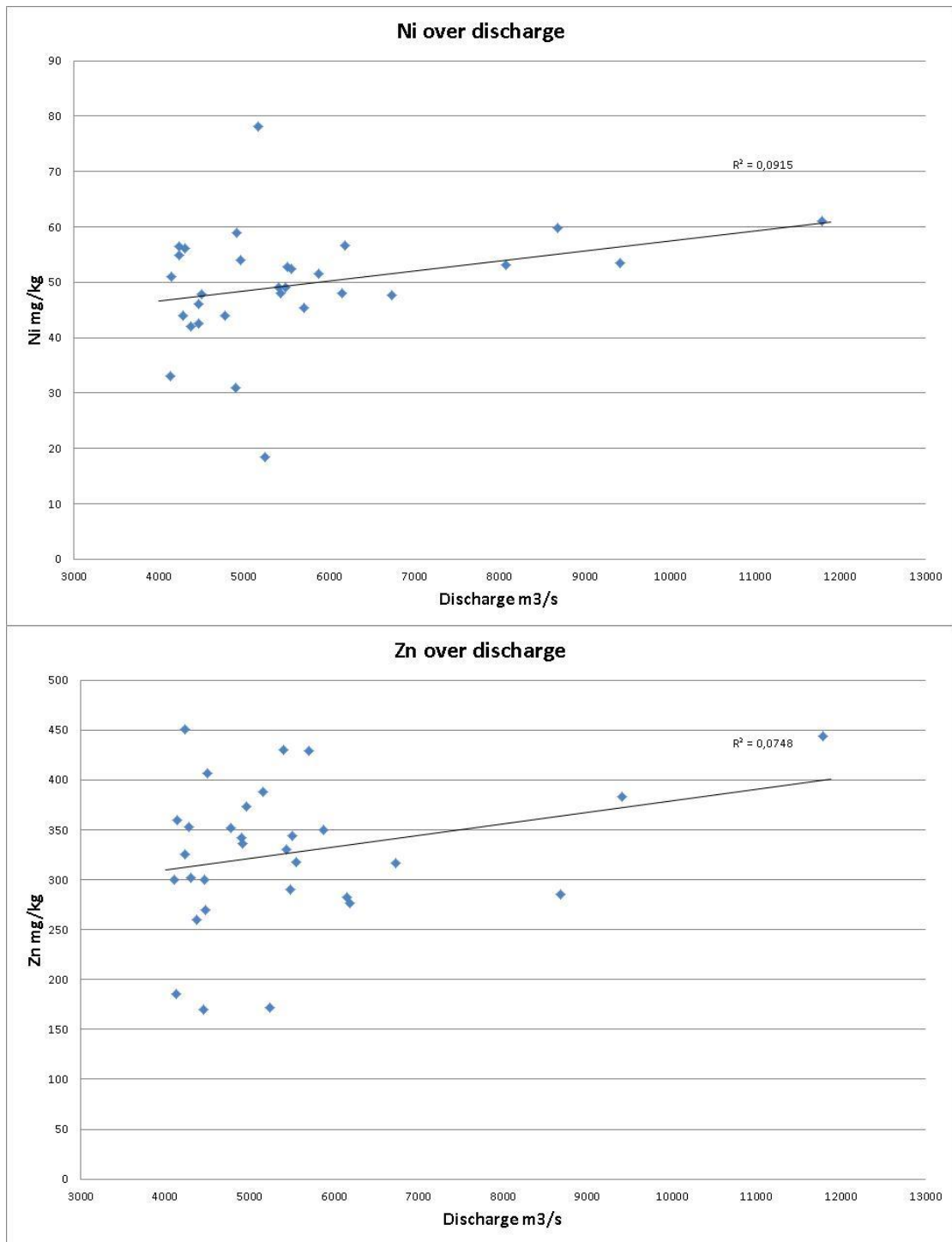


Figure 4.8: Relation between discharge above critical value and adsorbed metals (Period 1995-2009).

As can be seen in figure 4.7 and 4.8, metal concentration decreases with increasing discharge below the critical discharge while metal concentration increases with increasing discharge above the critical discharge. This may indicate a dilution due to higher discharges at first, however, when discharge increases contaminated sediment layers may be remobilized.

To compare the values above and below the critical discharge value, from both groups, averages and standard deviations are calculated as shown in table 4.1.

All Q	Cu	Ni	Zn
average	77,06898	46,77517	445,1962
st. dev	54,19338	7,339829	120,8339

Low Q	Cu n=400	Ni n=405	Zn n=387
average	78,92125	46,56938	454,6925
st. dev	55,83629	7,027066	118,9681

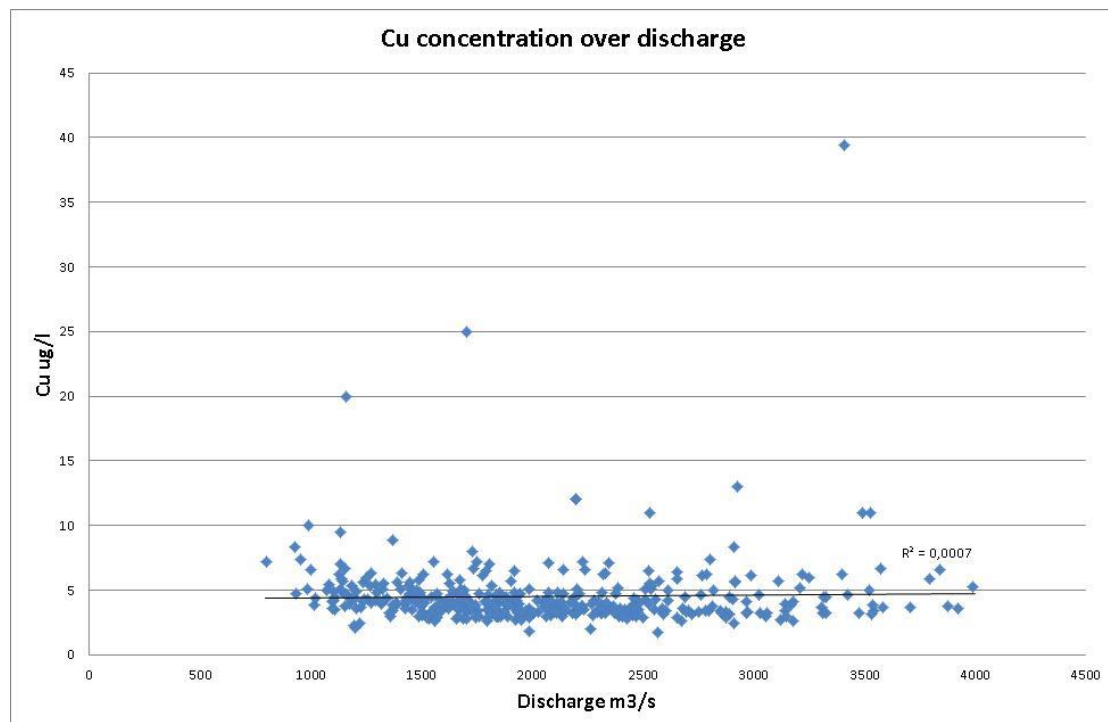
High Q	Cu n= 32	Ni n=30	Zn n=31
average	53,91563	49,55333	326,6452
st. dev	9,91694	10,3075	70,7538

Table 4.1: Average values and standard deviations of adsorbed metal concentrations below and above critical discharge value.

From table 4.1 it appears that during high discharges, the amount of contaminants adsorbed to SPM is on average lower than during low discharges. One of the reasons for this observation can be due to masking effects and dilution. Note that is important to realize that the amount of data points decreases significantly with increasing discharge.

4.1.3 Total concentrations

Also total concentrations are administrated. In the figures below, discharge and total metal concentration (dissolved and unfiltered) are plotted.



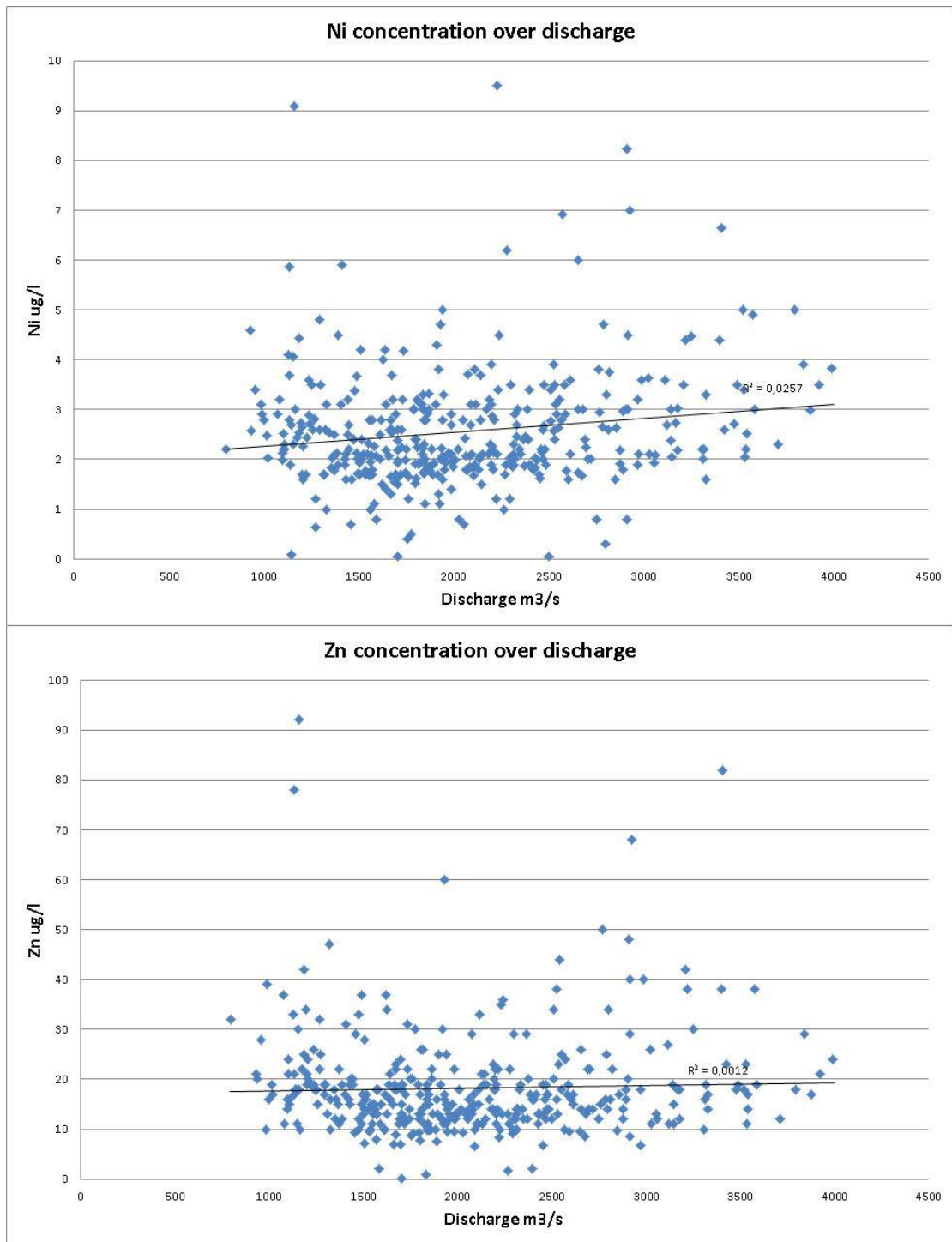
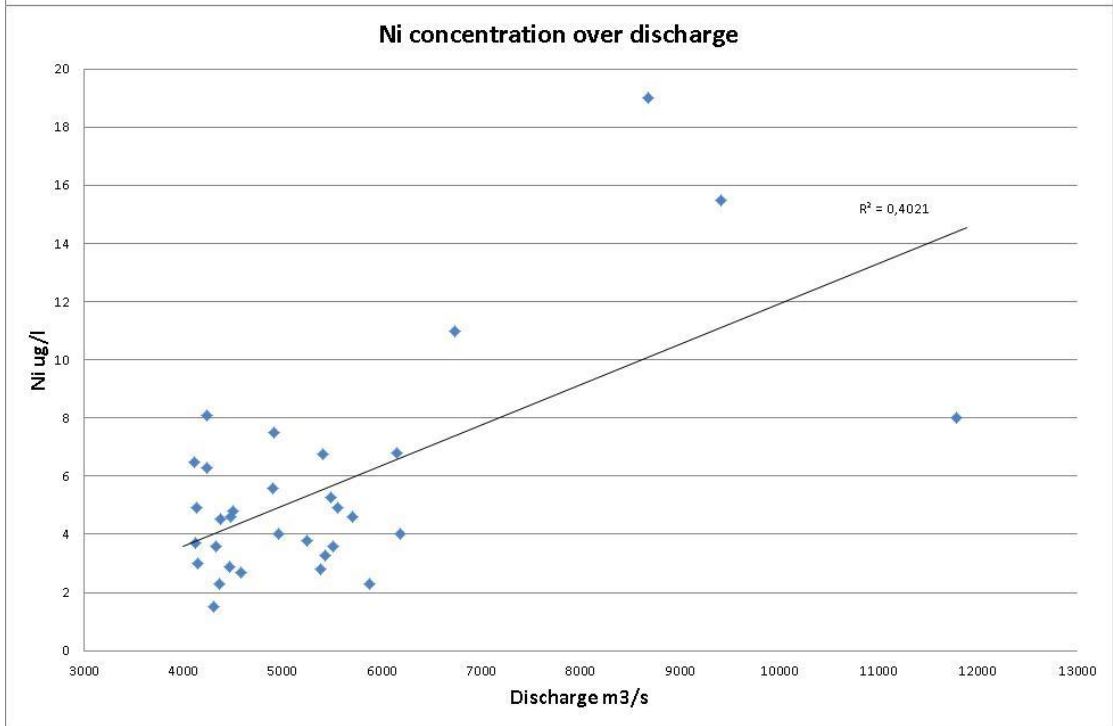
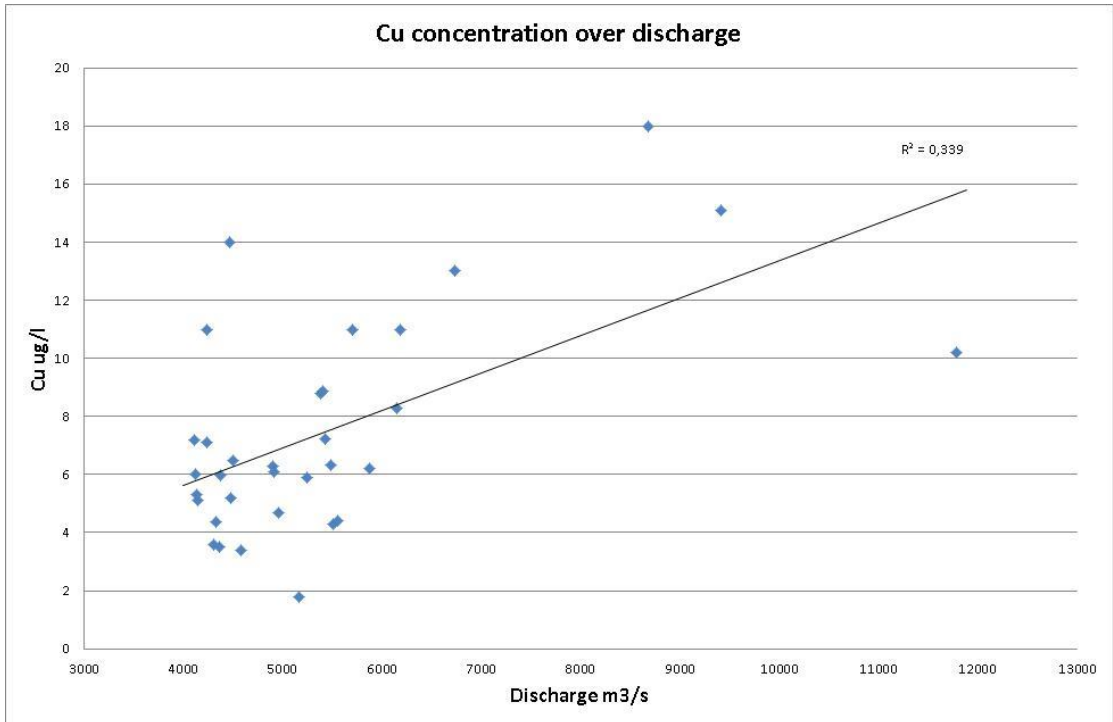


Figure 4.9: Relation between total, unfiltered, metal concentration and discharge below critical value (Period 1995-2009).



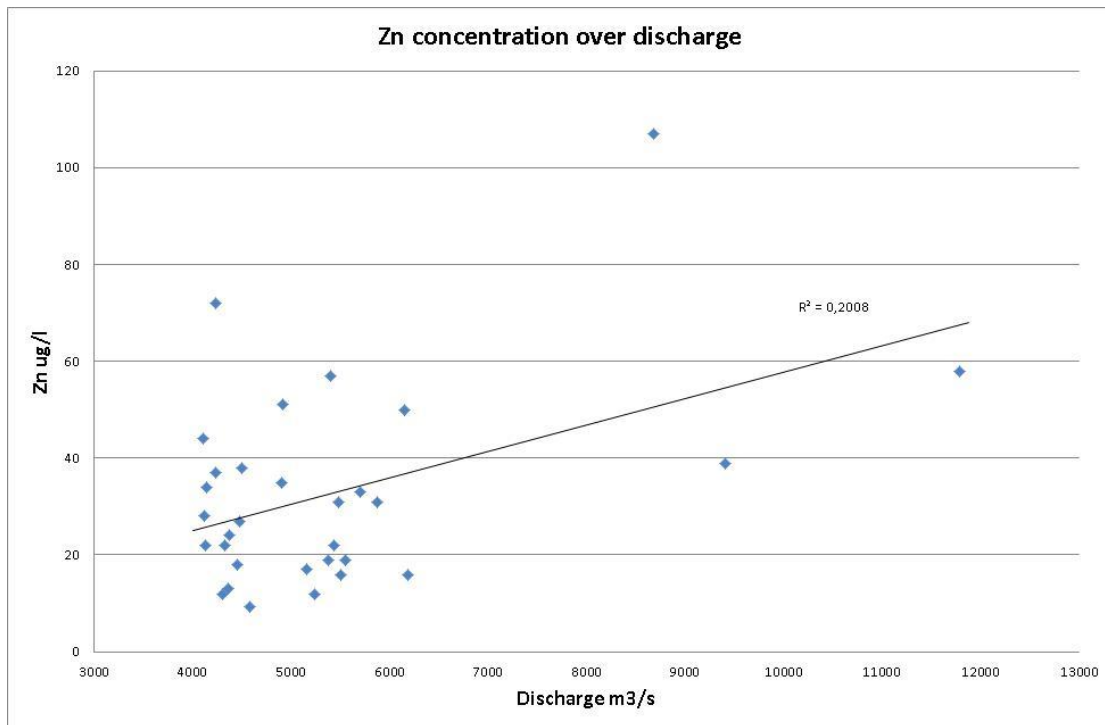


Figure 4.10: Relation between total, unfiltered, metal concentration and discharge above critical value (Period 1995-2009).

As becomes clear from figure 4.9 and 4.10 concentrations remain fairly constant below critical value and increase above critical value, indicating remobilization of Altlasten. A possible reason for the increasing nickel concentration during increasing discharge may be resuspension of iron due to higher discharges. Nickel adsorbs to iron very well, so resuspension increases sorption capacity for nickel.

Table 4.2 shows the average and standard deviations of metal concentration below and above critical discharge.

all Q	cu n=446	zn n=434	ni n=443
average	4,69603139	19,17322581	2,763205418
st dev	2,832167422	11,85984942	1,687068898

low Q	cu n=412	zn n=402	ni n=410
average	4,466578	18,05642	2,530707
st dev	2,631671	10,11517	1,135126

high Q	cu n=34	zn n=32	ni n=33
average	7,476471	33,20313	5,651818
st dev	3,644931	20,53702	3,68062

Table 4.2: Average values and standard deviations for total unfiltered metal concentrations below and above critical discharge value.

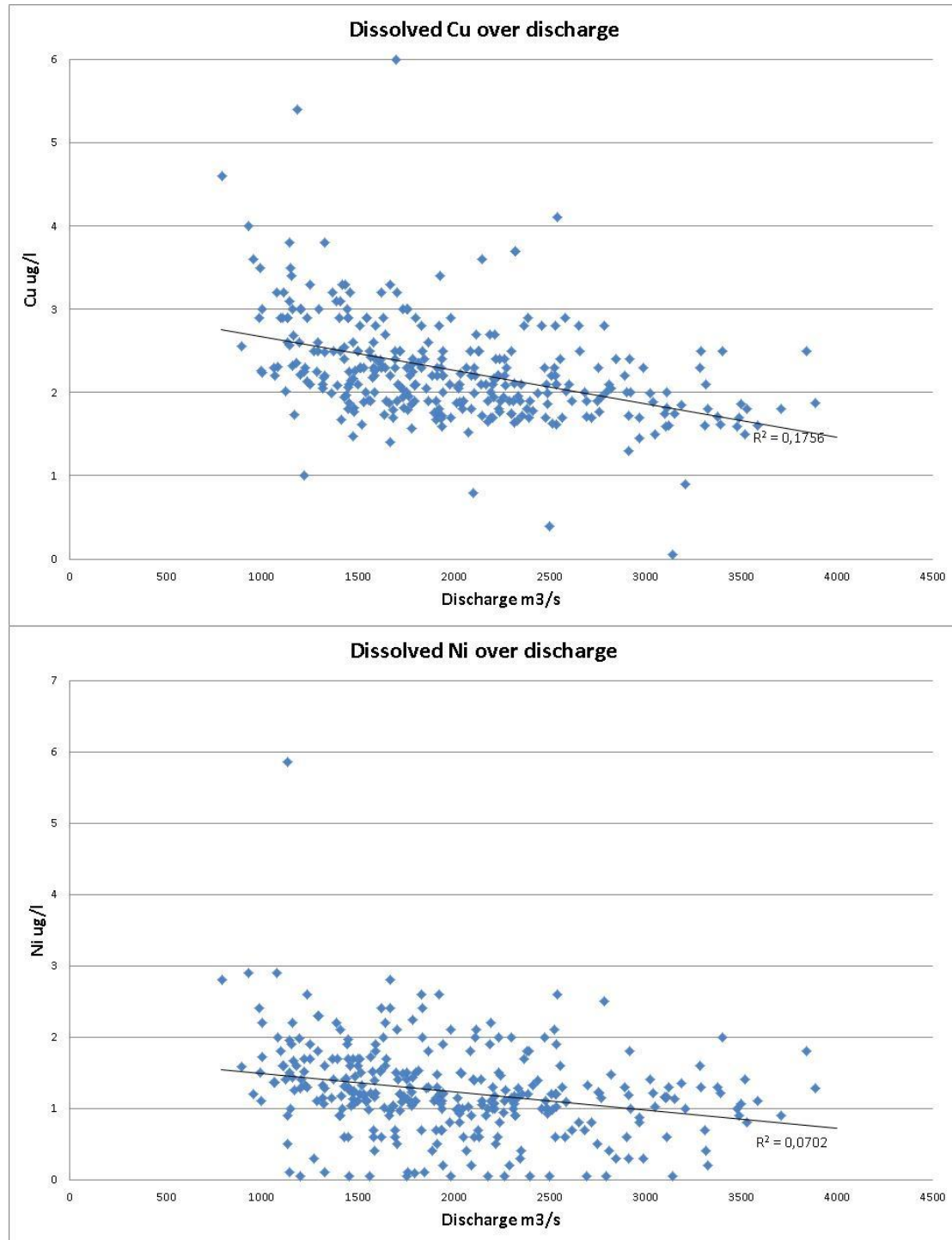
From table 4.2 it appears that total concentration of copper, nickel and zinc increase with increasing discharge. This suggests remobilization of Altlasten.

4.1.4 Dissolved contaminants (filtered < 0.45µ)

Besides transport of contaminants by means of adsorption to SPM, pollutants can travel in the dissolved phase.

Similar to SPM quality, concentrations during discharges above and below the critical value are compared.

In the figures below, dissolved concentrations of Copper, Nickel and Zinc are plotted over high discharge events.



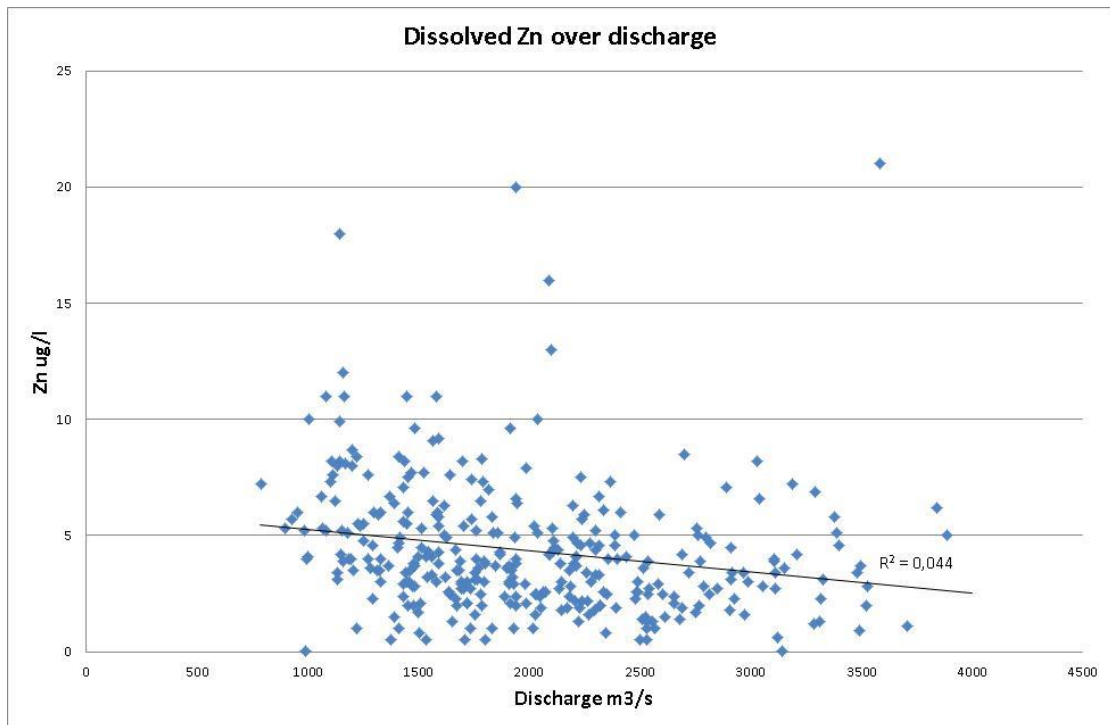
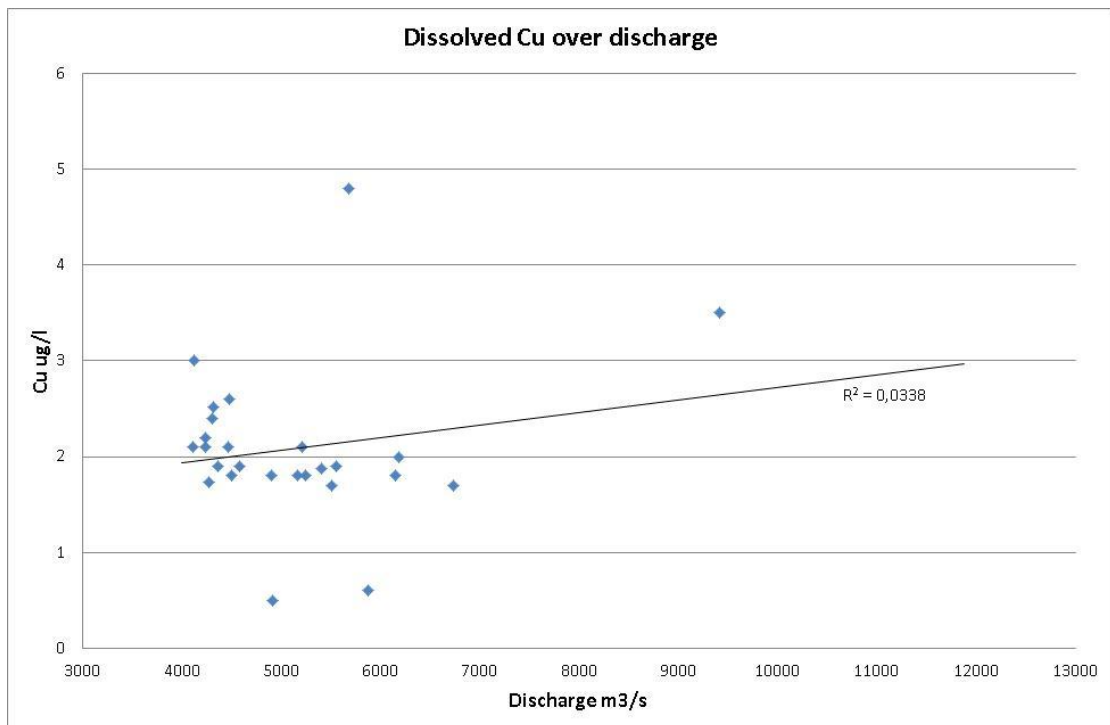


Figure 4.11: Relation between discharge below critical value and dissolved metals (after filtration) (Period 1995-2009).

Corresponding to adsorbed metals, again metal concentration decreases with increasing discharge for discharges below the critical value as can be seen in figure 4.11. In figure 4.12 the concentrations of dissolved metals above the critical value is showed.



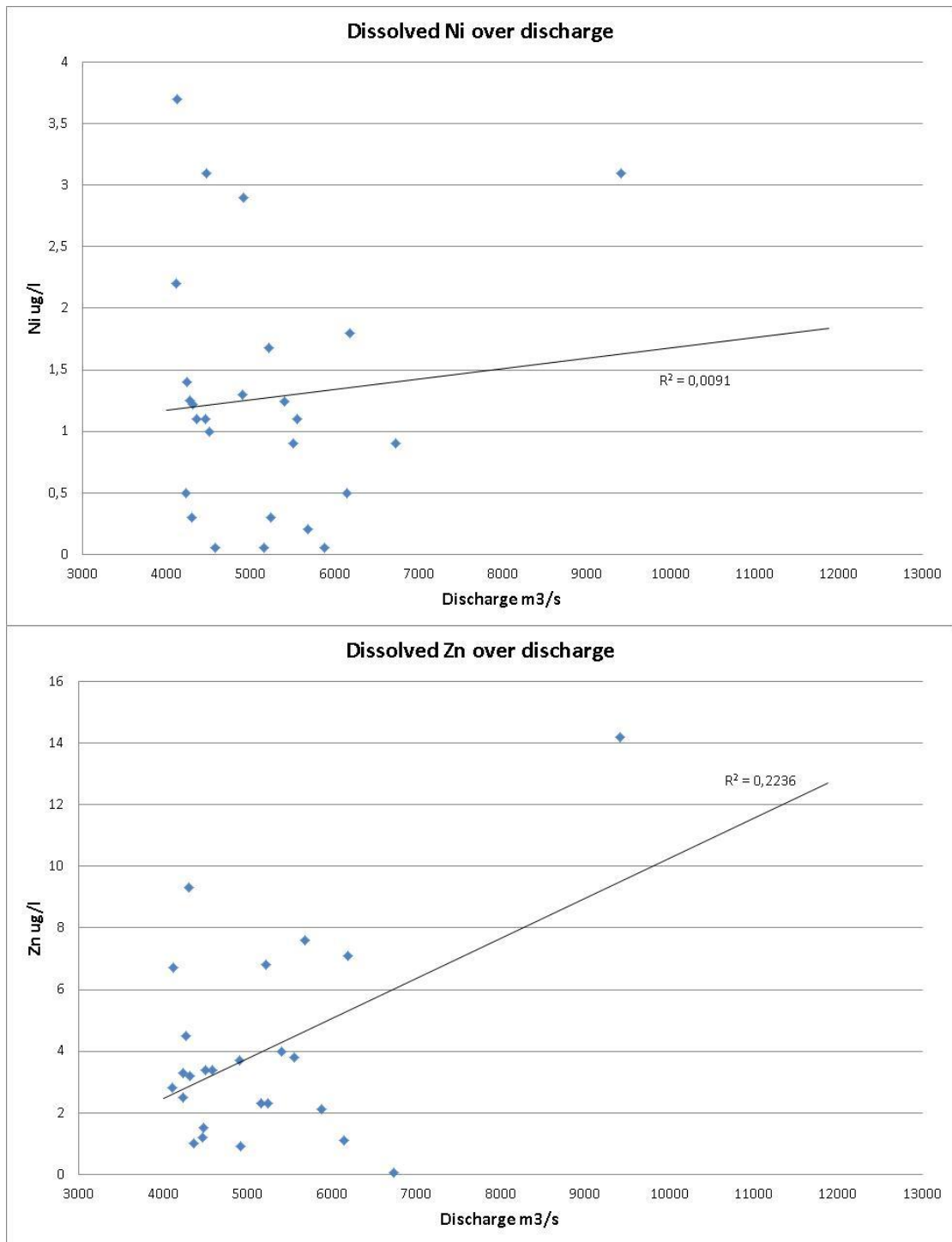


Figure 4.12: Relation between discharge above critical value and dissolved metals (after filtration) (Period 1995-2009).

Similar to adsorbed metals, a decreasing concentration with increasing discharge is observed below critical value and an increasing concentration above critical value. Although relations may not be very strong a dilution effect is only visible below the critical discharge while concentrations above critical discharge tend to increase again.

Table 4.3 shows the average concentrations and standards deviations of copper, nickel and zinc during periods below and above critical discharge value.

all Q	Cu n=354	Zn n=354	Ni n=347
average	2,255904	4,321328	1,239084
st dev	0,638131	2,842313	0,66747

low Q	cu n=328	zn n=329	ni n=321
average	2,26939	4,349544	1,236829
st. dev	0,620918	2,814583	0,632507

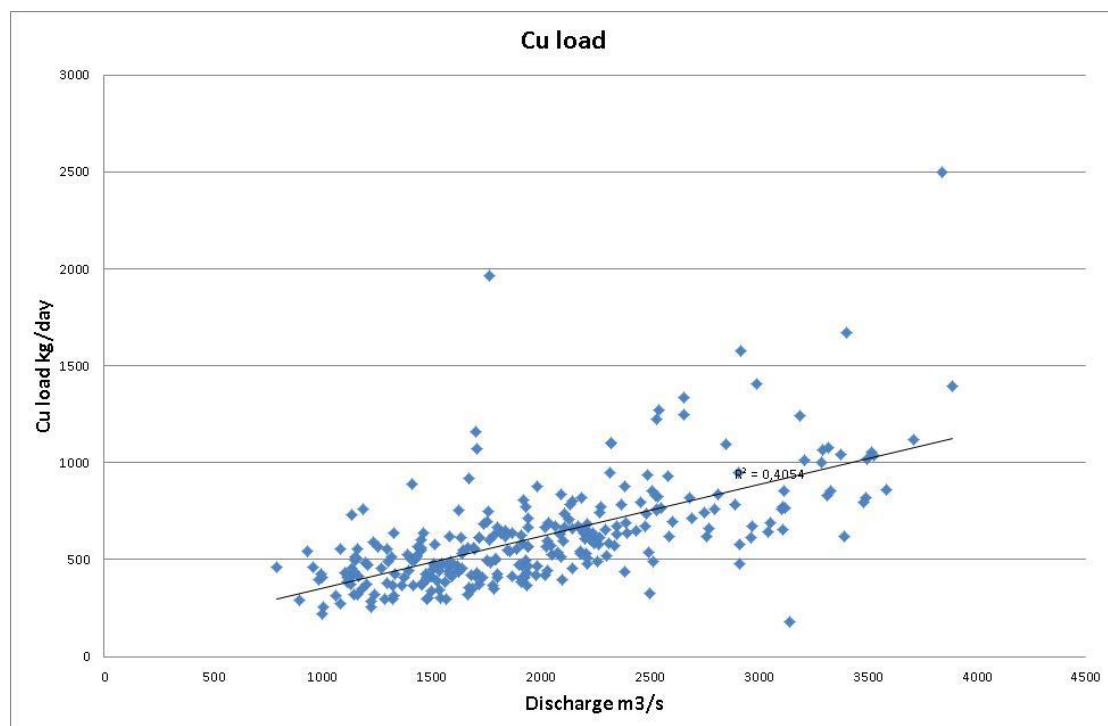
high Q	cu n=26	zn n=25	ni n=26
average	2,085769	3,95	1,266923
st dev	0,796058	3,10992	0,994329

Table 4.3: Average values and standard deviations for filtered dissolved metal concentrations below and above critical discharge value.

From table 4.3 it appears that increasing discharge does not induce in an increasing dissolved contaminant concentration. Again, it is important to realize the scarcity of data points during higher discharges and a dilution effect with increasing discharge.

4.1.5 Loads

When the metals of interest, Copper, Nickel and Zinc, are examined it becomes clear that a strong relation exist between discharge and contaminated load.



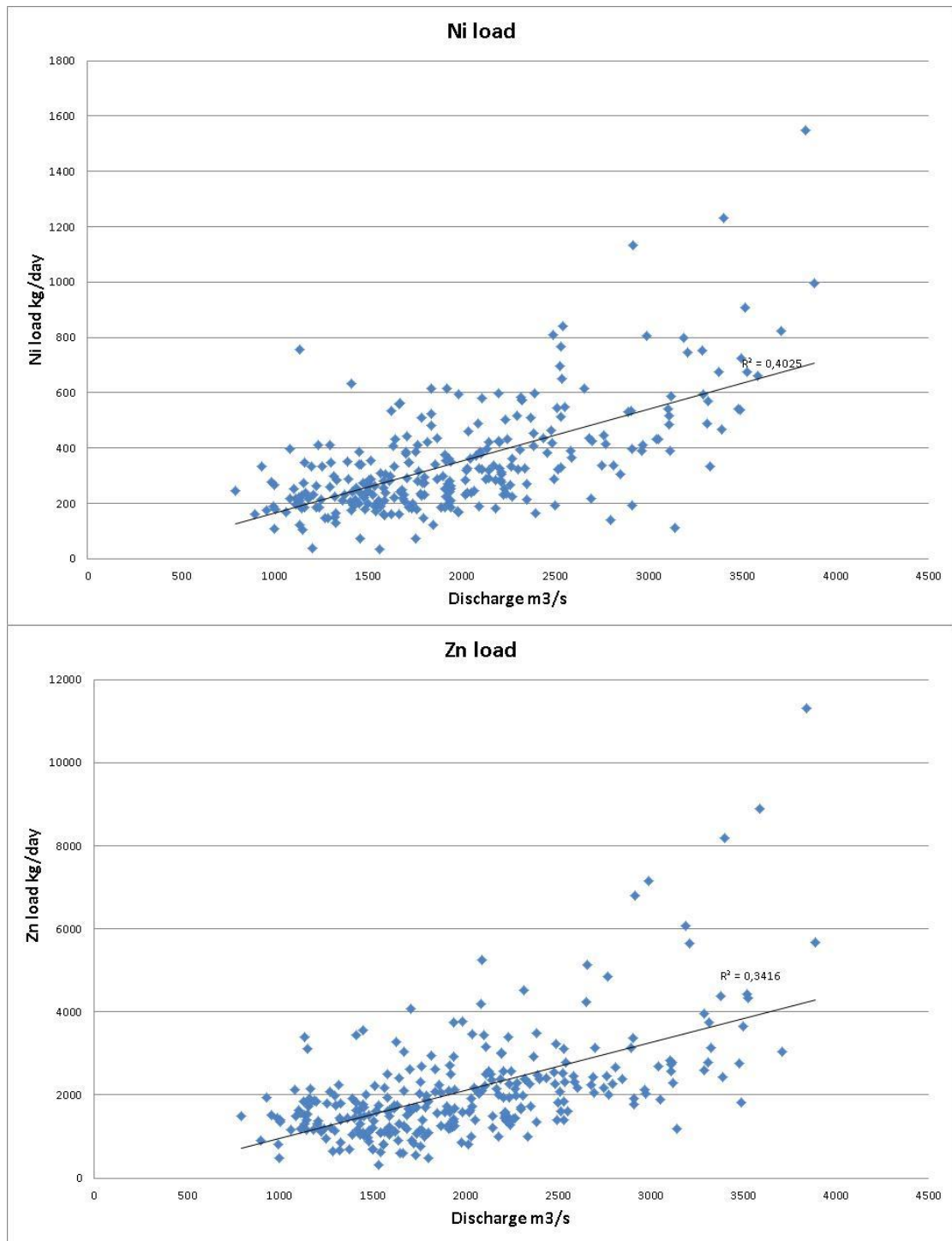
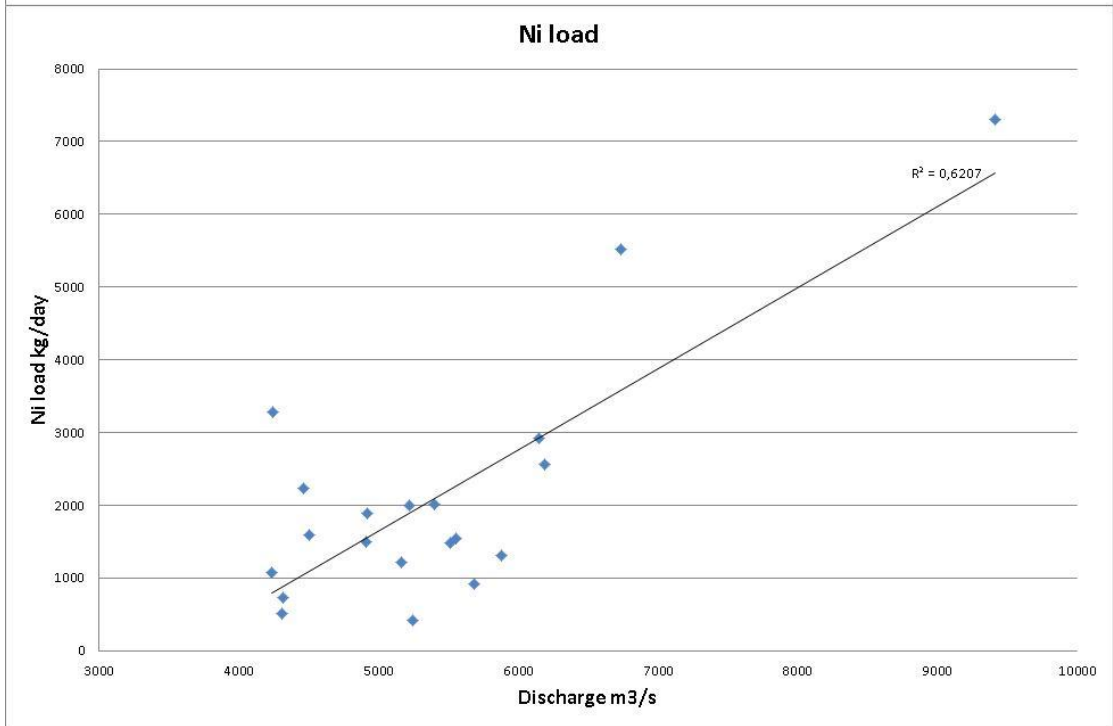
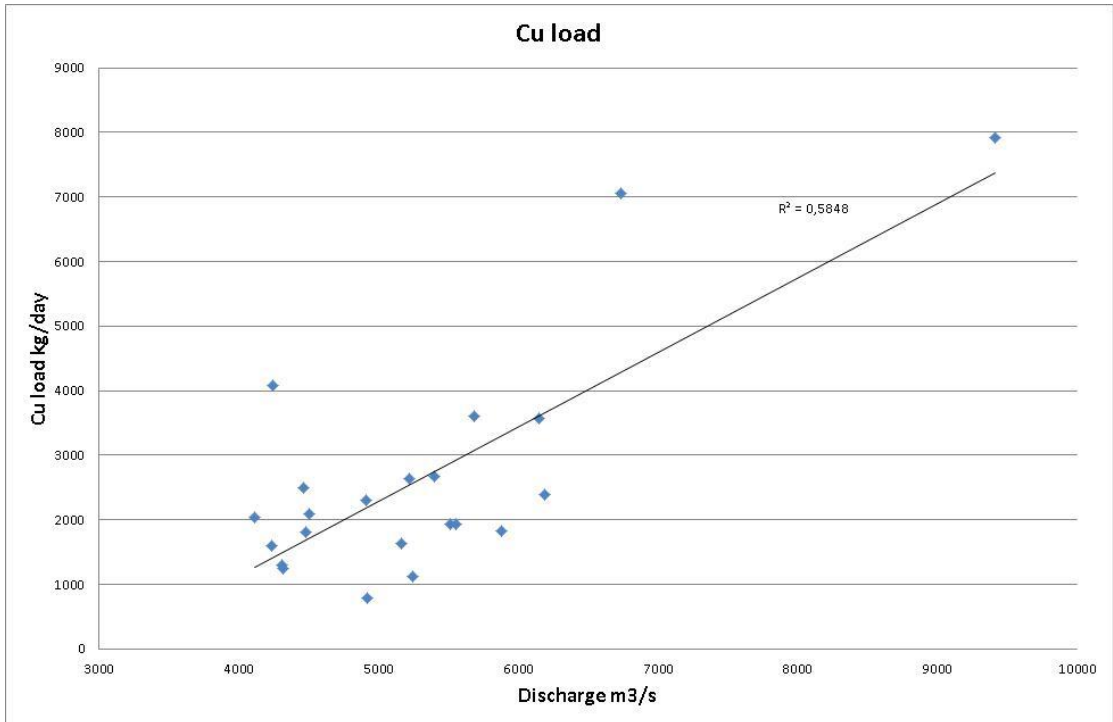


Figure 4.13: Relation between total metal load and discharge above critical value (Period 1995-2009).



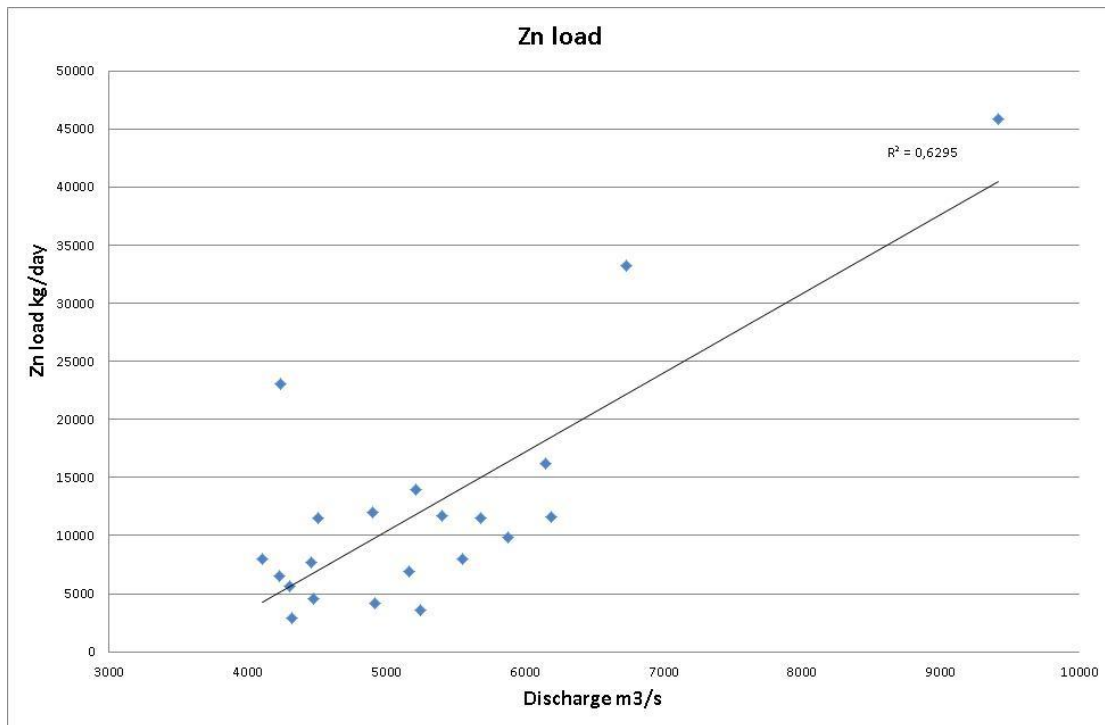
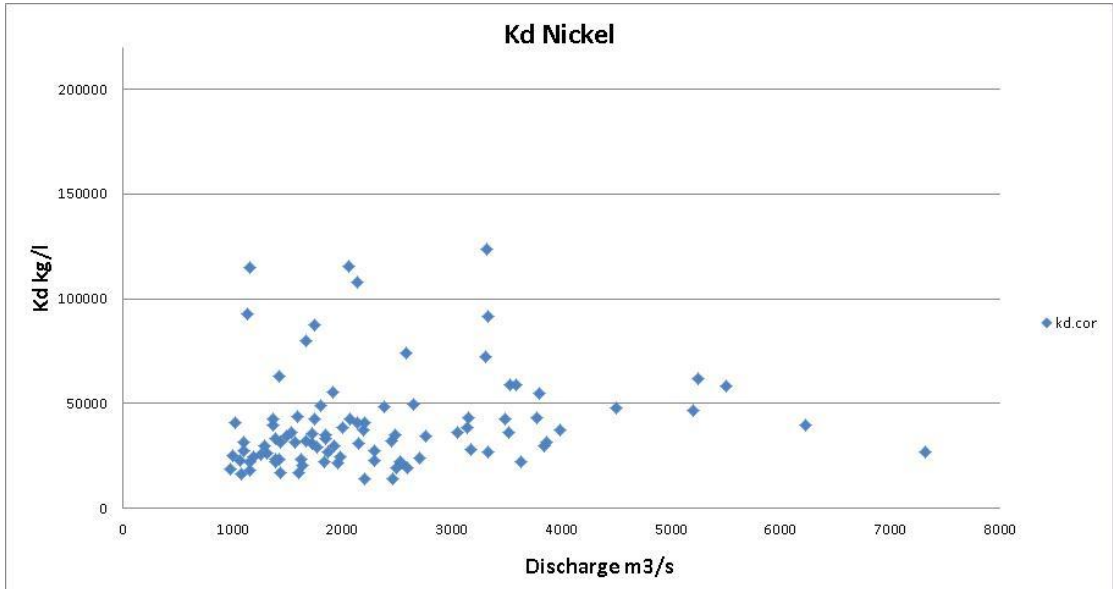
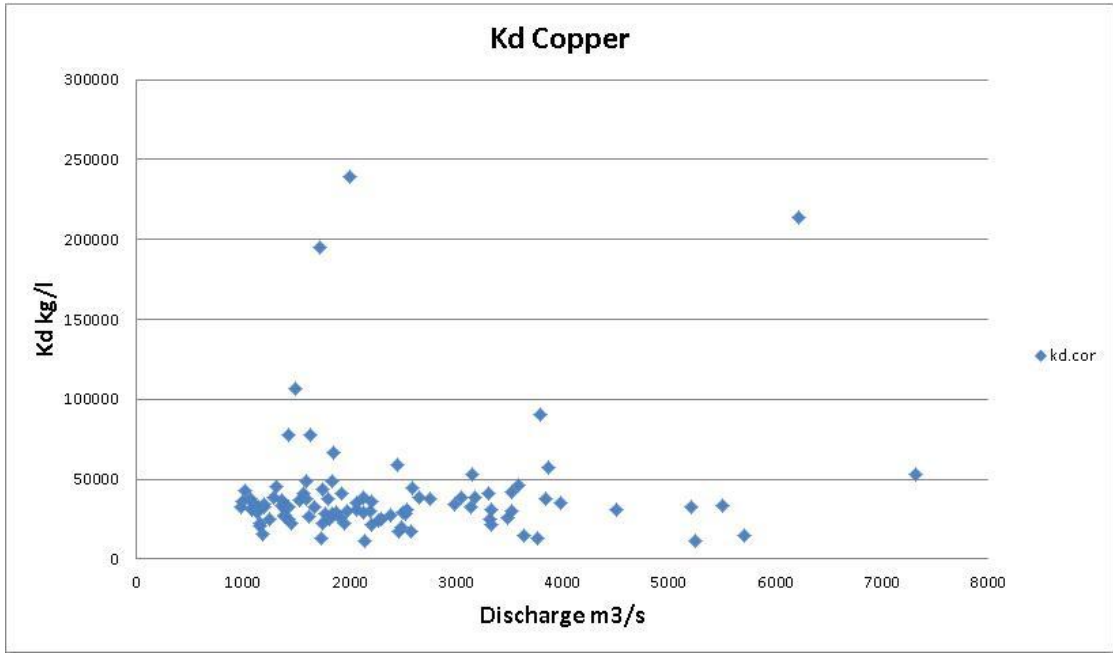


Figure 4.14 Relation between total metal load and discharge above critical value (*Period 1995-2009*).

Figure 4.13 and 4.14 show that higher discharges lead to higher metal loads. This relation may be straightforward since increasing discharges cause more water to be transported per time unit, therefore also more contaminants are transported per time unit. Nevertheless, it is important to demonstrate that this relation really exists.

4.1.6 Partitioning coefficient

As mentioned above the partitioning coefficient describes the distribution of a component in the solid and in the aqueous phase. However, in the literature it is found that this value is not constant but depends on both water and sediment composition and reactivity. Therefore, K_d values are examined during this study.



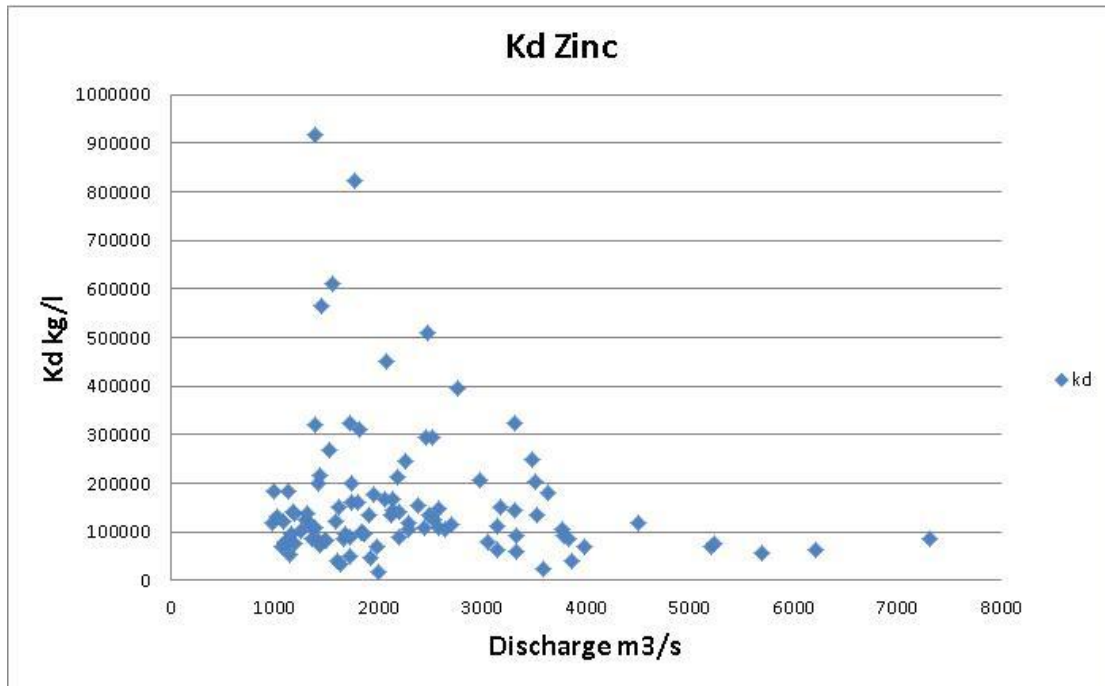


Figure 4.11 This figure shows the Kd values of zinc, copper and nickel over discharge. (Period 1996-2009).

The graphs above show a constant Kd value of Copper and Nickel with discharge. The graph of Zinc suggests a decreasing Kd value with increasing discharge. This may be caused by the fact that during low discharges, SPM composition is dominated by smaller fractions while during higher discharges relatively more sand is suspended. During the modeling phase, both a constant Kd as a variable Kd should be investigated.

4.1.7 Water quality standards

One of the reasons that Copper, Nickel and Zinc are examined is because of the fact that water quality standards are formulated, and as a consequence it is possible to determine in which cases these standards are exceeded. Table 4.4 shows a table with values, for metal concentrations. Measurement values are supposed to stay below this.

	log Kp	Oppw AC	Oppw Streefwaarde	Oppw MTR	Oppw JG-MKN	Oppw MAC-MKN
	ZS	ug/l				
Cu	4,7	0,4	1,1 (totaal)	3,8		
Ni	3,9				20	
Zn	5,04	3 Rijn			7,8+AC	15,6+AC

Table 4.4: Water quality standards for copper, nickel and zinc. For copper we are interested in MTR, which means maximum permitted risk. For nickel and zinc we are interested in JG-MKN, which means yearly average environmental quality standard.

In general these values are not supposed to be exceeded, however some compounds do exceed these values, as becomes clear from the figures below.

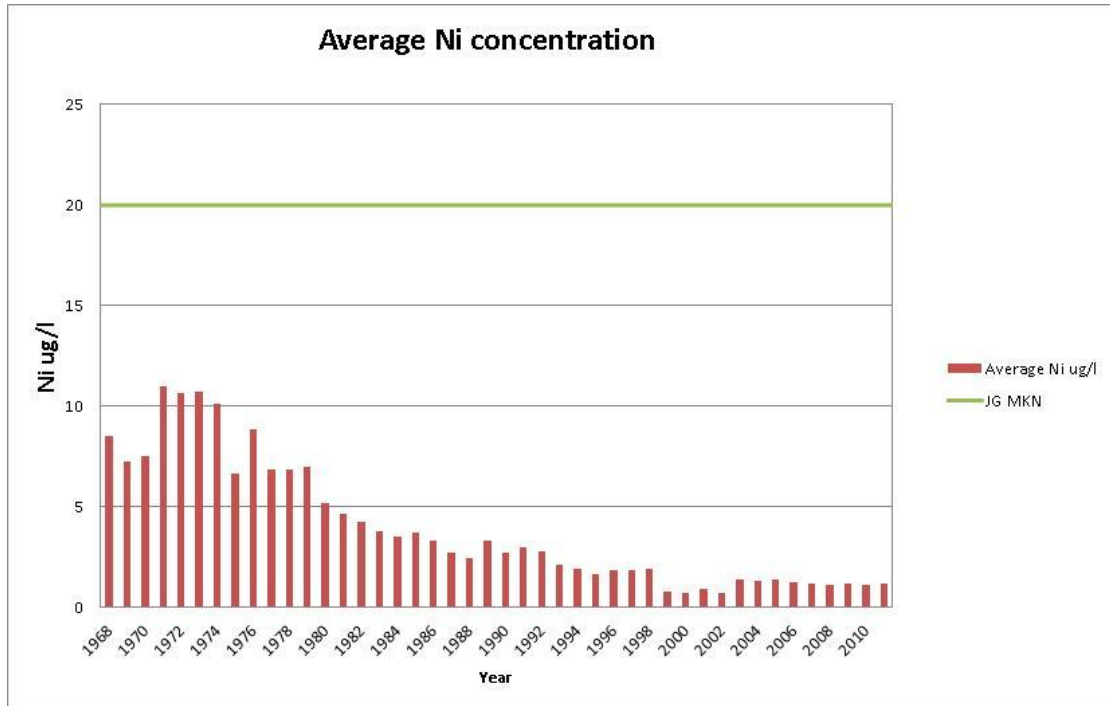


Figure 4.16: In this figure the yearly average Nickel concentration is shown together with the standard (green line). Nickel concentrations stay fairly below standards.

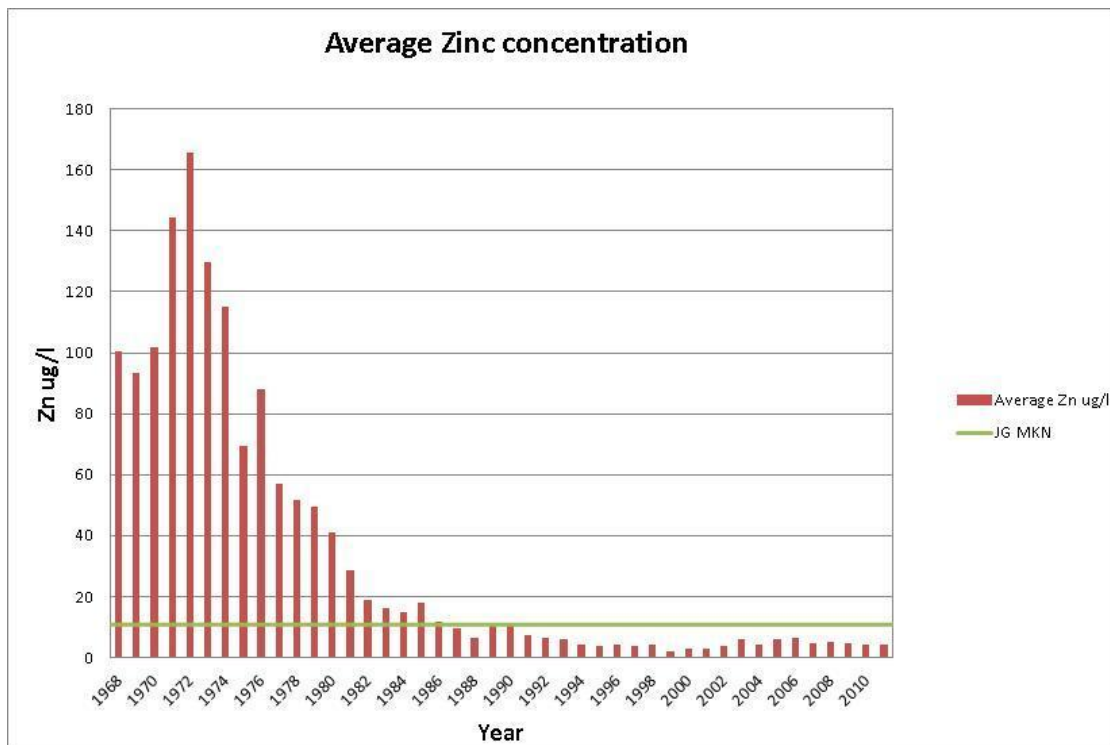


Figure 4.17: This figure shows the yearly average Zinc concentration together with its standard (green line). From 1968 till 1986 standards are exceeded every year, since then concentrations stay below standards.

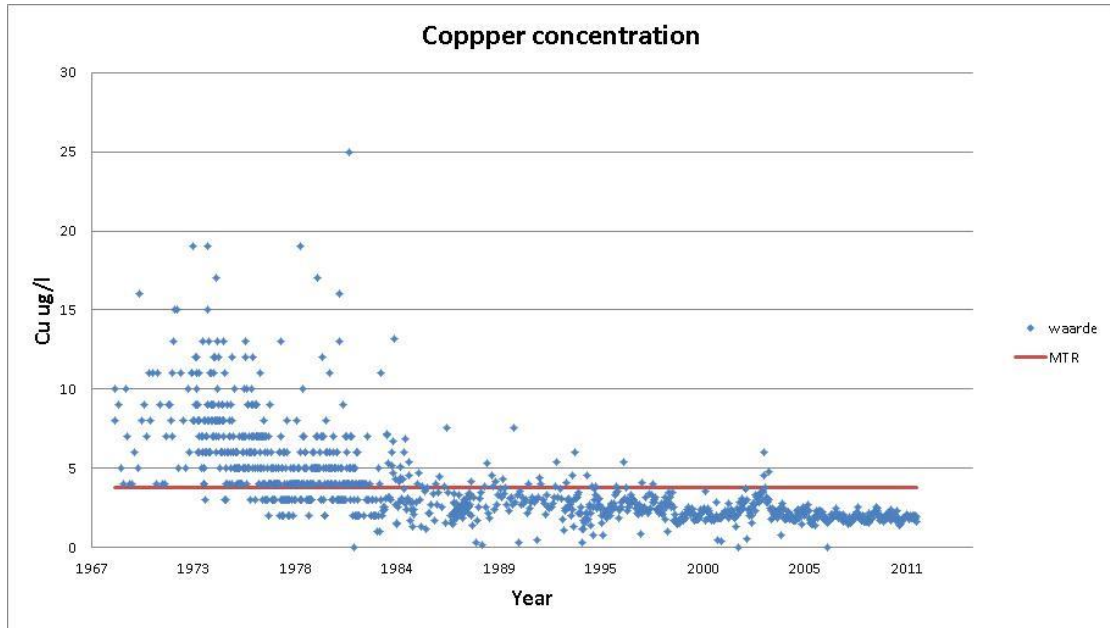


Figure 4.18: The figure shows Copper concentration and maximum permitted risk. As becomes clear from this figure Copper concentrations are exceeded many times, especially during higher discharges.

From the figures above it becomes clear that concentrations of copper, nickel and zinc has been higher in the past. Nowadays, concentrations stay fairly below standards, however, in the past standards were exceeded for both copper and zinc.

4.2 Model simulation

There are several ways to judge the performance of a model. Quality of model results refers to their ability to reproduce measured data and hence their applicability as prognostic tools.

For the set-up and calibration of the model first of all a SPM simulations are performed to check main transport characteristics. Hereby, the model is judged on realistic behaviour of SPM both with time and with discharge. In all cases, results of the Rhine at Lobith are examined since measured data is available for this location.

By changing several parameters the model can calibrated in such a way that results approach reality. In the matter of sensitivity, especially shear stresses and settling velocity of IM1 and IM2 prove to be important. An overview of parameters as used for the modelling is shown in appendix 2.

4.2.1 Single cell model simulation

Single cell simulations have been carried out to obtain a better understanding of the processes and their interactions. Especially the relation between shear stresses, erosion and sedimentation has been examined.

4.2.2 SPM calibration

In order to get a better grip on shear stresses and critical shear stresses, an extra option is added to the model. Instead of homogeneous critical shear stress, critical shear stress is now dependent and equal to a certain frequency of occurrence of the local shear stresses. By means of this option it is possible to determine the frequency of periods that critical shear stress for erosion and sedimentation is exceeded, and therefore, control resuspension and sedimentation events. If the model would have been very detailed in its representation of the river cross-sections, this would have made the model less realistic. Since WFLOW does not provide very detailed river cross-sections, the calculated shear stresses are anyhow not accurate and the modification above does not really reduce the accuracy while it enables users to control moments of sedimentation and resuspension or model calibration purposes.

After calibration, the model can be used and scenarios are calculated. Results of SPM concentration and residence time are shown in figures below 4.19 and 4.20.

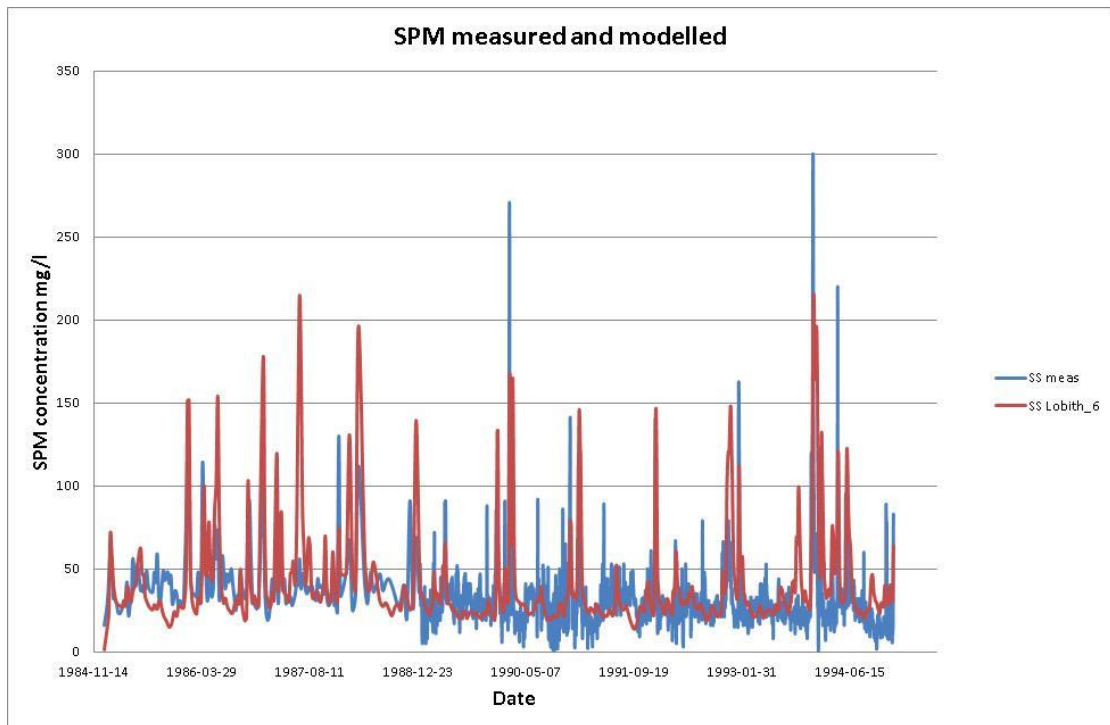


Figure 4.19: Measured (blue line) and modelled (red line) SPM concentration in time.

This same figure can be displayed as a plot of measured and modelled SPM concentration:

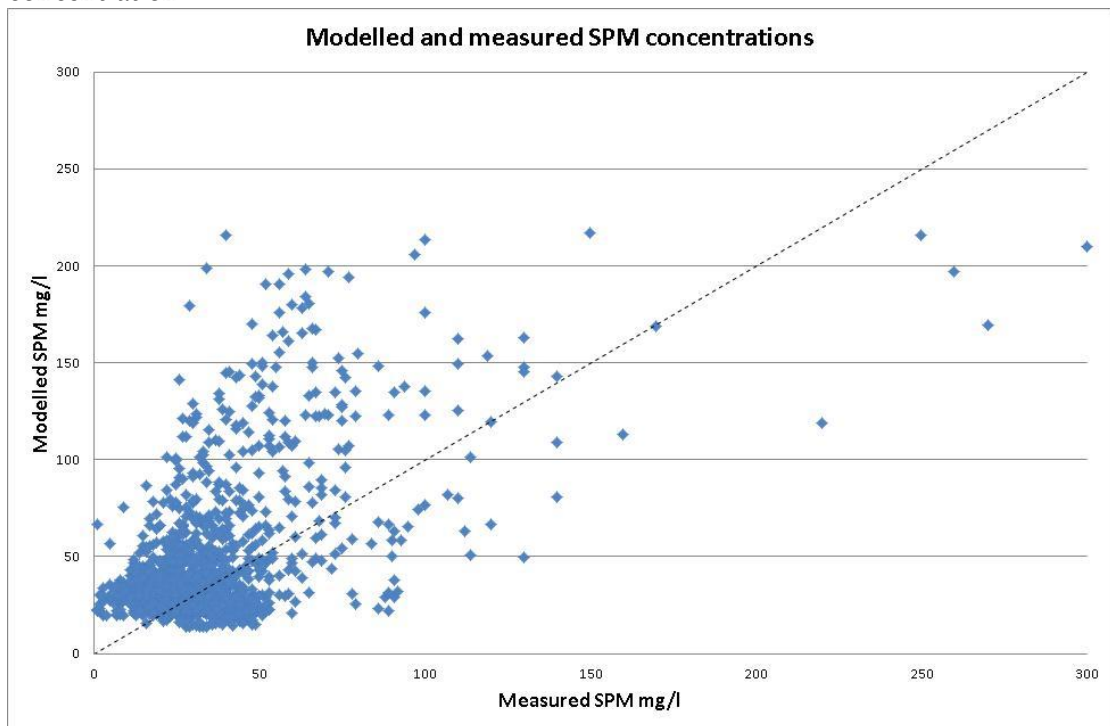


Figure 4.20: Measured SPM concentration plotted over modelled SPM concentration with 1:1 line plotted.

When both modelled and measured SPM concentrations are plotted over time, measured values of SPM seem to be reproduced by modelled results quite fairly. However, when measured and modelled data are plotted versus each other it becomes

clear that there is a lot of discrepancy between measured and modelled data, nevertheless, the general trends correspond.

In addition the relation between modelled SPM concentrations and river discharge is shown in figure 4.21.

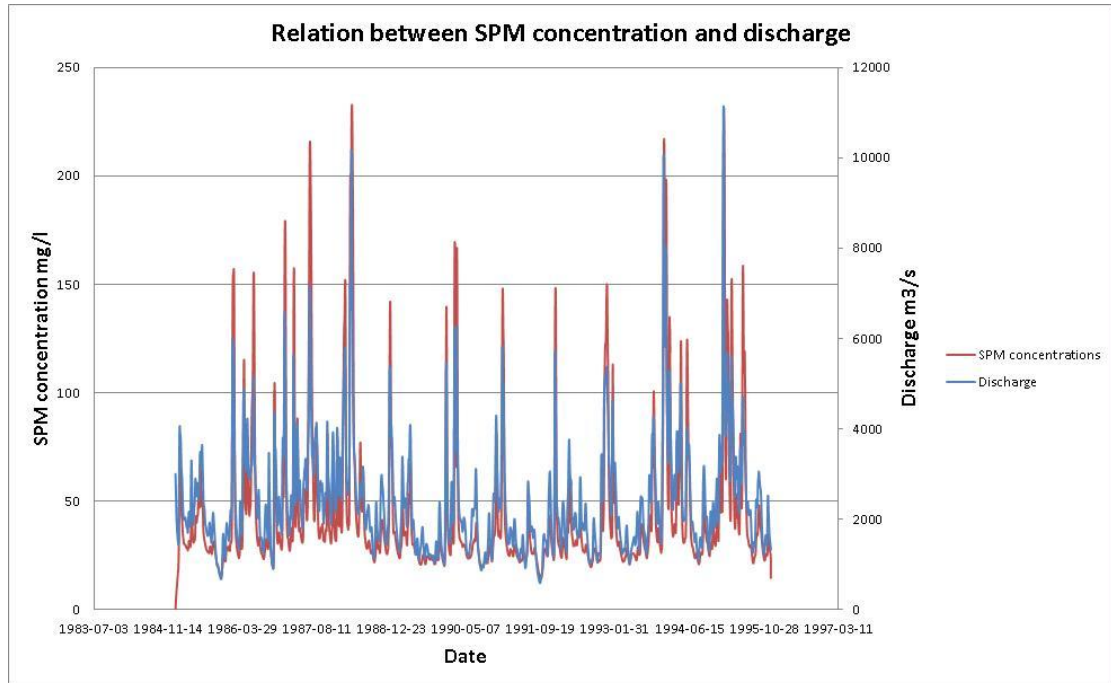


Figure 4.21: Relation between modelled SPM concentration and measured river discharge.

4.2.3 Residence time

The results of the tracer experiment, as described in 3.3.2, are shown in the figures below.

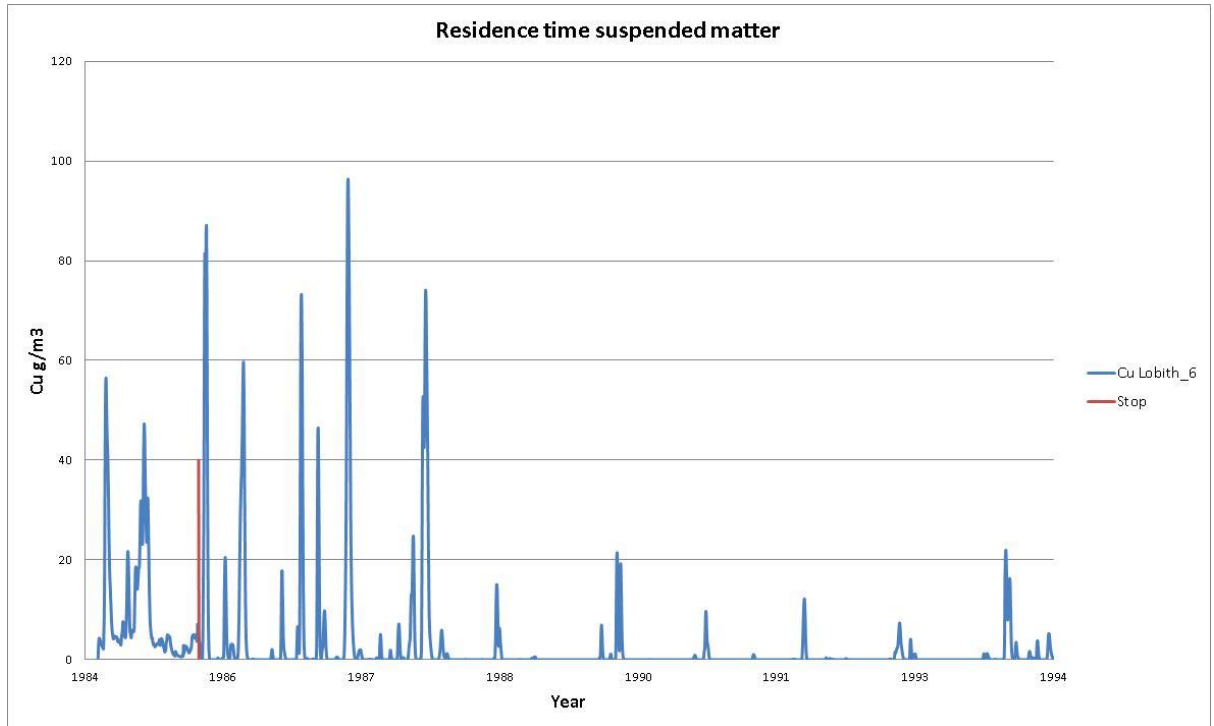


Figure 4.22: This figure shows the concentration of zinc over 10 years. The 'stop' line indicates the moment where no more zinc is injected in the system. Zinc peaks after this line are caused by resuspension of deposited material. Due to the infinitesimally high partitioning coefficient of zinc and the 1 on 1 injection of zinc and SPM, this concentration indicates the concentration of SPM injected during the first year. As becomes clear from this figure residence time is certainly more than 10 years.

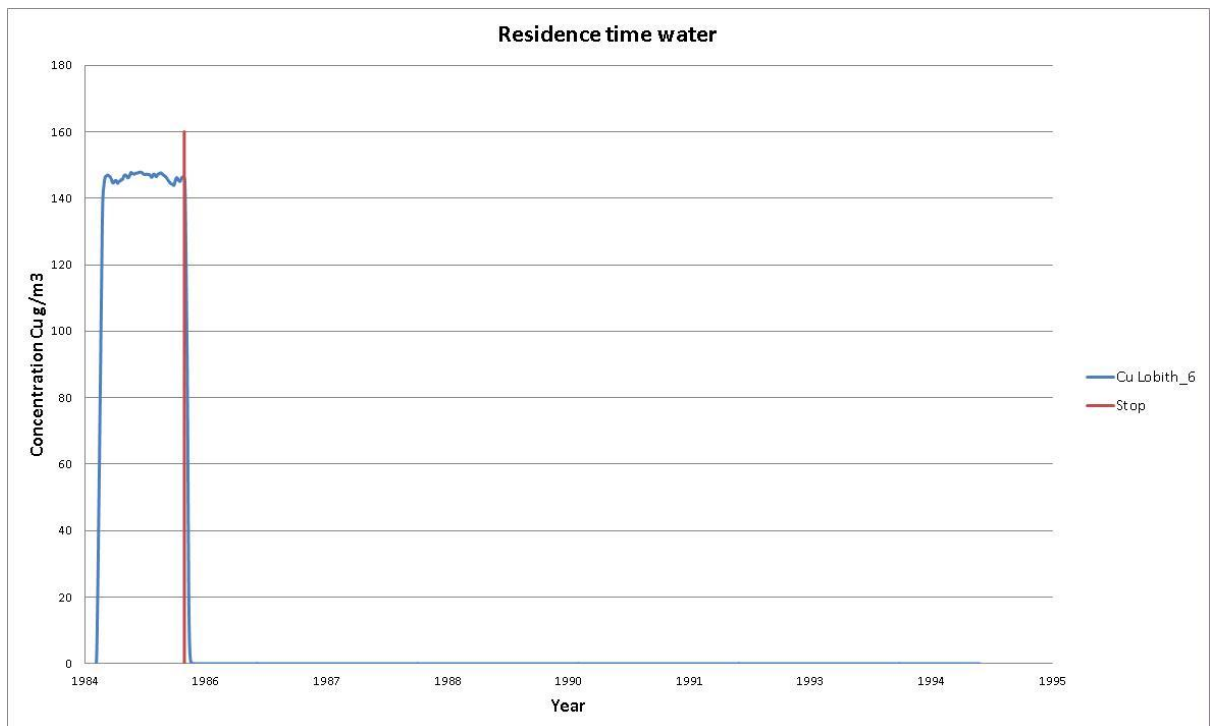


Figure 4.23: This figure also shows the concentration of zinc but in this case the partitioning coefficient goes to zero. Therefore the zinc concentration reflects the residence time of water. It is evident that water flows out of the system almost immediately.

This test proves that the model is able to store sediment for a longer time. Unfortunately, with these results we get a very unrealistic behaviour of SPM, so a balance needs to be found that gives both satisfactory residence times and a realistic behaviour of SPM. However, the fact that we have a residence time of more than one decennium is a very important result since it enables us to model a subsequent delivery of copper into the water column from historically contaminated sediments.

Residence time after calibration

One of the outcomes of the model is a balance file. This file gives users insight in in- and out fluxes. The tracer experiment, as described in chapter 3.3.2 is repeated whereby the SPM, marked with an infinitesimally high K_d for zinc, is traced for 20 years. Figure 4.24 shows the amount of zinc, emitted during the first year, that is stored as sediment and the amount that is flushed out.

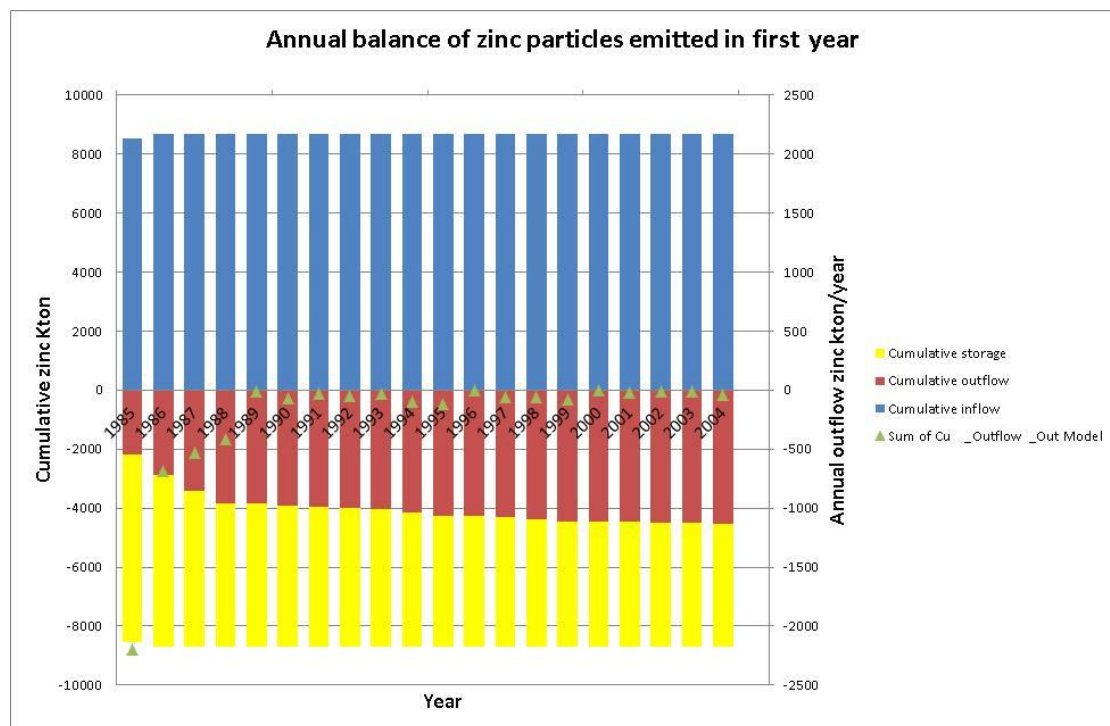


Figure 4.24 This figure shows the amount of zinc that flushed out and the amount that is stored in sediment.

As becomes clear from figure 4.24, during the first year a significant amount of zinc is directly flushed out, hereafter however, the release of zinc from the first year is slowly. After 20 years approximately 50% of zinc, that is emitted during the first year, is still stored as sediment.

In general, the model works in such a way that it is able to produce realistic behaviour of SPM as a function of time and discharge. In addition it generates long residence times of SPM as illustrated in figure 4.24.

4.2.4 Partitioning coefficient

During the analysis of the dataset from Lobith, it was found that K_p values have a wide range but there is not clear trend or relation with discharge. Zinc suggests a decreasing partitioning coefficient with increasing discharge, therefore, in this case a variable partitioning coefficient can be chosen.

In the other cases, the K_d that is used for the modelling is the median K_d of 102 data points. The reason that the median K_d is chosen instead of the average K_d is because of the fact that high peaks can be found in the data, causing the average K_d to be an overestimation of the actual data. The table below gives an overview of average, median and in the literature found K_d values.

	Zn	Cu	Ni
Median	120141	32687	34667
Literature	109647	3890	7943
Average	226839	47646	67025

Table 4.5: This table shows the K_d values from the used datasets and found in the literature.

For the variation of K_d values for zinc with discharge, as observed during data analysis, different K_d values of IM1 and IM2 can be adjusted, in order to simulate this behaviour. To do so, the composition of SPM is investigated with discharge.

Figure 4.25 shows the composition, in fraction IM1 and IM2, of SPM plotted over discharge. Note that this distribution depends on the definition of the concentrations of IM1 and IM2 in surface runoff and groundwater inflows, and on the processes parameters determined by model calibration.

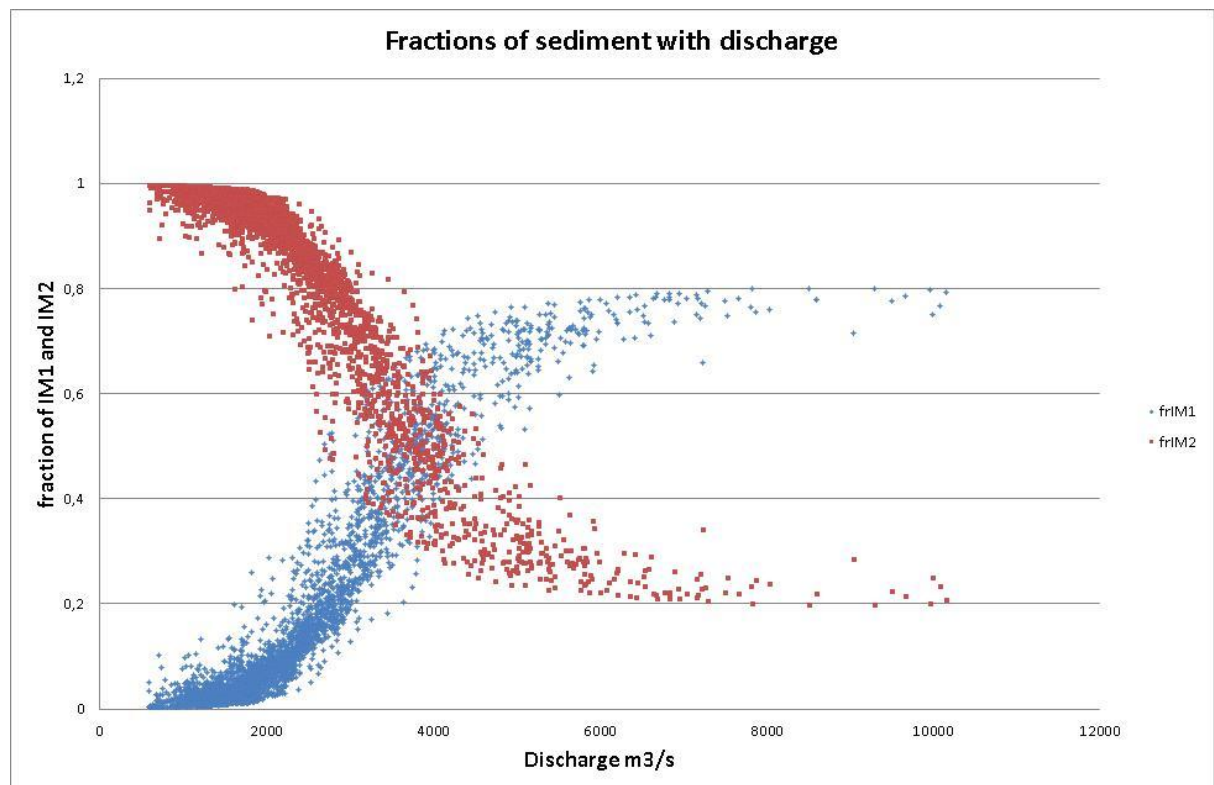


Figure 4.25: The contribution of IM1 and IM2 with discharge. As becomes clear from this figure, SPM consists only out of IM2 during lower discharge regimes. When discharge becomes higher also IM1 gets suspended and with discharges higher than $6000 \text{ m}^3/\text{s}$, SPM composition is around 80% IM1 and 20% IM2.

The different partitioning coefficient to each fraction gives us a varying total partitioning coefficient. In figure 4.26 the result of a varying K_d is shown in order that it corresponds to the observed K_d during the data analysis.

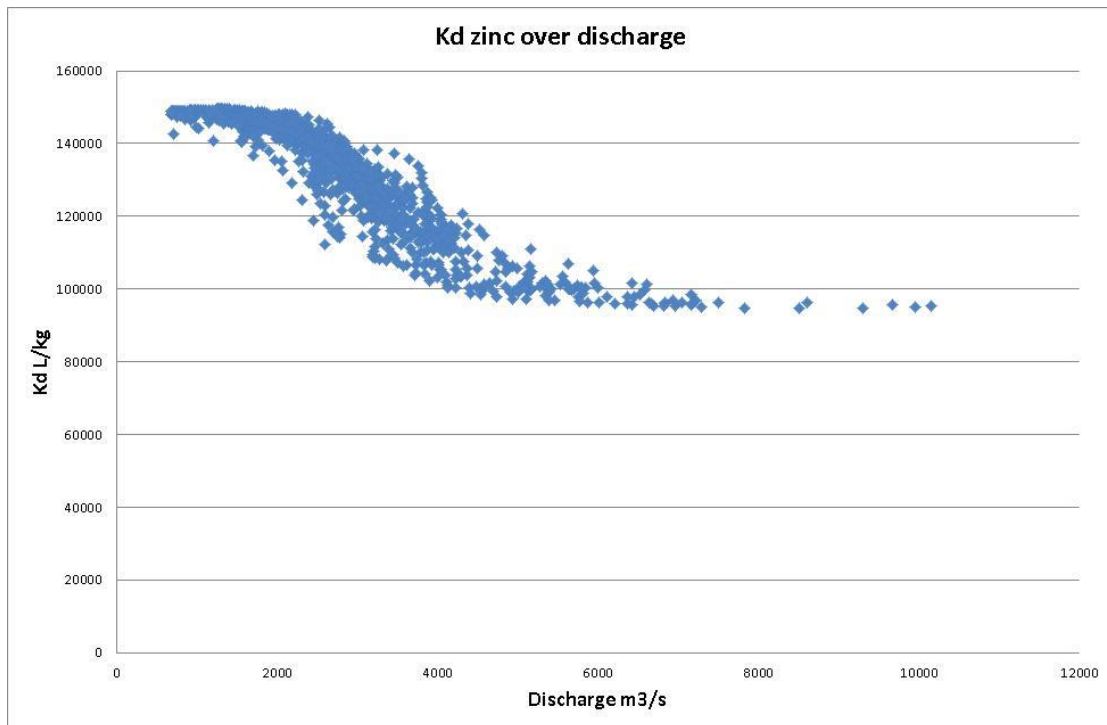


Figure 4.26: Modelled partitioning coefficient of Zinc, plotted over discharge.

This corresponds to the observed partitioning coefficient of Zinc, described in chapter 4.5.1.

To check whether this varying copper concentration makes a significant difference, both Cu concentrations are showed in the same plot as can be seen in figure 4.27.

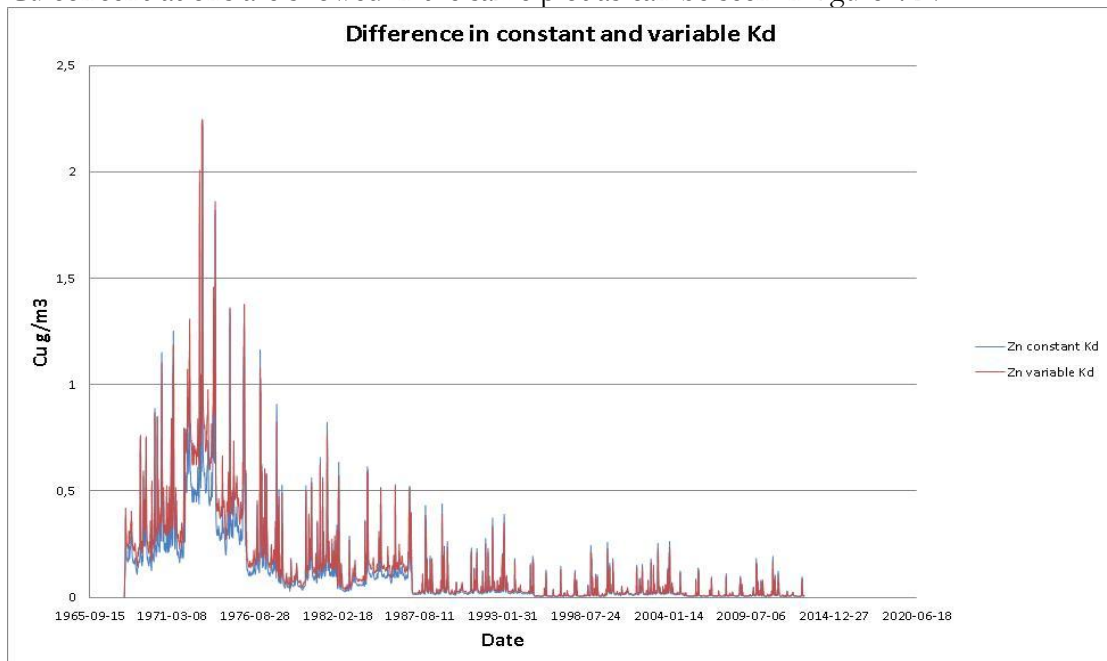


Figure 4.27: Copper concentrations with constant (blue) and variable (red) K_d , plotted from 1968 until 2010.

As becomes clear from figure 4.27, the result of a variable K_d does not create a significant difference in copper concentration compared to the result with constant K_d . Therefore, the focus will be on two different scenarios: one with a constant emission in time and the other with a variable emission in time.

4.2.5 Scenarios

Scenario 1

First the model is run with a constant emission of Zinc and a constant partitioning coefficient. As already mentioned, the median K_d , found in the datasets from waterbase is used. This is a K_d value of $120 \text{ m}^3/\text{kg}$.

According to van Duijnhoven and Venema (2012) the average zinc load in 2000 was around 1.24 tons/year as showed in table 4.6.

Aanvoer via de Rijn

Tabel 3: Jaarvrachten aanvoer via Rijn in kg of ton per jaar voor een beperkt aantal stoffen.

stofnaam	eenheid	1990	1995	2000	2005	2009	2010
jaardebiet	10 ⁶ m ³	58.500	88.100	79.700	60.000	59.100	68.400
stikstof	ton/jaar	328.715	396.922	261.729	221.557	186.135	212.317
fosfor	ton/jaar	17.062	18.344	14.274	8.012	7.594	9.096
arseen	kg/jaar	118.891	192.535	130.245	97.707	88.866	86.890
cadmium	kg/jaar	5.412	7.942	5.130	4.456	3.461	3.808
koper	kg/jaar	326.232	488.104	332.368	281.596	254.381	276.736
kwik	kg/jaar	2.857	3.282	1.584	1.286	745	774
lood	kg/jaar	280.426	445.501	241.735	171.422	123.156	133.850
nikkel	kg/jaar	208.960	341.092	196.212	195.747	168.132	189.874
zink	kg/jaar	2.244.609	2.263.734	1.240.479	1.355.856	1.096.946	1.258.027
anthraceen	kg/jaar	1.356	617	252	272	97	113
naftaleen	kg/jaar			208	261	97	143
fluorantheen	kg/jaar	3.095	3.925	1.866	1.371	540	898
benzo(a)anthraceen	kg/jaar	1.219	1.762	823	570	320	567
benzo(a)pyreen	kg/jaar	1.426	1.873	930	713	279	523
benzo(b)fluorantheen	kg/jaar	1.992	2.441	1.120	847	363	664
benzo(k)fluorantheen	kg/jaar	758	939	532	404	181	287
benzo(ghi)peryleen	kg/jaar	1.111	1.402	854	717	319	484
indeno(1,2,3-c,d)pyreen	kg/jaar	1.104	1.522	808	658	313	502
simazine	kg/jaar		1.962	710			
isoproturon	kg/jaar		5.312	3.339	1.881	1.551	2.205
diuron	kg/jaar		2.931	2.324	1.388	684	597
tributyltinoxide	kg/jaar			12	4,9	2,4	2,8

Table 4.6: This figure shows the year loads of different compounds between 1990-2010 in the River Rhine. (van Duijnhoven and Venema, 2012).

The average modelled zinc load in the period 1985 till 2035 is 1246110 kg/year. This is less than 0.5% different than the zinc load found in the literature, which is a very accurate result. The main focus for this study is the relation between discharge and SPM quality. Therefore Zinc in mg/kg is plotted over discharge in the next figure.

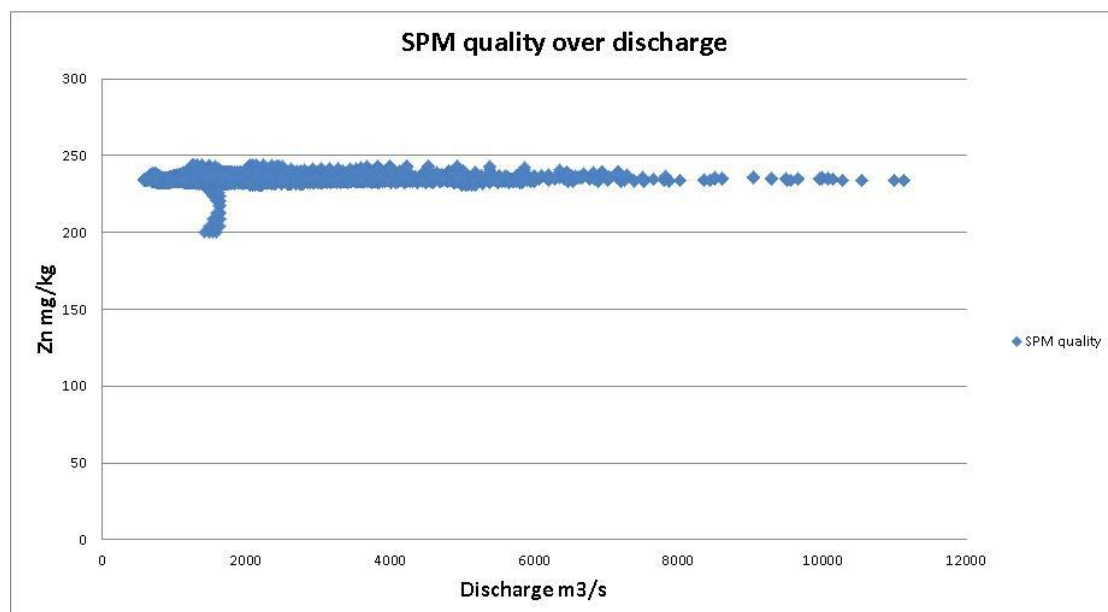


Figure 4.28: The amount of Zinc, adsorbed to SPM, as a function of discharge. The model has run for 50 years.

As becomes clear from figure 4.28 adsorbed zinc concentration does not depend on discharge when a constant emission pattern is chosen.

Scenario 2

During the second calculation, a variable emission pattern is chosen during the period 1968-2012. As already mentioned, total yearly loads are not available and therefore an estimation, based on total concentration is made.

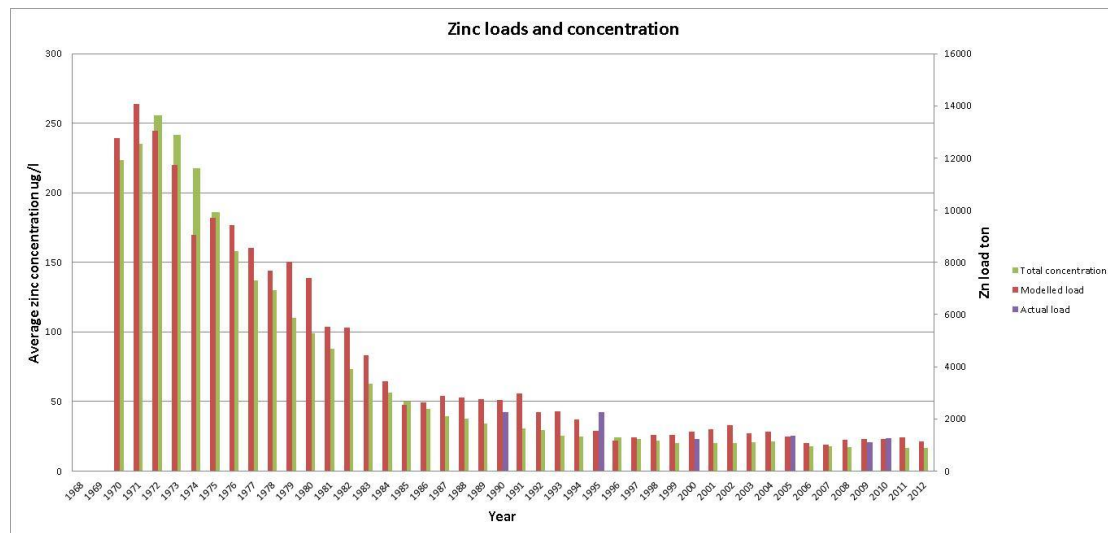


Figure 4.29: The (standardized) measured average Zinc concentration for each year and the (standardized) modelled Zinc load.

Figure 4.29 shows the modelled and observed load, together with measured unfiltered concentration. Since lots of seasonal variation exists in both modelled and observed data, each year is averaged with two years before and after, in order to remove seasonal fluctuations.

As can be seen in figure 4.29, a lot of zinc is emitted between 1968 and 1980. It is important to know what amount of injected copper has left the system and what amount is stored as sediment. Therefore a balance is made that shows in and outflow of zinc and storage of zinc, this can be seen in figure 4.30.

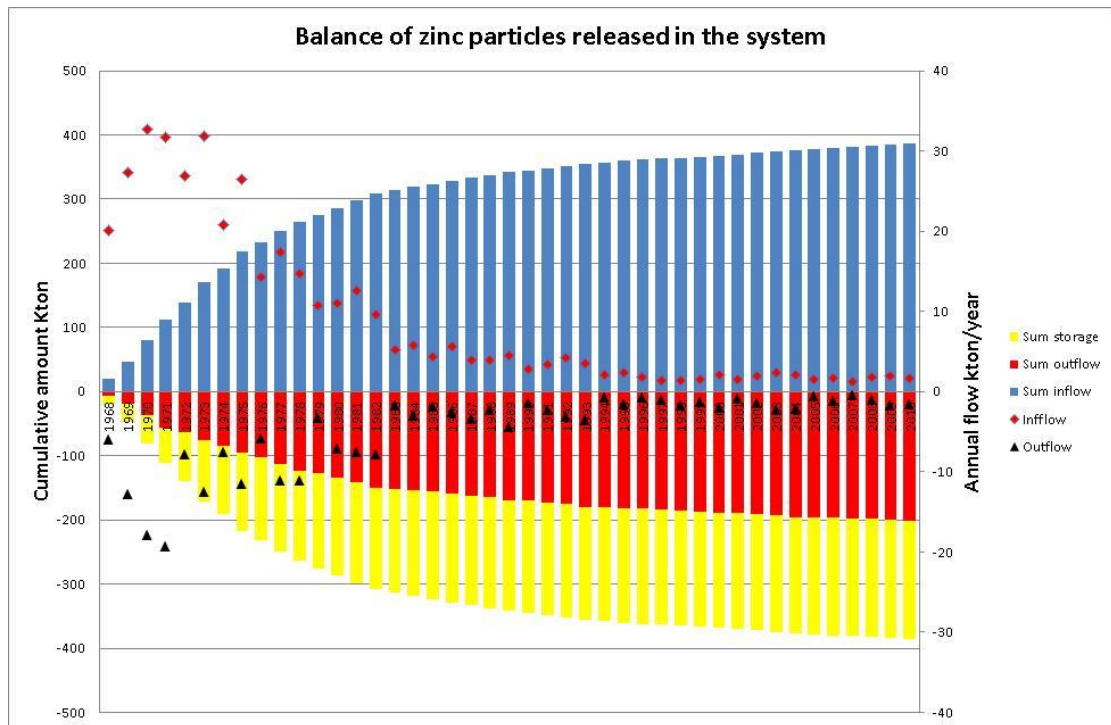


Figure 4.30: Balance of cumulate inflow, storage and outflow of zinc particles. Also showed in this graph is annual in and outflow.

As becomes clear from figure 4.30, a significant amount of total injected zinc, approximately 50%, is stored as sediment and is still in the system after 45 years.

Again, we are interested in the relation between discharge and SPM quality, which is showed in figure below 4.31.

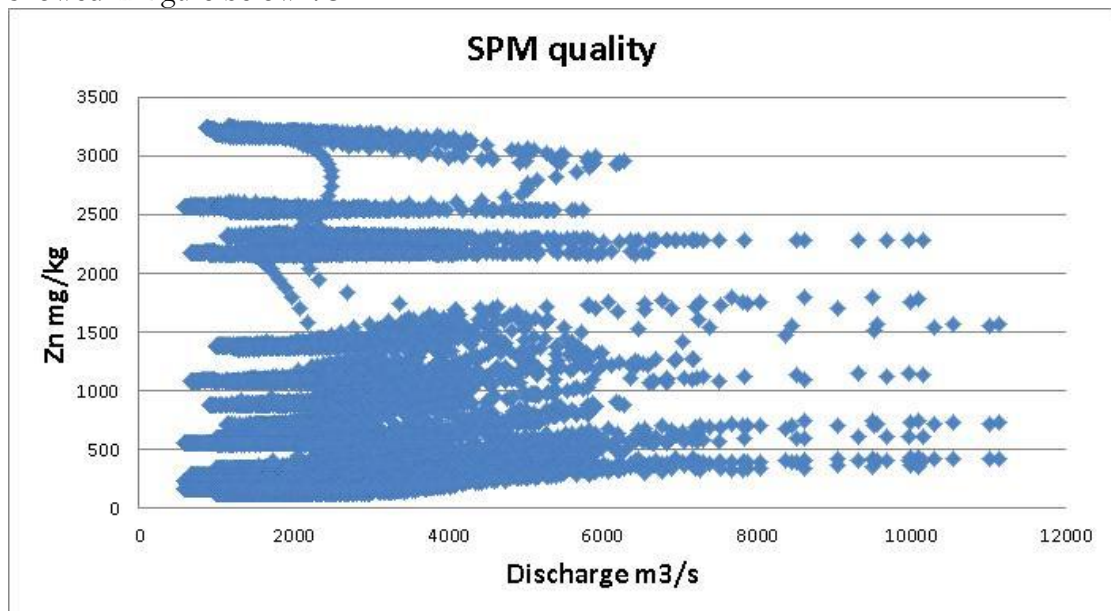


Figure 4.31: Amount of Zinc, adsorbed to SPM, as a function of discharge. The model has run for 45 years.

Since figure 4.31 contains a lot of data, the period 2007 until 2010 is investigated more closely. Again, zinc adsorbed to SPM is plotted over discharge as can be seen in figure 4.32.

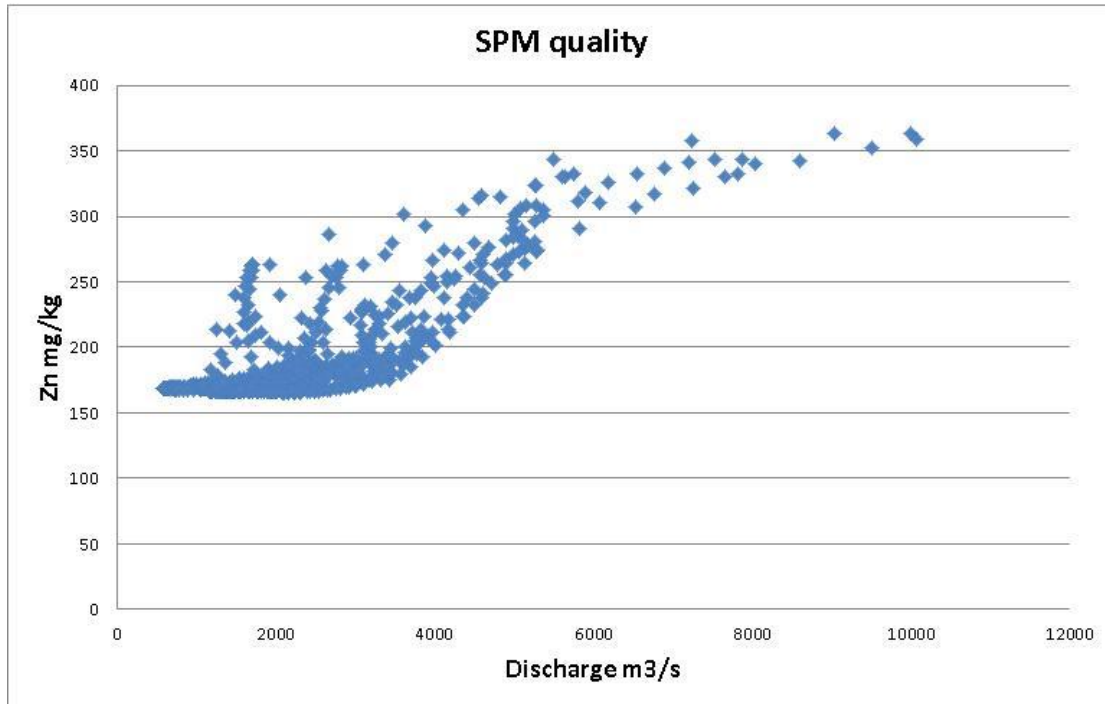


Figure 4.32: Zinc, adsorbed to SPM plotted over discharge in the period 2007-2010.

As becomes clear from figure 4.32, the amount of adsorbed zinc increases with increasing discharge. In figure 4.30 it was showed that a huge amount of zinc is stored as sediment. During high discharges, when erosion increases, old contaminated layers get in resuspension and due to the high zinc concentrations in the sediment SPM quality deteriorates significantly.

Scenario 3

As became clear from chapter 4.2.4, zinc concentrations are not very sensitive for changing partitioning coefficients. Therefore scenario 3 has become irrelevant.

5 Conclusions

5.1 Measurements

5.1.1 Adsorbed contaminants

Based on the data analysis during our study it is clear that SPM quality improves with increasing discharge in the lower regimes. This observation is also supported by the literature. One possible reason for this improvement is the dilution effect of suspension of relatively clean sediments. Data analysis also indicate that quality parameters (SPM and dissolved concentration) show different trends above approximately 4000 m³/s which is regarded as a 'critical' threshold value.

Although concentrations above the critical discharge value seem to increase, a comparison between concentrations during higher discharges and lower discharges does not indicate SPM quality deterioration based on average and standard deviations.

Important to keep in mind is that masking effects, like dilution and the reduction of sorption capacity with increasing grain sizes, can cover up actual contamination.

5.1.2 Total contamination

Unfiltered samples show a constant concentration below critical discharge value and an evident increasing concentration above critical value, especially for copper and nickel.

5.1.3 Dissolved contaminants (filtered < 0.45 µ)

In addition to adsorbed contaminants, also dissolved contaminants show a decreasing trend below critical discharge value and a slight increase above critical discharge value, however, differences are small.

An important remark is that in all cases, the amount of data points decrease significantly with increasing discharge. Therefore, it is hard to draw evident conclusions from the data analysis, which is one of the main reasons for the modelling process.

5.2 Model simulation

The model shows realistic behaviour for SPM trends both with time and with river discharges, compared to monitoring data. In addition it shows realistic residence times of SPM in the River Rhine network.

By means of numerical experiments, two different scenarios are carried out, one with a constant emission of zinc and the other with a variable emission pattern as observed during data analysis.

Scenario 1, with a constant emission pattern, suggests that there is no correlation between SPM quality and river discharge. In this case, SPM quality remains constant with increasing discharge.

Scenario 2, with a variable emission pattern, shows an increase in zinc concentration adsorbed to SPM with increasing discharge.

So to return to our research questions: Is it possible to model and predict contaminated fluxes and critical values for this to occur? From the model results, it becomes clear that it is possible to create a model that produces realistic behaviour for both SPM and zinc concentrations. In scenario 2, it is shown that zinc concentrations increase with increasing discharge from approximately 3000 m³/s.

So does SPM quality really deteriorate with increasing discharge? From the data analysis, this is hard to say because the amount of data significantly decreases with increasing discharge, and the actual effects are masked by many processes such as increasing grain sizes with increasing discharge and a dilution effect.

However, the model simulation shows that in the past decades, zinc has been deposited in such amounts that during higher discharges, resuspension of old sediments can cause SPM quality to deteriorate seriously.

6 References

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Appendices

Appendix 1

Parameters that are calculated by the model:

Check: Non reactive component, to check if the system works.

Cu: Copper [g/m³]

IM1: 1st fraction of silt [g/m³]

IM2: 2nd fraction of silt [g/m³]

IM1S1: Sedimentation flux of IM1 [g/m³/d]

IM2S1: Sedimentation flux of IM2 [g/m³/d]

fsedIM1: Sedimentation flux of IM1 [g/m²d]

fsedIM2: Sedimentation flux of IM2 [g/m²d]

QCuIM1: quality IM1 for Copper [g Cu/ g DM]

QCuIM2: quality IM2 for Copper [g Cu/ g DM]

FrCuIM1: fraction Cu adsorbed to IM1 [-]

FrCuIM2: fraction Cu adsorbed to IM2 [-]

fsedCu: sedimentation flux Cu [g Cu/m²d]

fResS1IM1 : resuspension flux of IM1 from layer 1 [g/m²d]

fResS1IM2 : resuspension flux of IM1 from layer 2 [g/m²d]

QCuIM1S1: quality IM1 for Cu in layer S1 [g Cu/ g DM]

QCuIM2S1: quality IM2 for Cu in layer S1 [g Cu/ g DM]

FResS1Cu: resuspension flux Cu from layer S1 [g Cu/m²d]

SS: suspended solids [g/m³]

Tau: total shear stress [N/m²]

fResS1DM: total resuspension flux from layer 1 [g/m²d]

FrIM1S1: fraction of IM1 in layer 1 [-]

FrIM2S1: fraction of IM2 in layer 1 [-]

FrCuDis: fraction free dissolved Cu in water column [-]

DisCu: free dissolved Cu in water column [g/m³]

QCuSS: Quality of SS to Cu [mg Cu/kg DM]

KdCuSS: overall partitioning coefficient for Cu SS [L/kg]

DMS1: total amount of dry matter in layer 1 [g DM]

FrCuDisS1: fraction dissolved Cu in layer 1 [-]

FrCuIM1S1: Fraction Cu adsorbed to IM1 in layer 1 [-]

FrCuIM2S1: Fraction Cu adsorbed to IM2 in layer 1 [-]

DisCuS1: free dissolved Cu in pore water in layer 1 [g Cu/ m³p]

QCuDMS1: overall sediment quality for Cu in layer S1 [mg Cu/kg DM]

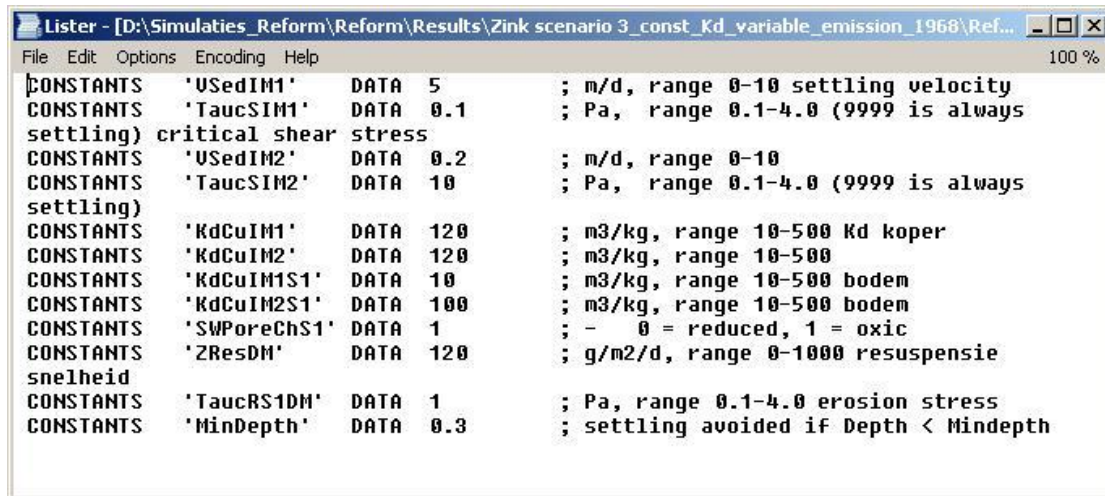
KdCuDMS1: overall partitioning coefficient Cu in layer S1 [m³/kg DM]

Velocity: water velocity [m²/s]

Surf: horizontal surface area of a DELWAQ segment [m²]

LocalDepth: depth from water surface to bottom of segment [m]

Appendix 2



The screenshot shows a text editor window titled 'Lister - [D:\Simulaties_Reform\Reform\Results\Zink scenario 3_const_Kd_variable_emission_1968\Ref...'. The window contains a list of model constants with their values and units. The constants are: 'USedIM1' (5 m/d), 'TaucSIM1' (0.1 Pa), 'USedIM2' (0.2 m/d), 'TaucSIM2' (10 Pa), 'KdCuIM1' (120 m3/kg), 'KdCuIM2' (120 m3/kg), 'KdCuIM1S1' (10 m3/kg), 'KdCuIM2S1' (100 m3/kg), 'SWPoreChS1' (1), 'ZResDM' (120 g/m2/d), 'TaucRS1DM' (1 Pa), and 'MinDepth' (0.3). The window also shows a menu bar with 'File', 'Edit', 'Options', 'Encoding', and 'Help', and a status bar indicating '100 %'.

```
CONSTANTS 'USedIM1' DATA 5 ; m/d, range 0-10 settling velocity
CONSTANTS 'TaucSIM1' DATA 0.1 ; Pa, range 0.1-4.0 (9999 is always
settling) critical shear stress
CONSTANTS 'USedIM2' DATA 0.2 ; m/d, range 0-10
CONSTANTS 'TaucSIM2' DATA 10 ; Pa, range 0.1-4.0 (9999 is always
settling)
CONSTANTS 'KdCuIM1' DATA 120 ; m3/kg, range 10-500 Kd koper
CONSTANTS 'KdCuIM2' DATA 120 ; m3/kg, range 10-500
CONSTANTS 'KdCuIM1S1' DATA 10 ; m3/kg, range 10-500 bodem
CONSTANTS 'KdCuIM2S1' DATA 100 ; m3/kg, range 10-500 bodem
CONSTANTS 'SWPoreChS1' DATA 1 ; - 0 = reduced, 1 = oxic
CONSTANTS 'ZResDM' DATA 120 ; g/m2/d, range 0-1000 resuspensie
snelheid
CONSTANTS 'TaucRS1DM' DATA 1 ; Pa, range 0.1-4.0 erosion stress
CONSTANTS 'MinDepth' DATA 0.3 ; settling avoided if Depth < Mindepth
```

Input file of the model. Note that sedimentation and erosion events are fixed and do not depend on tau. So model results are irrespective by TaucSIM1, TaucSIM2 and TaucRS1DM.