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Water quality monitoring in the Rhine-Meuse estuary

Research to select location(s) and sampling methods for the Rotterdam Waterway

Summary
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1 Introduction

The Institute for Inland Water Management and Waste Water Treatment (RIZA) of the Directorate General for Public Works and Water Management in the Ministry of Transport, Public Works and Water Management is planning to install a sampling station in the Rotterdam Waterway as part of a water quality monitoring network. The new station has to fulfil both national and international water quality monitoring needs in the main discharge of the river Rhine into the North Sea. Because the present bi-weekly monitoring activities in this region do not comply with the goals and methods agreed to within the International Rhine Commission, research was initiated to select one or more locations and to specify the required sampling frequencies and methods.

Within the framework of this study several reports were published:

- Problem analysis and project plan (Waterloopkundig Laboratorium, 1992);
- Analysis of the behaviour of water quality parameters in space and time (Waterloopkundig Laboratorium, 1993a);
- Optimization of sampling location and -method (Waterloopkundig Laboratorium, 1993b).
- Synthesis (Waterloopkundig Laboratorium, 1993c).
- Summary (this report).

1.1 Problem definition

The main goals of the new monitoring program at the selected station are specified as follows:

- To enable a 10% trend detection in the concentration of measured substances over a five year period.
- To enable the detection of uncontrolled (accidental) pollution inputs
- To determine the yearly pollution loads towards the North Sea with an accuracy of 10%.
- To determine the violation of (fresh) water quality standards.

With reference to these goals, research topics were specified to answer the following questions:

1. What is/are the optimal location(s) on the shore of the Rotterdam Waterway for the establishment of one or more sampling stations, given the requirements of the stated goals. The chosen location(s) should be insensitive to the planned opening of the Beerdam and should be located east of the storm surge barrier in the Rotterdam Waterway.

2. How is the accuracy of an individual measurement and the calculations of yearly load affected as a result of:
   - the concentration gradients in the area and the variation therein as a result of the tide, fresh/saline water layers, discharge, wind etc.;
- the dilution of river water with sea water, and physical, chemical and biological processes;
- sampling, storage, conservation and analysis of the samples.

3. What is the method and frequency of sampling that should be applied for load calculations in connection with the algorithm to be applied

1.2 Approach

The research has been conducted stepwise, with the analysis of the problem itself as the first step. The next step involved the inventory and analysis of all available measurements and effluent data. The topics for evaluation in the second step were:

- Which variability in concentration values can be seen in the measurements?
- Can the variations be connected to aspects like average sea level, river discharge etc.?
- Can the monitoring parameters (compounds) be grouped according to behaviour?
- Is it possible to identify the influence of processes, river discharge and sea level on concentration variability by using model simulations?
- Where are the most important pollutant discharges located and which parameters are involved?
- What is the spatial influence of pollutant discharges?
- Inventory of monitoring approaches abroad (Elbe estuary in Germany /Humber estuary in the U.K.);

The final step consisted of optimization of sampling location, method and frequency. The topics for evaluation in the final step were:

- What is the optimal sampling method?
- What is the optimal sampling frequency?
- What is the optimal sampling location?

Figure 1: Map of the Rhine-Meuse estuary. The present (A) and recommended sampling site (B) are indicated.
2 Problem analysis

Why is monitoring water quality a complicated matter in the Rotterdam Waterway?
The Rotterdam Waterway has a number of aspects that make monitoring especially complex:

1 The Rotterdam Waterway is situated in a tidal area. This results in a continuously varying water level, and an oscillating water movement with a net flow in the direction of the sea. As a consequence, no direct relationship between water level and river discharge can be found, which complicates the discharge assessment. A pollutant discharge in this dynamic flow pattern will result in a complex concentration profile, and in addition, a certain water mass may pass the monitoring location several times before reaching the sea. Finally, the influence of processes such as erosion and sedimentation will vary dependent on the tidal phase.

2 The Rotterdam Waterway is situated in the transition zone between saline and fresh water. The density difference between the water masses results in a vertically stratified system. As a result of friction on the boundary plane, saline water will be dragged along with the fresh river flow. This process results in a net landward flow in the saline lower layer, with a seaward flow in the upper (fresh water) layer. As a consequence of the mixing of the water masses, the fresh water concentration in the upper layer differs from the fresh water inflow. Additionally, the boundary between the two layers is not always very distinct.

3 The parameter concentrations in seawater influence the concentrations in the Rotterdam Waterway. For example, the return flow of dredged sludge discharged at "Loswal Noord" forms a significant part of the sediment inflow from the sea. As such associated parameters will influence the concentration values in the Rotterdam Waterway. However, the actual concentrations in the seawater entering the Rotterdam Waterway are not very well known.

4 The supply of water and substances to the Rotterdam Waterway is influenced by several factors. The inflow via the "Oude Maas" and "Nieuwe Maas" is dependent on the flows of the rivers Rhine and Meuse and the applied sluice operation. The harbours connected to the "Oude Maas" and "Nieuwe Maas" have their own complex pattern of inflow and outflow. There is a large concentration of industrial and shipping activities in the area in addition to a large population centre in the area and regular and incidental pollutant discharges are connected to these activities. Given the short distance from the pollutant discharges to the Rotterdam Waterway, a transversely inhomogeneous pollutant distribution can be expected.

5 To compensate for the high sedimentation in the bend of the Rotterdam Waterway near Maassluis, this section is regularly dredged in addition to the dredging of the harbours. These dredging activities can have a significant effect on the suspended solids concentrations.

6 Several processes specific for estuarine rivers occur in the Rotterdam Waterway. Adsorption, desorption and flocculation as a consequence of the salinity gradient are examples of these processes.
7 The busy shipping traffic in the Rotterdam Waterway leads to an extra disturbance in the measured system and limits the permanent sampling location to a position outside the main shipping lane.

Which considerations apply in a very general way to the choices that have to be made? Based on the general characteristics of the area to be sampled, the main considerations with regard to the station location and sampling methods can be named:

1 A westerly location is preferred when the net load to the North Sea has to be assessed. In this manner most pollutant discharges will be accounted for while most estuarine processes will have already taken place.

2 To minimize the influence of incomplete mixing at the confluence of the "oude Maas" and "Nieuwe Maas" and of pollutant discharges, a sampling location as far downstream as possible is preferred.

3 An easterly location is preferred when one wishes to minimize the sea influence (e.g. salinity and transport of pollutants from Loswal Noord). This consideration can be important for comparison of results with those from upstream stations (Lobith) and with freshwater standards.

4 The bend in the Rotterdam Waterway near Maassluis should be avoided as a sampling station due to the sedimentation and dredging activities which take place there.

5 The sampling method, frequency and location(s) as well as calculation techniques must be selected by reaching an optimal compromise between effort, costs and accuracy.

3 Data inventory

All available water quality data of the Rotterdam Waterway have been analyzed to gain insight into the existing temporal and spatial concentration variations. The data on pollutant discharges from the WIER database have been analyzed to gain insight in the relative and absolute influence of pollutant discharges on the sampling location and method.

Visits were made to the National Rivers Authority in England and GKSS and Wassergütestelle Elbe in Germany to evaluate the approach of these institutions to similar problems.

A field orientation was made by boat, where several locations were visited and discussed with local "Rijkswaterstaat" staff.

The "Regionaal model voor het Noordelijk Delta Bekken", a water quality model for the Rhine and Meuse estuary, was used to compare several sampling approaches for a few representative constituents.

With the aid of statistical optimization techniques (the Lettenmaier method) a frequency optimization was made for trend detection purposes on the basis of the most recent time series collected at the current sampling station at Maassluis.
3.1 Evaluation of water quality parameters

For purposes of data management, the constituents to be measured have been grouped based on environmental behaviour. From each group of constituents a number of representative parameters have been selected. The constituents are grouped in the following categories:

- Dissolved and conservative (Chloride);
- Dissolved and subject to seasonal variations (Ammonium, Nitrate, Ortho-phosphate);
- Particulate and conservative (PAH’s, PCB’s);
- Particulate/Dissolved (Lindane);
- Particulate/Dissolved and seasonal (ad/desorption dependend on e.g. var. in pH) (Cadmium, Nickel, Lead, Total-Nitrogen, Total-phosphate).

Original measurements and data from reports have been analyzed.

With the help of an numerical test model, the concentration variations during a tidal cycles was simulated for several categories of parameters in a schematic tidal canal with saltwater intrusion. The numerical model was developed in the framework of another study, and is based on the coupling of DELWAQ en CHARON water quality programs and the DISTRO hydrodynamic model. DELWAQ is used as the main program for transport and slow water quality processes, while CHARON is used to calculate the thermodynamic equilibrium.

3.2 Evaluation of pollutant discharges

The discharge data have been selected and analyzed based on the nearness to the potential sampling location and their contribution to the concentration levels in the Rotterdam Waterway. Areas where an disproportional disturbance of concentrations is expected have been identified.

3.3 Experiences in the Elbe and Humber estuaries

The sampling approach in the Elbe and Humber estuaries has been evaluated.

In the Elbe estuary the pollutant load is determined based on a sampling program in the cross-section of the river downstream from the harbour and industry of Hamburg. However this location is still upstream of the salt intrusion zone.

In the Humber estuary the river loads are determined at the tidal boundary. All pollutant discharges occurring downstream from this point are added to the determined load to estimate the load to the estuary and sea.

The english and german approaches are incomparable with the approach as aimed at in the Rotterdam Waterway with its complex system. As such the experiences in the Elbe and Humber do not provide additional insights in the solution of the encountered difficulties.
4 Variability and inhomogeneity

4.1 Variability in measured concentrations

The conservative compound chloride shows a high variability as a results of the tidally influenced salt intrusion. For this compound the influences of fluctuations of river discharge and sea level are very strong. The variations in concentrations occur in time as well as spatially (vertical stratification and longitudinal gradient).

For the parameters temperature, oxygen, nitrite and nitrate, a correction for the seasonal variation results in a strong reduction of the variability. For ammonium and ortho-phosphate this is not the case. The most important variability for these compounds occurs during the winter when the algal consumption of nutrients is at its minimum. After correction for seasonal effects oxygen shows the smallest relative variation (variance coefficient \(C_v\) smaller than 0.1), temperature, nitrite and nitrate follow (\(C_v\) between 0.1 and 0.2), the largest variabilities occur for Kjeldahl-nitrogen, total-phosphate, ortho-phosphate and ammonium (\(C_v\) larger than 0.3). Part of this variability can be explained by the variability in inflowing river water and pollutant discharges. The spatial variability of most compounds is limited with the exception of total phosphate and ortho-phosphate. This is also influenced by the relatively weak gradient in concentration values in the direction of the sea.

Of the metals nickel shows the lowest variability (\(C_v = 0.15\)), while the variability of the remaining metals is in the order of magnitude equal to that of suspended solids (\(C_v\) between 0.3 and 0.7). The variability of compounds with generally low concentration levels is relatively high. The influence of the inaccuracy of analysis becomes an important factor in these cases. This holds especially for lead, PAH and BaP.

An important observation from cross-sectional profile research is the large gradient in both the vertical and transverse directions. Especially for discharged compounds and compounds that strongly associate with suspended solids, the variations in the cross-section are larger that the variation in time as observed in the current sampling program. For example, the range in suspended solids concentrations observed in the current measurements is around 150 mg/l while the observed range in the cross-section amounts to 1000 mg/l. Consequently, the concentration measured using the current sampling approach in the Rotterdam Waterway is only representative (special circumstances excluded) for the upper layer at low tide and can not be considered representative for the concentration in the cross-section nor for the 'river concentration' with regard to these substances.

4.2 The influence of pollutant discharges

Most pollutant discharges that can be considered of influence on the transversal inhomogeneity of concentrations are located near the confluence of the "Oude Maas" and "Nieuwe Maas". Their importance can be evaluated based on the size of the discharge relative to the observed load at Maassluis (manual sampling scheme). For the (organic) micropollutants 1,3-xylene, 1,4-xylene, benzene, fluoride, tetrachloroethene, tetrachloromethane, trichloroethene, trichloromethane and toluene local discharges can be expected to have an important impact on the total load based on their relative size. Similarly, the relative
importance of local discharges for metals like arsenic, cadmium, chromium, mercury, manganese, nickel and lead is noted, as well as for calcium and total-phosphate. With regard to the organic micropollutants, allowance must be made for the volatility of some of these compounds. The locally discharged load of trichloromethane and tetrachloromethane proves to be substantially larger than the load measured at Maassluis, which illustrated the importance of loss processes. By far the largest part of the chloromethanes is discharged in the harbours, not directly in the Rotterdam Waterway or the "Nieuwe Maas".

5 The sampling location

During the analysis, an evaluation was made based on the goals set for the sampling station. Important factors determining the choice of location are: the degree of vertical and transversal inhomogeneity (as a result of incomplete mixing, processes etc), the dilution with sea water, disturbances and available infrastructure.

It proved that trend detection and load estimation favoured a location to the west of the bend at Maassluis, while detection of incidental spills and standard violations favoured locations east of Maassluis. Based on an overall evaluation, a location westwards of the bend at Maassluis is advised as the new sampling location. It is suggested to make optimal use of the existing infrastructure such as the existing landing at Poortershaven (Kruitsteiger) which is suitable for use as a permanent sampling station.

Because there are insufficient data to justify the choice of just one station it is advisable to collect data on the transversal variability of concentrations at the suggested cross-section, on which a well-founded choice of sampling locations in the cross-section can be based. Two options are suggested:
- An intensive ship-based sampling campaign with regular profile sampling in the cross-section. Sampling should be planned in order to sample at various hydrologic conditions;
- Installation of two (temporary) shore stations on the northern and southern shores with additional incidental sampling campaigns in the cross-section under various conditions.

Probably a sequence of the two options for a period of approximately two years will prove the most efficient approach.

6 The sampling strategy

The correct weighting of concentrations with the river discharge is essential for the reliable estimation of loads. For load estimation the reconstruction of concentration levels from point measurements to continuous data based on the salinity and the dilution curve proves to be a better approach than the direct use of point measurements. If actual river discharge can not be measured directly, model calculations based on actual upstream river discharges, tidal information and sea levels, may form an acceptable alternative.

Other sampling methods can also be used to make estimates of loads. Proportional sampling, where the volume of the sample is directly related to river discharge, can give a good
estimation of the load at the sampling point if the reversal of flow is taken into account for those compounds that are not affected by the mixture of water types. Composite samples not based on a relationship with river discharge do not supply any additional information when compared with grab samples. The interpretation of the resulting concentration in the composite sample is even less straightforward than the concentration at a certain location at a certain period of the tide.

Given the choice of an location westward of Maassluis, with some measurements at both high tide as well as in the lower water layer, it is evident that samples will not always contain fresh water. Considering the risk of introducing additional errors and from the viewpoint of comparability, the use of separate fresh water and salt water analytical techniques is considered inadvisable. A choice for one analysis technique (for salt water) is advised for all heavy metal assessments.

7 The sampling frequency

The optimal sampling frequency will depend on the goals set. A relatively high frequency is advised for the initial trial period: once a week at both high and low tide in both the upper as well as the lower layer. After this period, a decision can be made for the sampling frequency related to each goal based on the observed variability in concentrations.

7.1 Trend detection

In case of sampling for trend detection in concentrations, the variability in time (after correction for explainable variations) compared to the trend that has to be detected is important. It is striking that for all compounds (with the exception of oxygen) a trend of 10% of the mean concentration over a period of 5 years can not be detected with any reliability based on two weekly samples. An increase in sampling frequency will not improve the reliability significantly due to autocorrelation and tidal effects. The fact that it is possible for a number of compounds to detect a trend of a certain set relevant margin can be explained by the rather wide settings. It can be concluded that the originally set goal of detecting trends of 10% of the mean is not a realistic option. When using the set relevant margins, the compounds can be divided into three groups:

- Those compounds for which the relevant margin is set a such a large value that a very low sampling frequency will suffice (e.g. BaP, γHCH, Ni);
- Those compound for which the set relevant margin is so low that it will not be possible to detect this trend over a period of 5 years (e.g.: NH4, PO4, Cl, Cd);
- Those compounds for which an increase in sampling frequency will make a trend detection possible (e.g.: O2, Kj N, NO3, P).

7.2 Detection of standard violations and accidental spills

The frequency for standard violation detection is set in the regulation stipulating this kind of sampling.
Considering the short distance between the area with potential accidental spills and the monitoring location, a high frequency of sampling will be required to detect all spills. The time a spill with a length of two kilometers will be detectable at the sampling point ranges between once for 40 minutes and several times with a total duration of seven hours over two days, depending on the time and location of pollutant discharge. The final frequency required will be dependent on the required probability of detection.

7.3 Load estimation

Considering the complex combination of factors affecting the actual load, a quantitative assessment of the required sampling frequency is not possible with the available data. However, it can be concluded that continuous river discharge monitoring (or modelling) and monitoring of chloride concentration will increase the reliability of load estimations considerably.
8 Conclusions and recommendations

8.1 Sampling location

conclusions
- A location westwards of the bend at Maassluis is most suitable from the viewpoint of having the most complete transversal mixing.
- The existing infrastructure at the landing of Poortershaven (Kruitsteiger) can be used for the new sampling location.
- The English and German approaches are incomparable with the approach as aimed at in the Rotterdam Waterway with its complex system. As such the experiences in the Elbe and Humber do not provide additional insights in the solution of the encountered difficulties.

recommendations
- It is advisable to collect data on the transversal variability of concentrations at the suggested cross-section, on which a well-founded choice of sampling locations in the cross-section can be based. Two options are suggested:
  - An intensive ship-based sampling campaign with regular profile sampling in the cross-section. Sampling should be planned in order to sample at various hydrologic conditions;
  - Installation of two (temporary) shore stations on the northern and southern shores with additional incidental sampling campaigns in the cross-section under various conditions.
- It is recommended to evaluate the sampling program after at least one year.

8.2 Sampling strategy

conclusions
- A sampling strategy that includes the monitoring of river discharge is essential for a reliable estimation of loads.
- Sampling in the lower layer gives important information about the concentration of suspended solids and the compounds that associate with suspended solids, especially with regard to the effluents that have a high density.
- Based on present knowledge an error of 30-50% in the estimation of annual loads is to be expected.

recommendations
- It is recommended to apply one (salt water) analytical method for the determination of heavy metal concentrations for all samples of the Rotterdam Waterway.
- When applying fresh water standards in the Rotterdam Waterway one should be aware of the fact that the Rotterdam Waterway contains both fresh and salt water.
8.3 Sampling frequency

conclusions
- When considering trend detection based on the set relevant margin the compounds can be divided into three groups (see chapter 7.1).
- The goal of detecting a trend of 10% of the mean concentration over 5 years is not realistic for all components.
- The goal of detecting accidental spills can be specified as a probability of detection.

recommendation
- A relatively high frequency is advised for the initial trial period: once a week at both high- and low tide in both the upper as well as the lower layer. After this period a funded choice can be made for the sampling frequency for each goal based on the observed variability.
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