Texte

Texte

Texte

26
07

ISSN
1862-4804

**Effects of sampling and sample
preparation on results
during determination of
selected prioritary substances
according to the Water
Framework Directive**

**Umwelt
Bundes
Amt**

Für Mensch und Umwelt

TEXTE

ENVIRONMENTAL RESEARCH OF THE
FEDERAL MINISTRY OF THE ENVIRONMENT,
NATURE CONSERVATION AND NUCLEAR SAFETY

Research Report 204 22 213
UBA-FB 000982

Texte

26
07

ISSN
1862-4804

Effects of sampling and sample preparation on results during determination of selected prioritary substances according to the Water Framework Directive

by

Dr. Dieter Busch
Dr. Klaus Furtmann
Annette Schneiderwind
Irina Zyuzina
Rolf Reupert
Dr. Klaus Sielex

North Rhine-Westphalia State Environment Agency

UMWELTBUNDESAMT

The contents of this publication do not necessarily
reflect the official opinions.

Environmental Research Plan
of the German Federal Ministry of the Environment,
Nature Conservation and Reactor Safety

Water Framework Directive

Reference number (UFOPLAN) 204 22 213

Effects of sampling and sample preparation on results
during determination of selected prioritary substances
according to the Water Framework Directive

Authors:
Dr. Dieter Busch, Dr. Klaus Furtmann,
Annette Schneiderwind, Irina Zyuzina,
Rolf Reupert, Dr. Klaus Sielex

Landesumweltamt NRW[1]
Düsseldorf

President
Dr. Harald Irmer

PRODUCED FOR
UMWELTBUNDESAMT[2]

September 2006

---

[1] North Rhine-Westphalia State Environment Agency
[2] Federal German Environment Agency

Adress :

Landesumweltamt NRW
Wallneyerstraße 6

45133 E s s e n
Germany

Change of adress within restructuration
of the environmental authorities of NRW in 2007 :

LANUV
Landesamt für Natur, Umwelt und Verbraucherschutz
Nordrhein-Westfalen(LANUV)

Wallneyerstraße 6
45133 E s s e n

Germany

Contents

Chapter   **Page**

List of tables

List of figures

List of abbreviations

AQS	Analytical Quality Assurance
DL	Detection limit
D	Germany
DIN	German Standards Institute
DV	Data processing
EN	European standard
EPA	Environmental Protection Agency
EU	European Union
EWG	Einwohnerwerte i.e.
	Population equivalents (sewage treatment)
Fig	Figure
FR	Filter residue
FSS	Abfiltrierbare Substanzen i.e. Filterable suspended solids
IMBL	Bimmen / Lobith international monitoring station
KGV	Korngrößenverteilung i.e. Grain-size distribution
K_{ow}-value	Coefficient of distribution n-octanol / water
LAWA	German Working Group on water issues of the
	Federal States
log K_{ow}	Coefficient of partition distribution n-octanol / water
MP	Mixed sample
MW	Average
NL	The Netherlands
NRW	Federal state of North-Rhine Westphalia
OP	Original sample

PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyls
PE	Polyethylene
PN	Probenahme i.e. Sampling
PSM	Pesticides
PTFE	Polytetrafluor ethylene
QN	Quality standard
RLP	Federal state of Rheinland-Pfalz
SM	Schwermetalle i.e. Heavy metals
SP	Stichprobe i.e. Random sample
SS	Suspended matter
Stabw	Standard deviation
StUA	Regional Environment Agency of NRW
TOC	Total Organic Carbon
TS	Trockensubstanz i.e. Dry matter
UBA	Federal German Environment Agency
WDF	Retrieval rate
WKST	Water control stations
WFD	Water Framework Directive

Acknowledgments

We would like to thank all those whose commitment has contributed to the success of the project and who offered advice and assistance to the authors, including:

- Staff of the North-Rhine-Westphalia state environmental agency (LUA) departments 13, 22, 23, 51 and 54, who provided assistance with the determination of readings and the generation of graphics in the laboratory or during sampling.

- The Institute of Statistics of Bremen University, whose advice allowed an extensive statistical evaluation of data.

- Regional environmental agency (StUA) Düsseldorf, which assisted us with optimization of the filtration method and co-organized a comparative test to sampling.

- Regional environmental agency (StUA) Hagen, which provided a selection of sampling equipment on loan and supported the comparative test for sampling by their participation.

- Regional environmental agency (StUA) Herten, which assisted us with overcoming staff shortages during sampling and supported the comparative test for sampling by their participation.

1 Introduction

The EU Water Framework Directive (WFD) lays down new requirements for surface water monitoring, including 33 substances or groups of substances subject to a high ecotoxicological risk potential as so-called prioritary substances in Annex X of this directive. Environmental discharges of these substances must be prevented and their concentration in the environment reduced as much as possible.

As part of the EU WFD, EU-wide quality standards were developed for these prioritary substances that represent the "desired condition" to be achieved by surface waters that must be regularly monitored. Compliance with quality targets (concentrations) should rule out any risk to the aquatic ecosystem as a result of pollution by prioritary substances.

In the case of non-compliance with these targets, monitoring programs describe the contamination of affected surface waters and action to be taken for a gradual reduction of discharges (BÖHM et al 2002). Current framework conditions for any future chemical analysis monitoring throughout the EU are stipulated in the Proposal for a Directive on Environmental Quality Standards in the Field of Water Policy, amending Directive 2000/60/EC (KOM 2006).

It is the aim of the new quality targets to include ecotoxicological aspects in the assessment of present contamination. Contamination relevant to the ecosystems of waters from an ecotoxicological point of view, consisting of organic compounds (e.g. pesticides) and inorganic substances (e.g. heavy metal ions) are dissolved in water or attached to fine-particular seston and will be absorbed, starting with very low concentrations of aquatic organisms, which in some cases cannot be analytically proven (BUSCH et al 1995).

In the aquatic environment, deposited pollutants are subject to chemical/physical changes. Various factors, such as the concentration and composition of suspended matter in water, biological activities and chemical/physical conditions in surface water will influence the distribution of metals between the

liquid and the solid phase. These factors also influence the bio-availability of metals to aquatic biota (FÖRSTNER et al. 1985).

There is not necessarily a correlation between the biological availability and absolute concentrations in abiotic sections (water, seston, sediment) of the eco system (BUSCH et al. 1995). At the same time, synergistic increases in toxicity as a result of interaction with other substances contained in water may occur. Toxicity and bio-availability of heavy metals will, for instance, increase significantly with decreasing degrees of hardness and reduced pH-values of water (WACHS 1994). There are also clear correlations between the bio-availability of heavy metals and the salinity of river water (BUSCH et al 1996).

Organisms resorb heavy metals predominantly in dissolved form. The EU consequently stipulated the analysis of dissolved heavy metal proportions **- in filtered water samples –** for prioritary heavy metals. For prioritary organic pollutants tests of original samples have been scheduled.

From an analytical point of view, monitoring of environmental pollutants should, however, take place in the matrix including the highest concentrations and allowing the most reliable detection. Consequently, heavy metal contamination has in the past either been monitored in the suspended matter of surface waters or in the original sample. Lipophilic organic pollutants (e.g. PAH, chlorinated pesticides) have in the past been predominantly monitored in suspended solids.

Changes in the matrix to be analysed, as proposed by the EC, may cause analytical problems, as most standard processes were not validated for water containing suspended matter. In addition, changes in matrix will mean that existing monitoring data can no longer be directly compared with new data to be collected.

The aim of this project was to investigate the influence of sampling, sample preparation and their effect on monitoring results for the new matrixes to be analysed throughout the EU under the practical conditions of routine water monitoring.

As part of this project, the influence of sampling and sample preparation on results of the determination of prioritary substances in water and suspended matter has consequently been systematically investigated. For this purpose, the concentrations of pollutants in unfiltered water samples, filtered water samples and in suspended matter, removed by centrifugation, were concurrently analysed and subjected to comparative evaluations. Many years of qualified experience and an excellent infrastructure were made available for this project.

From 1976, the North-Rhine Westphalian State Environmental Agency has been involved in regular research, monitoring of water quality of the Rhine and its tributaries by permanent monitoring stations and the "Max Prüss" laboratory vessel. Because of the contamination of surface waters in this densely populated and highly industrialized region, the significance of the river Rhine and the inclusion in international monitoring programs (IKSR), strict requirements for surface water monitoring exist. Therefore, compared with the national average, an extensive environmental analysis, based on a high quality standard is applied in this region (LUA NRW 2000).

The results of the project carried out on various types of surface waters may be regarded as representative for surface waters subject to significant anthropogenic pollution in densely populated and industrialized catchment areas within Central Europe.

2 Monitoring programme

A prerequisite for implementation of the project is that surface waters contain a measurable contamination of any substances to be analysed. Consequently, out of 33 prioritary substances, some representative substances were selected that currently contribute to the environmental contamination of the industrialized Lower Rhine region and that can be easily detected in at least one of the matrixes to be analysed (original sample, filtered sample, suspended matter). However, some of the group of substances that have been regulated for some time (e.g. chlorinated pesticides) can, however, still be detected occasionally. Data collectives gathered for these substances in this project consequently remain incomplete. In addition, other substances that could be analytically detected together with any examined substances, were also tested.

2.1 Analysed groups of substances / parameters and matrixes

Prioritary substances and PCBs

Metals: cadmium, mercury, nickel and lead

PAHs: anthracene, fluoranthene, naphthalene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene

chlorinated pesticides : HCH, DDT, Aldrin, Dieldrin, Endrin, Isodrin

Water-soluble herbicides: Diuron, Isoproturon

PCB congeners: PCB-28, -52, -101, -118, -138, -153, -180

Other pollutants and parameters for characterizing specific boundary conditions of surface waters:

Metals: aluminium, arsenic, calcium, cobalt, chromium, copper, iron, potassium, magnesium, manganese, sodium, zinc

PAHs: methyl naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, pyrene, benz[a]anthracene, chrysene, dibenz[a,h]anthracene

chlorinated pesticides : Telodrin, 2,4-DDD, 4,4-DDD, 2,4-DDE, 4,4-DDE

Accompanying parameters (in situ): pH-value, temperature, conductivity, substances suitable for removal by filtering (FSS), discharge

Other accompanying parameters : total phosphate, chloride, sulphate, nitrite, nitrate, TOC

Fig. 2.1 provides a summary of all analysed groups of substances / parameters and matrixes.
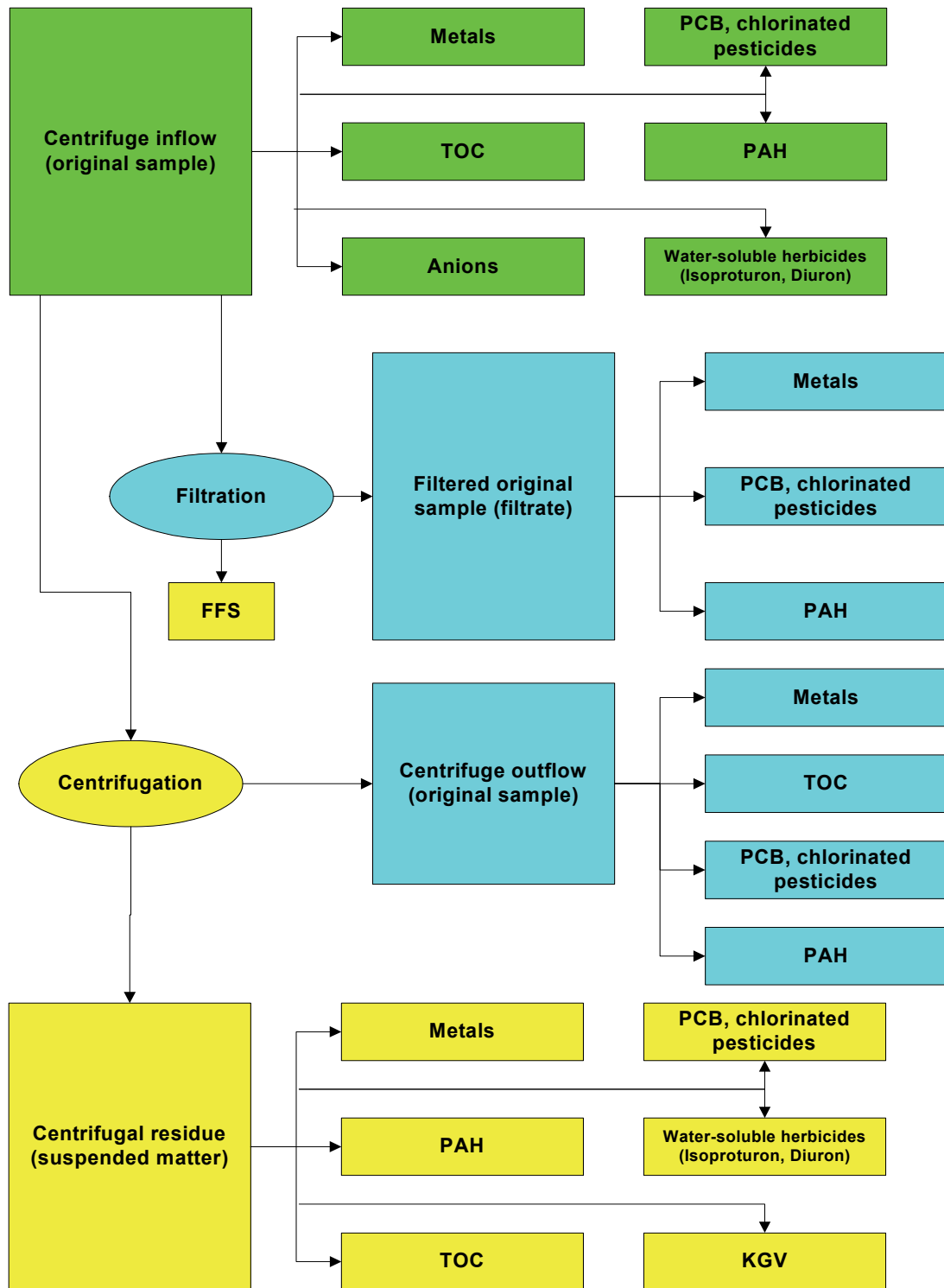
Fig. 2.1: **Summary of group of substances and parameters analysed in various matrixes**

2.2 Monitoring stations

From the monitoring stations used for official routine water monitoring, two representative monitoring stations on the river Rhine and four monitoring stations on major tributaries, subject to very different contamination levels, just prior to their mouth into the river Rhine, were selected (Fig. 2-2). Between May 2005 and March 2006 monthly samples were taken by these monitoring stations.

Tab. 2.2-1: Monitoring stations

SURFACE WATERS	NAME OF STATION	SAMPLING CONDITIONS	COMMENTS
Rhine, km 640	Bad Honnef	Water monitoring laboratory, Continuous-flow centrifuge	Concentration levels entering NRW
Rhine, km 865	Bimmen/Lobith	Water monitoring laboratory, continuous-flow centrifuge	Concentration levels leaving NRW to the Netherlands
Emscher	Dinslaken (prior to flowing into the Rhine)	Mobile continuous-flow centrifuge	Industrially and municipally contaminated wastewater effluent downstream from wastewater treatment plants at river mouth; mining influence (hard coal)
Lippe	Wesel (prior to flowing into the Rhine)	Mobile continuous-flow centrifuge or continuous-flow centrifuge on "Max Prüss" laboratory vessel	Agriculturally and industrially contaminated river of low mountain range region; mining influence (hard coal)
Wupper	Opladen (prior to flowing into the Rhine)	Mobile continuous-flow centrifuge	Industrially and municipally contaminated river
Erft	Eppinghoven (prior to flowing into the Rhine)	Continuous-flow centrifuge on "Max Prüss" laboratory vessel	Agriculturally and municipally contaminated river of low mountain range region. SM contamination from Mechernich ore deposit and brown coal open-cast mining

Today, some groups of substances e.g. chlorinated pesticides, can only be found in such small quantities in surface waters that detection limits of methods applied to the original sample and suspended matter is not exceeded. For these groups of substances a full matrix-specific analysis could not be carried out. The detection of PCB and PAH concentrations in filtered and unfiltered water samples also proved a problem, as frequently concentrations were below detection limits.

In order to ensure that the distribution of PCB and PAH contaminations between the dissolved and particle-bound phase in flowing waters can still be assessed, two special monitoring stations with high substance-specific contamination were also used for sampling (see Fig. 2.2):

Emscher upstream from Dinslaken river treatment plant on river mouth

Increased PAH contamination due to discharge from industrial sources (BUSCH et al 2001).

Fossa Eugeniana

Increased PCB contamination due to drainage water (hard-coal mines).

The surface water selection is of a typical European character for surface water contamination in densely populated regions subject to industrial and agricultural use. Results should be transferable to other similarly structured surface waters.
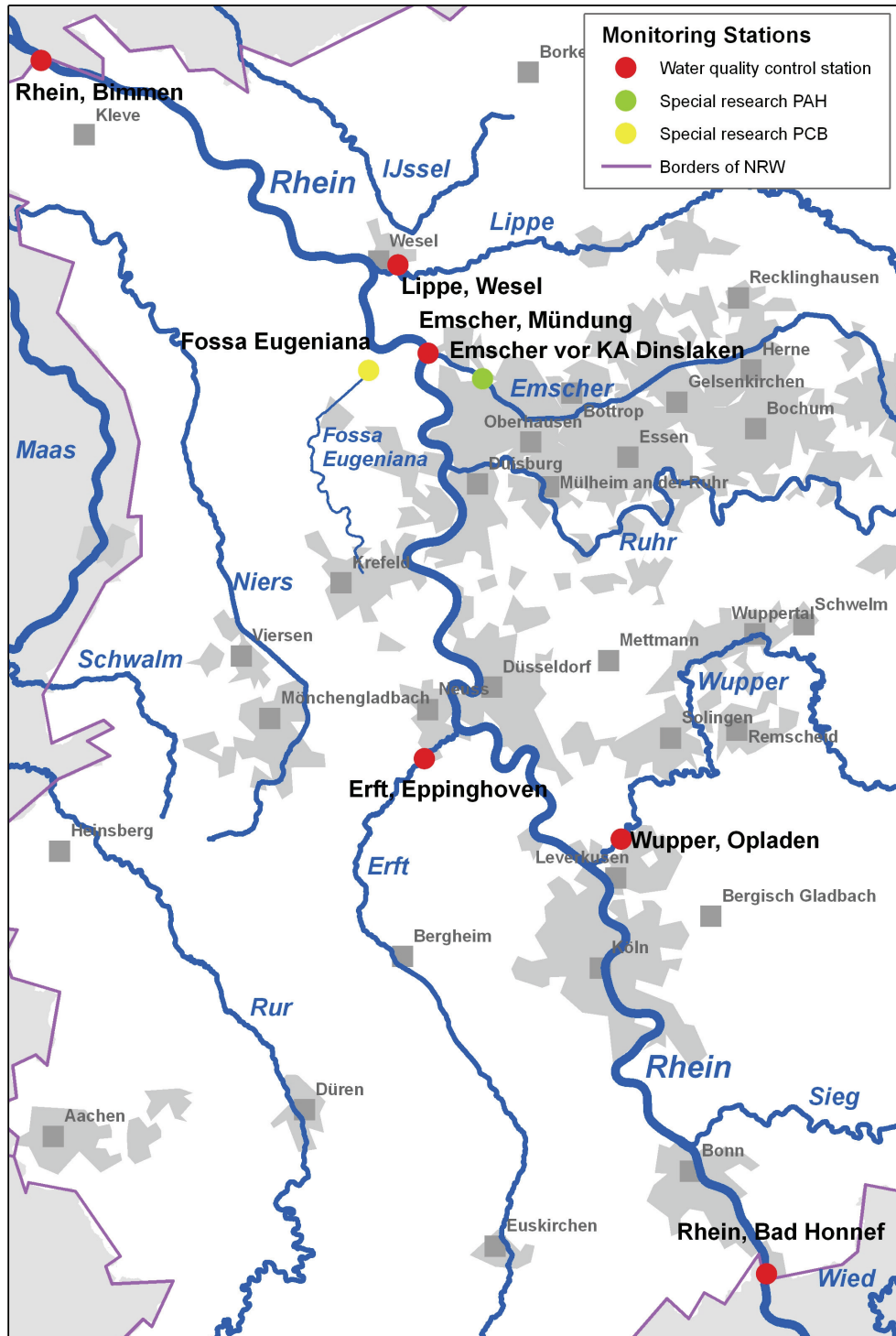
Fig. 2-2: Map of monitoring stations used for sampling

2.3 Characterisation of selected surface waters

Rhine

The river Rhine is a lowland river based on predominantly sandy river bed.

The catchment area of the Rhine covers approx. 185 000 km² and is home to approx. 50 million people. The Rhine provides drinking water for a population of approx. 5.5 million. At the same time, a treated wastewater volume based on a population equivalent of approx. 80 million is discharged into the Rhine. The length of the Rhine in NRW is 225 km. The average discharge is approx. 2200 m^3/s.

Contamination factors:

- Discharges from municipal wastewater treatment plants
- Discharges from industrial/commercial wastewater treatment plants
- Cooling water discharges
- Use of the Rhine as a Federal waterway
- High degree of catchment area is sealed, erosion of areas
- Contamination from inflowing tributaries

The average chloride content of the Rhine is approx. 80 mg/l. Average calcium concentrations (2000-2006) were 65 ± 7 mg/l (n=97) in Bad Honnef (Rhine km 640, right) and 77 ± 10 mg/l (n=161) in Bimmen (km 865, left). For an assessment of cadmium contamination according to the EU, these calcium values correspond to cadmium assessment class 3 (KOM 2006).

Wupper

The river Wupper is a low mountain range river based on a gravel bed and subject to industrial and municipal contamination. The catchment area of the Wupper covers approx. 800 km² and is home to approx. 890 000 people. The river has a length of 115 km. The average discharge is around 14.8 m^3/s.

Contamination factors:

- Discharges from municipal wastewater treatment plants

- Discharges from industrial/commercial wastewater treatment plants

- Cooling water discharges

- Precipitation and rain water discharges

The Wupper contains soft, mildly buffered water of a low acid-building capacity (approx. 1 mmol/l). Its chloride content fluctuates between 30 and 50 mg/l (summer) and 160 mg/l (winter). Average calcium concentrations (in 2000-2006) were 34 ± 6 mg/l at the Opladen monitoring station. For an assessment of cadmium contamination in compliance with EU regulations, these calcium values comply with cadmium assessment category 1 (KOM 2006).

Emscher

In its upper reaches, the river Emscher is a lowland stream, based on a loess and clay bed, and a sand and clay bed lowland stream in its middle and lower reaches. The river receives industrial and municipal discharges and is cleaned by a central sewage treatment plant at the river mouth prior to flowing into the Rhine. The selected monitoring station is located downstream from the wastewater treatment plants. The catchment area covers approx. 860 km^2 and is home to 2.3 million people. The length of the stream is 85 km, the average discharge is around 16.3 m^3/s.

Large sections of the bottom and embankments of the straightened, reinforced and dammed-in lowland stream are secured by concrete slabs.

Contamination factors:

- Industrial and commercial discharges from conurbations

- Introduction of rainwater and precipitation, high level of sealing

- Mine water inflow

- Groundwater contaminated by pollutants

As a result of the sump water of mines, the Emscher is heavily contaminated with chloride throughout the year. Average measured concentrations are approx. 600 mg/l (BUSCH et al 2001). Average calcium concentrations (in 2000-2006) at the mouth of the Emscher were around 157 ± 31 mg/l. For an assessment of cadmium contamination in compliance with EU regulations, these calcium values comply with cadmium assessment category 4 (KOM 2006).

Lippe

The river Lippe is a slow-flowing lowland river based on a predominantly sandy bed, contaminated by agricultural and industrial discharges. Drainage of hard coal mines also represents a considerable contamination factor. The catchment area covers approx. 4880 km^2 and is home to approx. 2 million people. The river is 220 km long. The average discharge is around 44.5 m^3/s.

Contamination factors:

- Municipal and industrial wastewater

- Inflow of Seseke, a wastewater containing tributary stream at Lünen

- Cooling water discharges

- Agricultural discharges

As a result of sump water of coalmines, the river Lippe is heavily contaminated with chloride (200-1000 mg/l). Average measured calcium concentrations (2000-2006) were approx. 133 ± 16 mg/l at the Wesel monitoring station. For an assessment of cadmium contamination in compliance with EU regulations, these calcium values comply with cadmium assessment category 4 (KOM 2006).

Erft

The river Erft is a lowland river with a gravel bed and subject to contamination from agriculture, ore deposits and brown coal open-cast mining, measuring approx. 107 km in length. The catchment area covers approx. 1800 km^2 and is home to approx. 600 000 people. The average discharge is around 17.3 m^3/s.

Contamination factors:

- Agricultural discharges

- Increased heavy-metal contents in the river and sediments around the Mechernich lead/zinc deposit

- Discharges from brown coal open-cast mining

- Cooling water discharges

The chloride contamination of the Erft is generally less than 200 mg/l. Average calcium concentrations (2000-2006) were approx. 57 ± 6 mg/l at the Eppingho-ven monitoring station. For an assessment of cadmium contamination in compliance with EU regulations, these calcium values are compliant with cadmium assessment category 3 (KOM 2006).

Fossa Eugeniana

The Fossa Eugeniana is the remnant of an ancient canal linking the rivers Maas and Rhine, the construction of which was commenced in the 17th century. The catchment area covers approx. 65 km^2 and is characterized by hard coal mining. The canal's high chloride contents of approx. 3500 mg/l are caused by draining hard-coal mines.

Contamination factors:

- Drainage water from mines (saline pit water)

- Municipal and industrial wastewater discharges

- Precipitation and rainwater discharges

3 Material and method

3.1 Examined matrixes

Within the scope of the project, the pollutant load was examined at selected monitoring stations and in each case in different matrixes. The frequency of individual examinations is shown in Tab. 3.1-1. Water samples were taken in compliance with DIN 38402-15 based on the LAWA-AQS Code of Practice P-8/3 (1997). The following samples were taken:

Inflow of the centrifuge (original sample) at the beginning and end of each centrifugation period, random samples.

Outflow of the centrifuge (drain) at the beginning and end of each centrifugation period, random samples. Random samples of entering and discharged water was initially decanted into a 2-l PE bottle pre-rinsed with sample water and then split into partial samples.

Mixed sample of inlet water taken during the entire centrifuging period. The sample was decanted into a 5-l glass bottle and then homogenized prior to being split into partial samples.

Filtered original sample (random sample, filtrate), by in-situ filtration.

Suspended matter (centrifuging residue).

Filter cake was only analysed as part of special tests on the river Emscher.

Tab. 3.1-1: Summary of number of tested samples for each parameter and matrix

	Water								
	Metals			Chlorinated pesticides	PAH	PCB		Herbicides	
	OP	Fil	Out-flow	OP	OP	OP	Fil	OP	Fil
Honnef	12	12	12	12	---	12	2	11	---
Bimmen**	12	12	12	12	4	12	2	10	3
Wupper	12	12	12	12	---	12	1	11	---
Erft	9	9	9	9	---	9	1	9	3
Emscher***	11	11	11	11	4	9	2	11	---
Lippe	11	11	11	11	3	10	1	9	4
Fossa E.****	---	---	---	---	---	2	2	---	---

	Suspended solids					
	Metals	Chlorinated pesticides	PAH	Herbicides*	PCB	Grain-size
Honnef	12	12	12	---	12	12
Bimmen**	12	12	12	3	12	12
Wupper	12	12	12	---	12	12
Erft	9	9	9	3	9	9
Emscher***	11	11	11	---	11	11
Lippe	11	11	11	4	11	11
Fossa E.****	---	---	---	---	2	---

OP = original sample; Fil = filtered sample, Outflow = Outflow of centrifuge; PAHs = Polycyclic aromatic hydrocarbons;
Herbicides -Fil* + Herbicides* = Further testing of Diuron and Isoproturon only if concentrations were detectable in original sample.

Bimmen ** = Parallel tests carried out on suspended matter from sedimentation box
Emscher *** = PAH special monitoring program at additional monitoring station
Fossa E. **** = PCB special monitoring program

3.2 Sampling and transport of samples

3.2.1 Sampling of suspended matter

Suspended matter is obtained from the continuous-flow centrifuge. At the Bimmen (Rhine) monitoring station, suspended matter was also collected from a sedimentation tank.

Centrifugation

Type Padberg Z61 continuous-flow centrifuges (centrifugation output of up to 1500 l/h) were used for monthly sampling at monitoring stations. At the same time, water samples were taken from inlet and discharge hoses as well as a mixed inlet water sample, using a sample collector.

In Bad Honnef and Bimmen (Rhine) and on the "Max Prüss" Laboratory vessel, centrifuges and pumps are permanently installed. At the other monitoring stations, samples were taken with a mobile centrifuge.

Suspended matter samples were taken in compliance with the recommendations of ISO 5667-17, taking into consideration LAWA-AQS Code of Practice p. 8/4 (1997). The duration of centrifugation depends on the suspended matter content of surface water and the required volume of suspended matter. In order to obtain 300 – 500 g of suspended matter (wet), centrifugation periods of up to 24 h were required.

Using a PTFE scraper, the suspended matter sample was transferred from the centrifuge foil to a 1-l brown-glass wide-neck bottle and transported, whilst protected against heat and light. Details of sampling suspended matter are shown in Tab. 1 of the Annex.

Sedimentation tank

The Bimmen monitoring station also used a sedimentation tank in addition to a continuous-flow centrifuge, thus allowing a comparison of these sampling methods. In case of the stationary sedimentation method, some of the water flowing through the monitoring station runs through a plexiglass sedimentation tank. The flow speed in the tank is reduced to approx. 0.01 m/s. The suspended matter contained in the water settles on a slope and slides down into the bottom section of the tank.

At the end of a four-week collection period, supernatant is drained off and the remaining water/ suspended matter mix is homogenized, using an agitator, and decanted into sampling bottles via a drain cock. In this way, approx. 5 l of wet substance can be collected over a period of four weeks. Disadvantages of the sedimentation tank are a low separating efficiency (around 30 – 40%) and ageing of suspended matter during sampling periods. Very fine suspended matter passes through the tank and is not collected.

3.2.2 Filtration of water sample (original sample)

The project utilized and developed a low-contamination "in-situ"" filtration method using the apparatus by Witt, allowing direct filtration into the sampling bottle or the receptacle used for metal analysis.

"In-situ" filtration method

Prior to each filtration, the equipment without a membrane filter was rinsed with 250 ml ultrapure water. The ultrapure water used (type 1, test water quality > 18 MΩ/cm) was removed immediately prior to sampling. Transportation receptacles were also rinsed prior to each use and checked for any signs of contamination, using blank values.

An untreated membrane filter (Satorius; 0.45 µm, Ø 50 mm, cellulose nitrate, No. 11 306) is removed from its original packaging by the use of plastic forceps, and placed in the equipment. Should the content of substances that can be filtered out also have to be determined, the filter must first be weighed.

Each filter is first pre-rinsed twice with 250 ml ultrapure water. The filtrate of the first rinse is discarded, whilst the filtrate of the second rinse is analysed as the blank filtration value.

Next, 250 ml of the sample are filtered into the PE sample bottle by using the same membrane filter.

3.2.3   Preservation of samples

For the analysis of heavy metals, standards and LAWA-AQS Codes of Practice stipulate acidification of samples by concentrated HNO_3 directly after sampling. During acidification of the samples one should make sure that any acid and tip of the pipette used are free from contamination. Due to an increased risk of contamination during field acidification, the preservation practice was modified. Instead of an immediate addition of acid to the samples, acidification of the samples is now only carried out in the laboratory.

Extensive trials by LUA NRW have shown that not stabilizing heavy metal samples (original sample as well as filtered sample) during sampling tests does not significantly affect results (see chapter 3.3.1.4).

3.2.4   Transportation of samples

After sampling, samples were immediately transferred to the cool box and taken to the laboratory the same day. Upon arrival, they were entered in the laboratory's computer system, stored in a refrigerator and then forwarded to laboratories. Where extended processing times were expected, suspended-matter samples were frozen.

3.3　Analysing method, quality assurance and detection limits

The laboratory uses a quality management system based on DIN EN ISO / IEC 17025. Where available, LAWA AQS Codes of Practice were used for analytical quality assurance. Individual methods are described in standard work instructions. Individual methods are shown in Tab. 3.3-1.

Tab. 3.3-1:　Summary of parameters, methods and detection limits

PARAMETERS	METHOD OF ANALYSIS in water	METHOD OF ANALYSIS in suspended solids	Lower application limit	
			Water [µg/l]	Suspended matter [mg/kg]
Cadmium	DIN EN ISO 17294-2 (ICP-MS)	DIN EN ISO 11885	0.01	0.12
Lead		DIN EN ISO 11885	0.05	1.7
Nickel	DIN EN ISO 17294-2 (ICP-MS)	DIN EN ISO 11885	0.1	0.33
Mercury	DIN EN ISO 17294-2 (ICP-MS) DIN EN 13506 (FSS)	DIN EN 1483, section 5	0.005	0.022
PAHs	DIN EN ISO 17993 (HPLC)	DIN 38414-S23, method B	0.005	0.03
Chlorinated pesticides	DIN 38407-F2	LUA method (GC)	0.005	0.001
Herbicides (Isoproturon Diuron)		LUA method (HPLC-MS/MS)	0.02	0.001
PCBs	DIN 38407-F3-1(GC)	DIN 38414-S20 (GC)	0.005	0.001
TOC	DIN EN 1484	DIN ISO 10694	500	500
Sulphate	DIN EN ISO 10304-1 (IC)		2	2
Chloride	DIN EN ISO 10304-1 (IC)		1	1
Disch. substances in original sample	Based on DIN 38409-H2-3			
Particle-size distributions in suspended matter		LUA method (wet-screening, laser diffraction spectroscopy)		

3.3.1 Heavy metal analysis: methodology and QA measures

As part of the project, metals such as lead, mercury, nickel and cadmium were determined in "original sample" matrix types (including suspended matter), "filtered sample" and "suspended matter".

3.3.1.1 Methodology

Original samples were taken in 250-ml PE bottles. Filtrates were stored in 50-ml PP centrifuge tubes and filtered samples for mercury analysis in glass jars. After sampling, the suspended matter was initially transferred into 1000-ml brown-glass wide-neck bottles. After freeze-drying, the suspended matter was stored in 100-ml brown glass jars.

Preparation of samples

Original samples were extracted with nitric acid using microwave pressure digestion in compliance with DIN EN ISO 15587-2. Filtered samples were directly measured without digestion. Digestion of suspended matter was carried out in compliance with DIN EN 13346 by the use of aqua regia subject to backflow.

Method of analysis

Determination of mercury in water was carried out in compliance with DIN EN 13506 using cold-vapour atomic fluorescence spectroscopyFSS. Determination of mercury in extracts of suspended matter samples was carried out in compliance with DIN EN 1483 using cold-vapour atomic absorption spectroscopy (AAS). Lead, cadmium and nickel were determined in original samples and in filtrates in compliance with DIN EN ISO 17294-2 by using ICP-MS. In suspended matter these elements were determined in compliance with DIN EN ISO 11885 by using ICP-OES.

3.3.1.2   Detection limits and measuring uncertainty

Detection limits were determined as specified in compliance with DIN 32645 (blank-value test method). Measuring uncertainty was determined in compliance with DEV 0-4 (extended measuring uncertainty according to chapters 7.2 and 8.2).

Tab. 3.3-2: Detection limits and measuring uncertainty for heavy metal analyses

Element	Matrix	Detection limit	Extended measuring uncertainty U in [%]. Extension factor k=2
Lead	Original sample & filtrate	0.05 µg/l	11
	Suspended matter	1.7 mg/kg	10.6
Cadmium	Original sample & filtrate	0.01 µg/l	15.4
	Suspended matter	0.12 mg/kg	9.4
Nickel	Original sample & filtrate	0.1 µg/l	11.2
	Suspended matter	0.33 mg/kg	12.6
Mercury	Original sample & filtrate	0.005 µg/l	18,6
	Suspended matter	0.022 mg/kg	16.4

3.3.1.3   Quality Assurance

The analysis is carried out as part of quality management based on DIN EN ISO 17025. Water samples were analysed as independent repeat tests (2 bottles from sampling). For suspended matter one digestion was carried out per sample; the digestion solution was analyzed several times. Blank values were monitored based on target values. In the case of water samples, the validity of calibration was verified in each series by a certified standard solution.

This was followed by target-value focused control and the documentation of ranges, blind values and values from certified standard solutions. Internal company reference material (e.g. residual material from inter-laboratory tests) was used for quality assurance of suspended matter analyses. Where possible, regular internal comparisons were made between analysing methods used.

For all matrix types continuous participation in public inter-laboratory tests and in validation studies is ensured so that at least annually but frequently more often than four times a year, information flows into Quality Assurance from regular successfully passed interlaboratory-tests.

The results of any analyses carried out on original samples were used for checking the plausibility of filtrate analysing results. When concentration in a filtrate was higher than in the original sample, the result was discarded.

3.3.1.4　　Deviations of methods from standards

Unlike wastewater monitoring, standard procedures are not mandatory for water monitoring. Where internal methods are used, comparability with standard methods should be ensured. The following deviations apply to heavy metal analyses:

1. Original samples were first acidified in the laboratory.

Acidification during sampling constitutes a considerable contamination risk. Acidification in the laboratory may be carried out under secure and reproducible conditions. As a result, LUA NRW has, since 2000, only stabilized samples in the laboratory upon arrival, i.e. 1-6 hours after sampling. Comparative tests carried out with regard to this modification in sampling showed no significant differences in analysing results for the two methods.

The influence of the point of time of acidification was also examined to ensure the quality of results of this project. For this purpose, original samples and filtrates were taken from three surface waters. One part each of the samples was acidified in-situ and another part only upon arrival of the sample (return of sampling person to laboratory).

Both for filtrates and original samples, there was a 95% certainty that the statistical evaluation (t-test) showed no significant differences (Tab. 3.3-3). For this analysis, 4 samples were in each case taken from two different surface waters (Figs. 3.1-1 to 3).

Tab. 3.3-3: Effects of in-situ/laboratory acidification, results of t-test

t-test parameters	Pb	Cd	Ni
n	6	6	6
$t_{krit}(0,95;5)$	2.571	2.571	2.571
t	0.652	0.674	0.436
Significant difference	no	no	no

36
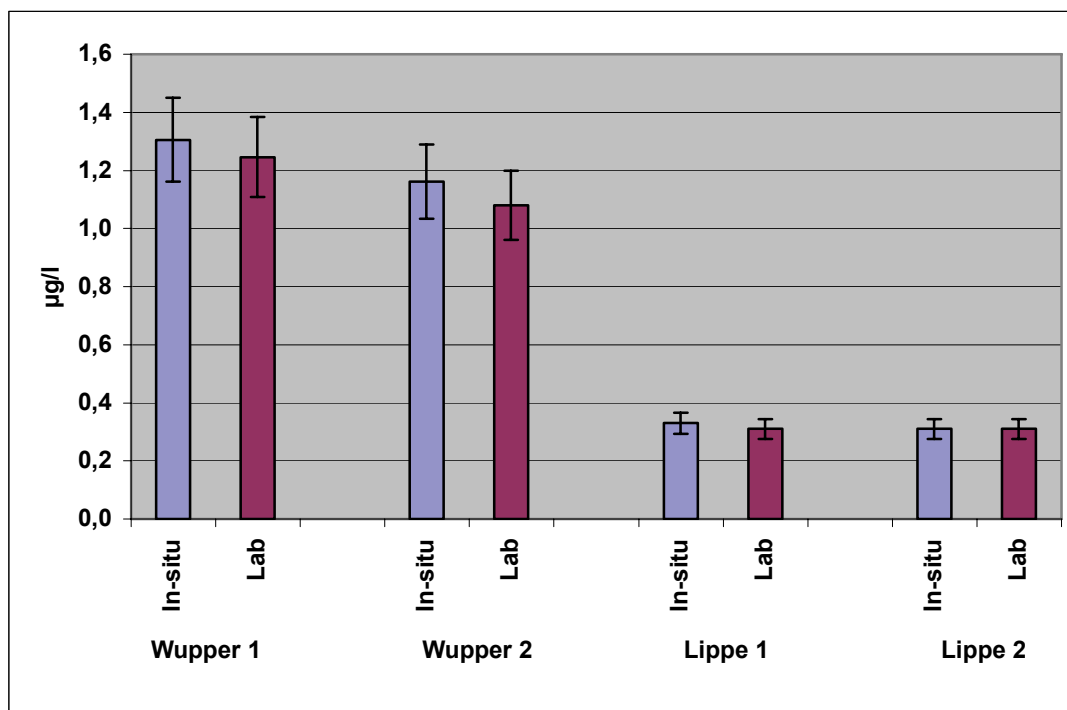
Fig. 3.3.-1: Influence of delayed acidification (in-situ/arrival at laboratory) on lead concentrations of original sample. Average value of repeat determinations (µg/l) and range of extended measuring uncertainty (U).
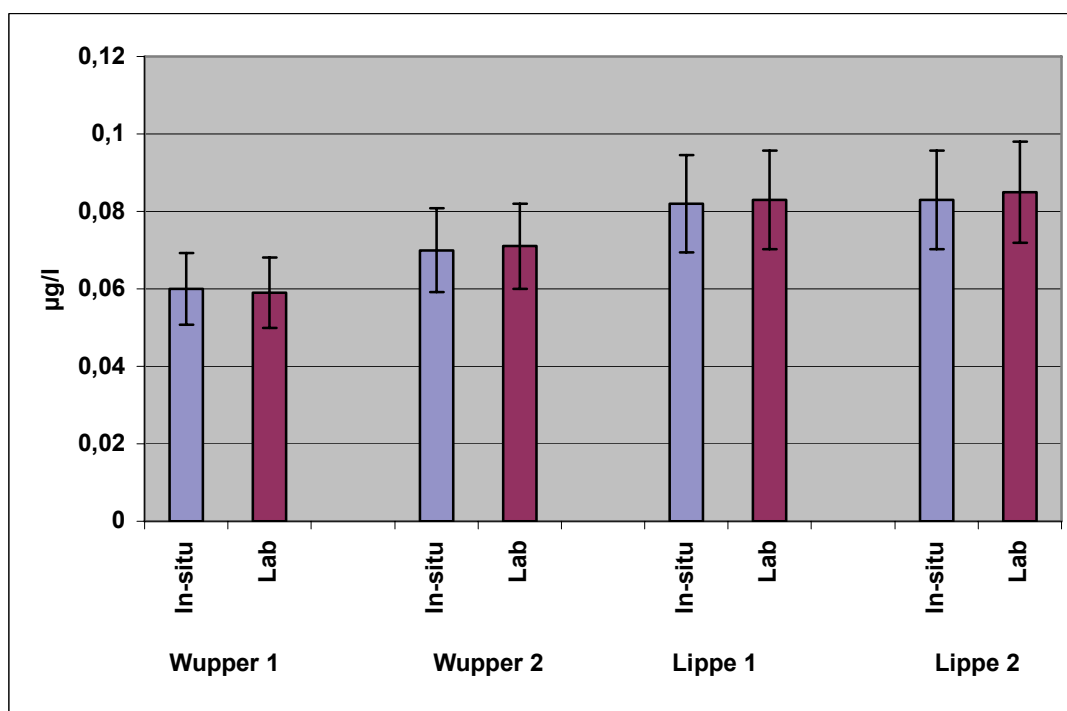
Fig. 3.3.-2: Influence of delayed acidification (in-situ/arrival at laboratory) on cadmium concentrations of original sample. Average value of repeat determinations (µg/l) and range of extended measuring uncertainty (U).
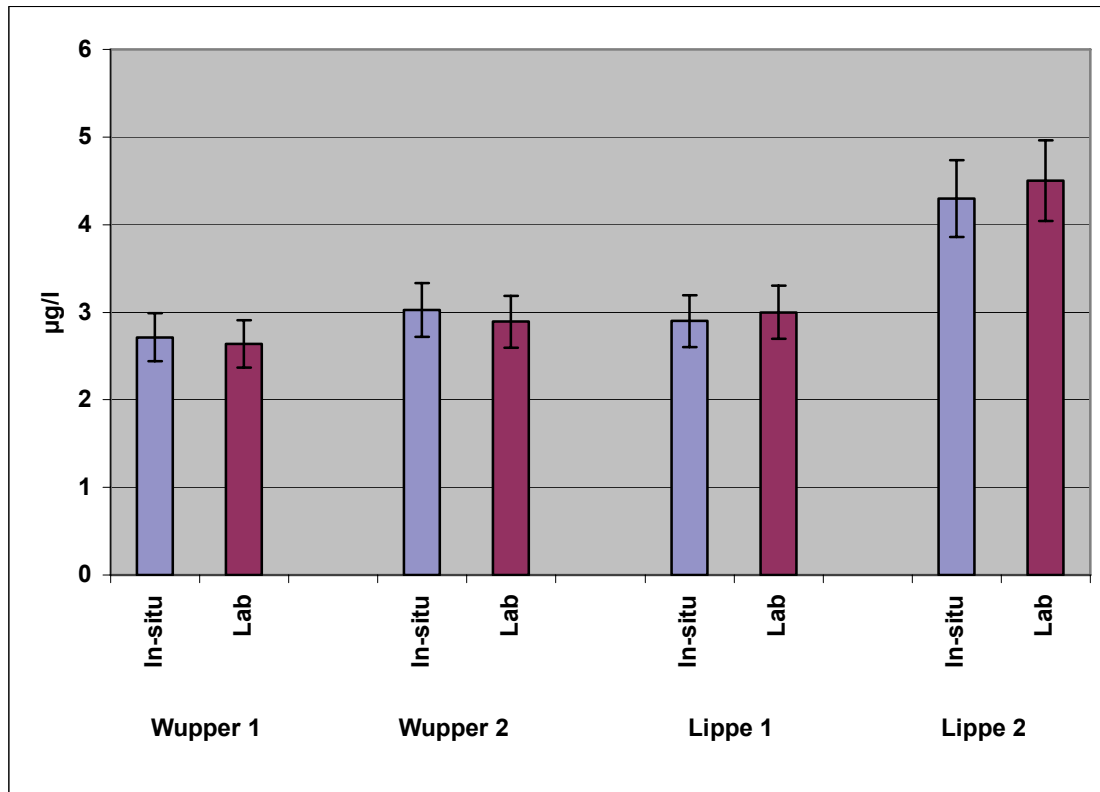
**Fig. 3.3-3: Influence of delayed acidification (in-situ/arrival at laboratory) on nickel con-
centrations of original sample. Average value of repeat determinations (µg/l) and range of
extended measuring uncertainty (U).**

2. Analysis of mercury concentrations from PE bottles

In the original sample, all four elements were analysed from one PE bottle. For
the determination of mercury, the standard stipulates the use of glass sampling
bottles. As the additional use of glass bottles more than doubles sampling and
quality assurance work during the routine monitoring of surface waters, trials for
establishing the suitability of favoured PE bottles were previously carried out in
2004 independently from this project.

As part of these trials, eight independent, similarly contaminated water samples
plus synthetic samples were stored in PE bottles for several months and re-
peatedly analysed in regular intervals. At the start of the trials, water samples
showed mercury contents of between 12 and 22 ng/l.

Over a period of three months, neither an increase of the content due to con-
tamination nor a reduction of the content due to absorption or migration was

determined for the water samples containing suspended matter (Fig. 3.3-4). Only synthetic samples prepared to Hg standard and free from suspended matter, showed expected adsorption losses.

The trial demonstrated that the use of PE bottles did not cause any significant mercury losses in unfiltered samples of surface waters containing suspended matter. Consequently it was decided not to use glass bottles for routine sampling of surface waters. The trial was repeated by another Government Environmental Laboratory and its findings were confirmed.

Development of mercury concentration in PE bottle over time

Hg standard solution, free from particles

Average of eight original samples

♦ Standard
■ Original sample
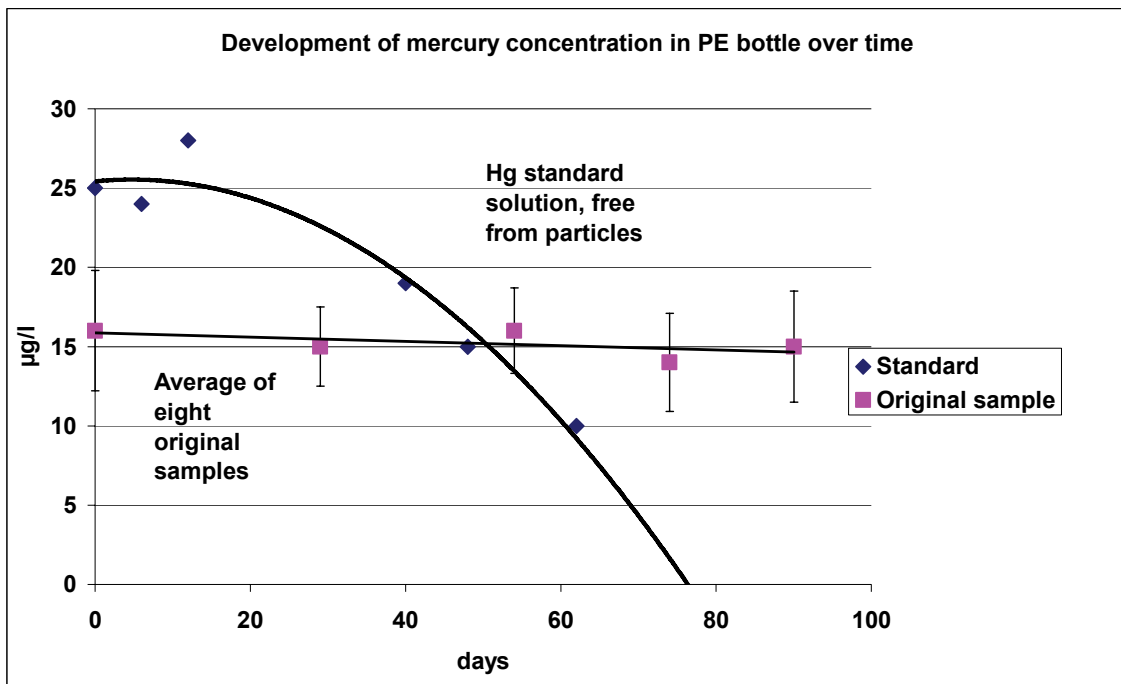
Fig. 3.3-4: Development of mercury concentrations in water samples over time, versus a standard solution, when stored for several weeks in PE bottles. Average values and standard deviations of concentrations of eight independent, similarly contaminated water samples.

3.3.2 Polychlorinated biphenyls (PCBs) and chlorinated pesticides: Methodology and QA measures

PCB analysis

Polychlorinated biphenyls were analysed in compliance with DIN 38407-F2 (02-1993) and 38407-F3 (07-1998). A gas chromatography, coupled with a mass-selective detector was used.

As part of the method described by DIN, inner ^{13}C-standards were added to water samples, extracted by cyclohexane, and the organic phase was isolated with the aid of a microseparator. The cyclohexane phase was concentrated to 1 ml. Coloured extracts were cleaned on the silica gel column coated with silver nitrate. Identification by means of retention time comparison with a standard solution and registration of 3 mass traces. Relative ion intensities of recorded masses in the sample and the standard may not deviate from each other by more than 30%. Internal standards are used for quantification throughout the entire procedure.

GC-MS conditions :

Detector:	MSD
Detector temperature:	300 °C
Transfer line temperature	300 °C
Ionisation energy	70 eV
Injector temperature:	240 °C
Column:	HP-5-MS; length: 60 m,
Filmthickness:	0.25 μm Ø = 0.25 mm
Temperature program:	10 min isothermal at 40 °C /8 °C min^{-1}
	$\rightarrow$72 °C / 11,5°C min^{-1}
	$\rightarrow$118°C / 4°C min^{-1}
	$\rightarrow$270°C / 10 min isothermal / 15°C min^{-1}
	$\rightarrow$ to 295°C / 4 min isothermal
Sample charging:	autosampler
Injection:	pulsed splittless
Flow:	1.2 ml/min
Carrier gas :	helium

After freeze-drying, sodium sulphate is added to suspended matter samples and extracted by hexane for approx. 7 hours, using soxhlet (100 extraction cycles). The extract was concentrated and cleaned by a silica gel column coated with silver nitrate. Subsequent identification and quantification was carried out by GC-MS, analogue to determination in the water sample.

Analysis of chlorinated pesticides

Chlorinated pesticides were analysed in compliance with DIN 38407-F2 (02-1993) and DIN EN ISO 6468 (02-1997). Only gas chromatography coupled with a mass-selective detector was used.

As part of the method described in the DIN standard, inner ^{13}C-standard was added to water samples, extracted by cyclohexane and the organic phase was isolated by a microseparator. The cyclohexane phase was concentrated to 1 ml. Coloured extracts were purified by treatment with a tetrabutyl ammonium hydrogensulphate solution and column chromatography on florisil. Identification by means of retention time comparisons with a standard solution and the registration of 3 mass traces. Relative ion intensities of recorded masses in both the sample and the standard may not deviate from each other by more than 30%. Internal standards were used for quantification throughout the entire procedure.

GC-MS conditions are the same as for the PCB analysis.

Suspended matter samples were extracted under the same conditions as previously described for PCB analysis. The extract was purified in water samples in the same way as for chlorinated pesticides analysed in water samples.

Quality assurance measures for PCB and chlorinated pesticides

Water samples:

For each analysis series a sample was analysed twice. Native standards were added to a water sample, which was then analysed throughout the entire procedure, and the amounts of detected individual compounds were entered on a control card. In general, retrieval rates of 90 to 100 % for PCBs and 80 to 100 % of selected chlorinated pesticides were detected. In addition, for each series a blank sample was co-analysed throughout the entire procedure and results were documented on a control card. ^{13}C-marked compounds were used as internal standards, consisting of 6 Ballschmiter-PCBs, $\alpha-$ and γ-HCH as well as p,p'-DDT.

The bottom application limit (UAWG) of methods used was 5 ng/l in the liquid phase and 10 ng/l for individually chlorinated pesticides. This UAWG represents the end point of the calibration line and differs from the determination limit (DL) and the detection limit (NG) established in compliance with DIN 38402, part 51. Generally it should be noted that UAWG data are more robust and better supported.

No PCBs and chlorinated pesticides could be detected in the liquid phase.

Samples of suspended matter:

Analytical quality assurance measures employed for the suspended matter phase were nearly identical with those of the liquid phase. For each series, a repeat test, a synthetic sample (standard, retrieval) and a blind value were carried out throughout the entire procedure. Values of synthetic samples and blind values were documented on control cards. Generally, the retrieval of standards was 80 to 100 %. The same ^{13}C-marked compounds as for water samples were used as internal standards.

The bottom application limit (UAWG) in the suspended matter phase was around 1 µg/kg for each individual compound. Generally, an original weight of

10 g was used. The detection limit, determined in compliance with DIN 38402, part 51, is based on a factor of 3 (in parts also a factor of 10) less than this UAWG. The information specified in "Water samples" also applies in this case. It should be noted that determined DL and NG strictly apply to 10-g samples. DL fluctuate depending on the mass used.

Measuring uncertainty

The measuring uncertainty for PCB and chlorinated pesticides in water and solids is based on expert estimates, taking into consideration data from inter-laboratory tests without any differentiation by matter and matrix. During this process, a measuring uncertainty of 30% resulted for a significance level of 68% and a measuring uncertainty of 60% for a significance level of 95%.

3.3.3 Polycyclic aromatic hydrocarbons (PAHs) : Methodology and QA measures

Analysis of PAHs

Determination of PAHs in water was based on DIN EN ISO 17993 (see References). Method B of DIN 38414-S23 was used for the analysis of suspended matter. In addition to the standardized HPLC method, individual PAHs were confirmed by online-fluorescence spectra, for which a 95% match with fluorescence spectra absorbed under standard conditions (excitation spectra) was required.

QA measures

QA measures for the analysis of water and suspended matter were identical to a large extent. In both cases, the entire procedure was controlled by the retrieval of 1-fluornaphthaline and 6-methyl chrysene. Retrievals were documented on retrieval cards based on target values of 80-120 % for each sample. For water samples, a blind value sample and a synthetic sample were analysed in each series of analyses in order to determine retrieval.

Measuring uncertainty

The extended measuring uncertainty (k=2) for the analysis of water samples was determined from retrieval experiments and inter-laboratory test data. For highly volatile PAHs (naphthalene, fluorene and acenaphthene), the average measuring uncertainty was around 62% and for higher condensed PAHs up to 38%.

The measuring uncertainty determined from reference materials for the analysis of suspended matter and sediments was around 23 - 52 %. The extended measuring uncertainty for benzo(a)pyrene was approx. 27% for a mass fraction of 1 mg/kg.

3.4 Correlations between contaminant concentrations and associated parameters

The entire data collective of results for the original sample was statistically checked for any generally valid associations between pollutants concentrations and associated parameters, using the Pearson correlation. 5% were chosen as the significant level ($s < 0.05$). A correlation was classed as relevant (in case of an existing significance) starting from a correlation coefficient of $r > 0.7$, as this correlation would then represent a variation of readings of $r^2 > 0.49$, of which at least 50 % would be declared.

Because of the considerable difference in size of analysed surface waters and consequently considerably differing discharges (Rhine = 2300 m³, Erft = 17 m³ average flow rate), potential correlations between flow rates and heavy-metal concentrations could not be analysed on a valid footing for the entire database. For easier comparison of results, a relative flow rate (RelAbfl) was calculated for individual monitoring stations, based on the following formula

RelAbfl = actual flow (at PN) / average flow (station) * 100 .

Increased flow rates were thus incorporated in correlations where figures exceeded 100% of the average flow rate.

3.5   Balancing of heavy metal quantities in various matrixes

Balancing is used to check and confirm readings. In this project, balancing plays an important role for the plausibility test for contaminant concentrations in individual matrixes. The following applies to the said checks:

Conc. in OP (mg/l) = Conc. Fil (mg/l) + Conc. SS (mg/kg) x SS quantity (kg/l)

The balancing is, however, made more difficult as a result of several sources of error during sampling and the type of analysis, caused by metal contaminations that are difficult to quantify, and losses of concentration.

a) Original sample :	Low risk of contamination
	Snapshot (seconds)

b) Filtered sample :	High risk of contamination and error
	Highest risk during filtration step
	Contamination and/or adsorption on filter
	Adsorption on surface of sample container as sample may not be preserved prior to filtration. Where applicable, concentration-lowering effects of delayed filtration
	Snapshot (seconds)

c) Water exiting centrifuge :	Snapshot (seconds)
	Contamination through centrifuge equipment

d) Centrifuged suspended matter:	Contamination through centrifuge equipment, in particular Al, Fe, Ni, Cu
	Integrated average (12-48 h)

One balancing approach is based on metal concentrations measured in the original sample (Metkonz-OP) and in the filtered sample (Metkonz-Fil). As during filtration of the water sample by a membrane filter (limited filtration volume) insufficient suspended matter material remains in the filter cake (Metkonz-SS) for analytic determination of the particle-bound part of the water sample, this is calculated from the following difference

MetKonz-OP – MetKonz-Fil = MetKonz-SS.

A second balancing approach is based on metal concentrations in suspended matter volumes MetZent-SS obtained by centrifugation, concentrations of FSS (filterable suspended solids) and metals exiting the centrifuge (MetKonz outflow) and in the original sample.

Metconc.outflow (mg/l) + MetZent-SS (mg/kg) x FSS volume (kg/l)

As both the original sample and discharge sample are random samples, whilst centrifugation integrates suspended matter loads over a period of up to 42 hrs., additional balancing differences may be caused by fluctuations of the load of

partial compartments over time. In order to determine the magnitude of potential error sources, differences versus original samples were determined.

Difference = OP concentration - (calculated of concentration in outflow water + concentration part of the filtered-out suspended matter volume/l)..

Analyses were regarded to be valid when the difference of different balancing approaches was less than 20%.

4 Results

An important analysis target was the observation of general associations in all surface water systems between the proportions of respective specific contaminant loads in different matrixes of a water sample. Amongst other things, it was examined whether concentrations in other matrixes could be estimated based on contaminant concentrations in an analysed matrix. In principle, a statistical analysis generated of the entire data collective was therefore made.

Analysis results are evaluated in several steps, separated by contaminant groups and matrixes. Established, typical associations were described and graphically illustrated, using results representative for individual monitoring stations.

4.1 Heavy metals

The spread, presence and bio-availability of heavy metals in surface waters are affected to a considerably degree by metal characteristics and thus also by distribution between the dissolved and particulate phase.

In order to asses the metal distribution to acqueous and suspended matter phases and the chemical/physical conditions of surface waters affecting distribution, the determination of metal concentrations in the original sample and the filtrate is of considerable significance (ARGE ELBE 1998 & 2003; MERIAN 1991).

4.1.1 Filtration tests of the original sample

4.1.1.1. Minimization of filtration blind values

Preliminary tests and initial results of the project, clearly indicated the necessity of filtration taking part as close to the time of sampling as possible. This will require special care during sampling, as an increased risk due to various contamination and error sources exists, which must be minimized.

Potential sources of contamination are checked step by step. Laboratory equipment, bottles, ultrapure water and acids used were checked for potential contamination. Results lead to the recommendation of using fresh ultrapure water for rinsing prior to each sampling cycle and for determining a blind value. The low-contamination method used as part of the project for in-situ filtration, is described in chapter 3.2.2 (p. 31).

Examination of the membrane filter used under routine sampling conditions (cellulose nitrate; 0.45µm, Satorius, No. 11308) showed that irregular contamination of the filter by specific elements had occurred in some batches. In addition to highly contaminated filters, the same batch also contains significantly less contaminated filters (Fig. 4.1.1-1). Maximum blind values were determined for zinc, although considerable nickel and copper contaminations were also found. Blind values for cadmium, lead und mercury were generally lower than the lower application limit.
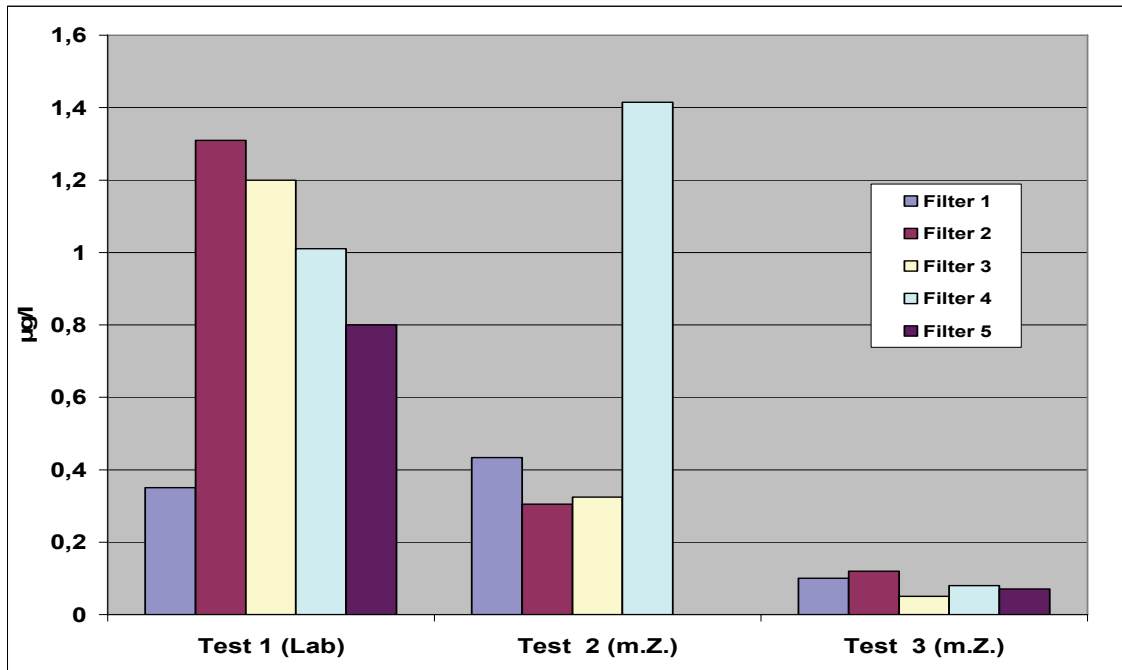
Fig. 4.1.1-1: Blind values of unrinsed filters for nickel (DL=0,1 µg/l) based on routine sampling conditions. Three filtration attempts using the apparatus by Witt and in each case four or five membrane filters from the same batch.
Test site : Lab : Düsseldorf lab, m.Z.: mobile centrifuge

In addition, it was also checked whether filtration blind values could be reduced by pre-rinsing filters and filter equipment several times. All tests were carried out on the same filter batch and the same apparatus by Witt. For the test, ultrapure water was filtered by the filter in two rinsing cycles and filtrates obtained were analysed. Examination of rinsing and/or flushing effects of the apparatus by Witt and filter confirmed irregular contamination of filters.
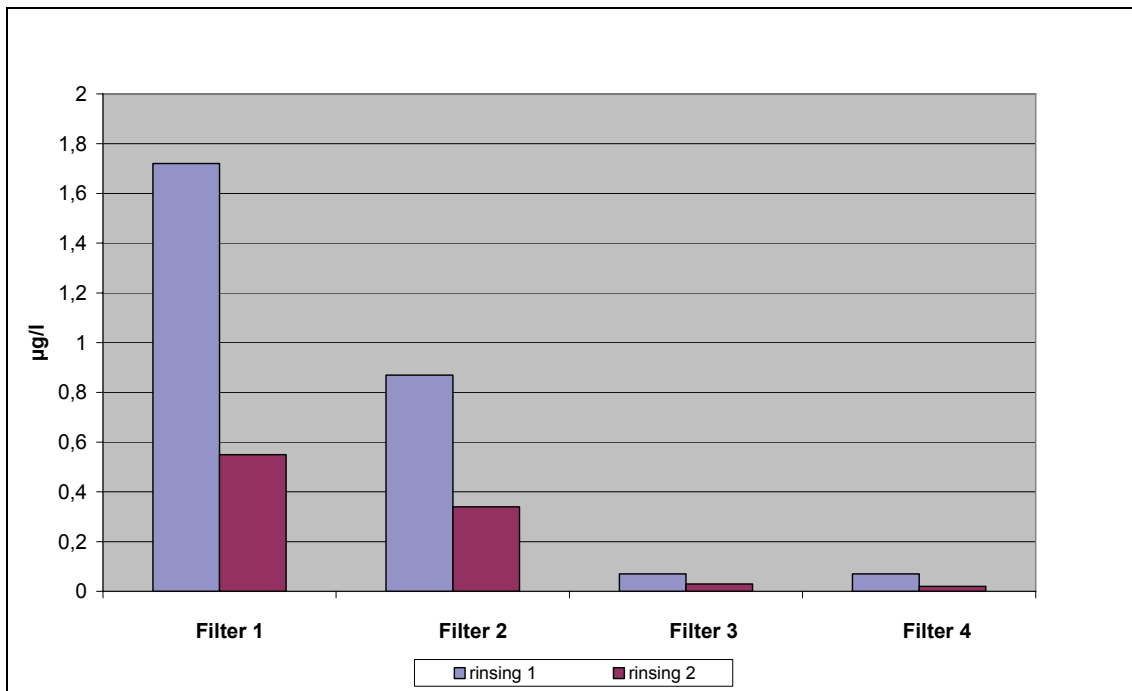
Fig. 4.1.1-2: Blind nickel values after first and second rinsing of the Apparatus by Witt and membrane filter. Results of individual filters.

These rinsing attempts show that by rinsing the equipment and filter twice, tolerable blind values may be achieved (Figs. 4.1.1-2). As a result of the blind value issue, filtration blind values of up to 20% of half the quality target were accepted after double flushing. This convention of the project has by now been incorporated in national SAA "in-situ filtration" as part of EU monitoring.

4.1.1.2   Comparison of different filtration methods

The question is what filtration method is best suited for monitoring dissolved heavy-metal fractions. For routine monitoring of surface waters and/or discharges, both pressure filtration and vacuum filtration is used. Prior to the project, potential effects of pressure and vacuum filtration on lead, cadmium and nickel subject to routine sampling conditions were tested. Mercury could regularly not be detected in filtered samples and could therefore not be assessed.

As part of the filtration trial, heavy metal concentrations in the original sample ("total volume") and in the discharge water ("dissolved fraction") of the centri-

fuge were also analysed as comparative parameters. Ideally, the results of filtrations (higher degree of separation than by centrifugation) should have been lower than concentrations in the discharge water of the centrifuge. Metal contents of the filtrate exceeding concentrations in the original sample are a clear indication of contamination.

Figs. 4.1.1-3-4 show the results of a parallel application of "in-situ" pressure and vacuum filtration. In pressure filtration, all tested metals showed maximum average values and maximum standard deviations. Penetration of particles through the membrane filter may thus not be excluded during pressure filtration. At the same time, the evaluation of results for nickel showed clear indications of a possible contamination in the pressure-filtered sample versus the original sample.

Lead and cadmium showed no significant increases in concentrations due to pressure filtration, although there is an increased concentration tendency in this case.
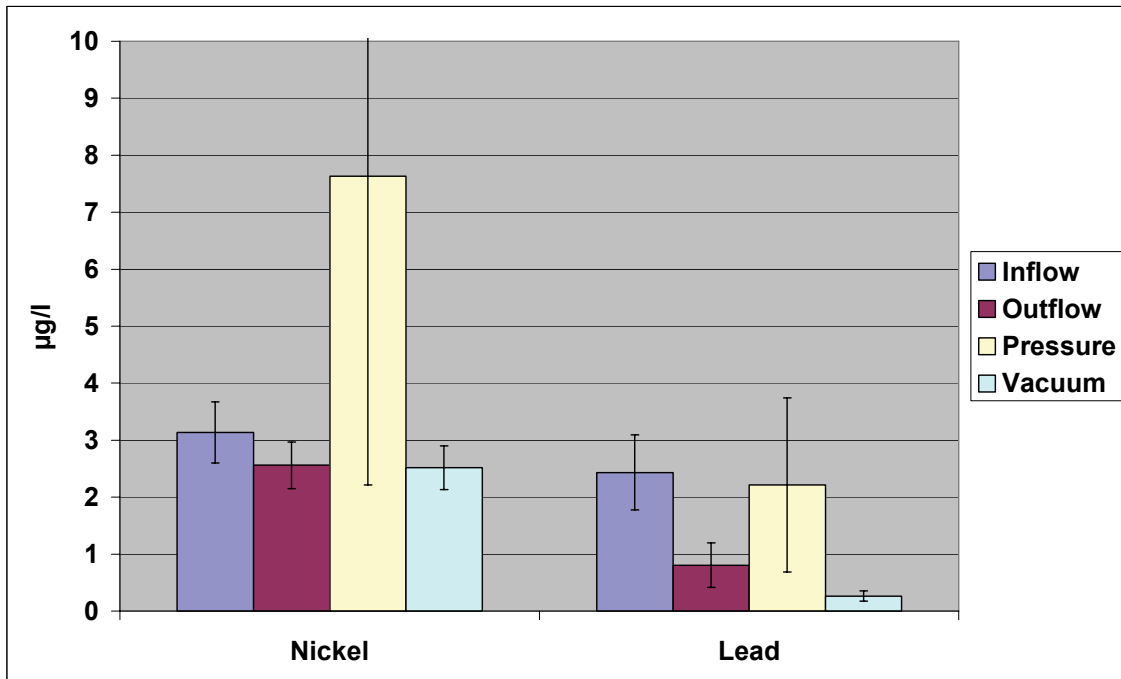
Fig. 4.1.1-3:   Comparison of pressure and vacuum filtration - example nickel and lead.
Averages of three successively removed samples (repeat tests in all cases) and standard deviation. Reference sizes:
Inflow and outflow of mobile centrifuge as control values for original sample and filtration.
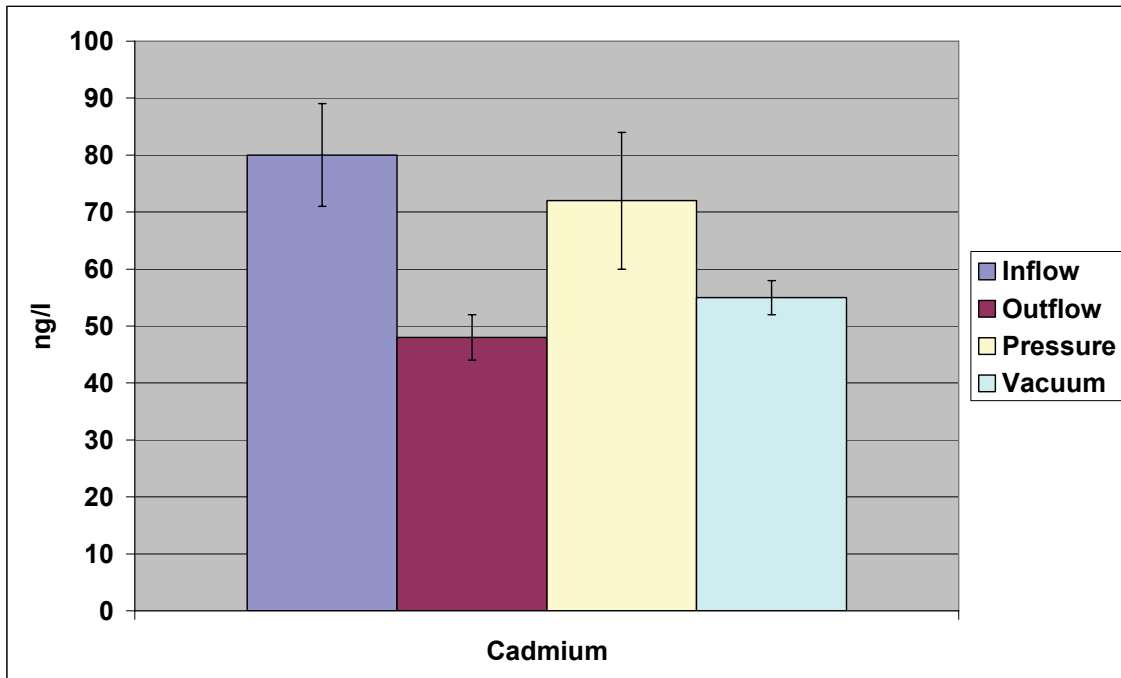
Fig. 4.1.1-4: Comparison of pressure and vacuum filtration – example: cadmium.
Averages of three successively removed samples (repeat tests in all cases) and standard deviation. Reference sizes:
Inflow and outflow of mobile centrifuge as control values for original sample and filtration.

After evaluation of results, a comparative test was carried out in-situ on the Wupper, involving sampling teams from four different laboratories, using four different filtration methods.

As part of the test, a water sample was taken in a 10-l homogenising container and split up into several samples. Apart from the apparatus by Witt (vacuum filtration) and pressure filtration, the teams also used syringe filters (e.g. Pall filters).

Findings confirmed results of preliminary trials. Pressure filtration showed significantly higher concentrations for elements such as Ni, Cr and Zn versus other methods (Figs. 4.1.1-7), whilst in the case of syringe filtration copper contamination must be suspected. Cadmium and lead showed no significant increases in concentration caused by these methods (Figs. 4.1.1-5 & -6).
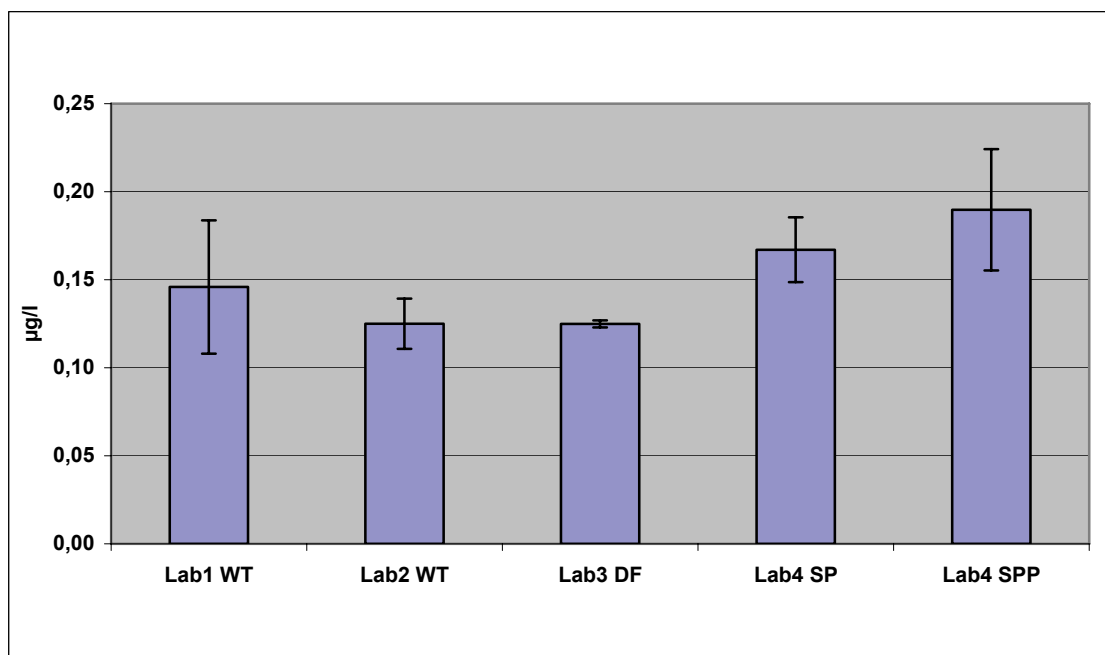
Fig. 4.1.1-5: Comparative test based on different filtration equipment: lead, averages of three parallel samples subject to standard deviation. In-situ filtration on the river Wupper.
WT=Apparatus by Witt, DF = pressure filtration, SP = Syringe filter, SPP (using Pall filter)
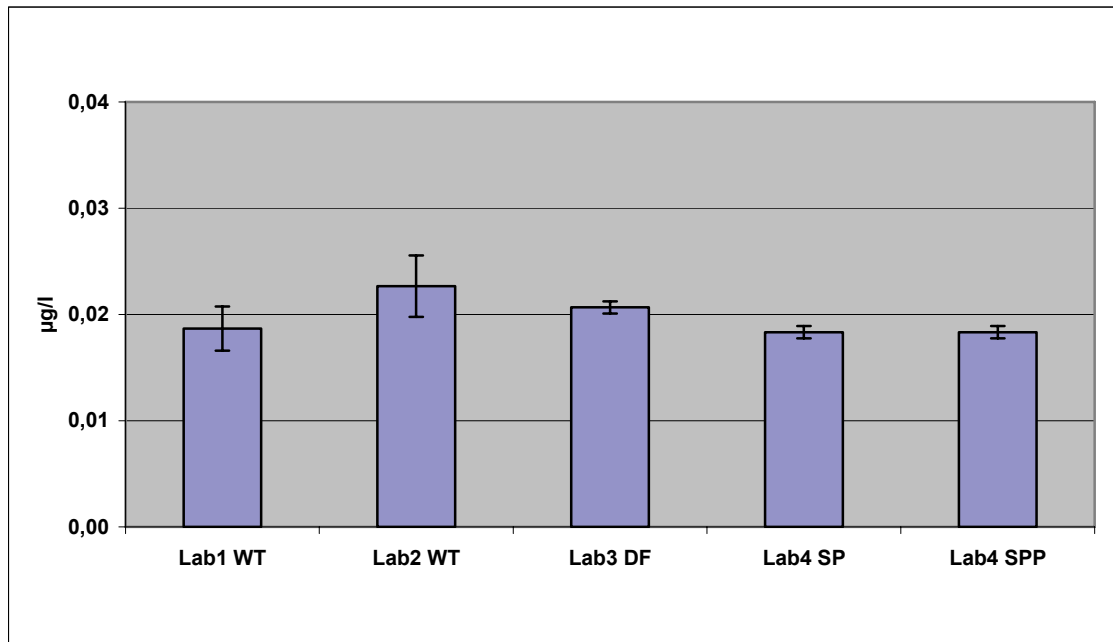
Fig. 4.1.1-6: Comparative test based on different filtration equipment: cadmium, averages of three parallel samples subject to standard deviation. In-situ filtration on the river Wupper. WT=Apparatus by Witt, DF = pressure filtration, SP = Syringe filter, SPP (using Pall filter)
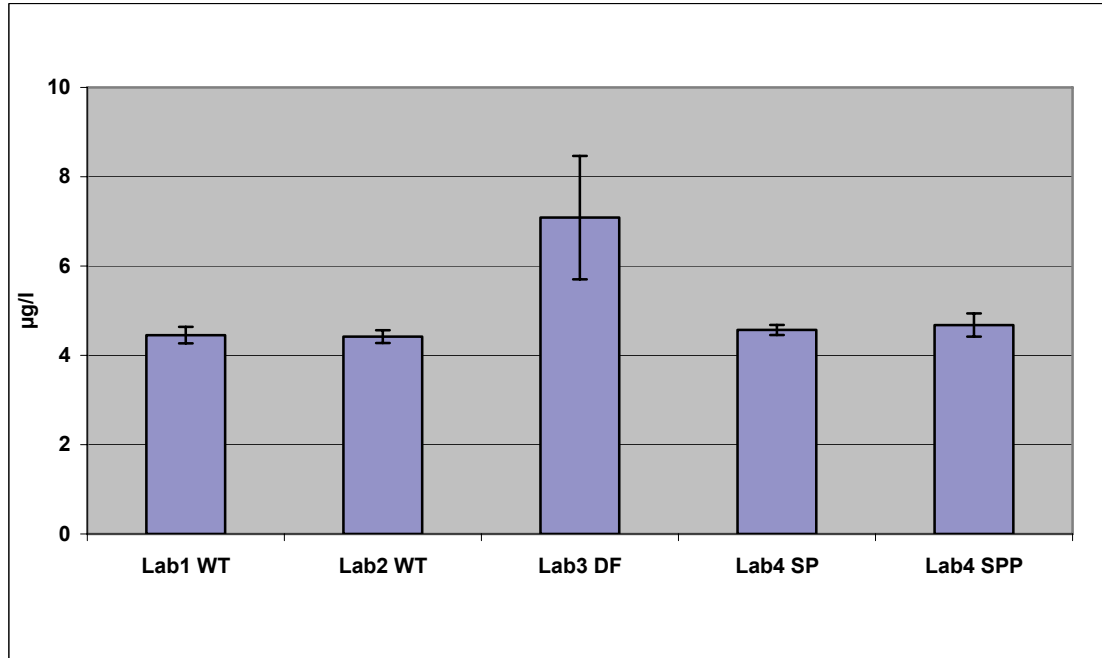
Fig. 4.1.1-7: Comparative test based on different filtration equipment: nickel, averages of three parallel samples subject to standard deviation. In-situ filtration on the river Wupper.
. WT=Apparatus by Witt, DF = pressure filtration, SP = Syringe filter, SPP (using Pall filter)

By using a apparatus by Witt for vacuum filtration, contamination caused by unnecessary transfers of sample material is avoided, as direct filtration into the tube (centrifuge tube), used for ICP-MS analysis, is possible.

4.1.1.3 Changes in concentration as a result of a delayed filtration start

Dissolved inorganic heavy metal ions (metal-specific) tend to have different levels of surface adsorption. Whilst in each case a relatively stable solution equilibrium has settled in the analysed surface water, there is a risk of some of the dissolved metals being adsorbed on the walls of the sampling bottle immediately after sampling. As a result, concentration of present dissolved metal fractions (and thus also concentration in the original sample) is reduced.

In order to prevent these losses in the original sample, samples are generally stabilized with acid. This acidification prevents adsorption but also transfers some of the particle-bound metal fractions to the solution. Acidification is a suitable stabilization method for the original sample.

There are, however, problems for the type of analysis of dissolved metal fractions. Should sample conservation be waived, one may expect that adsorption effects cause reductions in the concentration of the dissolved phase (POHL 2002). On the other hand, acidification of a sample does also not achieve the desired result due to re-dissolution effects on particle-bound metal ions.

The time of sample filtration therefore plays an important role for monitoring dissolved metal fractions. Because of adsorption kinetics, adsorption effects are probably particularly intense after sampling (SCHMITT 2002). Consequently, the influence of the time difference between sampling and filtration cycles on heavy metal concentrations in the dissolved phase was monitored.

A large water sample was taken at seven different monitoring stations without any acid stabilisation and split into divided samples. One of the divided samples was immediately filtered "in-situ" after sampling. The sample was filtered again

after transportation to the laboratory in intervals of several hours to days. Analyses of samples were always carried out by repeat tests. For the rivers Niers and Wupper, the test was also repeated on other dates.

After a period of two hours, the filtrate already showed clear, statistically significant losses of concentration for metals such as lead and cadmium (Tab. 4.1.1-1; Figs. 4.1.1-8, 4.1.1-10). In the case of nickel, these loss effects occurred to a significantly lesser degree (Fig. 4.1.1-12). The effects were particularly clear in the case of high levels of suspended matter in the original sample (more than 15 mg/l). Adsorption losses may also be anticipated for mercury. These losses could, however, not be quantified, as concentrations in filtered water samples regularly lie below detection limits.

Tab. 4.1.1-1 Comparison of "in-situ"/laboratory filtration, results of t-test

t-test parameters	Pb	Cd	Ni
n	8	9	9
t_{krit}	2.37	2.31	2.31
t	4.13	4.25	2.83
Significance fulfilled?	**yes**	**yes**	**yes**

The time dynamics for concentration losses of lead and cadmium is apparent from the example of three divided samples taken in-situ in intervals of 15 minutes from the Niers, a stream subject to metal contamination and high in suspended matter (special test by LUA and StUA Düsseldorf, Niers downstream of Viersen). Maximum dissolved concentrations were in each case determined in a sample filtered directly after sampling. After 15 minutes, concentration losses of between 40 – 50 % already occurred. (Figs. 4.1.1-9; 4.1.1-11). Further reductions in concentration were moderate. Nickel showed low concentration losses of approx. 10% and a more linear course of adsorption. (Fig. 4.1.1-13).

Illustrated events demonstrate that in case of delayed filtration considerable concentration losses for dissolved fractions of lead and cadmium cannot be excluded, in particular in the case of samples of a high suspended matter content.
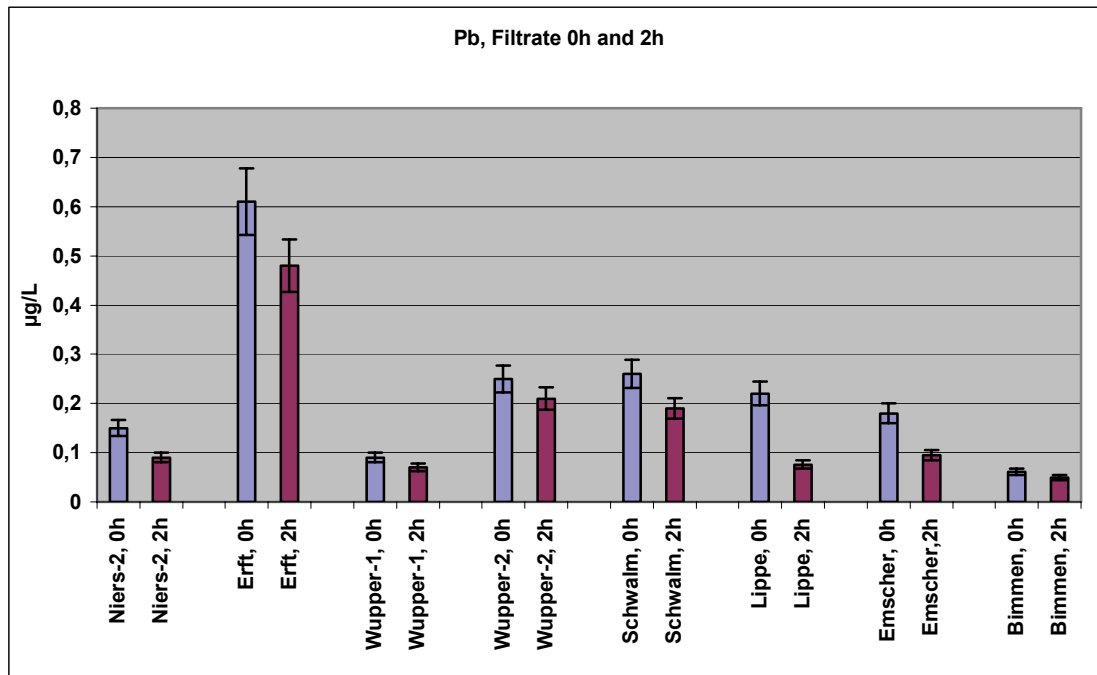
Fig. 4.1.1-8: Development of lead concentrations after immediate "in-situ" filtration and after two hours. Concentrations in divided samples (repeat test) based on extended measuring uncertainty (U). Samples from the rivers Niers and Wupper 1, 2 taken on different days
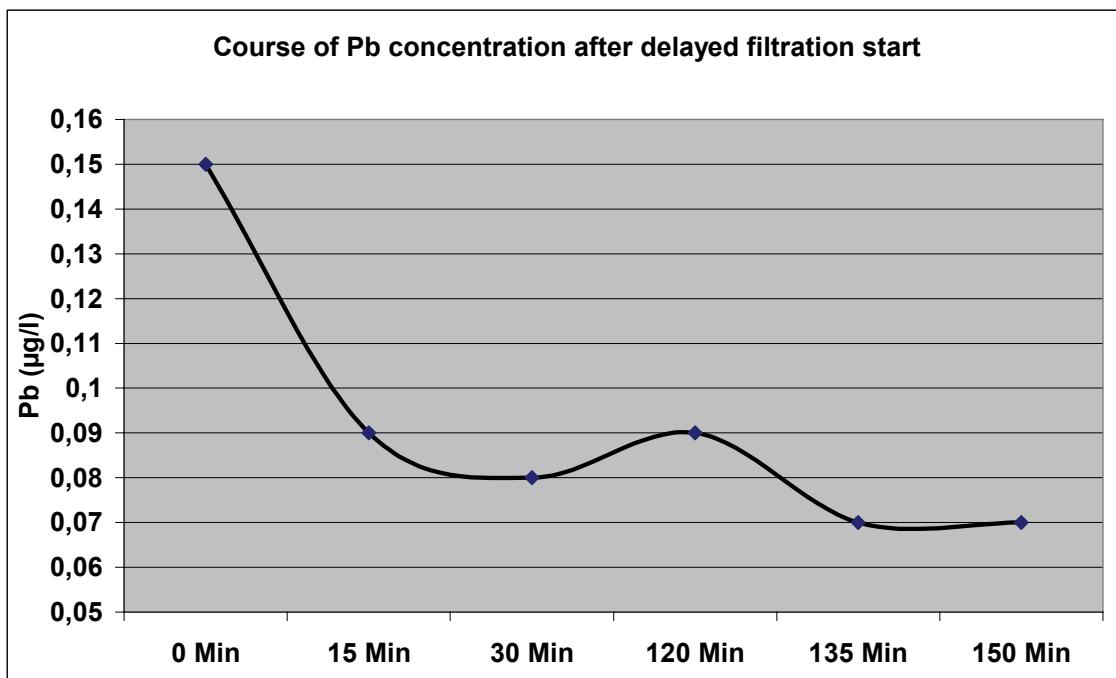
Fig. 4.1.1-9: Development of dissolved lead concentration in samples taken from contaminated surface water (river Niers downstr. of Viersen, sample Niers 1) after immediate filtration and delayed filtration (individual samples, repeat test).
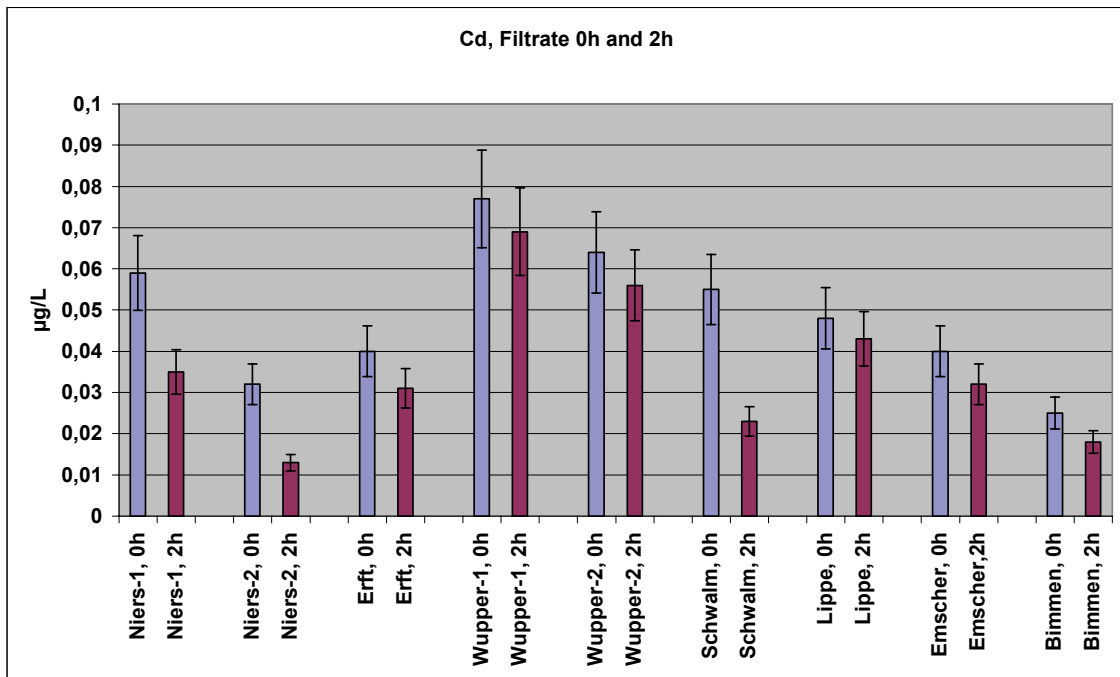
Fig. 4.1.1-10: Development of cadmium concentrations after immediate "in-situ" filtration and after two hours. Concentrations in divided samples (repeat test) of extended measuring uncertainty (U). Samples from the rivers Niers and Wupper 1, 2 taken on different days.
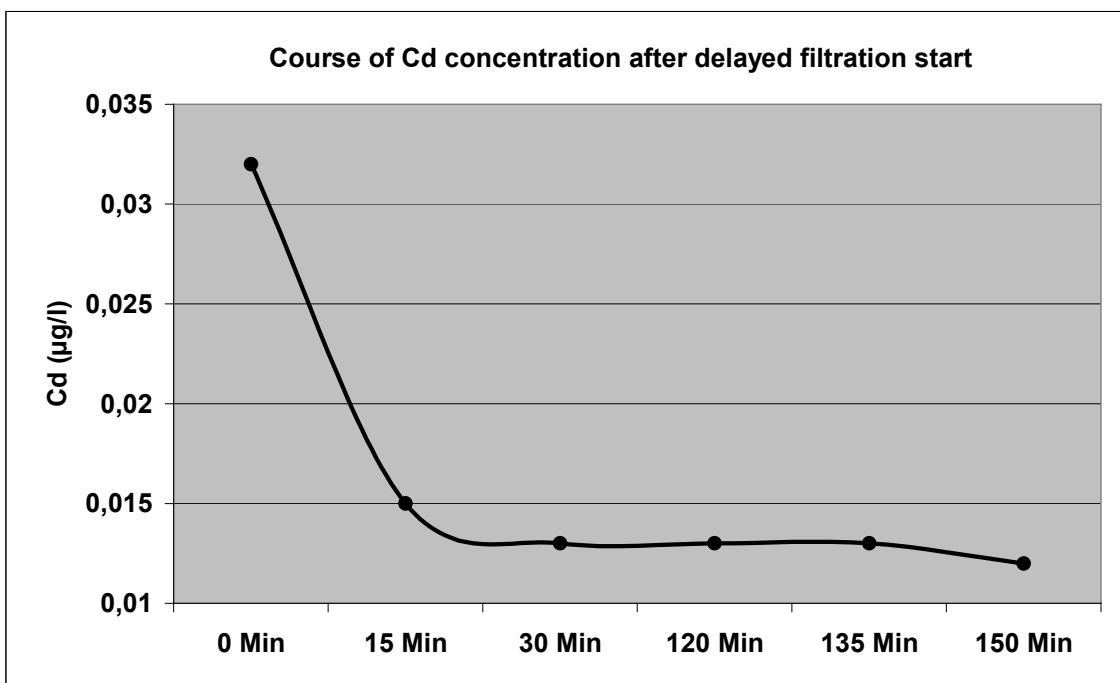
Fig. 4.1.1-11: Development of dissolved calcium concentration in samples taken from contaminated surface water (river Niers downstr. of Viersen, sample Niers 2) after immediate filtration and delayed filtration (individual samples, repeat test).
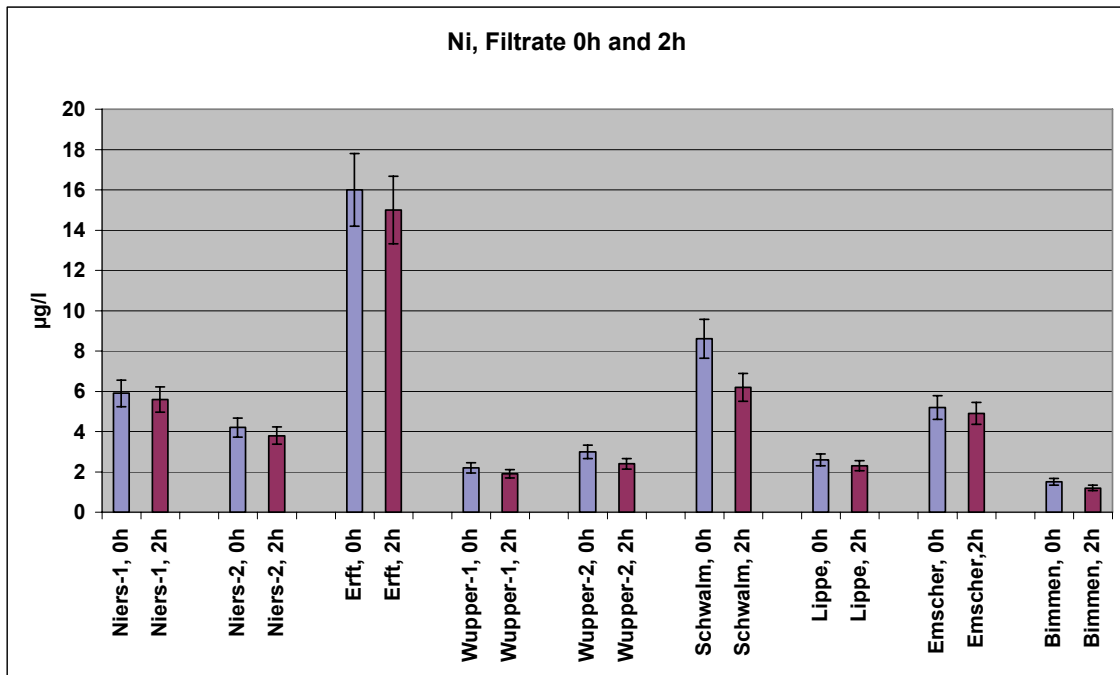
Fig. 4.1.1-12: **Development of nickel concentrations after immediate "in-situ" filtration and after two hours.** Concentrations in divided samples (repeat test) of extended measuring uncertainty (U). Samples from the rivers Niers and Wupper 1, 2 taken on different days.
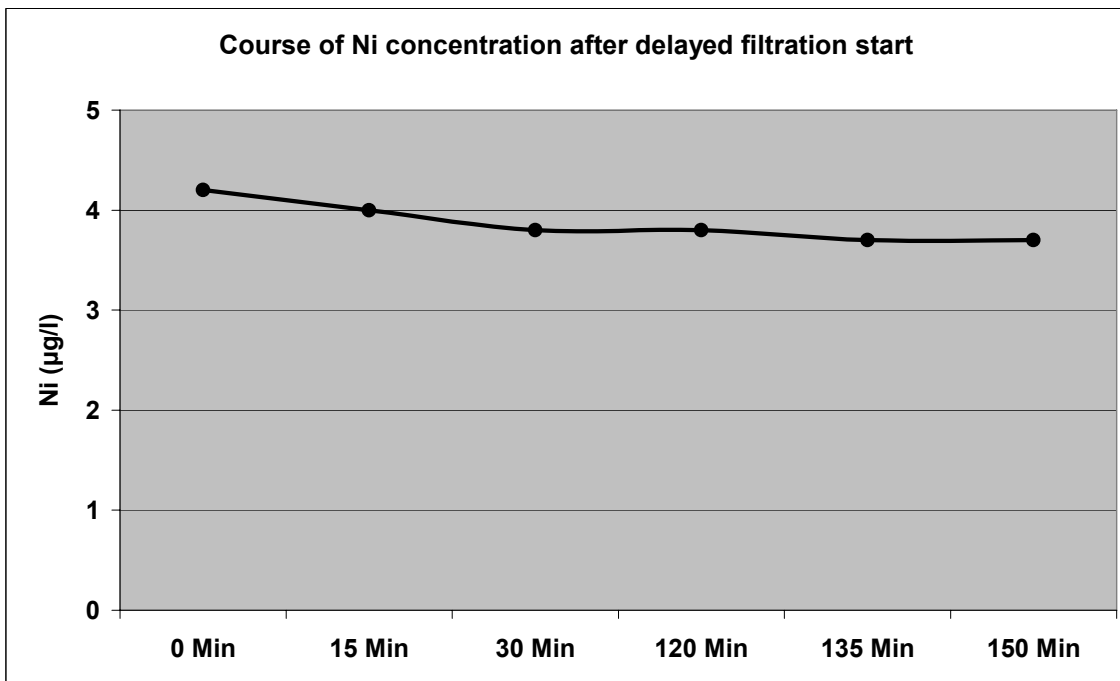
Fig. 4.1.1-13: **Development of concentration of dissolved nickel in samples taken from contaminated surface water (river Niers downstr. of Viersen, sample Niers 2) after immediate filtration and delayed filtration (individual samples, repeat test).**

4.1.2 Heavy metal concentrations at monitoring stations

4.1.2.1 Heavy metal concentrations in original sample

The method used for analysing the original sample (unfiltered water sample) is simple and also caries the lowest risks of contamination. Metal concentrations in surface waters of the densely populated and industrialised Rhine catchment area can be easily monitored by the detection limits of the ICP-(OES or MS) method.

Tab. 4.1.2-1 and Figs. 4.1.2-1 to -4 show the summarized results of the analysis for prioritary heavy metals in the original sample of individual monitoring stations. In addition, the results of sampling subject to increased discharges (end of August 2005 and Mach 2006) were included in the evaluation.

The following results were obtained from the evaluation of all data records :

1. Metal discharges from the densely populated and industrialised river Rhine catchment area are reflected at the international monitoring station (IMBL), Bimmen in its generally higher metal concentrations than in the Bad Honnef monitoring station.

2. Versus its tributaries, the river Rhine shows lower fluctuation amplitudes in its metal concentrations. The tributaries of the Rhine regularly show a higher contamination than the Rhine.

3. The contaminant load at monitoring stations is clearly subject to time-related fluctuations. This is partly due to different discharge volumes, fluctuations in suspended matter contents and discontinuous contaminant additions (e.g. higher metal contamination with increasing additions).

4. The tributaries Wupper and Erft show the greatest fluctuation range for metal concentrations. For the river Erft, particularly high and strongly fluctuating lead and cadmium contaminations are apparent.

5. Concentrations of mercury were frequently close to or below detection limits. Average concentrations at monitoring stations therefore show higher standard deviations.

6. Results for the river Emscher show a highly contaminated surface water system, the discharge of which predominantly consists of treated municipal and industrial wastewater.
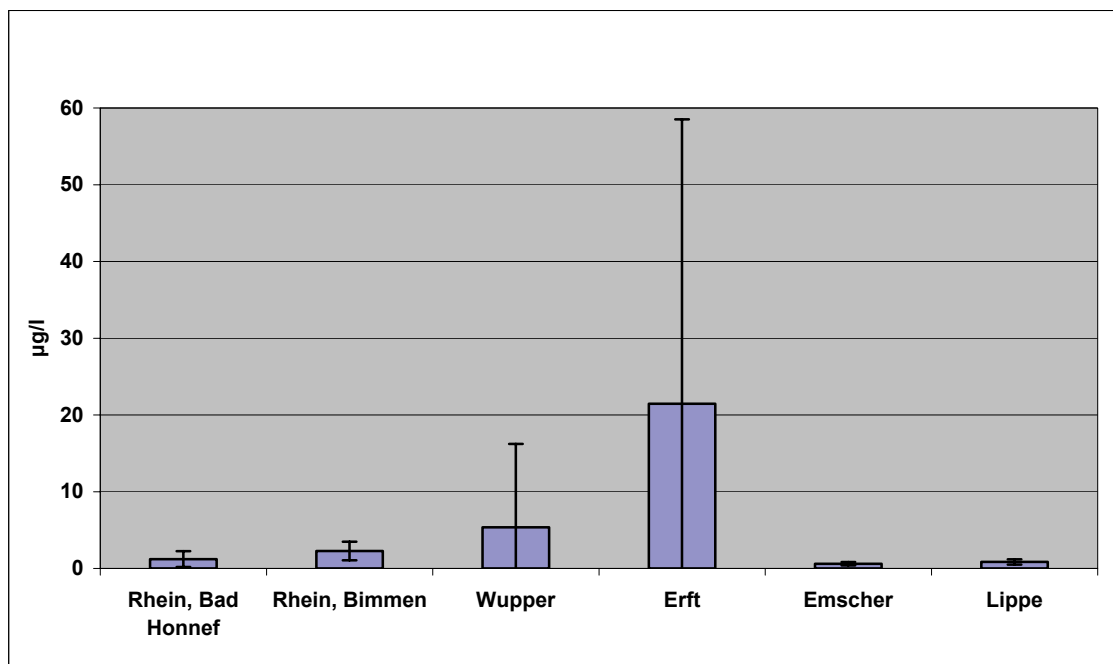
Fig. 4.1.2-1: Lead in the original sample. Average concentration values and standard deviation for all monitoring stations

Tab. 4.1.2-1: Characteristic values for heavy metal concentrations in original samples

Ort	n	MW	ST. D.	CV %	Median	1st quarter	3rd quarter	Min	Max
					Lead [µg/l]				
HON	12	1.22	1.04	85	0.77	0.70	1.30	0.41	4.20
BIM	12	2.27	1.22	53	1.90	1.65	2.51	0.96	5.30
WUP	11	2.05	0.98	48	1.55	1.33	2.33	1.20	3.85
ERF	9	23.7	37.9	160	9.90	3.10	17.05	2.15	118.0
EMS	11	0.65	0.24	37	0.59	0.49	0.80	0.31	1.03
LIP	10	1.16	1.03	89	0.91	0.64	1.09	0.32	3.95
					Cadmium [ng/l]				
HON	12	31	12	39	30	24	31	19	66
BIM	12	56	21	38	54	44	63	30	113
WUP	11	73	11	16	72	68	78	49	90
ERF	9	343	563	164	125	51	218	40	1745
EMS	11	53	26	49	47	40	49	38	130
LIP	10	87	14	16	86	81	94	62	110
					Nickel [µg/l]				
HON	12	2.13	1.07	50	1.75	1.55	2.35	1.30	5.10
BIM	12	2.69	0.83	31	2.53	2.29	2.75	1.70	4.45
WUP	11	2.89	0.44	15	2.85	2.78	3.08	2.00	3.80
ERF	9	32.34	50.37	156	13.50	5.90	24.80	3.80	160.00
EMS	11	7.64	2.53	33	6.70	6.23	7.83	6.05	14.50
LIP	10	3.40	0.80	24	3.05	2.91	3.64	2.70	5.30
					Mercury [ng/l]				
HON	12	12	13	108	6	6	10	5	45
BIM	12	17	7	44	14	12	24	8	29
WUP	11	18	12	68	14	12	28	3	40
ERF	9	19	23	119	8	8	12	6	72
EMS	11	7	10	138	3	3	6	3	35
LIP	10	11	5	42	11	7	16	6	18

HON = Rhine, Bad Honnef; BIM = Rhine, Bimmen; WUP = Wupper; ERF = Erft; EMS = Emscher; LIP = Lippe
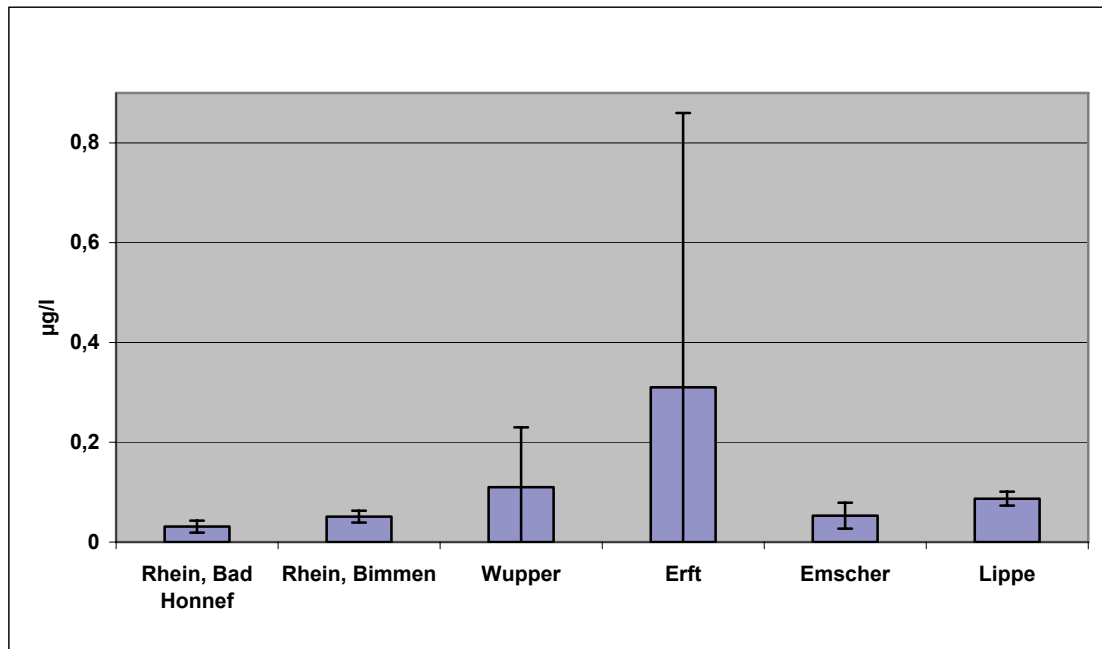
Fig. 4.1.2-2: Cadmium in original sample. Average concentration values and standard deviation for all monitoring stations
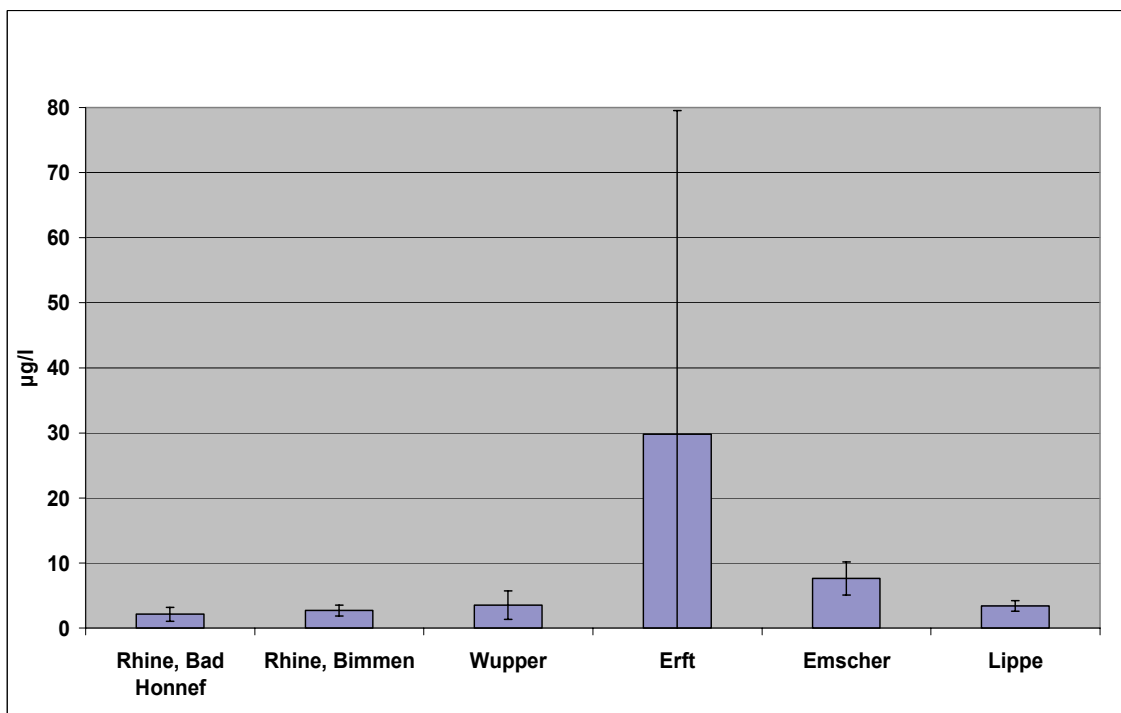
Fig. 4.1.2-3: Nickel in original sample. Average concentration values and standard deviation for all monitoring stations
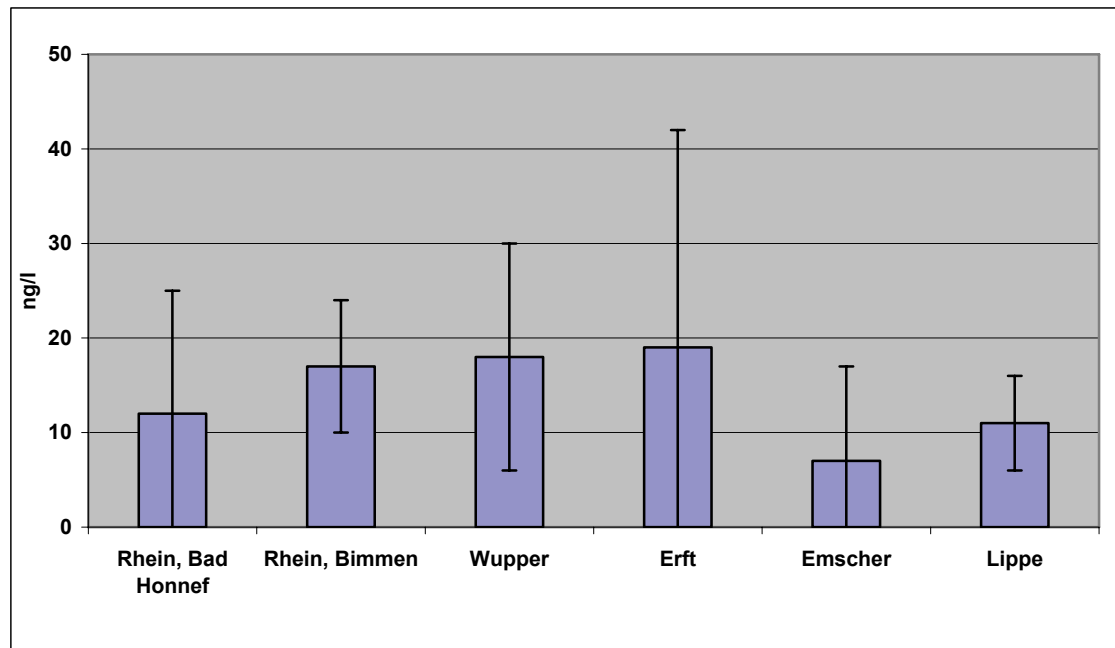
Fig. 4.1.2-4:   Mercury in original sample. Average concentration values and standard deviation for all monitoring stations

Interactions between metal concentrations in original samples and associated parameters

Determined heavy metal data were correlated with measured associated parameters (FSS, conductivity and others) (Tab. 4.1.2-2).

Tab. 4.1.2-2: Correlation of metal concentrations / associated parameters in original sample

	OP-Pb	OP-Cd	OP-Ni	OP-Hg
FSS	r = 0.902 s <0.0001	r = 0.896 s <0.0001	r = 0.895 s <0.0001	r = 0.696 s <0.0001
Conductivity	--	--	--	r = -0.250 s = 0.0480
Chloride	--	--	--	r = -0.297 s = 0.0162
Potassium	--	--	--	r = -0.253 s = 0.0370
Sodium	--	--	--	r = -0.306 s = 0.0131

n = depending on parameters of 54 – 65, grey and bold: relevant correlation

Filterable suspended solids (FSS)

For the entire data collective, positive significant and relevant correlations between metal concentrations in original sample and the volume of filterable suspended solids (FSS) were established. The said correlations may also be shown by individual monitoring stations.

In parallel to suspended matter sampling (centrifugation run), unfiltered water was taken as a mixed sample and two random samples (from the beginning and end of the centrifugation cycle). Figures 4.1.2-5 – 7 show concentrations in the mixed sample and averages of random sample concentrations together with filterable suspended solids.

Concentrations in the mixed sample and averages of both random samples often contain small irregular, fluctuating differences caused, amongst other things, by time-related fluctuations in the metal concentrations of surface waters.

In the case of two samplings showing parallel increased metal concentrations and filterable suspended solids (end of August 2005 and March 2006), increased discharges were observed at the monitoring stations.

For mercury, the data of individual monitoring stations often showed a weak or no correlation. The reason for this were very low mercury concentrations within

the range of detection limits (DL), therefore causing greater measuring uncer-
tainties. Values below DL were replaced by half the DL during analyses. In
some cases larger differences existed for mercury between random and mixed
samples. In general, mercury concentrations in mixed samples were lower than
in (immediately preserved) random samples. This was probably due to adsorp-
tion processes on the tube walls of the mixing sample collector.
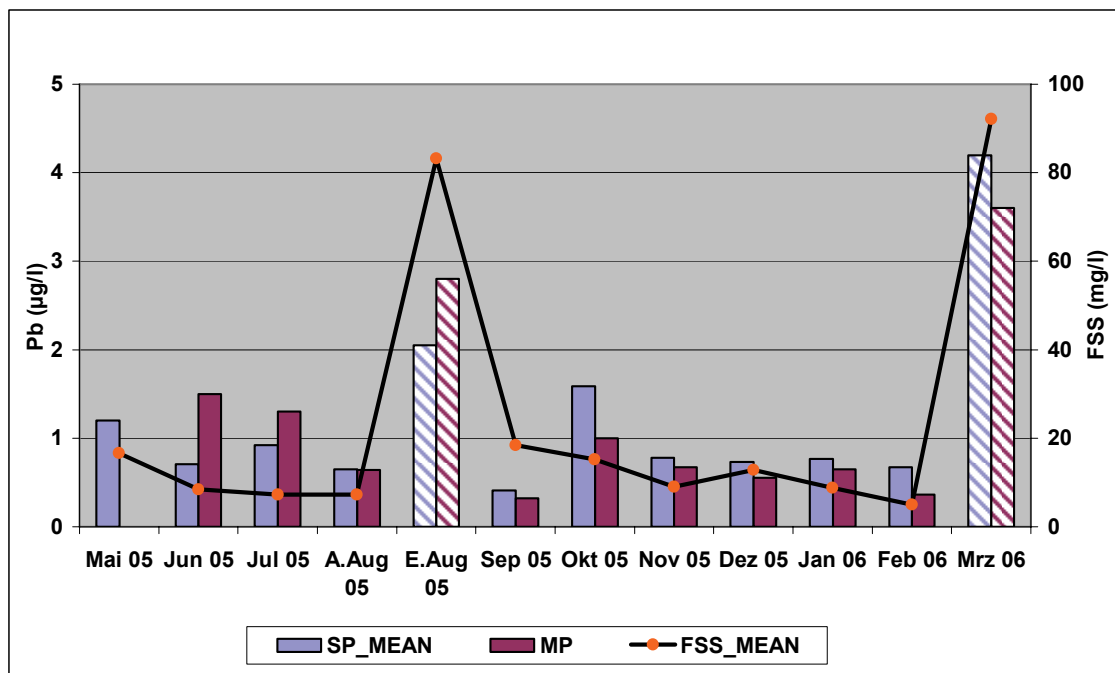
**Fig. 4.1.2-5: Concentrations of lead and filterable suspended solids in original sample
depending on sampling time at the Bad Honnef (Rhine) station** SP_MEAN = Average value from
two random samples; MP = Mixed sample; FSS_MEAN = Average value for filterable suspended solids; A. Aug. =
beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges.
Stat. parameters : r = 0.9; s <0.0001
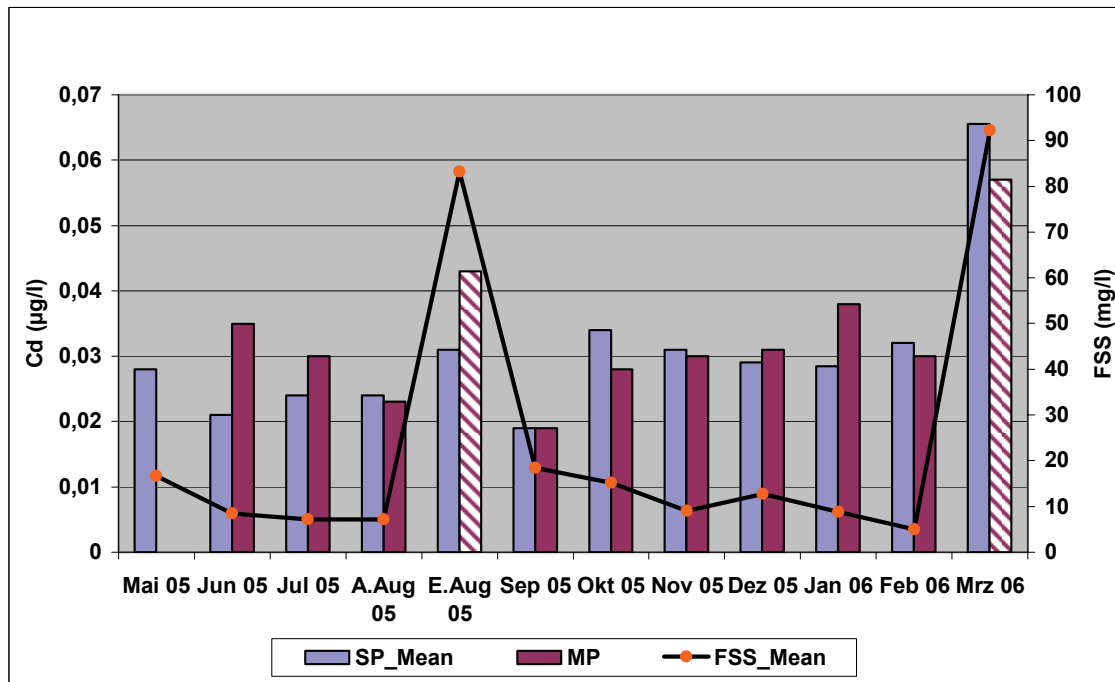
Fig. 4.1.2-6: Concentrations of cadmium and filterable suspended solids in original sample dependent on sampling time (Bad Honnef, Rhine) SP_MEAN = Average value from two random samples; MP = Mixed sample; AFS_MEAN = Average value for filterable suspended solids; A. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges.
Stat. parameters : r = 0.73; s = 0.007
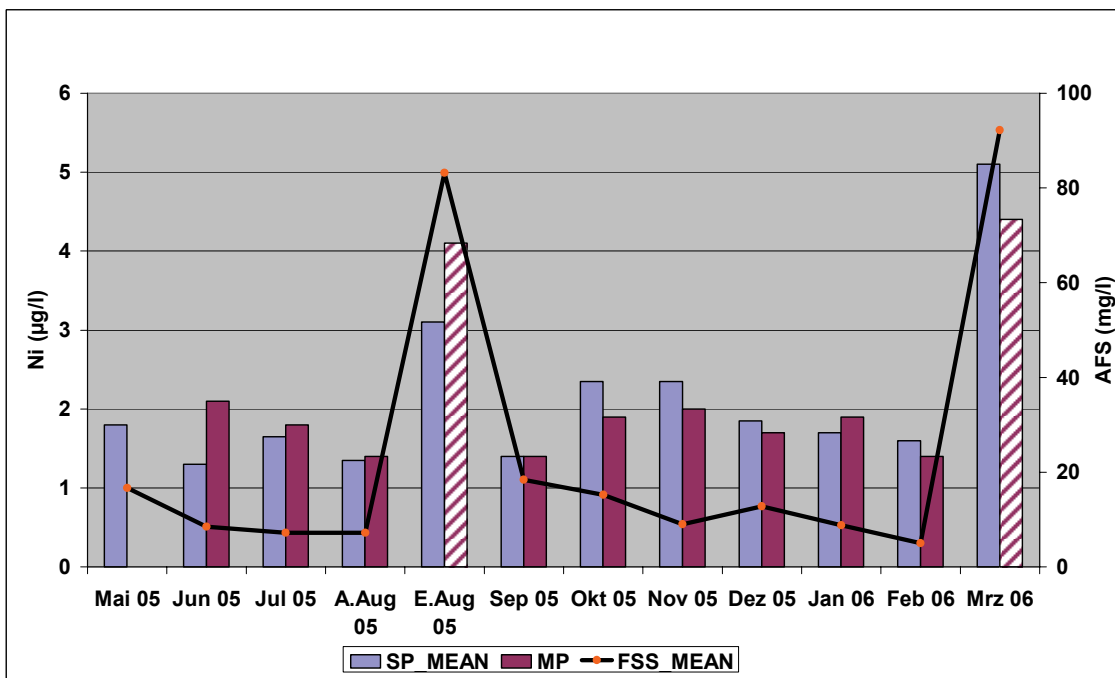
Fig. 4.1.2-7: Concentrations of nickel and filterable suspended solids in original sample in dependence of the sampling time (Bad Honnef (Rhine) SP_MEAN = Average value from two random samples; MP = Mixed sample; AFS_MEAN = Average value for filterable suspended solids; A. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges. Stat. parameters : r = 0.9;s <0.0001

Discharge

Analysis of the entire data collective showed no significant correlation to the relative discharge for prioritary metals. An analysis based on individual monitoring stations showed, however, positive, highly significant and relevant connections between lead, cadmium and nickel concentrations and respective discharges (Figs. 4.1.2-8 -10).
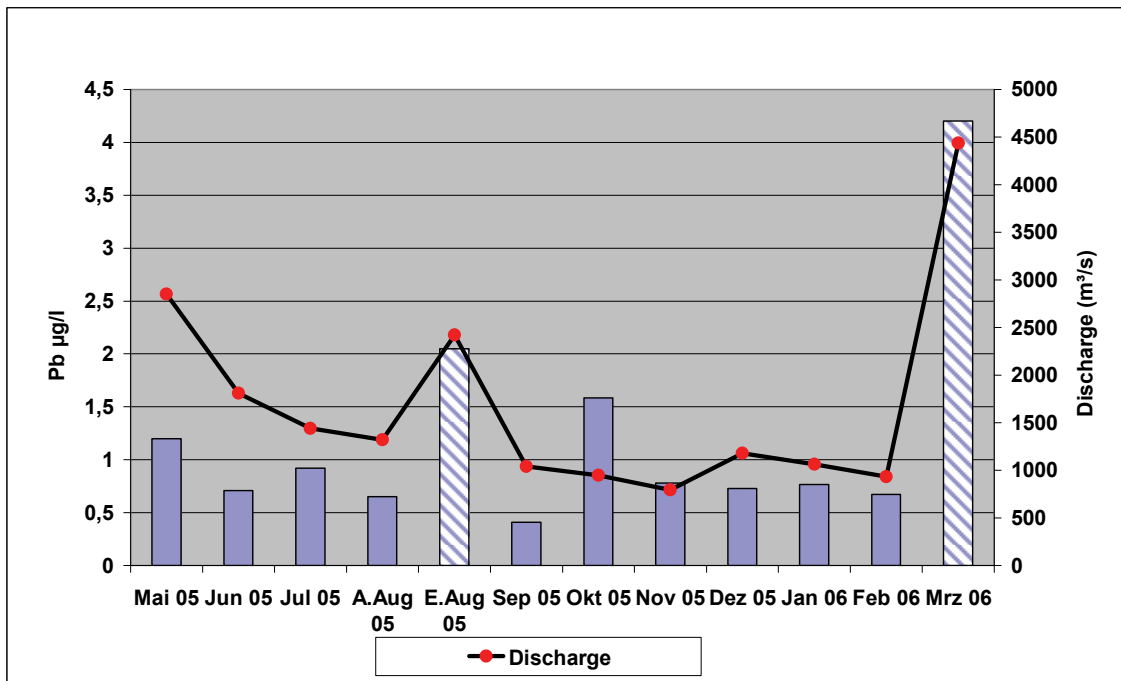
Fig. 4.1.2-8: Concentrations of lead in the original sample and flow volume depending on sampling time at the Bad Honnef station (Rhine). S. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges. Stat. parameters: r = 0.88; s = 0.0002
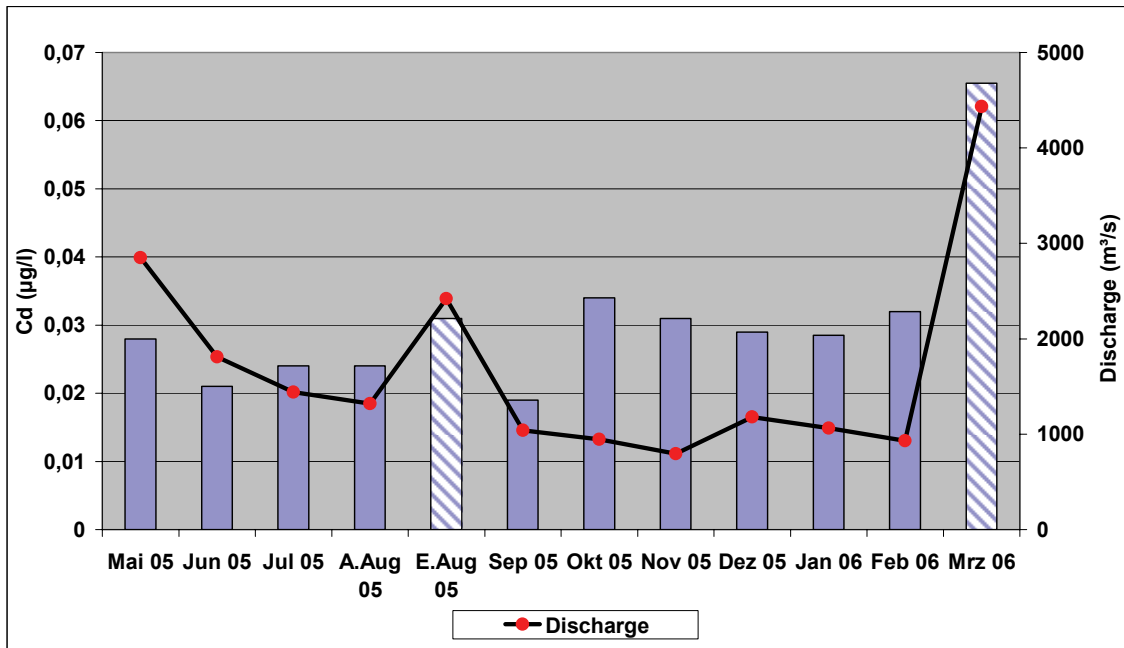
Fig. 4.1.2-9: Concentrations of cadmium in the original sample and flow volume depend-ing on sampling time at the Bad Honnef station (Rhine). S. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges. Stat. parameters: r = 0.77; s = 0.003
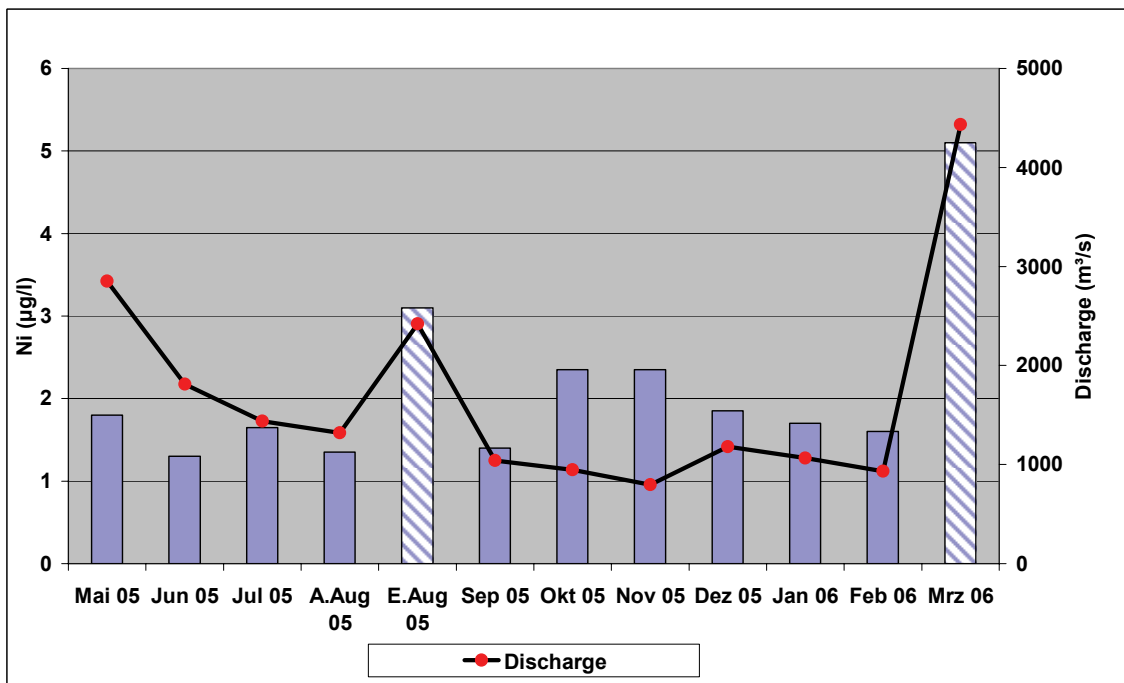
Fig. 4.1.2-10: Concentrations of nickel in the original sample and flow volume depending on sampling time at the Bad Honnef station (Rhine). S. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges. Stat. parameters: r = 0.88; s = 0.0002

Conductivity, saline-specific ions

For mercury, significant negative correlations were established with conductivity and saline-specific ions (chloride, potassium, sodium), which were, however, classed as irrelevant due to low correlation coefficients.

4.1.2.2 Heavy-metal concentrations in filtered water sample

In parallel to respective original samples (random samples), concentrations of heavy metal were analysed in filtered water samples. Preliminary tests of the project showed that as a result of adsorption processes, considerable losses of lead and cadmium concentrations could occur even after short transportation times (see chapter 4.1.1.3). Filtration should therefore be carried out directly "in-situ", immediately after sampling.

The parameters of metal concentrations measured in filtered samples, have been compiled in Tab. 4.1.2-3. Figs. 4.1.2-11 to -13, contain a graphic representation. Detection of mercury in filtered water samples is generally not even possible when surface waters are contaminated (DL: 5 ng/l).

Comparison of minimum and maximum metal concentrations in a filtrate and original sample showed lower fluctuations for filtrates. In the case of predominantly particular-bound lead, this difference is especially pronounced, probably due to different FSS volumes in the original sample:

	Lead concentrations	Minimum	Maximum	Factor
Erft	**Original sample**	**2.15 µg/l**	**118 µg/l**	**20**
	Filtrate	**0.06 µg/l**	**0.44 µg/l**	**6**

Tab. 4.1.2-3: Parameters of heavy metal concentrations in filtered sample

				Lead [µg/l]				
Location	n	AV	ST. D.	CV %	Median	1. quarter	3. quarter	Min	Max
HON	12	0.08	0.04	50	0.07	0.05	0.11	0.03	0.15
BIM	12	0.07	0.03	47	0.07	0.05	0.09	0.03	0.12
WUP	11	0.25	0.18	73	0.22	0.12	0.28	0.05	0.60
ERF	9	0.13	0.12	90	0.09	0.08	0.12	0.06	0.44
EMS	11	0.14	0.11	76	0.11	0.08	0.14	0.05	0.43
LIP	10	0.08	0.04	57	0.06	0.05	0.10	0.03	0.17
				Cadmium [ng/l]				
HON	12	18	5	26	19	14	20	10	25
BIM	12	26	6	24	27	23	30	14	38
WUP	11	51	8	15	54	48	56	33	59
ERF	9	25	18	70	20	16	20	15	71
EMS	11	51	36	70	43	38	45	30	158
LIP	10	60	10	17	65	54	67	42	70
				Nickel [µg/l]				
HON	12	1.11	0.36	32	1.18	1.09	1.30	0.10	1.45
BIM	12	1.50	0.23	16	1.50	1.35	1.70	1.10	1.90
WUP	11	2.44	0.46	19	2.30	2.10	2.73	1.90	3.45
ERF	9	6.71	3.83	57	7.30	3.30	7.95	2.40	14.50
EMS	11	6.78	1.27	19	6.60	5.83	7.35	5.25	9.65
LIP	10	2.57	0.25	10	2.55	2.36	2.78	2.25	2.95

HON = Rhine, Bad Honnef; BIM = Rhine, Bimmen; WUP = Wupper; ERF = Erft; EMS = Emscher; LIP = Lippe

Predominantly particle-bound mercury cannot be analysed in a filtered sample as all readings resulting from filtered samples were below detection limits.
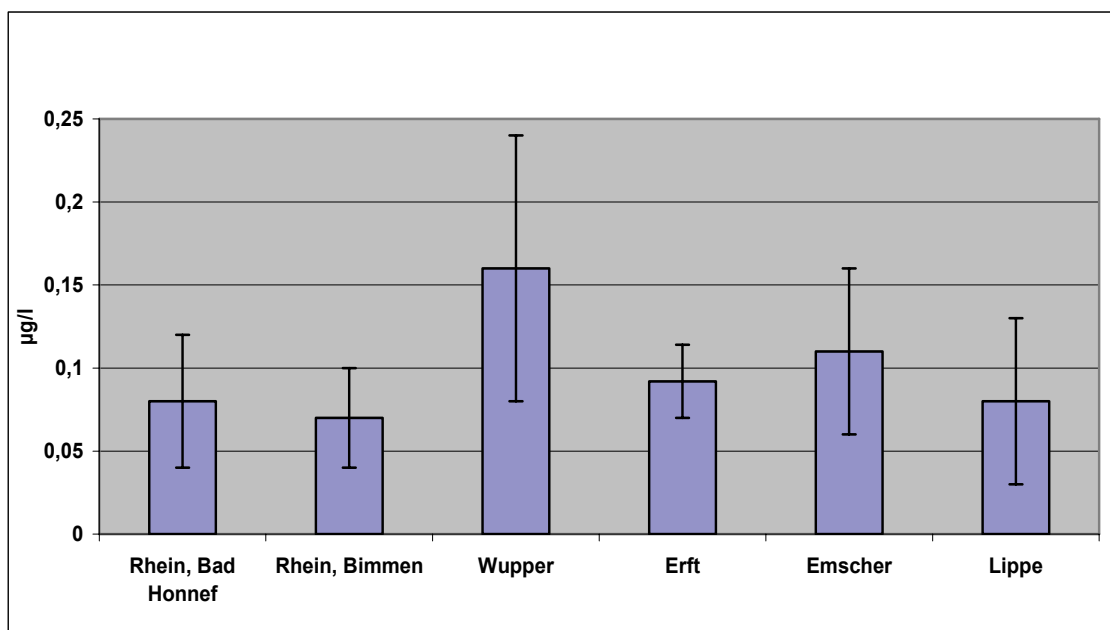
Fig. 4.1.2-11: Lead in filtered sample. Average values and standard deviation of concentration at all monitoring stations
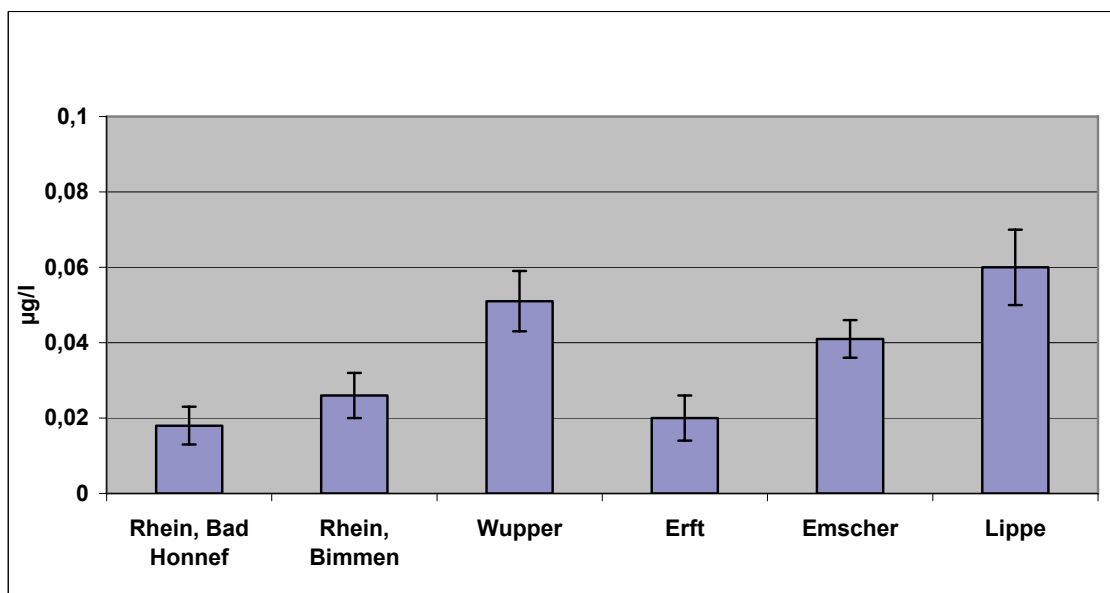
Fig. 4.1.2-12: Cadmium in filtered sample. Average values and standard deviation of concentration at all monitoring stations
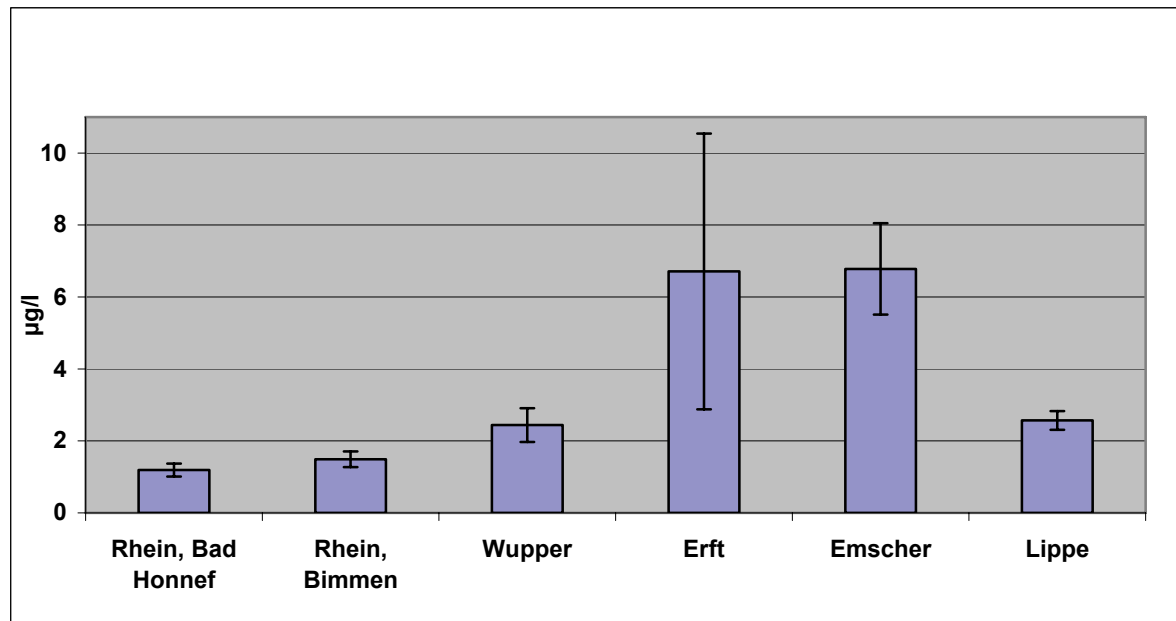
Fig. 4.1.2-13: Nickel in filtered sample. Average values and standard deviation of concentration at all monitoring stations

Interactions between metal concentrations in filtered samples and associated parameters

Determined heavy metal data were correlated with measured associated parameters (FSS,grain-size-distribution conductivity and others) (Tab. 4.1.2-4).

Tab. 4.1.2-4: Significant correlations between heavy metal concentrations in filtered samples and associated parameters

	FIL-Pb	FIL-Cd	FIL-Ni	FIL-Hg
FSS	--	--	r = 0.423 s = 0.0004	n.n.
Rel. discharge	--	--	r = - 0.271 s = 0.0477	n.n.
Calcium	--	r = 0.343 s = 0.0052	r = 0.343 s = 0.0052	n.n
Magnesium	--	--	r = 0.727 s <0.0001	n.n
Potassium	--	r = 0.351 s = 0.0041	r = 0.678 s <0.0001	n.n
Sodium	--	r = 0.409 s = 0.0007	r = 0.525 s <0.0001	n.n
Percentage of grain-size fractions				
	FIL-Pb	FIL-Cd	FIL-Ni	FIL-Hg
< 2 μm	--	r = - 0.371 s = 0.0025	r = - 0.504 s <0.0001	n.n
2-20 μm	--	r = - 0.363 s = 0.0032	r = - 0.566 s <0.0001	n.n
20-40 μm	--	--	--	n.n
40-63 μm	--	r = 0,344 s = 0,0053	r = 0,541 s <0,0001	n.n
63-125 μm	--	r = 0,323 s = 0,0099	r = 0,585 s <0,0001	n.n

n = depending on parameters between 60 – 65, grey and bold: relevant correlation

Filterable suspended solids (FSS) and particle size distribution

The entire data collective shows significant correlations to the suspended solids content (FSS) for nickel concentrations in the filtered sample only. For individual monitoring stations, dependencies between the FSS content and concentrations of other metals can, however, be verified. (Fig. 4.1.2-14).

Significant negative correlations to the percentage of small grainfractions (< 20 µm) and positive correlations to fractions with larger particles (40-125 µm) have been detected for dissolved cadmium and nickel concentrations. These mechanisms can be explained by a particularly high affinity of metal ions to fine suspended matter, which is increasingly particle-bonded, with a rising availability of fine suspended matter. All of the respective correlation coefficients are, however, rather small.
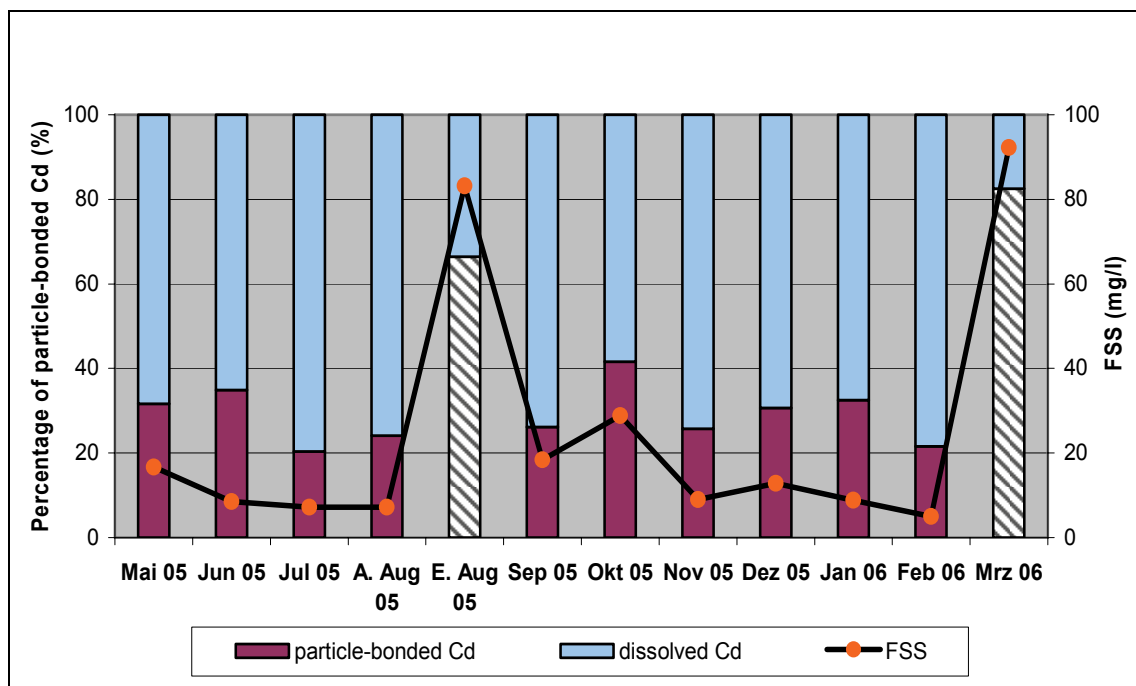
Fig. 4.1.2-14:   Particle-bound and dissolved Cd-fraction versus the contents of filterable suspended solids (AFS) at the Bad Honnef station (Rhine). S. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges.

Discharge

Increases in concentration detected with increasing discharge in the original sample do not occur in the filtrate. The suspended matter content, rising with increasing discharge, is more likely to lower dissolved metal fractions as a result of increased particle availability.

Conductivity, saline-specific ions

Alkaline earth and alkali ions compete with metals for bonding sites available on suspended matter. In the case of high alkaline (earth) concentrations, heavy metals are removed from their bonding sites and dissolved. This explains the significant number of positive correlations to dissolved cadmium (Ca, K, Na) and nickel concentrations (Ca, K, Na, Mg) found. Most of these correlations do, however, not reach a relevant level.

Relevant correlations do, however, also exist at individual monitoring stations. Fig. 4.1.2.15 shows a graph of concentration for nickel (µg/l), magnesium and potassium (mg/l) at the Bimmen station (Rhine).

4.1.2.3 Heavy metal concentrations in suspended matter

4.1.2.3.1 Volume and composition of suspended matter

During the project, the lowest suspended matter contents were generally detected in the river Emscher and the highest in the river Erft (Tab. 4.1.2-5). In addition, different surface waters also show distinct regional and time-related differences (Fig. 4.1.2-16) in the particle size distribution of their suspended matter. Suspended matter of the Rhine (Bad Honnef; Bimmen) showed the highest percentage of fine-grain fractions, whilst in the suspended matter from the Emscher coarse-grain fractions (in particular 63 – 125 µm) dominate.
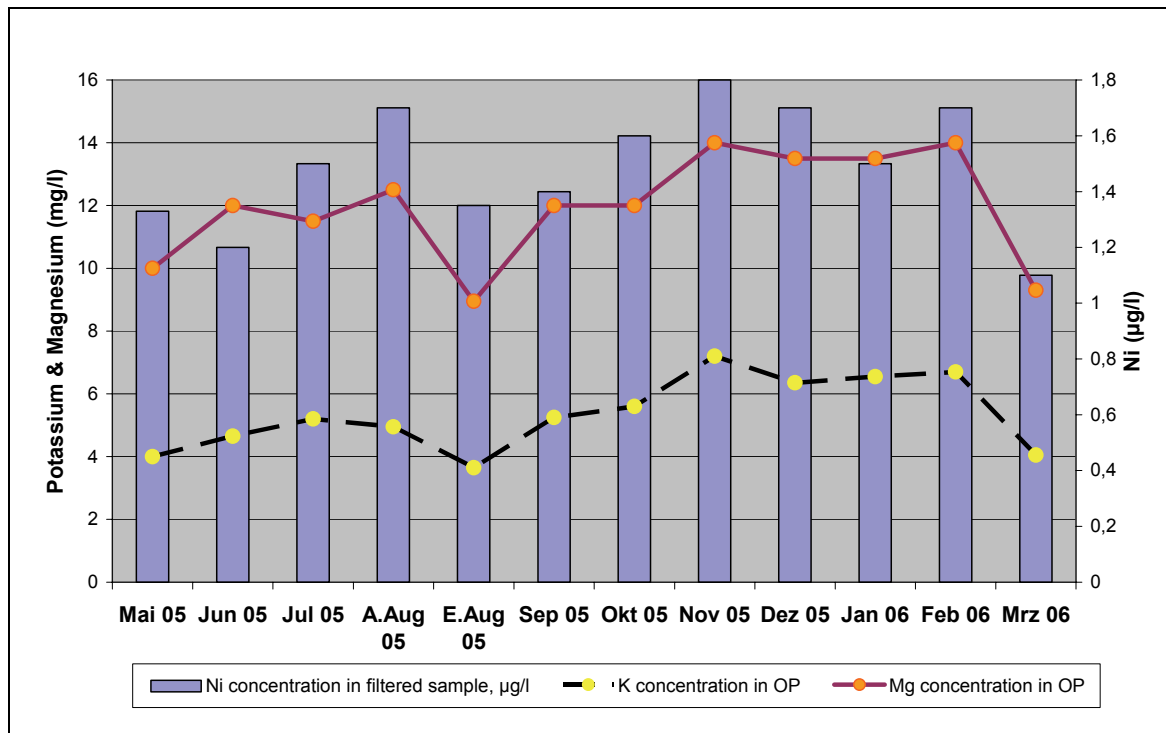
**Fig. 4.1.2-15:   Nickel concentration (µg/l) in filtered sample versus potassium and mag-
nesium concentrations (mg/l) at the Bimmen station (Rhine).** S. Aug. = beginning of August; E.
Aug. = end of August: Shaded sampling results with increased discharges.
 Stat. parameters: potassium   r = 0.61; s = 0.036;   magnesium   r = 0.77; s = 0.004

Versus other monitoring stations, suspended matter obtained from the Emscher
showed high TOC contents (29 %). This may be an effect caused by the
Dinslaken river treatment plant upstream, in which the whole Emscher is puri-
fied.

**Tab. 4.1.2-5   Parameters of suspended matter concentrations**

Location	n	AV	ST. D.	CV %	Median	1. quarter	3. quarter	Min	Max
				Filterable suspended solids [mg/l]					
HON	12	24.8	30.2	122	10.9	8.2	21.0	5.0	92.2
BIM	12	32.2	22.4	70	24.6	20.5	29.1	11.0	88.0
WUP	11	17.8	29.8	168	10.4	6.6	11.8	3.4	107.0
ERF	9	73.2	148.0	202	22.4	15.4	30.2	9.6	466.0
EMS	11	11.8	13.7	117	7.6	6.0	9.7	4.5	52.4
LIP	10	14.2	6.3	44	11.7	9.3	19.6	6.8	24.8

HON = Rhine, Bad Honnef; BIM = Rhine, Bimmen; WUP = Wupper; ERF = Erft; EMS = Emscher; LIP = Lippe
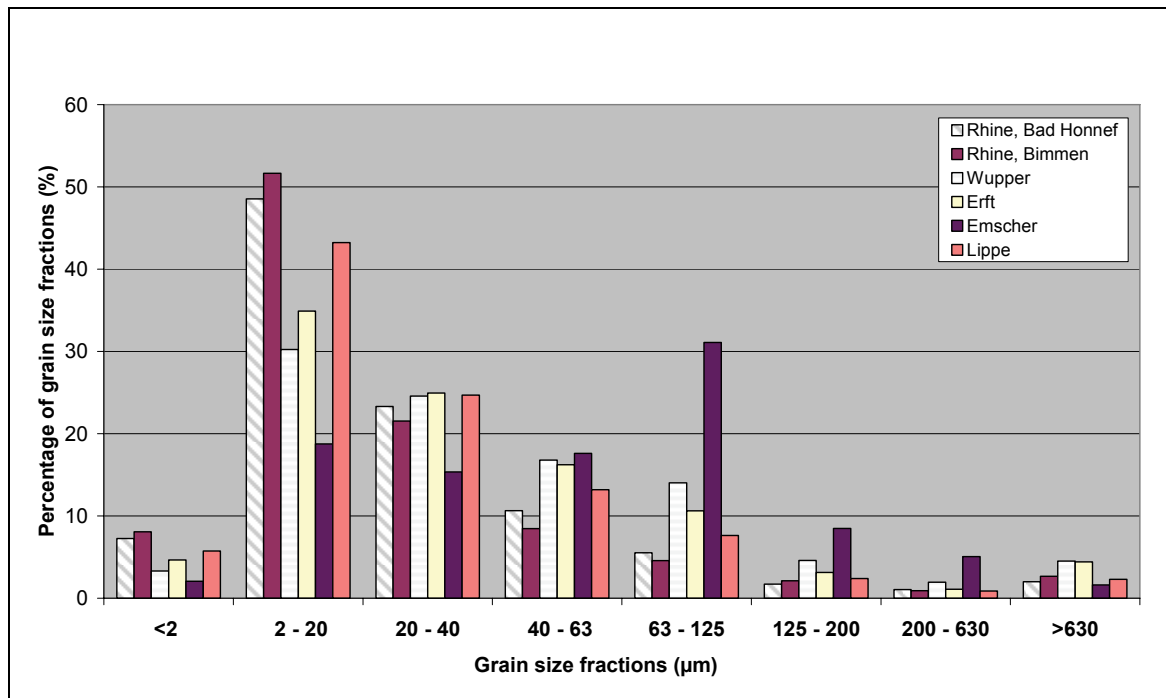
Fig. 4.1.2-16: Average values of percentage shares of particle size fractions of examined monitoring stations

Results confirm particle size distributions that change with discharge dynamics (Tab. 4.1.2-6). With increasing discharge, FSS concentrations and the percentage of particle size fractions also increase by up to 20 µm and fractions of over 20 µm decrease. These changes are particularly clear in considerably increased discharges.

Tab. 4.1.2-6: Correlation between the percentage share of particle size fractions of suspended matter removed by centrifugation and discharge

	Percentage of grain size fraction				
	< 2µm	2-20 µm	20-40 µm	40-63 µm	63-125 µm
Discharge	r = 0.558 s = 0.0002	**r = 0.663 s <0.0001**	r = - 0.410 s = 0.0085	**r = -0.666 s <0.0001**	r = -0.589 s = 0.001

r = correlation factor, s = significance level, s= 0.05 5% likelihood of error

Fig. 4.1.2-17 shows flow-dependent changes of suspended matter compositions in the Rhine at the Bad Honnef station. Changes in the relative percentage

share of particle size fractions are particularly apparent at the end of August 2005.
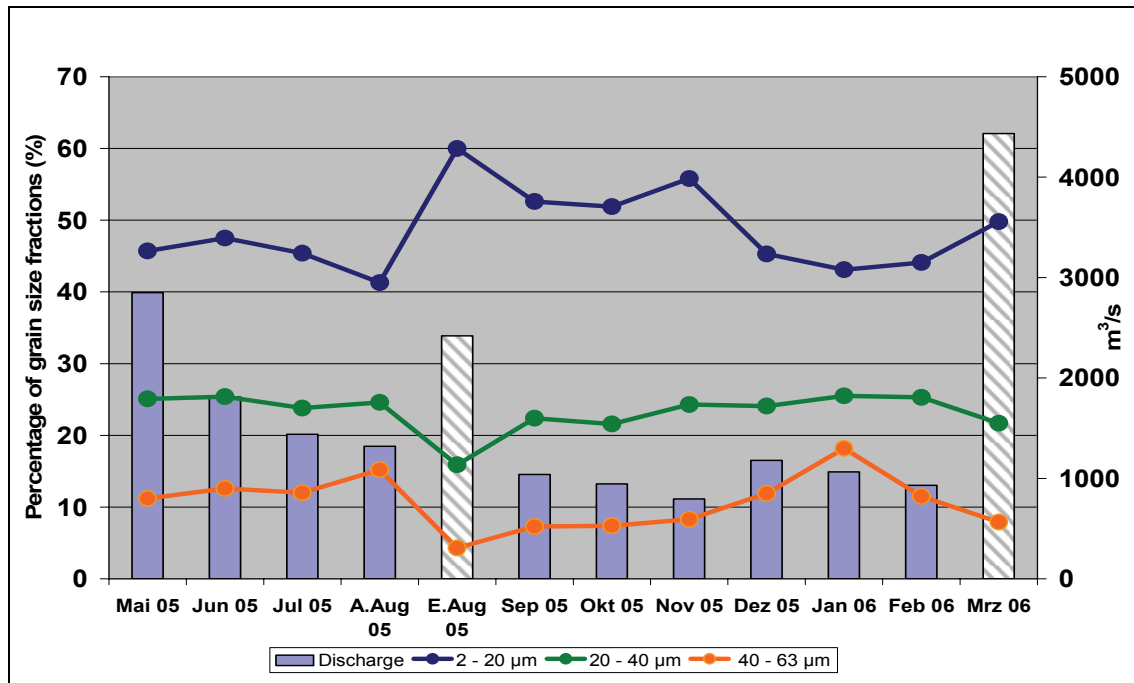
Fig. 4.1.2-17: Percentage share of suspended matter particle fractions depending on discharge, at the Bad Honnef station (Rhine) S. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges.

4.1.2.3.2 Effects of centrifugation and sedimentation on the composition of suspended matter

Suspended matter contents and concentrations of prioritary substances in surface waters may vary considerably over time. As a centrifugation period lasts one to two days at the most, whilst a sedimentation period lasts four weeks, natural differences in contamination of any suspended matter obtained cannot be ruled out.

As part of this project, potential sampling effects were analysed by comparing results from suspended matter obtained from centrifugation and passive sedimentation (sedimentation tanks) at the Bimmen station (Rhine).

Particle size distribution

Significant differences in the composition of particle sizes were found between centrifuged and sedimentated suspended matter (Tab. 4.1.2-7). In the case of centrifugation, the percentages of fine-particle fractions (< 20 μm) are significantly higher (Fig. 4.1.2-18) than for sedimentation and considerably lower for larger fractions (Fig. 4.1.2-19).

During centrifugation, considerably more fine-particle fractions are thus precipitated. Particle size distribution found in centrifuged suspended matter consequently correspond more to natural conditions of suspended matter in surface water.

Tab. 4.1.2-7: Significant differences in the shares of particle size fractions in centrifuged and settled suspended matter of surface waters, t-test

t-test parameters	Percentage of grain-size fraction			
	< 2 μm	2 - 20 μm	20 - 40 μm	40 - 63 μm
n	10	10	10	10
t_{krit}	2.26	2.26	2.26	2.26
t	5.17	8.81	-6.02	-12.98
Significant difference?	**yes**	**yes**	**yes**	**yes**

Zero hypothesis: $H0: \mu = \mu_0 = 0$; alternative hypothesis : $H1: \mu \neq \mu_0$; Signif. level: 5%
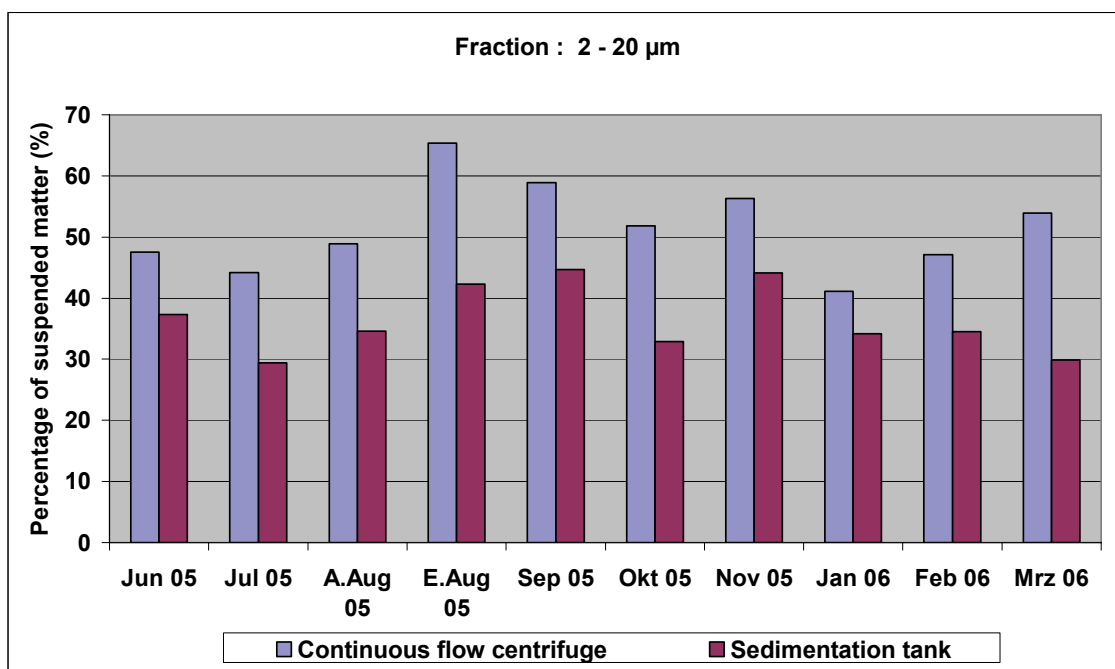
Fig. 4.1.2-18: Comparison of particle size distribution for continuous-flow centrifuges and sedimentation tanks, based on ten samplings. Percentage of fraction 2-20 µm.
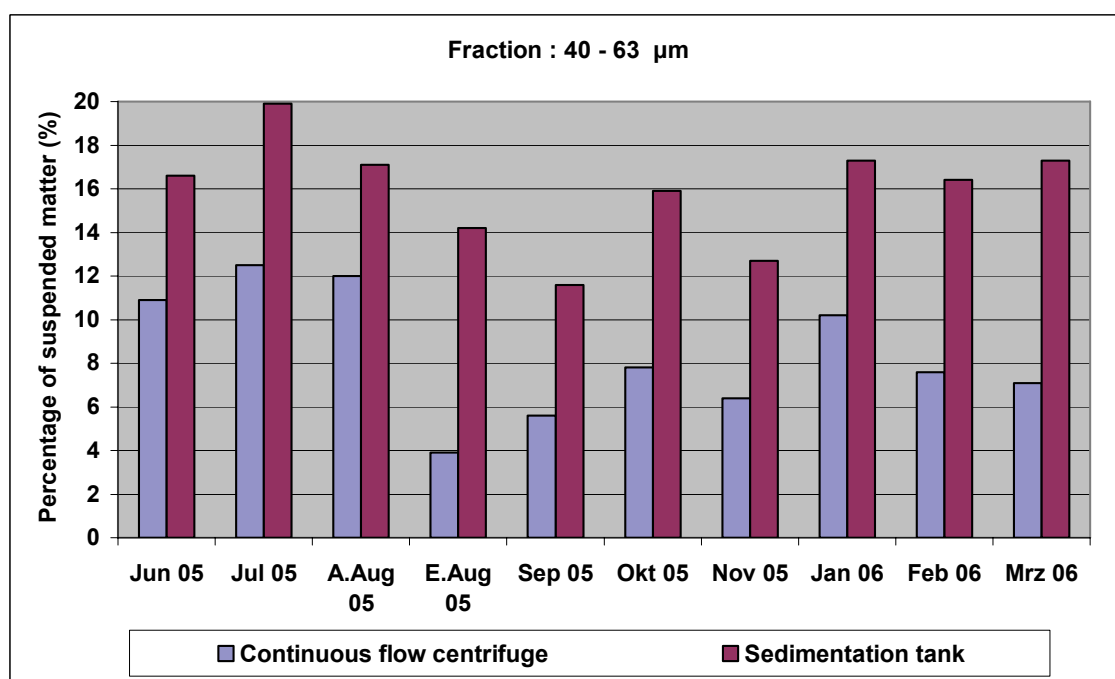
Fig. 4.1-2-19: Comparison of particle size distribution for continuous-flow centrifuges and sedimentation tanks, based on ten samplings. Percentage of fraction 40-63 µm.

4.1.2.3.3   Metal concentrations in suspended matter

Tab. 4.1.2-8 and Fig. 4.1.2-20 – 22 summarize the parameters of heavy metal analyses in suspended matter. Average values of these metal concentrations in suspended matter showed smaller relative standard deviations versus the original sample.
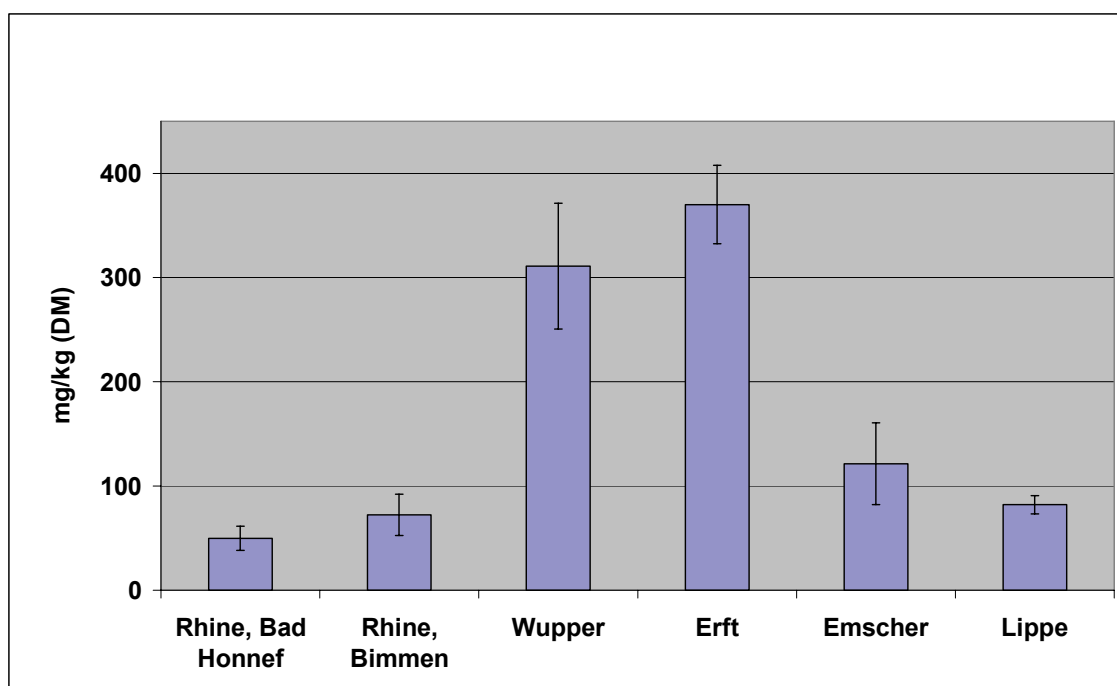
Fig. 4.1.2-20: Average values and standard deviations of lead concentrations in centri-fuged suspended matter in mg/kg versus dry mass.

Tab. 4.1.2-8: Parameters of heavy metal concentrations in suspended matter

Location	n	AV	ST. D.	CV %	Median	1. quarter	3. quarter	Min	Max
				Lead _mg/kg [DM]					
HON	12	49.9	11.6	23	50.0	41.0	57.8	28.0	66.0
BIM	12	72.2	19.8	27	73.0	61.8	83.0	30.0	110.0
WUP	11	310.9	60.4	19	300.0	270.0	345.0	230.0	450.0
ERF	9	370.0	37.7	10	360.0	340.0	390.0	330.0	440.0
EMS	11	121.3	39.3	32	110.0	98.5	155.0	68.0	190.0
LIP	10	82.0	8.6	10	81.0	76.5	86.3	72.0	97.0
				Cadmium mg/kg [DM]					
HON	12	0.57	0.16	27	0.56	0.47	0.66	0.29	0.81
BIM	12	1.13	0.51	45	1.01	0.82	1.50	0.34	2.20
WUP	11	3.58	0.65	18	3.50	3.20	3.85	2.70	5.00
ERF	9	4.07	0.77	19	3.80	3.60	4.10	3.40	5.90
EMS	11	2.05	0.49	24	1.80	1.75	2.25	1.50	3.10
LIP	10	2.31	0.26	11	2.25	2.10	2.48	2.00	2.80
				Nickel mg/kg [DM]					
HON	12	42.1	3.1	7	41.5	39.8	43.3	38.0	48.0
BIM	12	41.1	3.5	9	39.5	39.0	42.5	38.0	49.0
WUP	11	81.6	9.7	12	82.0	75.0	86.0	68.0	100.0
ERF	9	315.6	55.0	17	300.0	290.0	320.0	270.0	450.0
EMS	11	45.4	10.5	23	43.0	37.5	53.5	33.0	63.0
LIP	10	58.7	46.3	79	45.0	43.3	47.8	38.0	190.0
				Mercury mg/kg [DM]					
HON	12	0.41	0.12	30	0.42	0.33	0.46	0.21	0.67
BIM	12	0.63	0.31	49	0.59	0.49	0.77	0.21	1.40
WUP	11	3.04	0.54	18	3.00	2.85	3.30	2.00	3.89
ERF	9	0.25	0.05	19	0.26	0.24	0.27	0.16	0.34
EMS	11	0.87	0.14	16	0.88	0.77	0.91	0.67	1.10
LIP	10	1.13	0.54	48	1.05	0.85	1.10	0.65	2.60

HON = Rhine, Bad Honnef; BIM = Rhine, Bimmen; WUP = Wupper; ERF = Erft; EMS = Emscher; LIP = Lippe
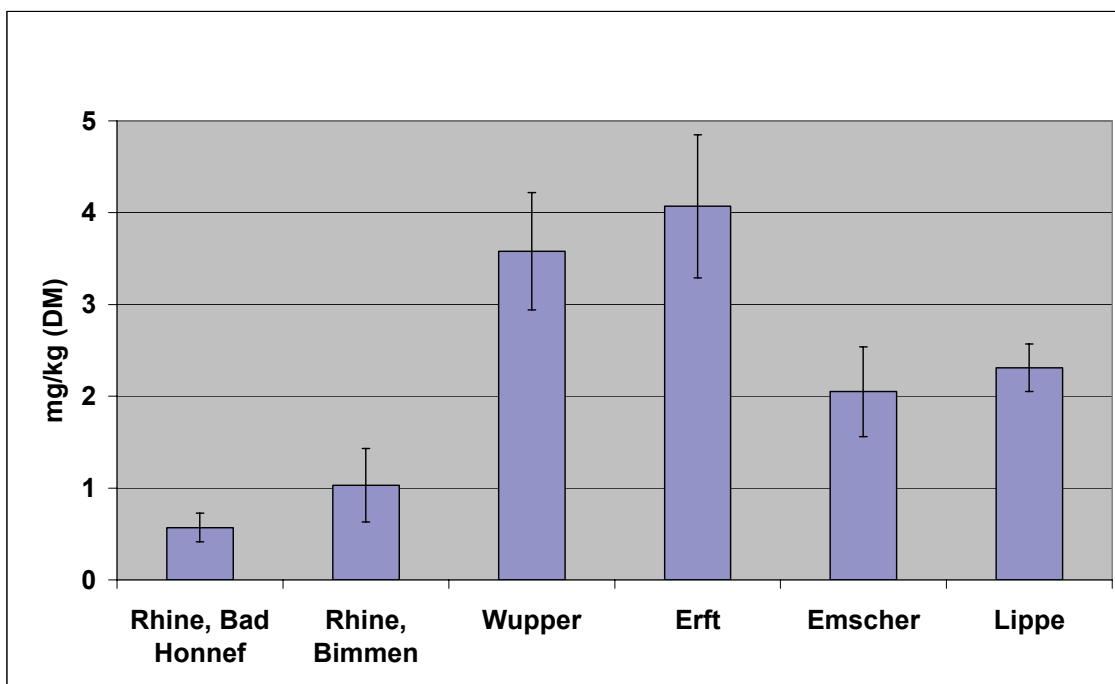
Fig. 4.1.2-21: Averages and standard deviations of cadmium concentrations in centri-fuged suspended matter in mg/kg versus dry mass.
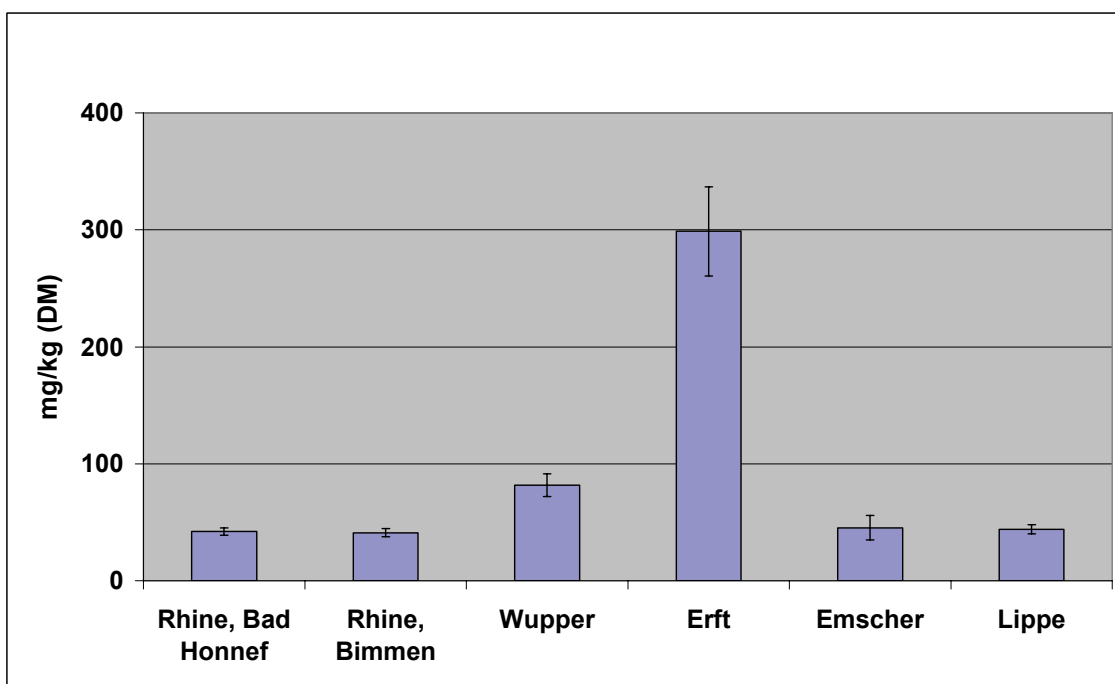
Fig. 4.1.2-22: Averages and standard deviations of nickel concentrations in centrifuged suspended matter in mg/kg versus dry mass.
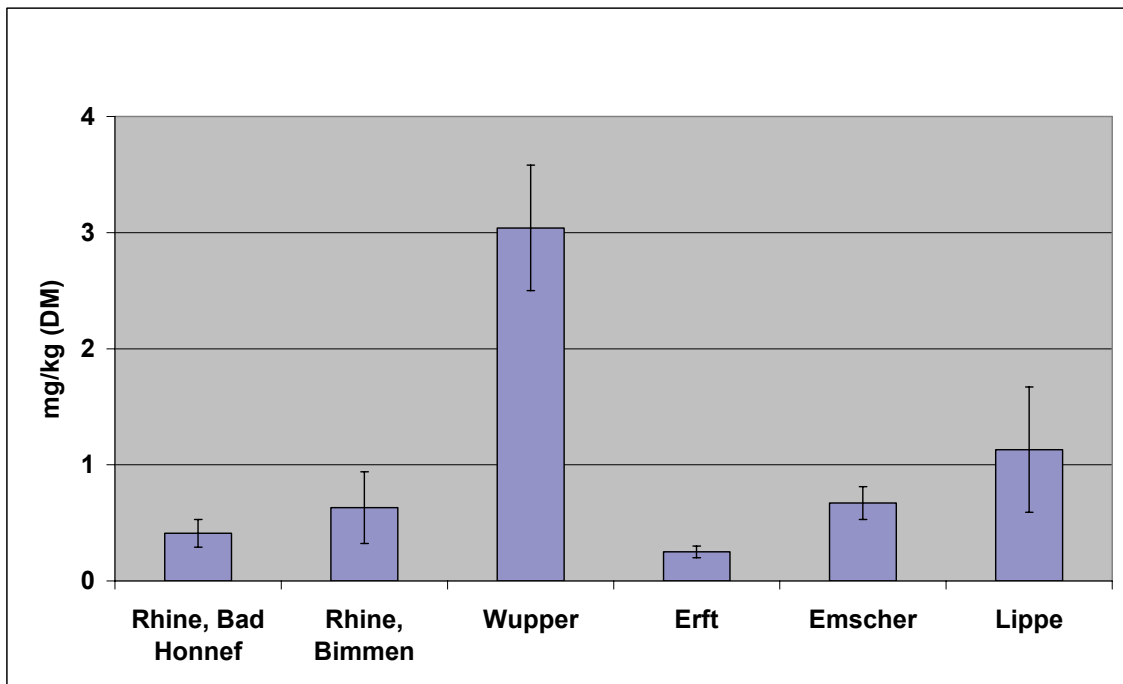
Fig. 4.1.2-23: Averages and standard deviations of mercury concentrations in centri-fuged suspended matter in mg/kg versus dry mass.

Interactions between metal concentrations in suspended matter and associated parameters

Determined heavy metal data were correlated to measured associated parameters (Tab. 4.1.2-9).

Tab. 4.1.2-9: Correlations between metal concentrations in suspended matter and associated parameters

	SS-Pb	SS-Cd	SS-Ni	SS-Hg
FSS	r = 0.255 s = 0.0406	r = 0.285 s = 0.0216	r = 0.447 s = 0.0002	--
Rel. flow	--	--	r = - 0.271 s = 0.0471	--
Calcium	r = -0.475 s <0.0001	--	r = -0.311 s = 0.0117	r = -0.302 s = 0.0146
Magnesium	--	--	--	r = -0.341 s = 0.0055
Potassium, sodium	--	--	--	--
Particle size fractions				
	SS-Pb	SS-Cd	SS-Ni	SS-Hg
< 2µm	r = - 0.468 s <0.0001	r = - 0.545 s <0.0001	--	r = - 0.395 s = 0.0012
2-20 µm	r = - 0.451 s = 0.0002	r = - 0.521 s <0.0001	--	r = - 0.359 s = 0.0036
20-40 µm	r = 0.292 s = 0.0189	r = 0.247 s = 0.0490	r = 0.286 s = 0.0220	--
40-63 µm	r = 0.570 s <0.0001	r = 0.623 s <0.0001	r = 0.331 s = 0.0076	r = 0.359 s = 0.0035
63-125 µm	--	--	--	--

n = depending on parameters 54 – 65; grey and bold: relevant correlation

Filterable suspended solids (FSS)

A significant negative correlation was found between the contents of filterable suspended solids and the heavy metal contents of suspended matter. Correlation coefficients are, however, relatively small.

Fig. 4.1.2-24 shows the levels of cadmium concentrations over time versus FSS contents at the Bad Honnef station (Rhine). Cd / FSS show a significant negative correlation, marked for both locations with increased discharges (End of August 2005; March 2006).
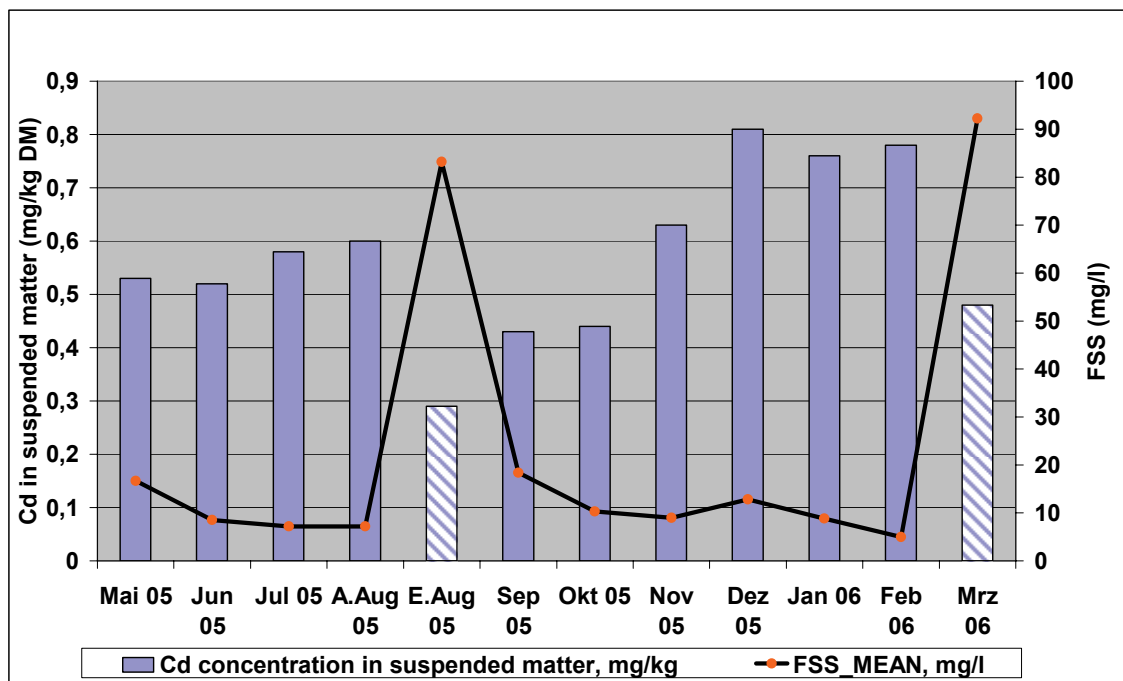
Fig. 4.1.2-24: Cadmium concentration in suspended matter depending on the content of filterable suspended solids (FSS) at the Bad Honnef station (Rhine). S. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges.   Stat. parameters: r = - 0.56 ; s = 0.05

The course of the contents of metal concentrations and filterable suspended solids is shown in Fig. 4.1.2-25 based on the example of the Bimmen station (Rhine). The lowering effects for lead caused by increased discharges (August 2005, March 2006) can be clearly recognized. The course of concentrations for predominantly dissolved nickel, which is relatively constant in comparison, shows no effects.
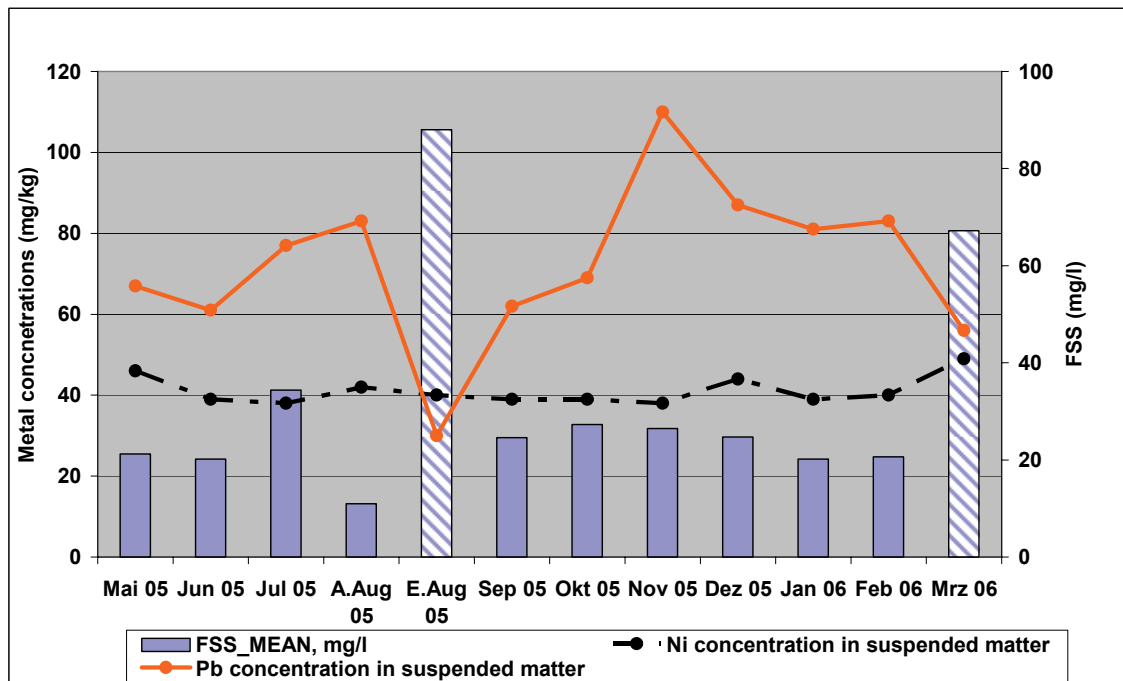
Fig. 4.1.2-25: Lead und nickel concentrations in suspended matter depending on the contents of filterable suspended solids at the Bimmen station (Rhine). S. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges.

Particle size distribution in suspended matter

Between the shares of different particle size fractions and metal concentrations in suspended matter, negative and positive correlations exist, with parts of fine grain fractions (< 2 µm; 2-20 µm) and positive correlations with parts of fraction of 40-63 µm (Tab. 4.1.2-9).

Mercury has the lowest correlation coefficients. In the case of predominantly dissolved nickel, correlations with small coefficients are only apparent for larger fractions of 20-40 µm and 40-63 µm.

Fig. 4.1.2-26 shows the development of lead concentrations versus the percentage of suspended matter fractions at the Bimmen station. At the time of increased flow (end of August), a diluting process can be clearly recognized. With the increase in fine sediments (probably with lower contamination), which

may be explained by leaching, the lead content of suspended matter also decreases.
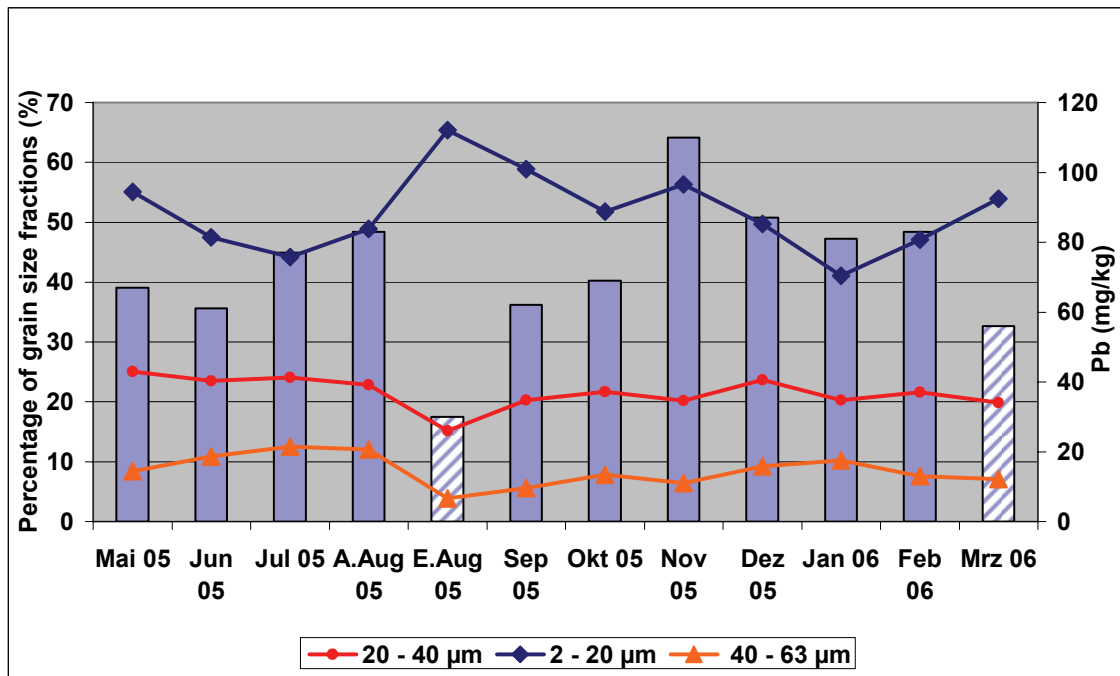
Fig. 4.1.2-26: Lead concentrations in suspended matter versus proportions of different suspended matter fractions at the Bimmen station (Rhine) S. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges. Statistical parameters of correlations to lead concentrations :   fraction 2-20 µm   r = -0.8   s = 0.001^   fraction 20-40 µm   r = 0.77 s = 0.004
fraction 40-63 µm   r = 0.88   s = 0.0002   fraction 63-125 µm   r = 0.69 s = 0.02

Negative correlations to small particle fractions, found for particle-bound lead, cadmium and mercury, seemed implausible at first, as heavy metals predominantly attach themselves to small suspended matter particles. In addition, there are negative correlations to small fractions (deposits on increased fine particles available) in filtered water samples.

In case of increased discharges, the volume of filterable suspended solids increases and their metal contamination is reduced at the same time. Coincidently, percentages of small fractions increase with discharge volumes. A plausible explanation for determined correlations is the considerable volume of low-contaminated fine suspended matter deposited by high-water waves, reducing on the one hand concentrations in suspended matter, whilst simultaneously par-

ticle-binding of the dissolved parts of metal concentrations occurs as a result of increased availability.

Discharge

Only particle-bound nickel concentrations showed correlations to relative discharges that were classed as being irrelevant.

Conductivity, saline-specific ions

For alkaline earth ions (calcium, magnesium) significant negative (Pb/Ca; Ni/Ca; Hg/Ca, Mg) correlations with low correlation coefficients result.

Effects of different suspended matter sampling methods on heavy metal concentrations

Results of four weeks of sedimentation and in each case of one centrifugation at the end of the sedimentation period were available for the comparison of sampling methods.

Due to the different proportions of particular-contaminated fine particle fractions of centrifuged and settled suspended matter, differences in concentration may be anticipated caused by the sampling method. Centrifuged suspended matter regularly has Pb, Cd and Ni contents that are significantly higher statistically than sedimented samples (Figs. 4.2.1-27 - 30, Tab. 4.1.2.10). In the case of increased discharges (end of August 05, March 06) these conditions are reversed in some cases.

Tab. 4.1.2-10: Significant differences in metal concentrations in centrifuged and settled suspended matter of surface waters, t-test

t-test parameters	Pb	Cd	Ni	Hg
n	10	10	10	10
t_{krit}:	2.201	2.201	2.201	2.201
t	-3.393	-3.085	-5.082	-1.532
Significant difference ?	**yes**	**yes**	**yes**	no

Zero hypothesis: H0:$\mu=\mu_0=0$; alternative hypothesis : H1:$\mu\neq\mu_0$; Signif. level: 5 %
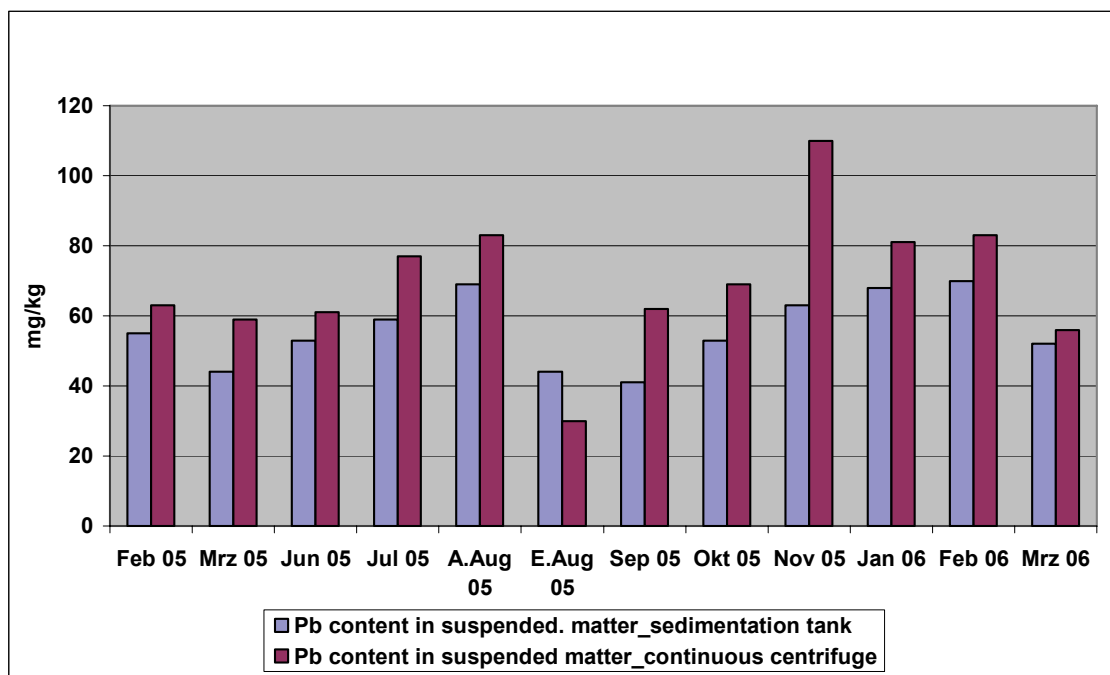
Fig. 4.1.2-27: Differences in lead concentrations in suspended matter when using different sampling methods (sedimentation/centrifugation)
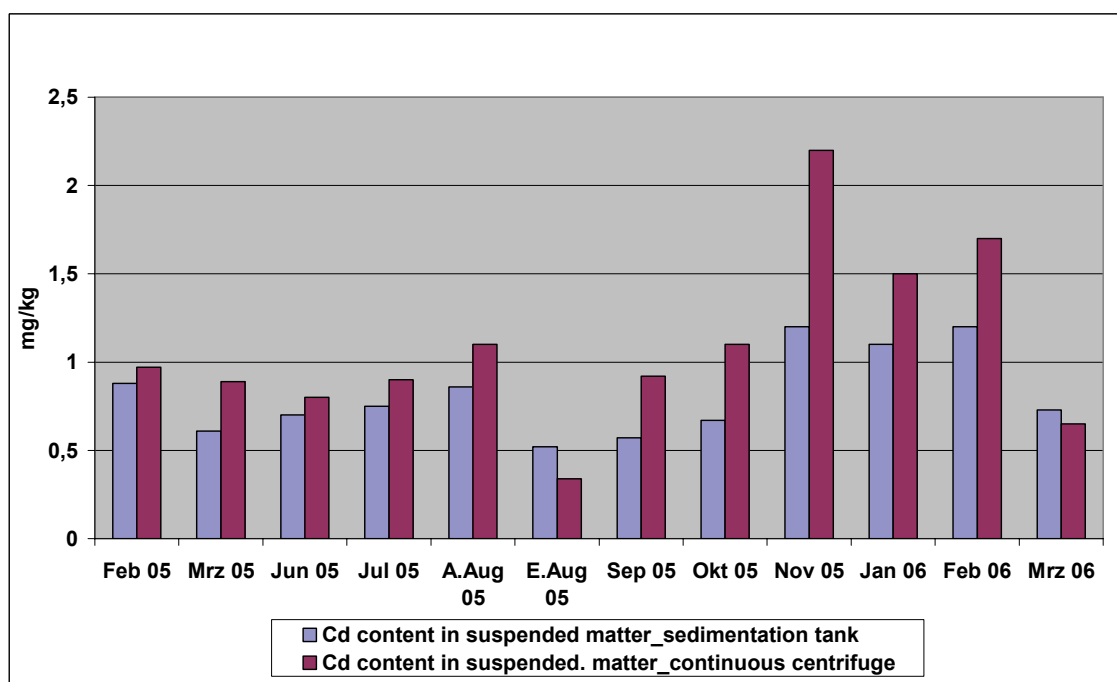
Fig. 4.1.2-28: Differences in cadmium concentrations in suspended matter when using different sampling methods (sedimentation/centrifugation)
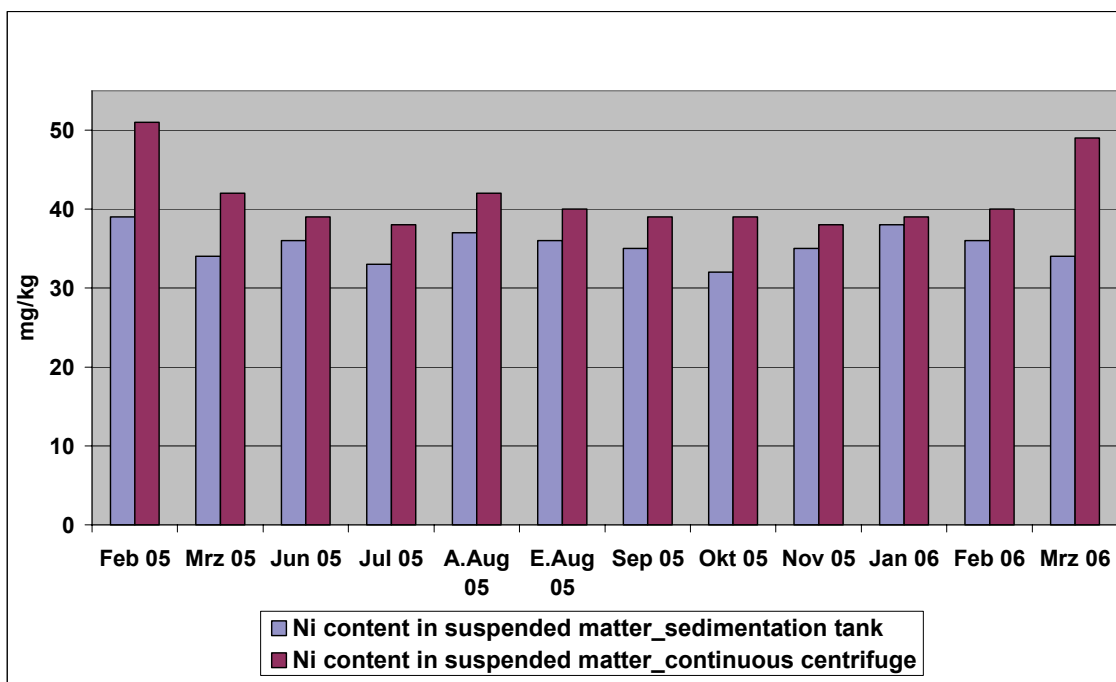
Fig. 4.1.2-29: Differences in nickel concentrations in suspended matter when using different sampling methods (sedimentation/centrifugation)
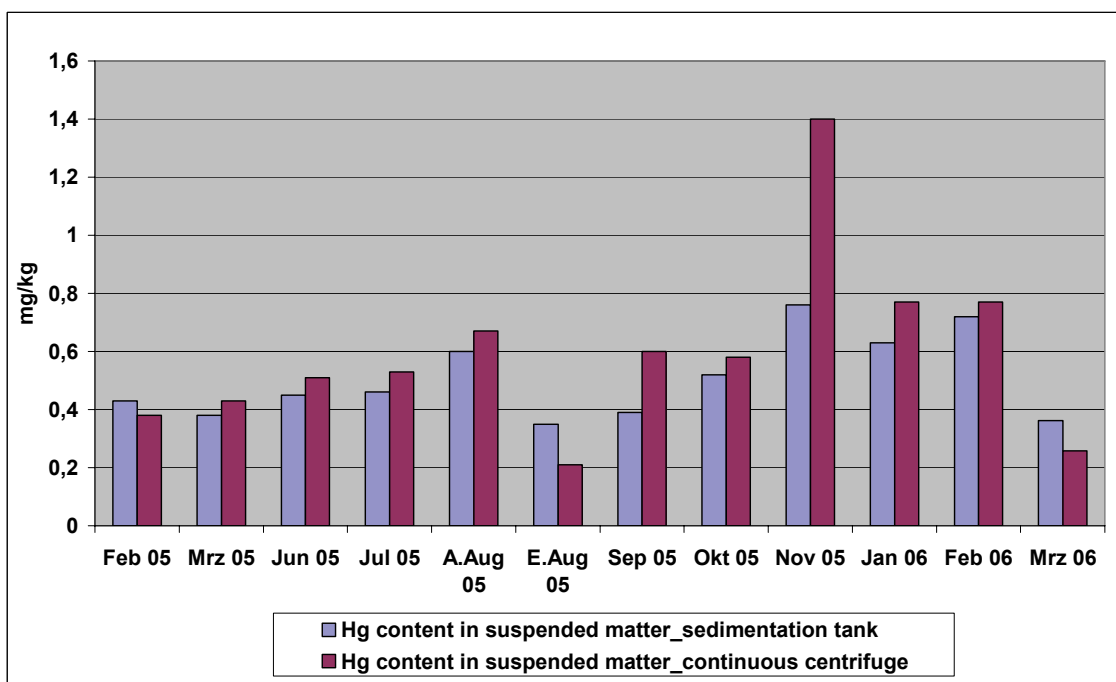
Fig. 4.1.2-30: Differences in mercury concentrations in suspended matter when using different sampling methods (sedimentation/centrifugation)

4.1.3 Dissolved and particle-bound metal shares

Suspended matter volumes obtained from filtration of original samples were extremely low and could therefore not be analysed in general. Respective percentages of particle-bound and dissolved heavy metals were therefore calculated . Averages of dissolved and particle-bound parts of lead, cadmium and nickel are shown in Figs. 4.1.3-1, -3 and -5.

When comparing the results of monitoring stations, it is apparent that particle-bound parts of heavy metals were highest in the river Erft, whilst the river Emscher generally showed the highest shares of dissolved heavy metals.

Lead

Lead showed a high affinity to the suspended matter of surface waters. Particle-bonded parts generally constituted around 90% of total contamination. Standard deviations of averages were relatively small versus cadmium and nickel. At the mouth of the Emscher, the particle-bonded share of lead was just about 80%, with the mean variation being considerably higher.

Despite a relatively small variation span, clear variations over time in the distribution between the dissolved and the particulate phase were also apparent for lead. The highest variation versus the particulate phase were observed during sampling, with increased discharges of suspended matter volumes. The result over time is shown in Fig. 4.1.3-2, based on the example of the Bad Honnef station (Rhine).
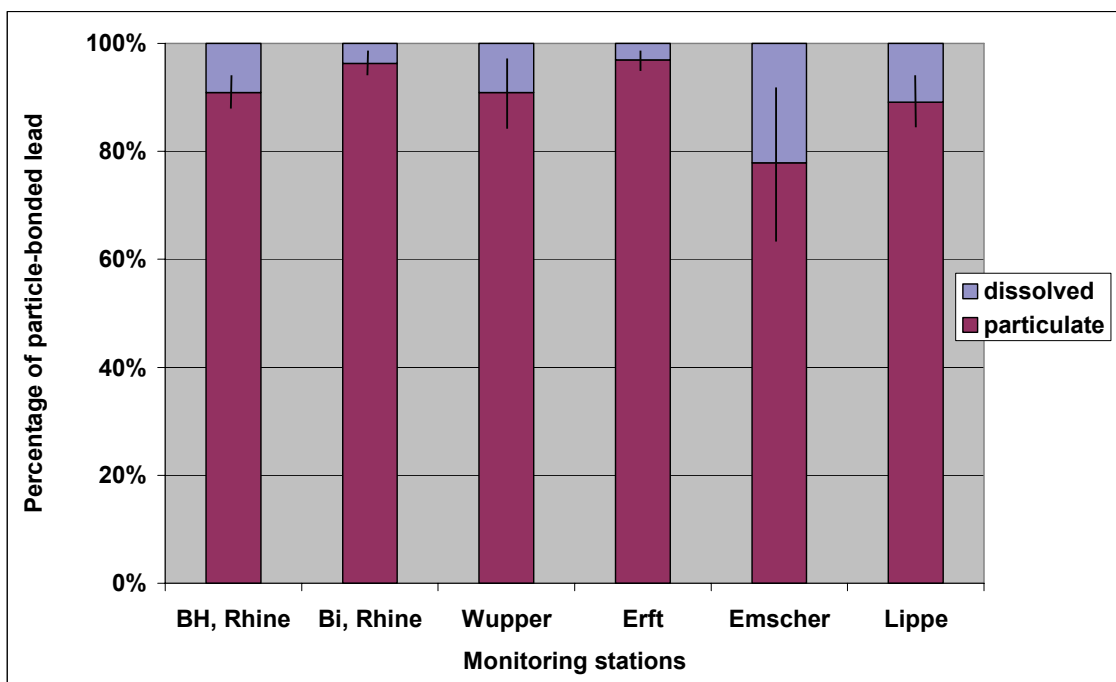
Fig. 4.1.3-1: Distribution of lead contamination over dissolved and particulate phases.
Averages and standard deviations of distribution. BH = Bad Honnef; Bi = Bimmen
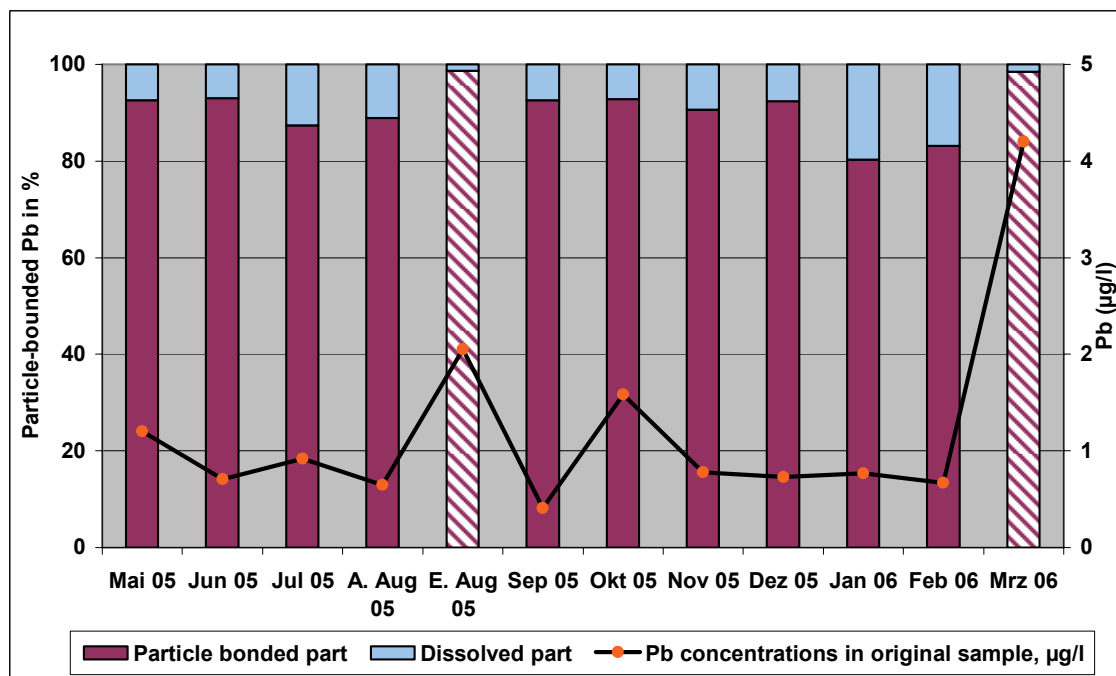
Fig. 4.1.3-2 : Distribution of lead contents over dissolved and particulate phases over time versus concentrations in the original sample in Bad Honnef (Rhine).
S. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges.

Cadmium

In the case of cadmium, comparison of the stations showed clear regional and time variations of particle-bound and dissolved parts. Dissolved parts in the river Rhine are between 50 and 65 %. The lowest percentages of dissolved cadmium of approx. 25 % are regularly found in the Erft, whilst the highest of over 85 % are found in the Emscher (Fig. 4.1.3-3). Fluctuations in readings are clearly higher than for lead.

Cadmium also showed a higher variation over time in the distribution between dissolved and particulate phases. Fig. 4.1.3-4 shows an example for the Bad Honnef (Rhine) station.
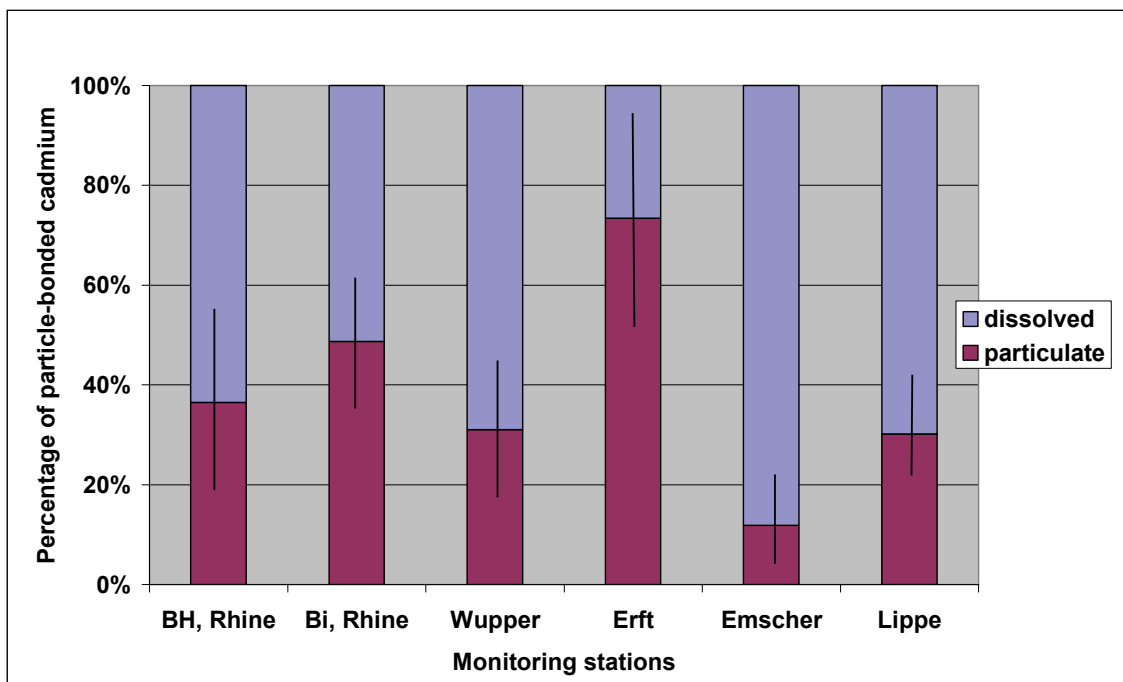
Fig. 4.1.3-3: Distribution of cadmium contamination over dissolved and particulate phases. Average values and standard deviations of distribution. BH = Bad Honnef; Bi = Bimmen
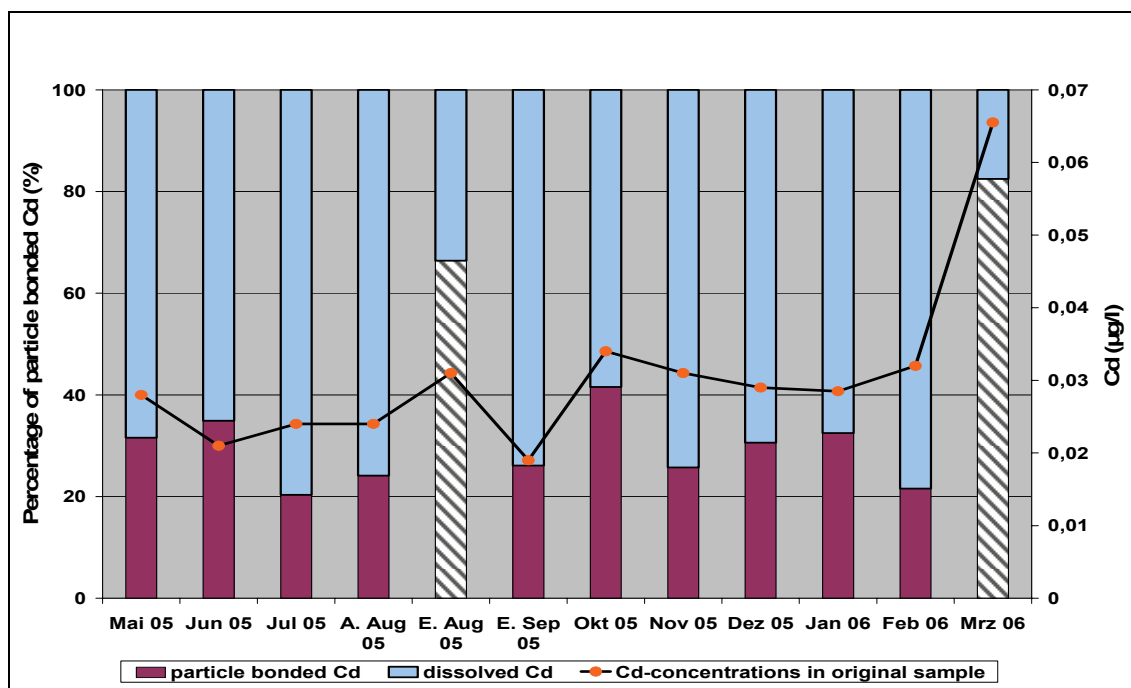
Fig. 4.1.3-4 :   Distribution of cadmium contents over dissolved and particulate phases over time versus concentrations in the original sample in Bad Honnef (Rhine).
S. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges.

Nickel

Nickel was predominantly determined in dissolved form at the tested monitoring stations and showed clear regional and time variations. Dissolved proportions in the river Rhine were around 60 and 65 %. The smallest dissolved proportions of approx. 45 % were regularly found in the Erft, whilst the Emscher showed highest dissolved proportions of nearly 90 % (Fig. 4.1.3-5).
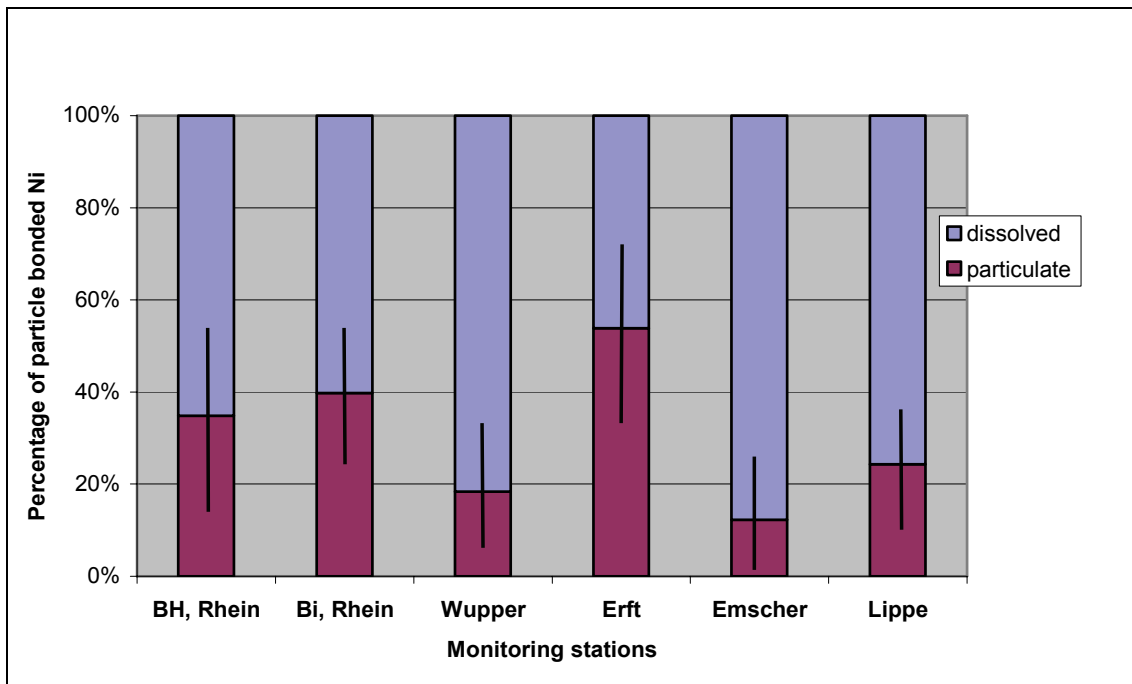
Fig. 4.1.3-5: Distribution of nickel contamination over dissolved and particulate phases. Average values and standard deviations of distribution. BH = Bad Honnef; Bi = Bimmen

Mercury

The dissolved proportions of mercury contaminations regularly remained below detection limits, as a result of which distribution of the metal could not be evaluated. One can, however, estimate from readings (maximum original sample: 0.06 µg/l) and the detection limit (0.005 µg/l) that the particle-bonded part of mercury contaminations in samples with higher mercury concentrations exceeded 90 %.

4.2 Organic parameters

4.2.1 Polychlorinated biphenyls (PCBs)

PCBs accumulate in aquatic ecosystems in the suspended matter of surface waters, sediment and also in the fatty tissues of biota through bioaccumulation. Tab. 4.2.1-1 shows the n-octanol / water-coefficient of distribution and water solubility of examined PCB congeners.

As part of this project, seven (Ballschmiter congeners + PCB-118) out of 209 possible congeners were examined based on different levels of chlorination (Tab. 4.2.1-1).

Tab. 4.2.1-1: Octanol/water-coefficients of distribution and water solubility of analysed PCB congeners

Congeners	PCB-28	PCB-52	PCB-101	PCB-118	PCB-138	PCB-153	PCB-180
log K_{ow}	5.607	5.919	6.376	6.416	6.781	6.834	7.162
Water solubility (mg/l) at 20 °C	0.13	0.055	0.012	0.0098	0.0036	0.0034	0.0012

4.2.1.1   PCB concentrations in suspended matter

The results of many years of monitoring suspended matter in surface waters have shown clearly measurable contamination at all selected monitoring stations as well as regional contamination differentials that were confirmed as part of this project. The range of test results at monitoring stations is shown in Tab. 4.2.1-2.

Tab. 4.2.1-2: Range (min/max) of PCB contamination of analysed suspended matter

Congeners	Rhine, Bad Honnef (µg/kg DM)	Rhine, Bimmen (µg/kg DM)	Emscher, Dinslaken (µg/kg DM)	Erft, Neuss (µg/kg DM)	Lippe, Wesel (µg/kg DM)	Wupper, Opladen (µg/kg DM)
n	12	12	11	9	10	11
PCB-28	<1 – 6.0	1 – 7.3	**11 – 26**	0.4 – 0.8	**8.6 - 14**	<1 – 3.1
PCB-52	1.1 – 3.9	1.2 – 11	**16 – 28**	<1 – 1.5	**7.5 - 13**	3.5 – 8.6
PCB-101	1.3 – 5.4	1.9 – 16	**19 – 31**	2.5 – 3.4	**7.5 – 15**	8.4 – 19
PCB-118	<1 – 3.4	1.4 – 7.7	**11 – 17**	1.2 – 2.7	**5.4 – 11**	**4 – 8.8**
PCB-138	3.1 – 12	3.2 - 18	**27 – 48**	8.2 – 11	10 - 20	**18 – 43**
PCB-153	2.4 – 9.2	2.9 – 17	**25 – 47**	6.6 – 9.2	8 - 19	**18 – 37**
PCB-180	1.4 – 6.1	1.6 – 9.5	**14 – 22**	4.6 – 7.2	4.9 – 11	**12 – 29**

n = number of samples; DM = dry mass

Different PCB samples were obtained from monitoring stations (Fig. 4.2.1-1). Some of the sump water from coal mines causes some of the PCB contaminations in surface waters, containing a greater share of low-chlorinated PCB congeners. This is clearly apparent in Fig. 4.2.1-1 by the example of the Fossa Eugeniana (special analysis) experiencing particularly high levels of mining-related contamination. The Emscher contains higher levels of contamination for all congeners, whilst increased concentrations of higher chlorinated congers are characteristic for the Wupper. The Lippe shows increased contamination by llow-chlorinated PCBs emitted by sump water of coal mines.

Correlations between PCBs in suspended matter and associated parameters

PCB data obtained were correlated with selected associated parameters (Tab. 4.2.1-3).
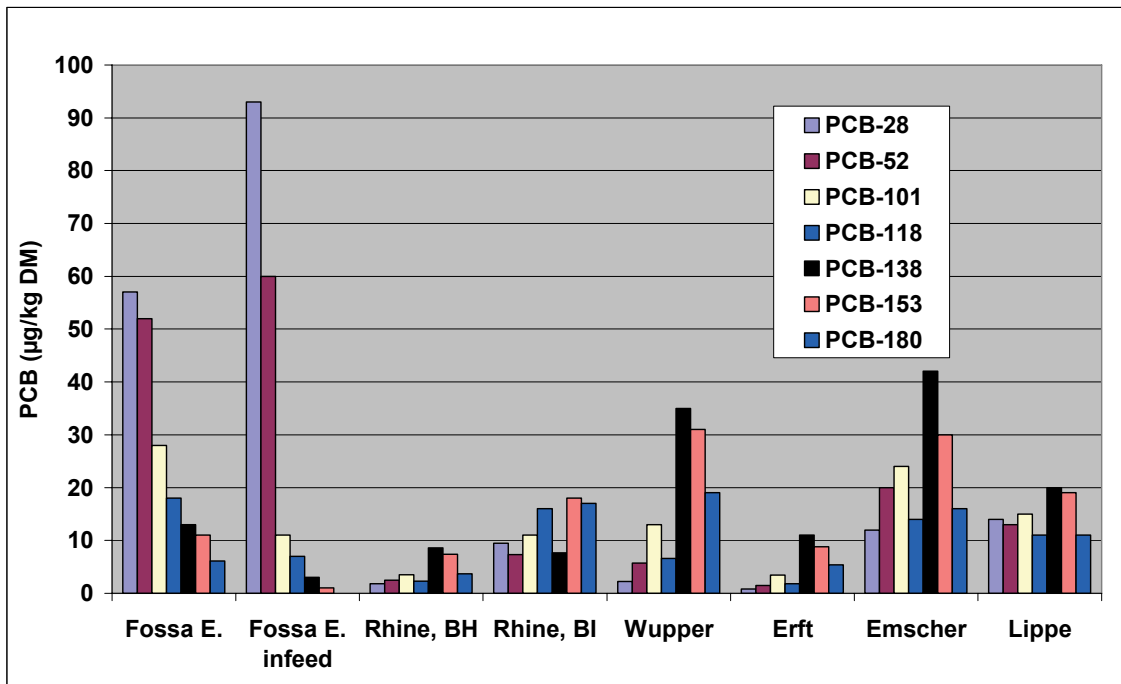
Fig. 4.2.1-1: PCB samples of suspended matter obtained from six monitoring stations versus two monitoring stations at the Fossa Eugeniana influenced by mining. DM = dry mass

Filterable suspended solids (FSS)

No correlation between PCB concentrations in the suspended matter and the contents of a sample of filterable suspended solids can be proven for the entire data collective. Correlations at individual stations were, however, significant. The influence of increasing the FSS content due to PCB contamination of suspended matter in the case of increased discharge (Fig. 4.2.1-2) is clearly apparent in the Rhine.

Tab. 4.2.1-3: Significant correlations between PCB concentrations in suspended matter and associated parameters

	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180

SS_P_TOC	r = 0.672 s <0.0001	**r = 0.860** **s <0.0001**	**r = 0.878** **s <0.0001**	**r = 0.853** **s <0.0001**	**r = 0.802** **s <0.0001**	**r = 0.821** **s <0.0001**	**r = 0.749** **s <0.0001**
Conductivity	**r = 0.860** **s <0.0001**	**r = 0.786** **s <0.0001**	r = 0.582 s <0.0001	**r = 0.714** **s <0.0001**	--	r = 0.297 s = 0.0250	--
Chloride	**r = 0.911** **s <0.0001**	**r = 0.896** **s <0.0001**	**r = 0.768** **s <0.0001**	**r = 0.844** **s <0.0001**	r = 0.501 s <0.0001	r = 0.552 s <0.0001	r = 0.423 s = 0.0005
Percentage of grain-size fractions							
< 2µm	r = - 0.363 s = 0.0051	r = - 0.506 s <0.0001	r = - 0.592 s <0.0001	r = - 0.569 s <0.0001	r = -0.675 s <0.0001	r = - 0.672 s <0.0001	r = - 0.669 s <0.0001
2-20 µm	r = - 0.456 s = 0.0003	r = -0.610 s <0.0001	**r = -0.689** **s <0.0001**	r = -0.665 s <0.0001	**r = -0.716** **s <0.0001**	**r = - 0.725** **s <0.0001**	**r = - 0.713** **s <0.0001**
20-40µm	r = - 0.554 s <0.0001	r = -0.635 s <0.0001	r = -0.570 s <0.0001	r = - 0.567 s <0.0001	r = -0.334 s = 0.0104	r = -0.380 s = 0.0104	r = -0.283 s = 0.0316
40-63 µm	--	r = 0.358 s <0.0058	r = 0.467 s = 0.0070	r = -0.443 s = 0.0005	r = 0.589 s <0.0001	r = 0.576 s <0.0001	r = 0.611 s <0.0001
63-125 µm	r = 0.640 s <0.001	**r = 0.785** **s <0.0001**	**r = 0.807** **s <0.0001**	**r = 0.793** **s <0.0001**	**r = 0.729** **s <0.0001**	**r = 0.750** **s <0.0001**	**r = 0.693** **s <0.0001**

n = between 54 – 65 depending on parameters, Grey and bold: relevant correlation
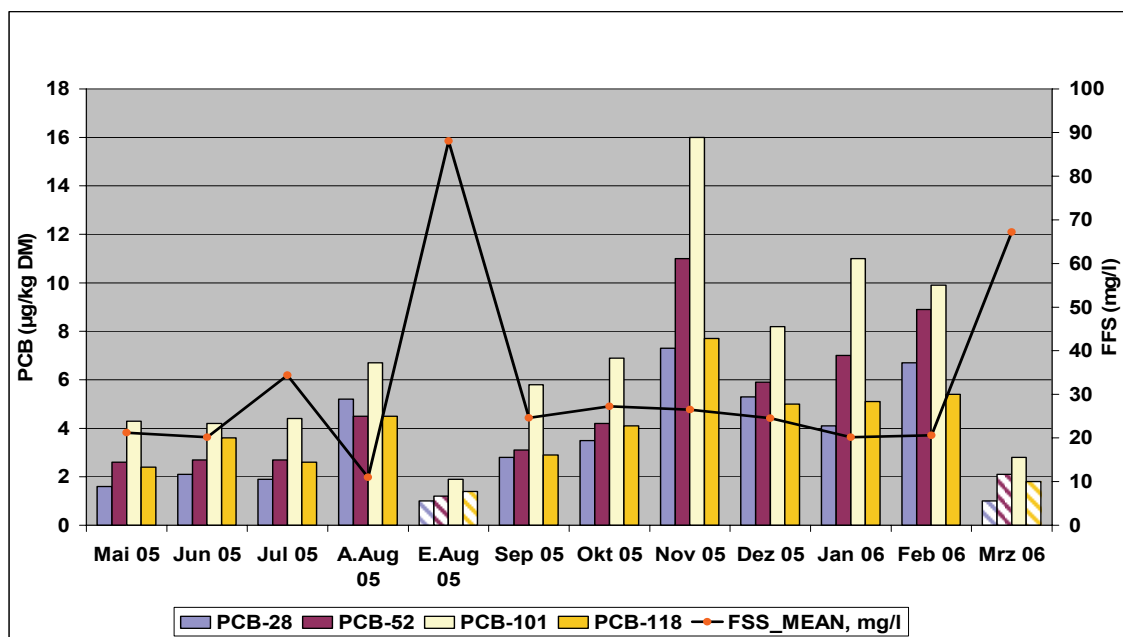
Fig. 4.2.1-2: Course of PCB concentration in suspended matter, depending on the contents of filterable suspended solids at the Bimmen (Rhine) monitoring station. S. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges. Correlations predominantly insignificant.

Particle size distribution in suspended matter

There are also significant correlations between particle size distributions in suspended matter and PCB concentrations. As in the case of heavy metals, negative correlations exist with parts of small particle size fractions and positive correlations with parts of the larger fractions. These correlations are particularly marked for the 40-63 µm fraction.
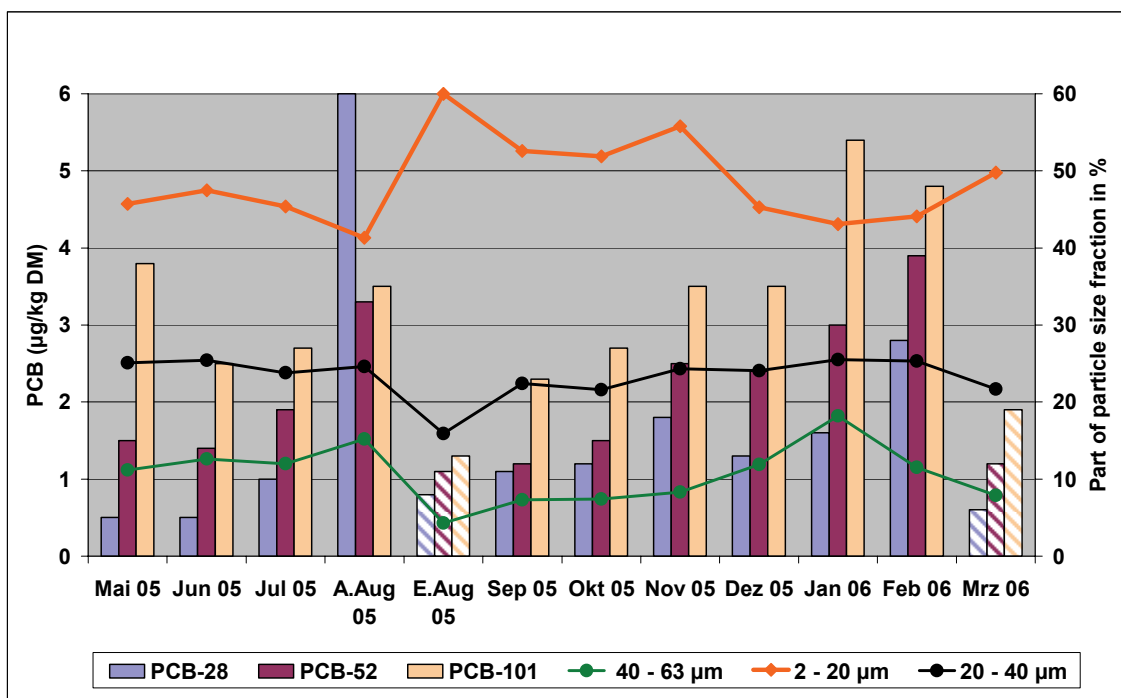
Fig. 4.2.1-3: Course of PCB concentration in suspended matter depending on particle size distribution at the Bad Honnef (Rhine) monitoring station. S. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges. All correlations between PCB congeners and particle size fractions are significant. Statistical parameters:

Fraction	PCB-28	PCB-52	PCB-101
2 – 20 µm	r= -0.45; s= 0.14	**r= -0.60; s= 0.037**	**r= -0.67; s= 0.018**
20 – 40 µm	r= 0.27; s= 0.40	r= 0.57; s= 0.055	**r= 0.75; s= 0.005**
40 – 63 µm	r= 0.43; s= 0.17	**r= 0.64; s= 0.03**	**r= 0.76; s= 0.004**
63 – 125 µm	r= 0.35; s= 0.30	r= 0.30; s= 0.36	r= 0.25; s= 0.46

For metals (see chapter. 4.1.2.3.3) these effects were associated with the increased introduction of low-contaminated, fine-grained sediments during high-water scenarios. For PCBs, similar correlations may be assumed, but cannot be confirmed, as PCB concentrations could not be determined in the dissolved phase.

TOCs in suspended matter

PCB concentrations for all congeners are significantly correlated to a TOC percentage of suspended matter of surface waters (Fig. 4.2.1-4). The relevance level of r > 0.7 was always exceeded, starting at evaluation of the full data collective (exception PCB-28) (Tab. 4.2.1-3).
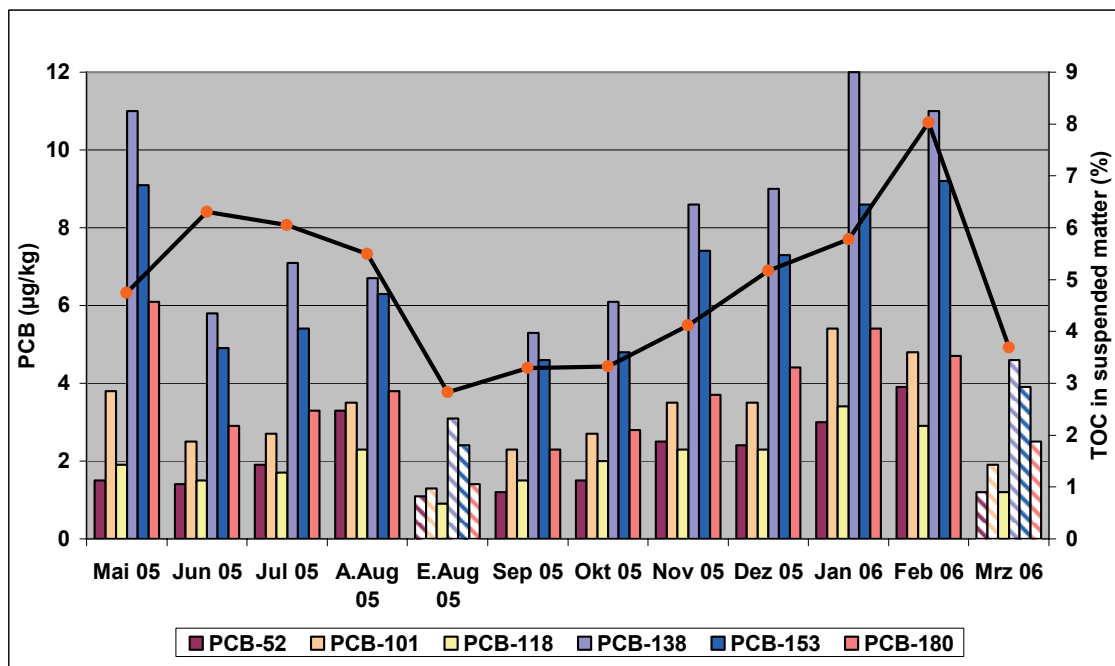
Fig. 4.2.1-4: Course of concentration of different PCB congeners versus the TOC proportion (%) in suspended matter, based on the example of the Bad Honnef (Rhine) monitoring station. S. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges. All correlations between PCB congeners and TOC are significant. Lowest coefficient:: PCB-180: r = 0.56 s = 0.06, highest coefficient: PCB-52: r = 0.72 s = 0.008

Discharge

No significant correlations were established between the relative discharge and PCB concentrations in the suspended matter of surface waters for the full data collective. Furthermore, significant correlations occurred only rarely at individual monitoring stations.

The concentration-lowering effect of high-water events, induced by increasing FSS volumes, was apparent from the concentration courses at some monitoring stations (Fig. 4.2.1-4), with a significant correlation to discharges only occurring for the PCB-118 congener.
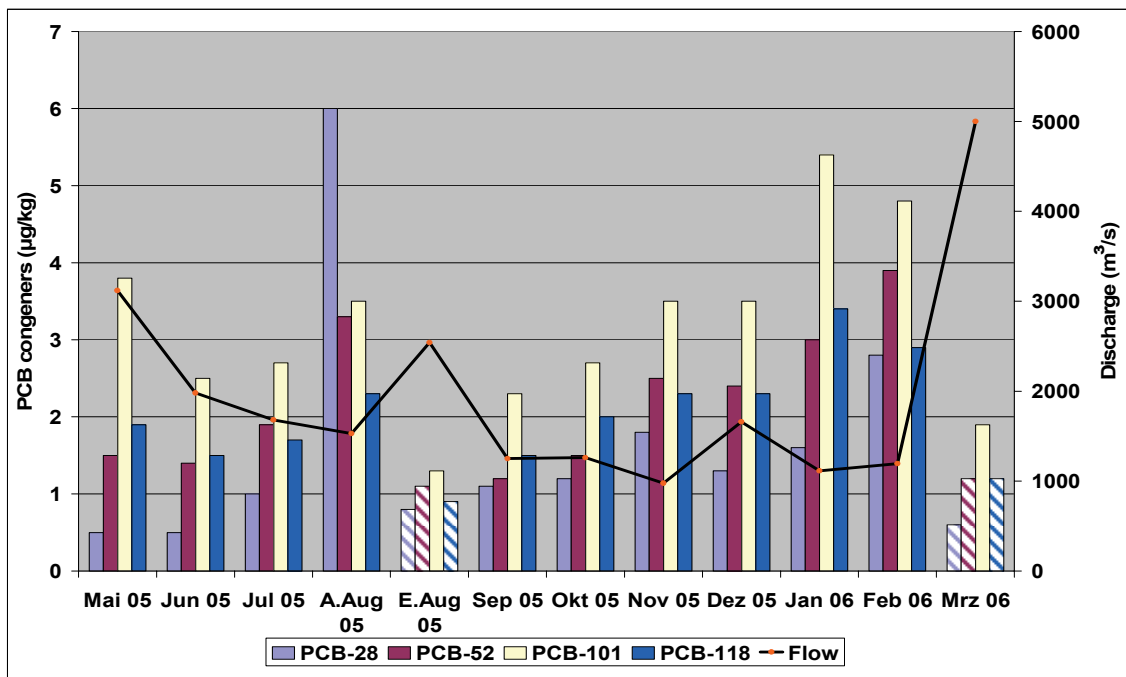
Fig. 4.2.1-5: Course of concentration of PCBs depending on discharge at the Bad Honnef (Rhine) monitoring station. S. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges. Correlations significant for PCB 118 only. r = -0.60; s = 0.04

Conductivity, saline-specific ions

Concentrations of low-chlorinated PCB congeners (PCB 28 – 118) show significant and relevant correlations to conductivity and chloride content. Saline contamination also predominantly enters surface waters within in the sump waters of hard-coal mines, in particular in the case of the Lippe and Emscher. Close correlations of PCB concentrations with conductivity and chloride confirm in particular the origin of low-chlorinated PCB congeners from the contaminants of hard-coal mining. Correlation coefficients are significantly lower for higher-chlorinated PCBs.

Influence of different methods for sampling suspended matter on PCB concentrations in suspended matter

The statistical evaluation of PCB concentrations produced negative correlations to small and positive correlations to the larger suspended matter fractions. One can therefore not rule out that sampling methods influence PCB concentrations, as fine fractions are recorded to a different degree during centrifugation and sedimentation.

The comparison of PCB concentrations from sedimentation and centrifugation at the Bimmen monitoring station did, however, rather show random variations in PCB patterns. No statistically significant tendency towards higher or lower PCB concentrations could be proven (Tab. 4.2.1-4).

Tab. 4.2.1-4: PCB concentrations in centrifuged and settled suspended matter, t-test

t-test parameters	PCB-28	PCB-52	PCB-101	PCB-118	PCB-138	PCB-153	PCB-180
n	10	10	10	10	10	10	10
t_{krit}:	2.201	2.201	2.201	2.201	2.201	2.201	2.201
t	-1.993	-1.206	-0.734	-0.268	-0.368	-0.032	0.186
Significant difference ?	no	no	no	no	no	no	no

Zero hypothesis: H0:$\mu=\mu_0=0$; alternative hypothesis : H1: $\mu\neq\mu_0$; signif. level: 5%

4.1.2.2 PCB-concentrations in original sample and filtrate

EU-WFD stipulates the original sample as the analysis matrix for prioritary organic contaminants. As part of this project, the unfiltered original sample was consequently regularly analysed for PCB contents in parallel with the suspended matter sample.

PCB concentrations in the original sample also fell below the detection limit of 5 ng/l at monitoring stations that showed increased PCB concentrations in suspended matter. After the first three sampling operations, the analysis of filtrate and centrifuge discharge water was waived, as any readings of the filtrate were also lower than detection limits, as expected.

Fossa Eugeniana special analysis

A special programme was carried out on the Fossa Eugeniana, a small tributary canal of the Moers stream, flowing into the left bank of the Rhine around Duisburg. This surface water currently shows a particularly high PCB contamination from mine drainage water. In the Fossa, individual low-chlorinated congeners (PCB-28) reached suspended matter concentrations of up to 90 µg/kg.

The objective of the analysis was to determine the distribution of PCB between dissolved and particle-bonded phases. Despite high levels of contamination, no PCBs could be detected in the original sample. Consequently, the results of special analyses do not provide any information either about the PCB distribution percentage in the original sample.

In the event that the analysis of PCBs is switched to the original water sample, as intended as part of monitoring according to EU-WFD for prioritary organic substances, one must anticipate that even increased PCB contaminations of surface waters can no longer be detected.

4.2.2 Chlorinated pesticides

Chlorinated pesticides were used to a considerable degree until the 1970s. Most substances and their metabolites are toxic, persistent and accumulate in the fatty tissues of animals. In order to protect humans and ecosystems, today most chlorinated pesticides are prohibited or their use is at least limited (BÖHM et al 2002).

As part of this project, the following chlorinated pesticides were analysed in water and suspended matter (Tab. 4.2.2-1):

Tab. 4.2.2-1:   Analysed chlorinated pesticides

α-HCH (hexachlorcyclohexane)	2,4-DDT	Aldrin
β-HCH	4,4-DDT	Dieldrin
γ-HCH (Lindan)	2,4-DDD	Endrin
δ-HCH (hexachlorcyclohexane)	4,4-DDD	Isodrin
	2,4-DDE	Telodrin
	4,4-DDE	

Most chlorinated pesticides are slightly polar and of a relatively low water solubility but good liposolubility (Tab. 4.2.2-2). Analyses show that today, contamination of surface waters with chlorinated pesticides is low. From analysed substances, only 4,4-DDE could be detected in a few instances in the Rhine at 1 and 3 µg/kg (range of DL) in suspended matter.

**Tab. 4.2.2-2:   n-octanol / water coefficient of distribution and water solubility of
prioritary-chlorinated pesticides (MÜLLER et al 1997)**

Pesticide	γ-HCH	DDT	Aldrin	Dieldrin	Endrin	Isodrin
log K_{ow}	4.0	6.19	5.59	5.9	4.56	6.5
Water solubility(mg/l) at 20 °C	6.2	0.0034	0.022	0.18	0.25	0.15

As expected, concentrations of chlorinated pesticides in all filtered and unfil-
tered water samples were below detection limits. The analysis of the filtered
water sample was therefore waived after the first sampling.

4.2.3   Polycyclic aromatic hydrocarbons (PAHs)

PAHs enter surface water through atmospheric deposition and industrial (e.g. coking plant) and communal discharges. Low-condensed PAHs such as naphthalene or methyl naphthalene are predominantly found dissolved in water, whilst higher condensed substances having a log K_{ow} > 6 (e.g. benzo(a)pyrene), are almost exclusively particle-bonded. Tab. 4.2.3-1 shows the water solubilities of PAHs. As part of the project, 16 PAHs were analysed in compliance with US-EPA.

Tab. 4.2.3-1: n-octanol/water partition coefficient of distribution and water solubility of selected prioritary PAHs (KOCH 1995; CHLUP 2004)

PAHs	log K_{ow}	Water solubility (mg/l) at 20 °C
Naphthalene	3.36	22 - 33.5
Anthracene	4.56	0.045
Fluoranthene	5.13	0.21
Benzo-(a)pyrene	6.13	0.0038
Benzo-(b)fluoranthene	6.57	0.0012
Benzo-(k)fluoranthene	6.3	0.00055
Benzo-(g,h,i)-perylene	6.63	0.00026
Indeno-(1,2,3-cd)-pyrene	7.66	0.062

4.2.3.1 PAH concentrations in suspended matter

Tab. 4.2.3-2 shows the range of PAH concentrations in suspended matter from which regional differences in contamination are apparent. As a result of contamination by industrial and municipal wastewater, highest PAH concentrations were found in the Emscher and Wupper.

Tab. 4.2.3-2: Ranges of concentration of regional contaminations of suspended matter with prioritary PAHs

	Bad Honnef, Rhine	Bimmen, Rhine	Emscher	Erft	Lippe	Wupper
n	12	12	11	9	10	11
Naphthalene	<0.03–0.04	0.10 – 0.62	0.51 – 3.3	<0.03	0.44 – 1.2	0.06 – 0.12
Anthracene	<0.03–0.05	<0.03–0.43	0.06 – 0.65	<0.03–0.05	0.1 – 0.17	0.16 – 0.37
Fluoranthene	0.19 – 0.76	0.19 – 1.5	1.9 – 5.9	0.42 – 0.99	0.91 – 1.3	1.9 – 4.2
Benzo-(b)-fluoranthene	0.13 – 0.52	0.14 – 0.91	1.5 – 2.7	0.33 – 0.57	0.62 – 0.98	1.4 – 3.3
Benzo-(a)-pyrene	0.10 – 0.39	0.10 – 0.62	0.96 – 1.7	0.22 – 0.35	0.37 – 0.57	1.1 – 2.2
Benzo-(ghi)-perylene	0.1 – 0.38	0.11 – 0.58	1 – 1.6	0.24 – 0.33	0.37 – 0.62	1.1 – 2.3
Indeno-(123-cd)-pyrene	0.08 – 0.36	0.08 – 0.52	0.83 – 1.4	0.2 – 0.3	0.38 – 0.6	1.2 – 2.1
Sum PAH EPA*	1.1 – 4.71	1.17 – 10.5	13.5 – 38.1	2.52 – 4.66	6.9 – 10.6	13.1 – 26.8

Sum PAH EPA – total of 16 PAHs in compliance with US EPA   n = number of samples, DL = 0, 03 mg/kg

Correlations between PAH concentrations in suspended matter and associated parameters

The entire data collective of PAH concentrations in suspended matter was examined for correlations to associated parameters (Tab. 4.2.3-3).

Tab. 4.2.3-3: Significant correlations between concentrations of prioritary PAHs in suspended matter and associated parameters

	Naph-thalene	Anthra-cene	Fluoran-thene	Benzo-(a)-pyrene	Benzo-(b)-fluoran-thene	Benzo-(ghi)-perylene	Indeno-(123-cd)-pyrene
FSS	r = -0.420 s = 0.0069	--	--	--	--	--	--
SS_P_TOC	**r = 0.704 s =<0.0001**	r = 0.475 s <0.0001	r = 0.541 s <0.0001	**r = 0.713 s <0.0001**	r = 0.687 s <0.0001	**r = 0.732 s <0.0001**	r = 0.628 s <0.0001
Percentage of grain-size fractions							
< 2 µm	r = -0.500 s = 0.0012	r = -0.312 s = 0.0134	r = -0.579 s <0.0001	r = -0.640 s <0.0001	r = -0.679 s <0.0001	r = -0.677 s <0.0001	r = -0.651 s <0.0001
2-20 µm	r = -0.555 s <0.0002	r = -0.383 s <0.0021	r = -0.626 s <0.0001	**r = -0.693 s <0.0001**	**r = -0.723 s <0.0001**	**r = -0.733 s <0.0001**	r = -0.672 s <0.0001
20 – 40 µm	r = - 0.570 s = 0.0002	r = -0.359 s = 0.0042	--	r = -0320. s = 0.0112	r = -0.255 s = 0.0455	r = -0.305 s = 0.0170	--
40-63 µm	r = 0.432 s <0.0061	--	r = 0.542 s <0.0001	r = 0.544 s <0.0001	r = 0.615 s <0.0001	r = 0.620 s <0.0001	r = 597 s <0.0001
63-125 µm	r = 0.681 s <0.0001	r = 0.409 s = 0.0011	r = 0.534 s <0.0001	r = 0.656 s <0.0001	r = 0.658 s <0.0001	r = 0.675 s <0.0001	r = 0.583 s <0.0001

n = 54 – 65 depending on parameter, grey and bold: relevant correlation

Discharge

No relevant correlations were established for PAH contents and relative discharges of surface waters. Increased discharges did, however, have a lowering effect on the PAH contents of suspended matter. This lowering effect is clearly apparent in the case of increased discharges (end of August 05) from the shown example (Rhine/Bimmen) (Fig. 4.2.3-1)
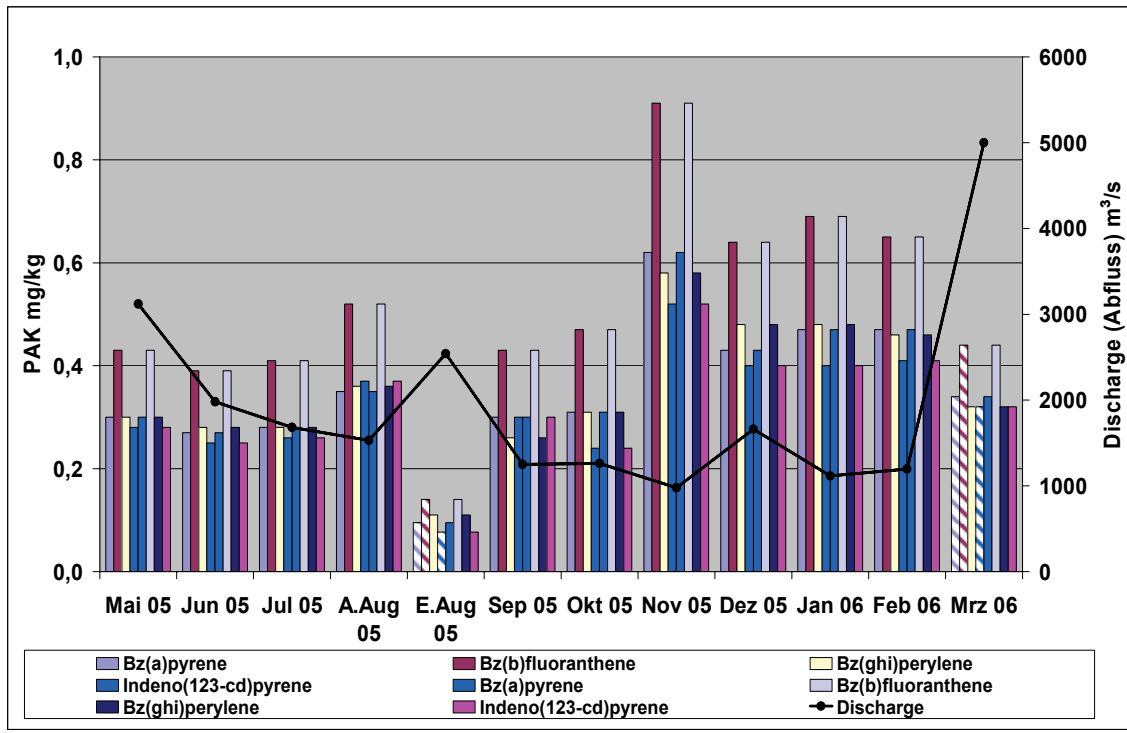
Fig. 4.2.3-1: **Course of concentration of PAHs in suspended matter versus discharges at the Bimmen (Rhine) monitoring station.** S. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges. No significant correlations between PAH concentrations and flow

Filterable suspended solids (FSS)

There were no significant correlations between PAH concentrations and FSS contents. At some monitoring stations, links between increasing FSS contents and reduced PAH concentrations were apparent (Fig. 4.2.3-2). These are probably diluting effects as a result of the entry of low-contaminated fine sediment in increased discharges.
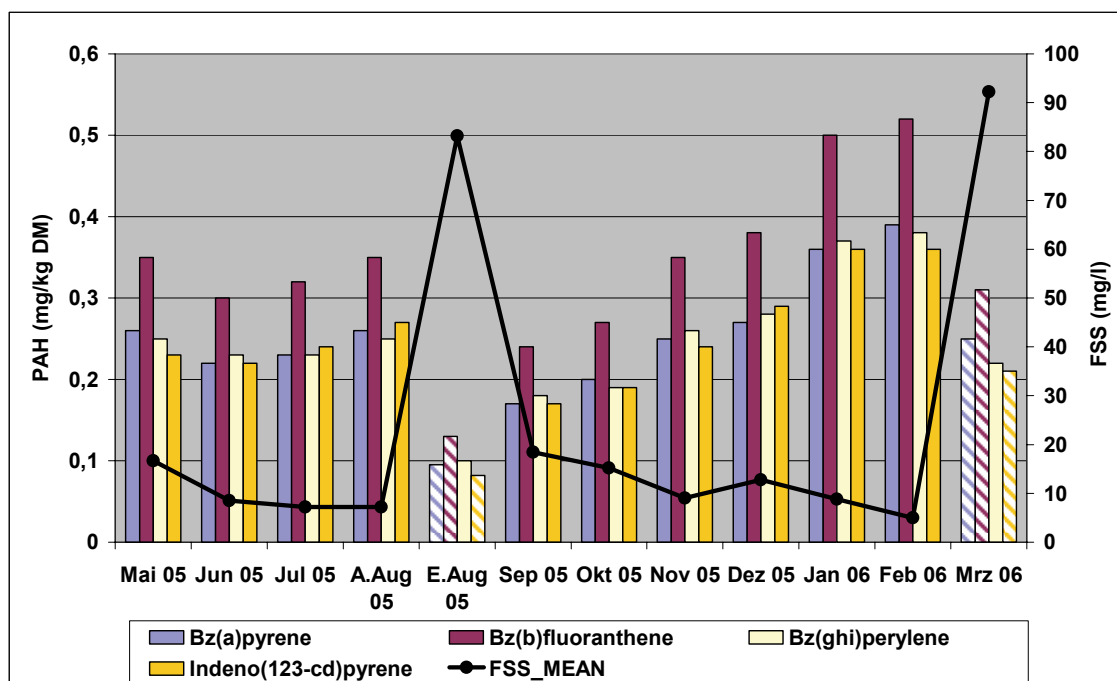
Fig. 4.2.3-2: PAHs in suspended matter and the contents of filterable suspended solids (AFS) in water at the Bad Honnef (Rhine) monitoring station. S. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges. Stat. parameters:
Bz(a)pyrene:	r= -0.50; s= 0.1	Bz(b)fluoranthene:	r= -0.57; s= 0.05;
Benzo(ghi)perylene	r= -0.59; s= 0.04	Indeno(123-cd)pyrene:	r= -0.62; s= 0.03

Particle size distribution

Significant correlations can also be demonstrated for PAHs in suspended mat-ter and particle size distribution (Tab. 4.2.3-3). Correlation coefficients are gen-erally significantly lower than those for PCBs (see chapter 4.2.1). Only negative correlations of higher-condensed PAHs with a fraction of 2-20 µm reach rele-vance level.

At some monitoring stations, the positive correlations of PAH contamination to larger fractions are clearly closer and are shown in the example of the Bad Honnef/ Rhine monitoring station in Fig. 4.2.3-3.
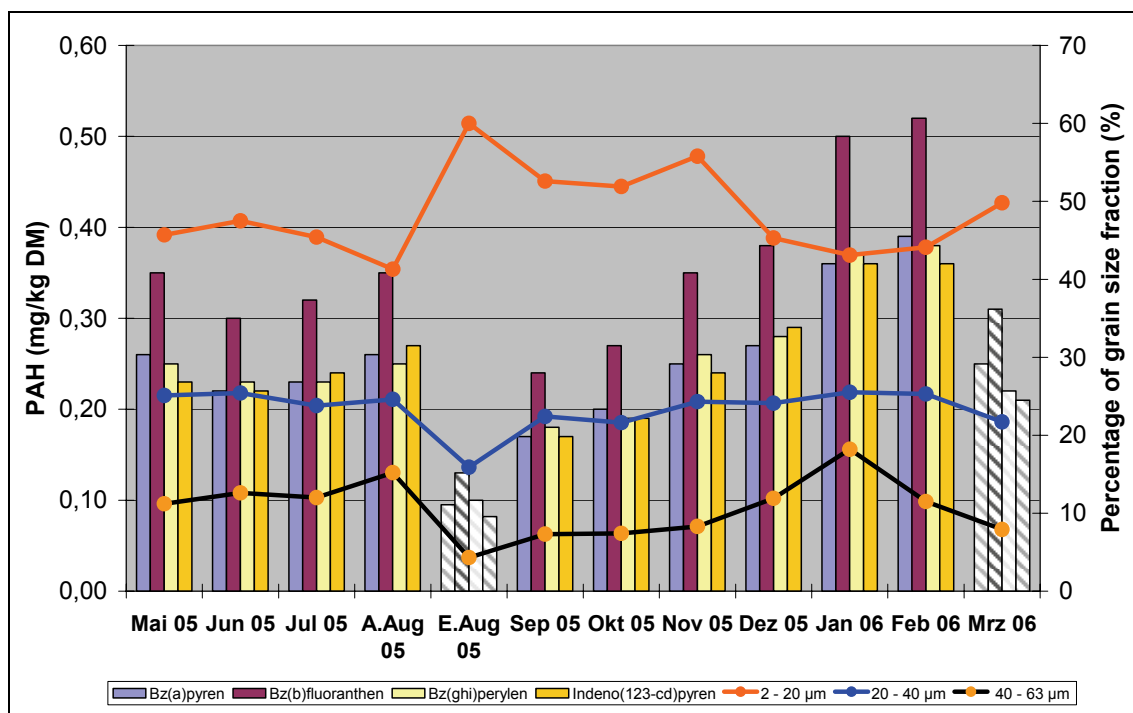
Fig. 4.2.3-3: PAH contents in suspended matter and particle size distribution at the Bad Honnef monitoring station (Rhine) S. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges. Stat. parameters:

KGV	Bz(a)pyrene		Bz(b)fluoranthene		Bz(ghi)perylene		Indeno(123-d)pyrene	
2 – 20 µm	r= -0.74	s= 0.006	r= -0.74	s= 0.006	r= -0.72	s= 0.008	r= -0.80	s= 0.002
20 – 40 µm	r= 0.77	s= 0.0035	r= 0.80	s= 0.002	r= 0.80	s= 0.002	r= 0.82	s= 0.001
40 – 63 µm	r= 0.72	s= 0.009	r= 0.75	s= 0.005	r= 0.75	s= 0.005	r= 0.81	s= 0.001
63 – 125 µm	r= 0.3	s= 0.38	r= 0.3	s= 0.36	r= 0.27	s= 0.41	r= 0.39	s= 0.24

Correlations to particle size distributions and the effects of reduced concentrations in the case of increased discharges were observed for prioritary metals (see chapter 4.1.3) and PCBs (see chapter 4.2.1). For metals, the effects are put down to the increased inflow of low-contaminated fine-grain sediments during high water levels.

Similar links may be assumed for higher condensed PAHs but cannot be confirmed, as insufficient results were available above detection limits in original and filtered samples.

TOC

All prioritary PAHs showed significant positive correlations with the TOC contents of suspended matter, reaching a relevance level of r = 0.7 for naphthalene, benzo(a)pyrene and benzo(ghi)perylene. These close correlations are shown in Fig. 4.2.3-4 based on the example of the Bad Honnef monitoring station (Rhine).
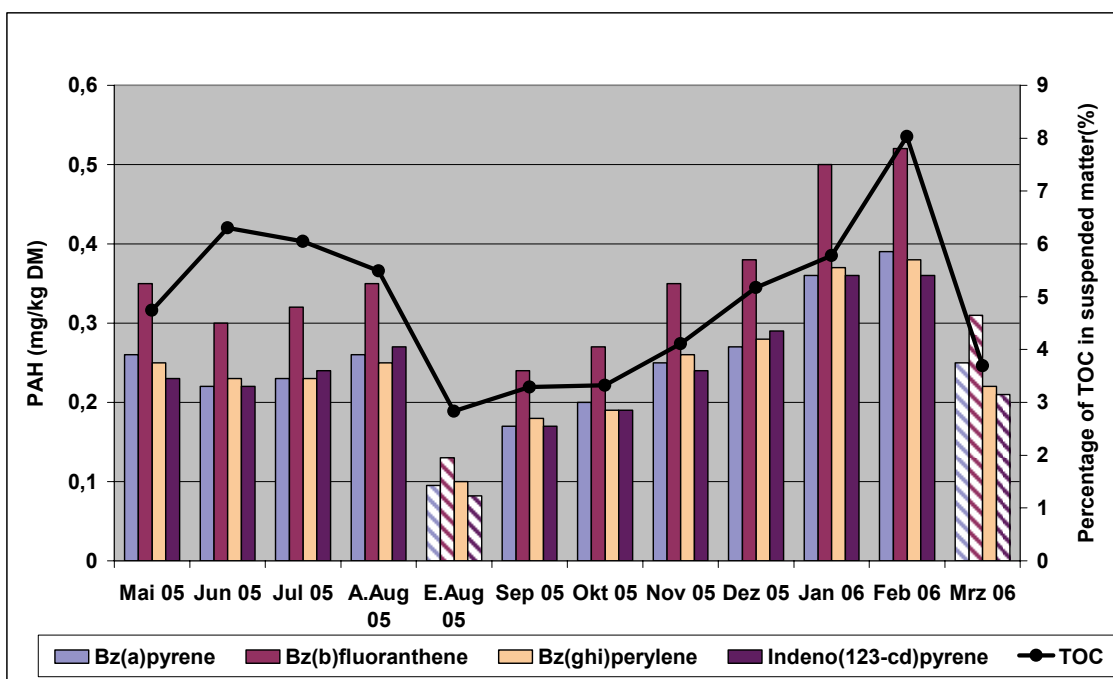
Fig. 4.2.3-4: PAH concentrations and percentage of TOC proportions in suspended matter at the Bad Honnef station (Rhine). S. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges. Stat. parameters:

Bz(a)pyrene:	r= 0.77	s= 0.003;	Bz(b)fluoranthene:	r= 0.78	s= 0.003;
Benzo(ghi)perylene:	r= 0.79	s= 0.002;	Indenopyrene:	r= 0.80	s= 0.002

Effects of different sampling methods on PAH concentrations in suspended matter

The results of four weeks of sedimentation and in each case of one centrifugation at the end of the sedimentation period were available for examining sampling effects on PAH concentrations.

Comparisons of PAH concentrations obtained at the Bimmen station from sedimentation and centrifugation showed a tendency towards higher PAH concentrations in the suspended matter, obtained by centrifugation (Fig. 4.2.3-5, Tab. 4.2.3-4).

Tab. 4.2.3-4:   Averages for PAH concentrations in suspended matter. Comparison of concentrations in suspended matter from sedimentation and centrifugation

	Fraction 40-63 µm	Fraction 63-125 µm
Centrifugation	8.5 %	4.6 %
Sedimentation	15.1%	11.3 %

	Naph-thalene	Anthra-cene	Fluoran-thene	Benzo-a-pyrene	Benzo-b-fluoran-thene	Benzo-ghi-perylene	Indeno-123-pyrene
Centrifugation	0.32	0.12	0.73	0.35	0.51	0.35	0.32
Sedimentation	0.27	0.13	0.85	0.42	0.59	0.39	0.36

Statistically significant higher concentrations of suspended matter obtained by centrifugation were only demonstrated for benzo(a)pyrene and benzo(B)fluoranthene. (Tab. 4.2.3.-5)

Tab. 4.2.3-5: PAH concentrations in centrifuged and sedimentated suspended matter, t-test

t-test parameters	Naphthalene	Fluoranthene	Phenanthrene	Anthracene	Benzo(a)pyrene	Pyrene
t_{krit}:	2.447	2.262	2.262	2.262	**2.262**	2.262
t	-1.57	1.87	-0.38	0.13	**2.62**	1.40
Significant difference?	no	no	no	no	**yes**	no
	Benzo(b) fluoranthene	**Chrysene**	**Benzo(ghi) perylene**	**Indeno(123-cd) pyrene**		**SumPAH EPA**
t_{krit}:	**2.262**	2.262	2.262	2.262		2.262
t	**2.265**	2.11	2.11	1.66		1.28
Significant difference?	**yes**	no	no	no		no

n = 10, Zero hypothesis: H0:μ=μ₀=0; alternative hypothesise : H1: μ≠μ₀; signif. level: 5%

From the comparison of different methods for obtaining suspended matter, one can deduct that a uniform sampling method must be determined for monitoring PAHs, in order to prevent any differences in concentration caused by different methods.
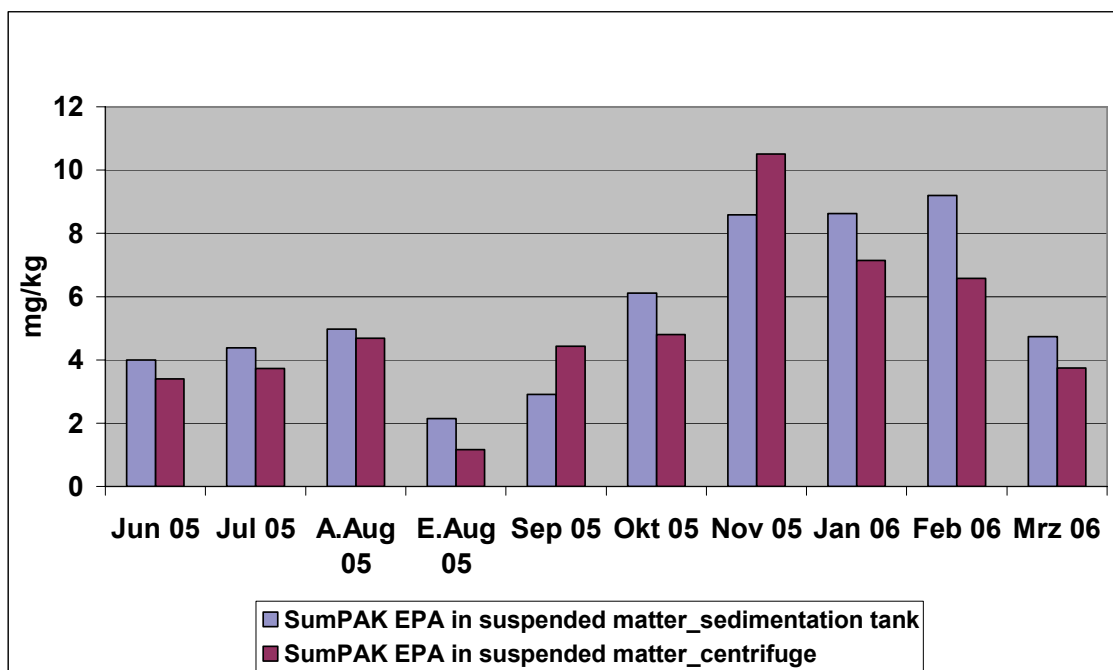
Fig. 4.2.3-5: Comparison of total of 16 PAHs in compliance with US-EPA in suspended matter when using different sampling methods

4.2.3.2 PAH concentrations in the original sample and filtrate

In the original sample and filtrate only low-condensed PAHs (naphthalene, 2-methyl naphthalene, phenantrene and fluoranthene) were regularly detected in the dissolved phase. Higher condensed PAHs in the liquid phase could frequently not be detected. Consequently, only the original samples from the monitoring stations Bimmen (Rhine), Wesel (Lippe) and Dinslaken (Emscher) were regularly analysed. Tab. 4.2.3-6 shows the obtained ranges of test results, with concentrations below or close to detection limits in most cases.

Tab. 4.2.3-6:   Regional contamination of selected PAHs in original sample at three analysed monitoring stations (DL = 5 ng/l)

	Bimmen, Rhine (ng/l)	Dinslaken, Emscher (ng/l)	Wesel, Lippe (ng/l)
Naphthalene	<5 – 15	14 – 35	10 – 29
Anthracene	<5 – 8	<5 – 6	<5
Fluoranthene	<5-27	9 – 54	8 – 34
Phenanthrene	8 – 14	11 – 59	8 – 31
Pyrene	<5-26	28 – 36	<5 – 25
Benzo(b)fluoranthene	<5 – 17	<5 – 14	<5 – 19
Benzo(a)pyrene	<5 – 11	<5 – 8	<5 – 12
Benzo(ghi)perylene	<5 – 9	<5	<5 – 10
Indeno(1,2,3cd)pyrene	<5 – 9	<5	<5 – 11

For four series of tests, PAH concentrations were also measured in filtrate and centrifugal discharges. Only naphthalene, 2-methyl naphthalene, phenanthrene and fluoranthene were detected on a regular base. Like in the original sample, test results of the filtrate and centrifugal discharge, frequently were within detection limits (Fig. 4.2.3-6).
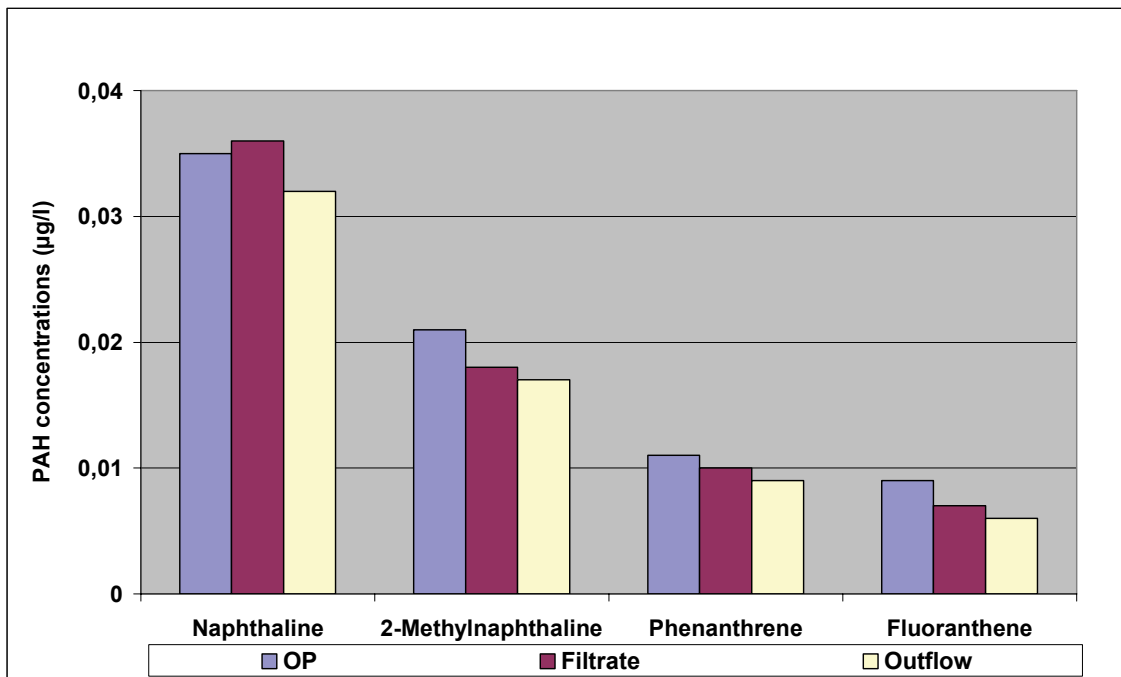
Fig. 4.2.3-6: Dissolved PAH concentrations of PAH representatives with low log K_{ow} of original samples, centrifugal outflow and filtrate from the Dinslaken monitoring station (Emscher)

Distribution of PAH contamination to dissolved and solids phases

An attempt was made to determine the distribution of PAH contamination in the dissolved and solids phases at the most contaminated monitoring station (Emscher). The composition at the mouth of the Emscher is, however, considerably influenced by the wastewater treatment plant at the mouth of the river and thus represents a special case.

Data from the Emscher confirm the tendency of PAHs to increasingly settle on suspended matter as condensing increases (and simultaneously increasing log K_{ow}) (Fig. 4.2.3-7). Concentrations of the four low-condensed PAHs detectable in water and the calculated part of particle-bonded PAHs are shown in Tab. 4.2.3-7. Determination of dissolved parts for higher condensed PAHs was not even possible at a monitoring station with obvious contamination in suspended matter.

Tab. 4.2.3-7: Distribution of PAHs detectable in water to dissolved and suspended matter phases

	PAH content in suspended matter (mg/kg)	Measured total contamination of water sample (ng/l)	Calculated particle-bonded PAHs in water samples (ng/l)	Particle-bonded PAH share (%)	log K_{ow}
Naphthalene	1.8	35	3.1	9%	3.36
2-Methyl-naphthalene	3	21	5.2	25%	4.0
Phenanthrene	1.6	11	2.8	25%	4.57
Fluoranthene	1.9	9	3.3	37%	5.02
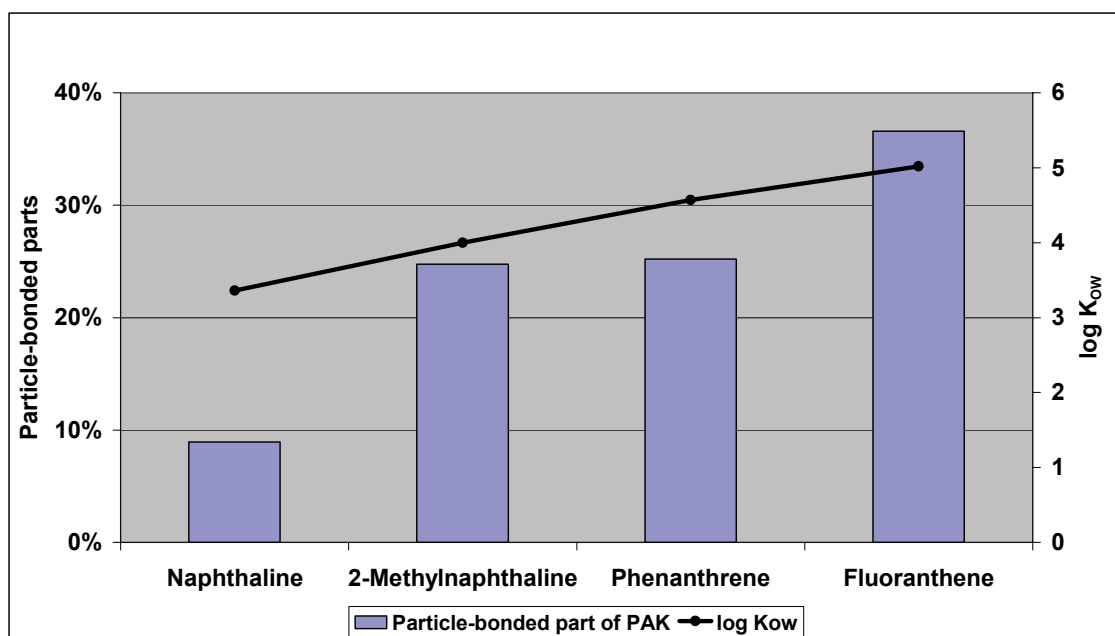
Fig. 4.2.3-7: Particle-bonded parts of PAHs detectable in water at the Dinslaken monitoring station (Emscher) and respective associated log K_{ow}

4.2.3.3 Special PAH analyses (Emscher upstream from wastewater treatment plant Dinslaken at river mouth)

In order to determine phase distribution, a special analysis was carried out in the river Emscher, highly contaminated with PAHs, upstream from the wastewater treatment plant at the river mouth, i.e. in mixed wastewater. Original samples, filtrate and filter residues were analysed. Samples were homogenized and split up in five part samples which were analysed simultaneously.

Fig. 4.2.3-8 shows the results of analyses for selected PAHs. As expected, the share of PAHs in the dissolved phase decreases with increasing condensation. There are no significant differences in concentration between the original sample and the filtered sample for water-soluble naphthalene. Naphthalene was determined in a nearly fully dissolved state.

As the level of the degree of condensation of PAH increases, concentrations in the original sample are reduced, falling under detection limits in the filtrate, whilst concentrations in the filter residue increase at the same time.

Concentrations of the higher condensed PAH found in filter residue significantly exceed, in the case of higher condensed PAHs, PAH values determined in the original sample, as particle-bonded PAHs cannot be fully extracted from the original sample by the extraction process. Earlier tests carried out by LUA showed that only approx. 40 – 60 % of the particle-bonded proportions were recorded during liquid-liquid extraction with n-hexane in compliance with EN ISO 17993. The mass balance (filter residue + filtrate = original sample) therefore does not work (due to the method).

The results of the special test illustrate the difficulties of PAH analyses. In the case of lower contaminated PAHs, concentrations determined for the original sample and/or in the filtrate, more or less represent the actual total content. Based on an analysis in suspended matter, the concentrations of low condensed PAHs are clearly underestimated.

124

For higher condensed PAHs, concentrations above detection limits were only found in case of severe contamination and higher FSS contents. There is also a problem of incomplete extraction of particle-bonded parts from the original sample so that lower results cannot be avoided (Fig. 4.2.3-8).

One cannot rule out that existing contamination with higher condensing PAHs has been overlooked during the analysis of original samples. In order to produce uniform and comparable PAH analyses for surface water evaluation in compliance with WFD, binding conventions for extraction and analysing methods to be used have to be agreed.
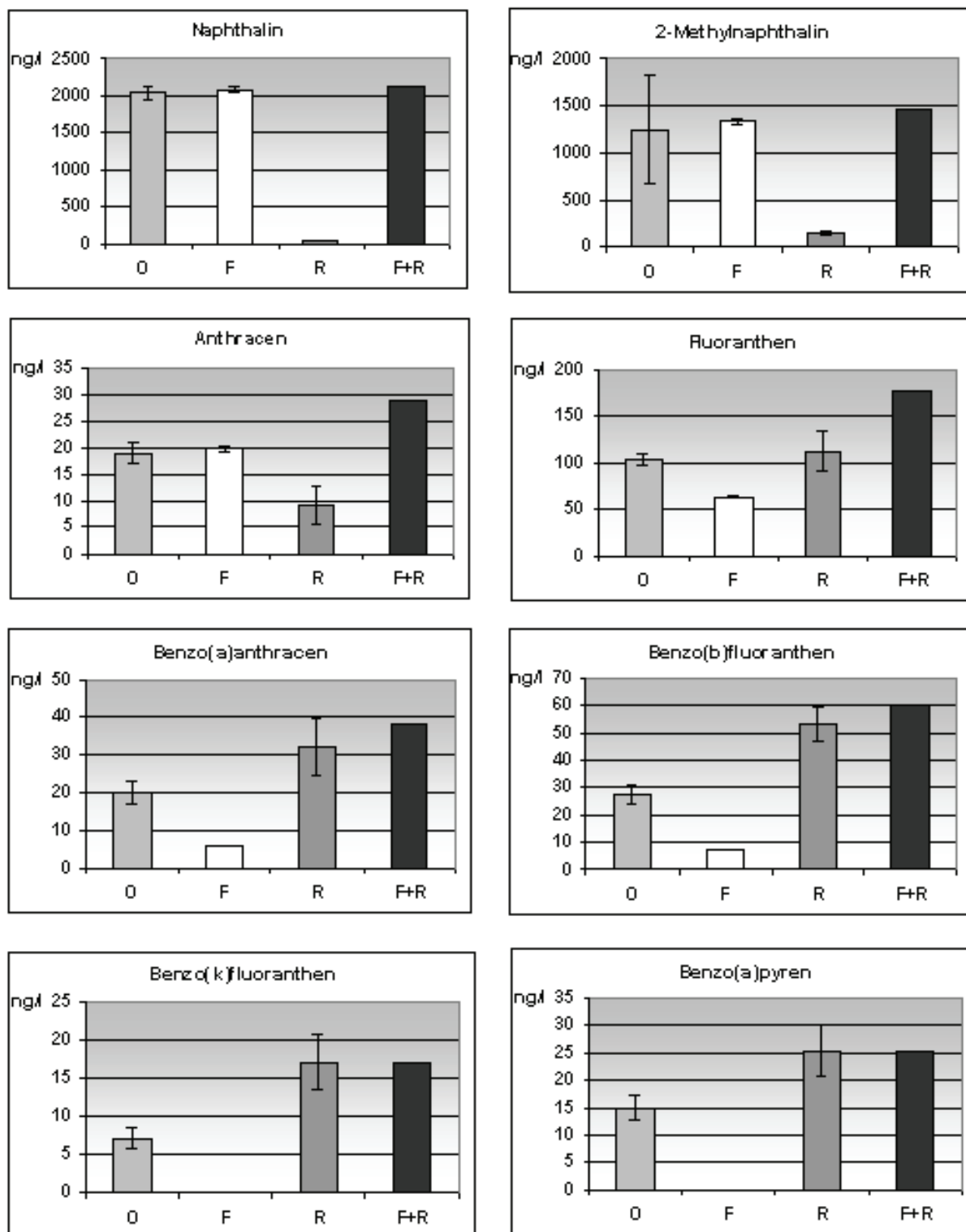
Fig. 4.2.3-8: Distribution of PAHs between dissolved and particle-bonded phases
O = original sample, F = filtered sample, R = filter residue, produced in compliance with DIN 38414-23, part B
F+R Total mass concentration of filtered sample and filter residue
Average values and standard deviation of five simultaneously analysed part samples

4.2.4 Polar herbicides (Isoproturon and Diuron)

Isoproturon and Diuron show a low octanol/water partition coefficient of distri-
bution and thus easily water-soluble (Tab. 4.2.4-1). Isoproturon is used as a
selective herbicide before and after sowing and mainly for the cultivation of
grain. Diuron is used as a global herbicide, e.g. for traffic areas. The use of both
substances is nowadays restricted by law.

Tab 4.2.4-1: n-octanol/water coefficients of distribution and water solubility of
Isoproturon and Diuron (RIPPEN 1987)

	log K_{ow}	Water solubility (mg/l)
Isoproturon	2.5	65
Diuron	2.82	42

Because of the method employed, the untreated original sample could not be
analysed by HPLC, as samples have to be centrifuged prior to analysis in order
to prevent blockages in the HPLC system. Apart from the centrifuged water
sample, concentrations in filtered water samples were also examined as part of
this project.

During the application period of the substances (Isoproturon : grain herbicide,
autumn, spring;   Diuron : total herbicide, vegetation period) Isoproturon or Di-
uron could only be detected in a few samples.

In samples, where Isoproturon and Diuron were detectable in water, the centri-
fuged suspended matter was also extracted and concentrations were analysed.
Quality assurance of results was based on determination of the retrieval rate
(deuterized standard). The particle-bonded proportions of herbicide contamina-
tion of water samples were calculated from test results. Tab. 4.2.4-2 contains
analyses and calculated results for Isoproturon.

In the case of the three samples with positive results, the filtrate was also ana-
lysed. As expected, concentrations in the filtered and centrifuged water sample
were always the same. Based on the results of the analyses, a negligible parti-
cle-bonded share of less than 0.5% may be calculated for Isoproturon.

Tab. 4.2.4-2:   Concentrations of Isoproturon in water and suspended matter

Monitoring stations	Suspended matter concentration (µg/kg)	FSS mg/l	Original sample concentration (µg/l)	Particle-bonded share (%)
Bimmen-Rhine	8.35	20.5	0.18	0.11
Bimmen-Rhine	3.92	21.2	0.05	0.09
Neuss Erft	5.13	26	0.03	0.24
Neuss-Erft	5.30	17.6	0.02	0.40
Wesel-Lippe	3.71	18.7	0.07	0.07
Wesel-Lippe	5.67	9	0.10	0.04
Wesel-Lippe	13.88	12.6	0.28	0.05
Wesel-Lippe	9.77	20	0.19	0.06

Fig. 4.2.4-1 shows the correlation of concentrations of Isoproturon in water and suspended matter. This correlation of results is considerably worsened in the area around detection limits due to analytical scatter.
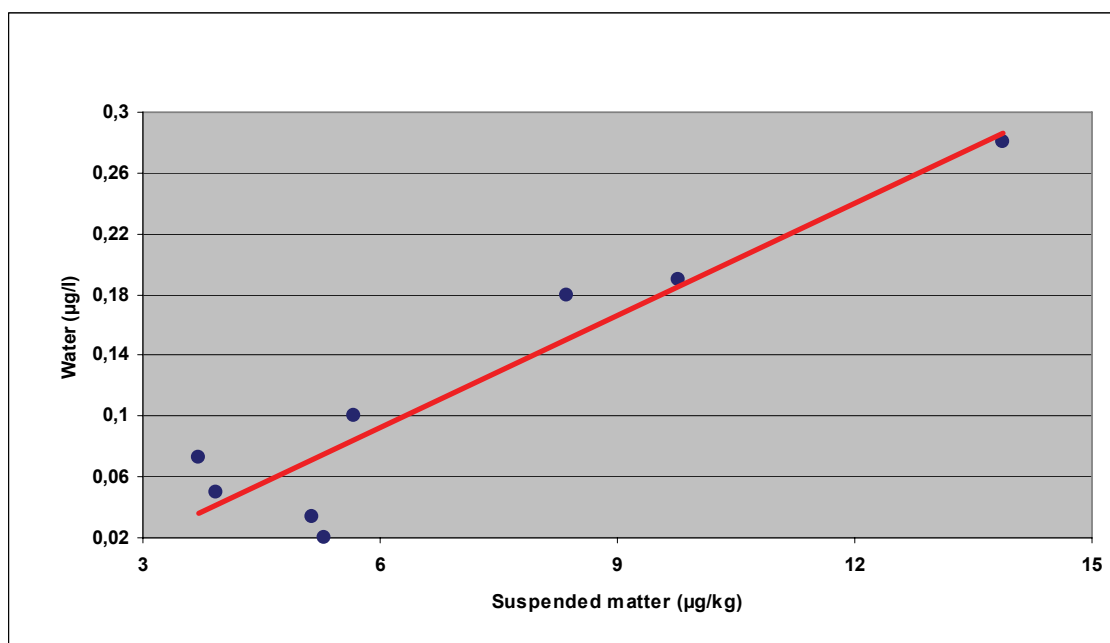
Fig. 4.2.4-1: Correlation of concentrations of Isoproturon in water and suspended matter

Tab. 4.2.4-3 represents a compilation of analytical results of concentrations of Diuron in water and suspended matter, the contents of filterable suspended solids and the share of particle-bonded Diuron determined by calculation.

A share of Diuron contents of less than 1.0 % may be derived from analytical results, which is therefore also negligible.

Isoproturon and Diuron are nearly fully dissolved in water. The best method for effectively monitoring the concentrations of these substances is the analysis of concentrations in the original sample (centrifugal, as stipulated by the method).

Tab. 4.2.4-3: Concentrations of Diuron in water and suspended matter

Monitoring station	Suspended matter concentration (µg/kg)	FSS mg/l	Original sample concentration (µg/l)	Particle-bonded share (%)
Bimmen-Rhine	12.12	11	0.03	0.27%
Bimmen-Rhine	6.64	24.6	0.02	0.56%
Bimmen-Rhine	12.15	21.2	0.04	0.34%
Neuss Erft	15.18	26	0.06	0.41%
Neuss Erft	23.70	17.6	0.04	0.89%
Neuss-Erft	22.65	25	0.08	0.46%
Wesel-Lippe	19.02	18.7	0.06	0.42%
Wesel-Lippe	36.47	12.6	0.04	0.86%
Wesel-Lippe	37.40	20	0.16	0.27%

5 Monitoring of water quality in compliance with EU-WFD Consequences of analysis matrix selection for assessment options of surface water contamination by prioritary substances

Quality standards for prioritary substances and respective matrix to be analysed currently stipulated by the EU, will have consequences for future surface water monitoring. Due to the change of the analysis matrix now required for many substances, the question of whether current contamination assessments are valid and compatible with future environmental monitoring is of great importance.

Based on the results of the project, carried out under routine conditions for monitoring surface waters, some of these issues relating to examined groups of contaminants, can already be solved.

5.1 Heavy metals

During present water monitoring activities, metal concentrations are determined in suspended matter or in unfiltered water samples. Analysing methods required for this have been established. A very extensive database is available for evaluating contamination. In addition to the four prioritary metals (lead, cadmium, nickel,mercury), chrome, zinc, copper and often other metals were analysed as a matter of routine.

In compliance with EU-WFD, existing dissolved parts of prioritary heavy metals should now be compared with harmonized EU quality standards derived from toxicological data.

Research carried out by CARPENTER & HUGGETT (1984) on the Susquehanna River (Chesapeake Bay) showed a highly fluctuating distribution of heavy metals in dissolved and particle-bonded phases for copper, nickel und zinc in the course of a year. Depending on the type of metal and season, 50 - 90 % of metal volumes were particle bonded. Similar findings were also made for examined metals as part of this project.

When comparing rivers with and without anthropogenic contamination, a higher share of dissolved heavy metals may be expected for contaminated surface waters (FÖRSTNER & SALOMONS 1984). Various tests show different distributions of heavy metals depending on physico-chemical parameters: nickel, zinc and cadmium preferably exist in a dissolved state under natural pH conditions, whilst lead and copper have a high affinity to suspended matter (FÖRSTNER & PATCHINEELAM 1976).

As many tests confirm the influence of chemical/physical characteristics of surface water on the distribution of metals between dissolved and particulate phases, these links were also investigated and evaluated as part of this project.

5.1.1 Influences during sampling

5.1.1.1 Adsorption effects

For the analysis of dissolved metal parts, samples cannot be preserved by acidification. As previously illustrated in the results section, significant losses may occur over a short period of time as a result of adsorption on sample container surface, in particular for samples of a high FSS content.

Where samples are only filtered in the laboratory, the results of findings may be lower, as concentration losses cannot be ruled out as a result of delayed filtration. In order to reduce the risk of assessing surface water contaminations incorrectly, it is recommended to carry out "in-situ" filtrations of water samples under standardized conditions and directly after sampling.

5.1.1.2 Particle-size effects as a result of different sampling methods

In the case of centrifugation, the percentage share of fractions of < 20 µm is significantly higher than that of sedimentation. The preferred accumulation of metal ions in fine-grain fractions thus leads to method-related, statistically sig-

nificantly higher concentrations of prioritary metals in centrifugal suspended matter.

In order to ensure better comparisons and evaluations of results of suspended matter analyses in compliance with EU-WFD, it is recommended to agree on uniform conventions for applicable sampling methods for obtaining suspended matter.

5.1.3 Factors influencing the distribution of metals between dissolved and particle-bound phases

The results of the project show that the part of dissolved fractions to be analysed in compliance with WFD is not only characterised by the volume of discharges but also by respective existing chemical/physical surface water conditions.

During evaluation of a data collective, significant correlations (acc. to Pearson) regularly occur between associated parameters and calculated metal distributions to different matrixes (Tab. 5.1-1).

Tab. 5.1-1:   Significant correlation between particle-bound parts of metal contaminations and associated parameters

	PAR_Pb	PAR_Cd	PAR_Ni		PAR_Pb	PAR_Cd	PAR_Ni
SS_P_TOC	r = - 0.510 s <0.0001	r = - 0.540 s <0.0001	r = - 0.481 s <0.0001	**FSS**	--	r = 0.504 s <0.0001	r = 0.570 s <0.0001
Conductivity	r = - 0.484 s <0.0001	r = - 0.408 s = 0.0009	r = - 0.318 s = 0.0110	**Percentage of grains-size fraction**			
Chloride	r = - 0.540 s <0.0001	r = - 0.535 s <0.0001	r = - 0.440 s = 0.0002	**< 2 µm**	r = 0.472 s <0.0001	r = 0.411 s = 0.0007	r = 0.494 s < 0.0001
Ca	r = - 0.452 s = 0.00021	r = - 0.450 s = 0.0002	r = - 0.341 s = 0.0055	**2 - 20 µm**	r = 0.455 s = 0.0002	r = 0.382 s = 0.0018	r = 0.409 s = 0.0008
Mg	r = - 0.471 s <0.0001	r = - 0.264 s = 0.0334	--	**20 - 40 µm**	r = 0.309 s = 0.0129	r = 0.356 s = 0.0039	--
K	r = - 0.532 s <0.0001	r = - 0.265 s = 0.0334	--	**40 - 63 µm**	r = -0.324 s = 0.0090	--	r = -0.320 s = 0.0100
Na	r = - 0.537 s <0.0001	r = - 0.531 s <0.0001	r = - 0.432 s = 0.0003	**63 - 125 µm**	r = -0.544 s <0.0001	r = -0.452 s <0.0002	r = -0.436 s = 0.0004

**n = 54 – 65 depending on the parameter, FSS = filterable suspended solids,
SS_P_TOC = carbon proportions (total) of suspended matter in %**

5.1.3.1 Available filterable suspended solids (FSS)

The FSS volume may be used as an indication for binding sites (surfaces) of dissolved ions. A considerably number of metals, such as nickel and cadmium, large parts of which are normally in a dissolved state, are forming particular bonds with an increasing availability of (finely grained) suspended matter (Fig. 5.1-2). Close connections between available suspended matter and any metal parts bonded in the suspended matter phase, can be verified for the entire data collective (Figs. 5.1-3 to -5).

The decreasing effects of increasing FSS concentrations on dissolved parts of prioritary heavy metals should be taken into consideration in future evaluations of the quality of surface waters. Determination of an existing FSS volume should therefore be included in future programs for monitoring prioritary heavy metals.
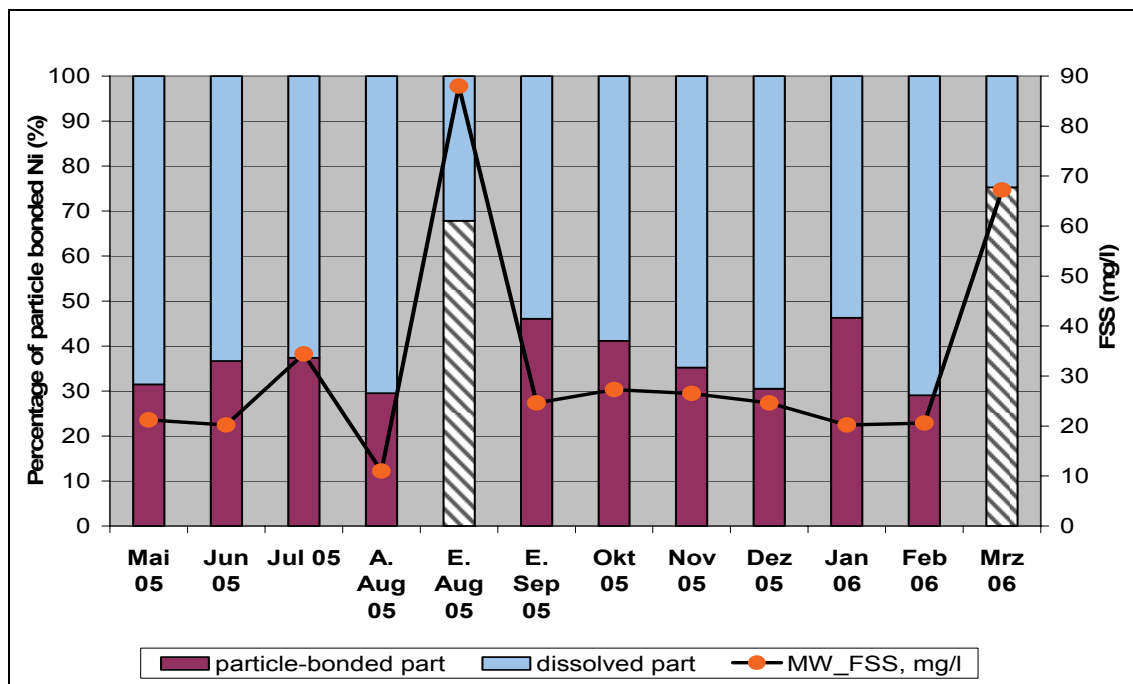
Fig. 5.1-1:   Particle-bonded and dissolved nickel proportion compared to the content of filterable suspended solids at the Bimmen station (Rhine). S. Aug. = beginning of August; E. Aug. = end of August: Shaded sampling results with increased discharges. Stat. parameters: r = 0.94; s <0.0001
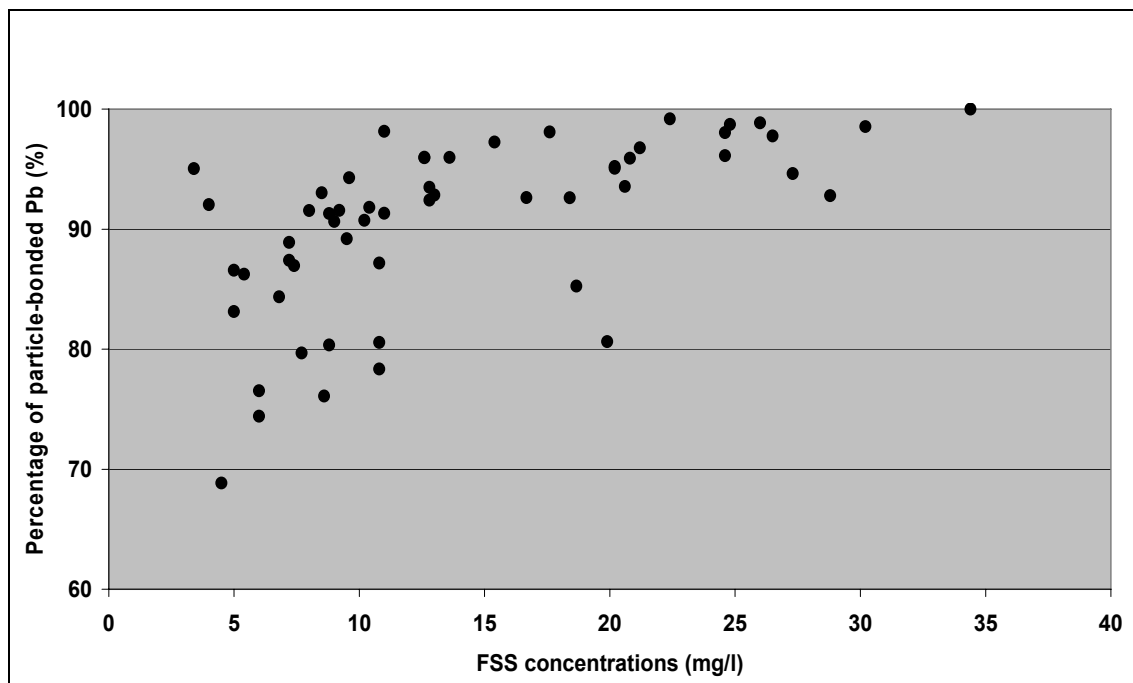
Fig. 5.1-2:   Particle-bonded shares of lead contents depending on available filterable suspended solids (FFS) (total data collective)

Fig. 5.1-3: Particle-bonded parts of cadmium contents depending on available filterable suspended solids (FFS) (total data collective)

Fig. 5.1-4: Particle-bonded parts of nickel contents depending on available filterable suspended solids (FSS) (total data collective)

5.1.3.2 Characteristics of filterable suspended solids (FSS)

a) TOC content

Statistical evaluation demonstrated significant positive correlations to the TOC content (%) of FSS for particle-bonded lead, cadmium and nickel. These interactions may also be explained by adsorption processes of dissolved metal proportions on active biological surfaces (cell walls) and by intracellular absorption (bio-accumulation) of metals by bacteria, algae, etc.

b) Particle size

As the surface size of particles increases, so does the bonding capacity for metal ions. The higher the fine grain proportions of suspended matter, the higher the increased availability of bonding sites, synonymous with the increasing percentages of fine grain in suspended matter.

These mechanisms are confirmed by the results of Pearson correlations. For the particle-bonded proportions of lead, cadmium and nickel, significant positive correlations to the two smaller fractions (< 20 µm) and negative correlations to the larger fractions (> 63 µm) have been verified (see chapter 4.1.2.3.3).

5.1.3.3 Saline content/competing ions

For the particle-bonded metal proportions of lead, cadmium and nickel, significant negative correlations to conductivity, chloride content and concentrations of calcium and potassium have been verified (see chapters 4.1.2.2 ; 4.1.2.3.3). Close correlations exist between alkaline and alkaline-earth ions and dissolved concentrations of cadmium and nickel (Tab. 5.1-2).

Tab. 5.1-2: Correlations of dissolved shares of cadmium and nickel to the concentrations of potassium, sodium, calcium und magnesium

Alkali metals	FIL-Cd	FIL-Ni		Alkaline earth metals	FIL-Cd	FIL-Ni
K	r = 0.351 s = 0.0041	r = 0.678 s <0.0001		Ca	r = 0.343 s = 0.0052	r = 0.343 s = 0.0052
Na	r = 0.409 s = 0.0007	r = 0.525 s <0.0001		Mg	--	**r = 0.727 s <0.0001**

Alkaline and alkaline earth metals compete with metal ions for available bonding sites on suspended matter particles. As salinity increases, increased shares of dissolved heavy metals can, in particular, be found in estuaries (GKSS 1997), as metal ions are driven away from their bonding sites by other ions.

These competitive effects may increase during increased discharges by dilution effects. In the case of decreasing concentrations of competing ions, the number of available bonding sites will increase at the same time. Negative correlations between sodium and calcium concentrations and particle-bonded cadmium pro-portions are shown in Fig. 5.1-6, based on the results from the

monitoring station on the Lippe.
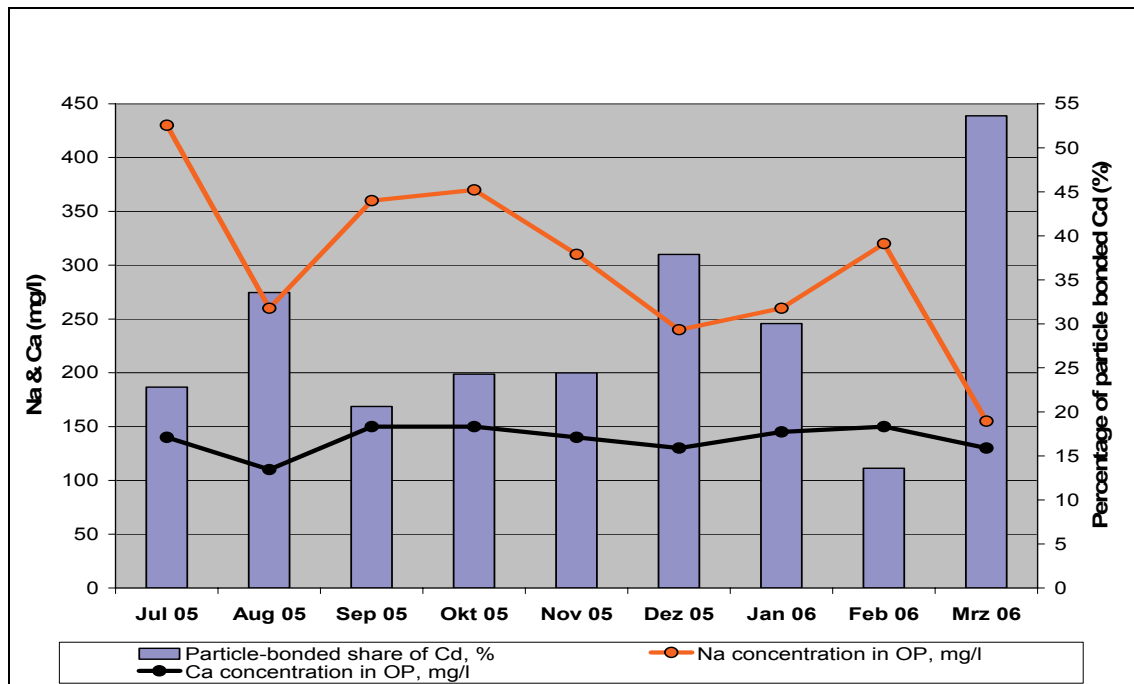
Fig. 5.1-5: Particle-bonded cadmium part versus sodium and calcium concentrations in the original sample of the Lippe. Stat. parameters for Na : r = - 0.82; s = 0.003; Ca: r = -0.65, s = 0.04

5.1.3.4 Discharge of surface waters

Correlations to concentrations of prioritary heavy metals may also be demonstrated in various matrixes for the discharge of surface waters. These are mainly a combined effect of:

1. Dilution effects on metal, alkaline and alkaline-earth concentrations

2. Increased material charges, e.g. by erosion

3. Increased entry of (low-contaminated) fine suspended matter

4. Increases in metal concentrations in the original sample as a result of increasing FSS contents

Changes in metal distribution with increasing discharges are thus mainly caused by simultaneous quantitative and qualitative changes in available suspended matter and salinity (see chapter 4.1.2.3).

5.1.4 Consequences of monitoring requirements changed by EU WFD

Present monitoring of heavy metals in surface waters is based on the evaluation of concentrations in original samples or in suspended matter of surface waters, in order to guarantee the protection of aquatic biocenoses by limiting total contamination.

The EU now stipulates that the four prioritary metals are monitored in filtered water samples. The following quality standards (QN) were suggested for permissible annual averages of the four prioritary metals (KOM 2006) (Tab. 5.1-3).

Tab. 5.1-3 : Pan-EU proposal of quality standards for prioritary metals (dissolved)

Metal	QN in µg/l
Cadmium	0.08 – 0.25 (depending on hardness)
Lead	7.2
Mercury	0.05
Nickel	20

In Germany, national quality standards (or proposals) have existed in the past for concentrations of heavy metals in original samples and/or suspended matter.

The results of the project show that at all six obviously contaminated monitoring stations, the QN for prioritary metals in filtered samples is complied with (Tab. 5.1-4).

With the exception of periodically high concentrations in the Erft, heavy metal concentrations measured in original samples, already regularly comply with the QN for filtered samples.

Tab. 5.1-4 : Comparison of averages of metal concentrations in filtered samples with new EU-WFD quality standards.

		Lead (µg/l)			
Location	n	AV	Max	QN MW	QN MAX
HON	12	0.08	0.15		
BIM	12	0.07	0.12		
WUP	11	0.25	0.60	7.2	not defined
ERF	9	0.13	0.44		
EMS	11	0.14	0.43		
LIP	10	0.08	0.17		
		Nickel (µg/l)			
Location	n	AV	Max	QN MW	QN MAX
HON	12	1.11	1.45		
BIM	12	1.50	1.90		
WUP	11	2.44	3.45	20	not defined
ERF	9	6.71	14.50		
EMS	11	6.78	9.65		
LIP	10	2.57	2.95		
		Mercury, original sample (ng/l) (filtered sample : n.n.)			
Location	n	AV	Max	QN MW	QN MAX
HON	12	12 (n.n.)	45 (n.n.)		
BIM	12	17 (n.n.)	29 (n.n.)		
WUP	11	18 (n.n.)	40 (n.n.)	50	70
ERF	9	19 (n.n.)	72 (n.n.)		
EMS	11	7 (n.n.)	35 (n.n.)		
LIP	10	11 (n.n.)	18 (n.n.)		
		Cadmium (ng/l)			
Location	n	AV	Max	Ca cat.	QN MW	QN MAX
HON	12	18	25	2	80	450
BIM	12	26	38	3	90	600
WUP	11	51	59	1	< 80	< 450
ERF	9	25	71	3	90	600
EMS	11	51	158	4	150	900
LIP	10	60	70	4	150	900

Ca = hardness class: classification for cadmium, based on calcium content of sample
HON =Bad Honnef, Rhine, BIM = Bimmen, Rhine; WUP = Wupper; ERF = Erft;
EMS = Emscher; LIP = Lippe

The change of analyses to filtered water samples will have a number of conse-
quences (see Tab. 5.1-7):

1 The EU has only proposed binding quality standards for the dissolved phase
for prioritary metals. All other metals are evaluated based on current national
quality standards for original samples. As a result, metal concentrations
must be simultaneously determined both in the filtrate and the original sam-
ple or the national QN for all other metals must be adapted.

2 Monitoring the dissolved parts of metals is not compatible with data of pre-
sent monitoring system of surface waters. In addition, the results of the pro-
ject show that satisfactory forecasts for concentrations in other matrixes (fil-
tered sample, suspended matter) cannot be derived from metal concentra-
tions of a matrix (e.g. an original sample).

3 It is clear that future evaluations of the conditions of surface waters to be
carried out according to EU regulations, will vary from those of the first in-
ventory in compliance with WFD from the analysis of suspended matter and
original samples.

4 For metals, whose dissolved concentration shares regularly are below de-
tection limits (e.g. mercury), regional differences in contamination and time-
related contamination trends cannot be recognized and assessed.

5 The distribution of metals over dissolved and solids phases is subject to
physico-chemical influencing factors. A qualified evaluation of the condition
of surface waters (differences in contamination, development of trends, ef-
fectiveness of rehabilitation arrangements) based on metal proportions in
the dissolved phase, is more difficult than in the original sample, as in gen-
eral the effect of influencing factors cannot be quantified with certainty.

6 Concentrations of dissolved metal proportions are not suitable for contami-
nation calculations, as only a variable part of the full contamination will be

included. Under marine conditions one must assume that considerable mo-
bilisation of heavy metals from the solids phase will be possible.

5.1.5 The use of analysis results of original samples for evaluating compliance of EU quality standards for filtered samples

Metal concentrations in the original sample are generally higher than concentrations of a filtered sample, as at most 100% of metal contaminations may be present in dissolved form. The evaluation of data shows that, at most of the monitoring stations original samples already comply with quality standards for filtered samples. In these cases, compliance with the QN for filtered samples may already be documented based on an analysis in the original sample.

In order to check this pragmatic approach, all heavy metal readings of the original sample available for watercourses in NRW were evaluated for the period of 2003-2006. Depending on the metal, between 6200 and 8700 data records from up to 724 monitoring stations were available. The suitability of each available data record (individual measurements) for the evaluation of dissolved shares was checked. Results have been compiled in Tab. 5.1-6.

One must observe that in this case, individual values are compared with the quality standards for QN of average annual values. Contamination events at monitoring stations, in which only some readings exceed the QN, will not automatically cause the QN to be exceeded.

No averages were produced for individual monitoring stations as part of this evaluation, as a considerable proportion of readings taken for specific metals were below highly variable detection limits. A reliable calculation of average values, incorporating readings below the DL (for simplification as concentrations of ½ DL) will require a uniformly applied DL, where possible, below half of the QN.

If all readings fell below the QN during evaluation, the average would also meet the quality target. At monitoring stations, where individual or all readings for the original sample exceed the QN for the filtered sample, analyses of filtered samples should also be carried out until a decision about the future procedure can be taken, based on a solid database.

At the beginning of the evaluation period, some laboratories still used methods subject to relatively high detection limits. For mercury and cadmium, a considerable data volume could therefore not be evaluated as although the samples contained concentrations that fell below detection limits, these were above quality targets (only defined after 2003) for filtered samples. In the meantime, detection limits were adapted to current requirements of the associated Draft Directive.

Mercury

Concentrations of 34% of the 6297 readings for the original sample were below and 2% above the QN, whilst the remaining 64% could not be used due to the high DL of methods used. Based on the results of this project, one could estimate that in case of samples subject to higher contamination, less than 10% of mercury proportions are present in dissolved form. One may assume that the QN for filtered samples is already complied with by the original sample at numerous monitoring stations.

Tab 5.1-5: Evaluation of monitoring of prioritary heavy metals in original samples carried out in NRW between 2003-2006 in view of the QN of WFD for filtered samples.

	Number of measure-ments 2003-2006	Readings above DL			Readings below DL			Suitability of all tests for use of new EU Quality Standards		Tests fully complying with QN	
		Total	of which		total	of which		suitable	unsuitable		
	n	N	Values < QN	Values > QN		DL < QN	DL > QN	part in %	part in %	n	part in %
Lead	6247	886	316	570	5361	4736	625	90	10	5052	81
Nickel	8706	4801	4588	213	3905	3905	0	100	0	8493	98
Mercury	6297	874	745	129	5423	1397	4026	36	64	2142	34
Cadmium evaluated by calcium categories											
Cat. 1	1769	493	94	399	1276	21	1255	29	71	115	7
Cat. 2	552	166	41	125	386	2	384	30	70	43	8
Cat. 3	3036	789	406	383	2247	40	2207	27	73	446	15
Cat. 4	1823	353	165	188	1470	65	1405	23	77	230	13
Cat. 5	84	13	3	10	71	13	58	31	69	16	19
Cadmium total	**7264**	**1814**	**709**	**1105**	**5450**	**141**	**5309**	**27**	**73**	**850**	**12**

Number of monitoring stations : differs for each metal, up to 724

Lead

Concentrations of 81 % of the 6247 readings for the original sample were below and 9% above the QN, whilst the remaining 10 % could not be used due to the high DL of methods used. One may therefore assume that for monitoring the QN for dissolved lead, analyses of original samples will suffices for the majority of the monitoring stations.

Nickel

Concentrations of 98 % of the 8706 readings taken for the original sample were below than and 2% above the QN. The evaluation shows that for monitoring the QN for dissolved nickel, an analysis of an original sample will suffice for nearly all monitoring stations.

Cadmium

The situation for cadmium was more problematic – and also more complicated because of the additional staggering of quality standards based on hardness classes. 12 % of the 7264 readings of the original sample were below and 15% above the QN, whilst the remaining 73 % could not be evaluated due to the high DL of methods used.

5.1.6 Conclusions for heavy metal monitoring

The preceding evaluation shows that monitoring of the QN for lead, nickel and mercury could already be completed for a considerable part of monitoring stations based on the analysis of original samples. Based on available data, no final assessment for the cadmium scenario can be made as yet. One may expect that a major proportion of samples will also have to be analysed as filtered samples for determining cadmium contamination.

The results of the project confirm the dependence of dissolved proportions of heavy metals on the underlying chemical/physical conditions of surface waters. Consequently, the quantity and condition of suspended matter in surface waters (particle size composition, TOC content), pH value, DOC and the concentrations of Na, K, Ca,

Mg should be taken into consideration for a full and EU-wide evaluation of dissolved prioritary heavy metals.

Analysis of the filtrate does not provide the required results for the calculation of total loads of contamination. The original sample must therefore always be analysed for this purpose. When using modern analysis methods (e.g. ICP-MS), synergising effects may be used when analysing original samples, as numerous other metals subject to a national QN can be analysed for the original sample.

In order to continue the present observation of the development of contamination, the emphasis of future monitoring should, where possible, be placed on analyzing original samples. For a more detailed evaluation, the filtrate and suspended matter may also be analysed.

Tab. 5-1-6: **Monitoring of metals in compliance with EU-WFD, consequences of matrix selection**

Metals	Filtered sample	Original sample	Suspended matter
Quality standard	EU-wide QN defined for prioritary metals Pb, Cd, Ni and Hg	National QN (LAWA) defined for a number of metals	
	No compatibility with analyses in OP or suspended matter, conversion impossible, new evaluation systems required	Continuation of previous monitoring strategies. Limited compatibility between analyses of suspended matter and original sample, conversion based on FSS of original sample for evaluating the level of contamination of each matrix.	
Regional contamination differences	No or only limited determination of Cd and Hg, as readings never or rarely are above DL.	Easily determined for most metals.	Easily determined for most metals.
Trend		Easily determined	Easily determined
Load calculation	No satisfactory load calculation possible, as particle-bonded shares are not determined.	Easy to calculate	No satisfactory load calculation possible, as dissolved parts are not determined.

5.2 Polycyclic aromatic hydrocarbons (PAHs)

Previous water monitoring considered the concentrations of substances under the generic term of PAHs in suspended matter. Methods have been established. Long-term databases and national QNs for original samples are available for environmental evaluation. In addition to prioritary PAHs, other representatives of this group of substances are included in the same analysis step.

Compliance with national QN was checked, based on the analysis, in suspended matter and subsequent conversion (based on the FSS contents of water samples) to concentrations in a water sample.

In the affiliated draft Directive to EU-WFD (KOM 2006), the EU has proposed quality standards for original samples for PAHs (Tab 5.2-1). It is, however, not an explicit requirement that analyses must take place of original samples. When a substance is nearly completely bonded to suspended matter, the latter may also be analysed. The determined concentration must then be converted into µg/l based on the suspended matter content of the original sample and be compared with the QN.

Tab. 5.2-1: EU proposal for quality standards for prioritary PAHs in the original sample

PAHs	(µg/l)
Naphthalene	2.4
Anthracene	0.1
Fluoranthene	0.1
Benzo(a)pyrene	0.05
Benzo(b)fluoranthene	Σ 0.03
Benzo(k)fluoranthene	
Benzo(ghi)perylene	Σ 0.002
Indeno(1,2,3-cd)pyrene	

National Quality Standards for original samples exist for pyrene, chrysene, dibenzo(ah)anthracene, benzo(a)anthracene, phenanthrene, fluorene and acenaphthene.

Changing analyses to the original sample will have the following consequences:

In an unfiltered water sample (original sample) only low-condensed PAHs may be analysed. Regular determination will generally only be possible for naphthalene, methyl naphthalene, phenanthrene and fluoranthene. All other PAHs examined were below detection limits, including samples from contaminated surface waters. Monitoring of PAHs in an original sample will therefore only produce an incomplete determination of contamination including higher condensed PAHs (increased log K_{ow}).

Detailed evaluations available in the past (contamination differentials, development of trend, effectiveness of clean-up arrangements) of water contaminations including higher condensed PAHs, cannot be guaranteed by analysing original samples. Regional and time-related differences in contamination known from preliminary examinations can no longer be determined even in the case of increased levels of contamination.

The problem with current examinations of suspended matter is that the determination of water-soluble PAHs will only be incomplete. The results of analyses of the original sample for both higher condensed and water-soluble PAHs are thus not compatible with the results of current surface water monitoring of suspended matter.

The above findings confirm that better matching of the matrix to be analysed to respective substance characteristics would be required for better agreement of the matrix of PAH contamination to be monitored. For monitoring medium and highly condensed PAHs, the analysis of concentrations in the suspended matter is advantageous, whilst low-condensed PAHs should be analysed in the filtrate or the original sample.

Tab. 5.2-2: **Monitoring of PAHs in compliance with EU-WFD, consequences of matrix selection**

PAHs	Original sample	Suspended matter
Quality standard	QN defined by EU Meaningful monitoring will only be possible for low-condensed water-soluble PAHs. Higher-condensed PAHs may also not be detected at contaminated monitoring stations and will at best at DL level. No compatibility with previous water monitoring. Should be extended by monitoring of higher condensed PAHs in suspended matter.	National QN for OP Method of previous monitoring strategy. Evaluation by converting the FSS content to concentrations expected in the original sample. Higher condensed PAHs can always be detected in case of contamination. Contamination can only be reliably evaluated for higher condensed PAHs. Should be extended by monitoring of low-condensed (water-soluble) PAHs in the original sample.
Regional differences in contamination	Detection only possible for low condensed PAHs	Detection of higher-condensed PAHs is easily possible in case of contamination.
Trend	Monitoring only possible for low condensed PAHs	Monitoring possible for highly condensed PAHs.
Load calculation	Possible for low condensed PAHs. Serious shortfalls for the load of higher condensed PAHs.	Loads determined by calculating expected concentrations in the original sample based on the FSS content. Satisfactory results for higher-condensed PAHs. Serious shortfalls for water-soluble low condensed PAHs.

5.3 Chlorinated pesticides

In previous water monitoring, predominantly concentrations of chlorinated pesticides in suspended matter were considered. Methods used are established, with a long-term database being available for environmental evaluation. In addition to prioritary representatives of this group of substances, other substances or metabolites are determined during the same analysing step. chlorinated pesticides exist, depending on water solubility and suspended matter conditions, partly dissolved in water but predominantly particle-bonded.

National quality standards exist for original samples. Compliance with these QN has been examined based on the analysis of original samples and predominantly based on the analysis of suspended matter (followed by conversion from FSS to concentrations in OP). The following EU-wide quality standards have been proposed (KOM 2006):

Tab. 5.3.1: **EU proposals for quality standards for prioritary chlorinated pesticides in original samples**

Pesticide	EU -quality standard (µg/l)
Alachlor	0.3
DDT total	0.025
p-p-DDT	0.01
HCH	0.02
Aldrin	
Dieldrin	Σ 0.01
Endrin	
Isodrin	

Contamination of analysed surface waters has been reduced by now to such an extent that the quantification of analysed substances as part of the project was neither possible in the original sample nor in the suspended matter sample (see chapter 4.2.2). DDE only was sporadically found around detection limit level in suspended matter of surface waters. From an ecotoxicological point of view, chlorinated pesticides are therefore no longer substances requiring high-intensity monitoring.

A description of the distribution of chlorinated pesticides over dissolved and particle-bonded proportions of contaminations could not be derived from the results of this project, as analyticalresults were lower than detection limits.

Similar to PAHs, the group of chlorinated pesticides has considerable differing water solubilities. The analysis of this group of substances in the original sample is, as already practiced in Germany, in principle possible for pesticides of a low log K_{ow} (see Tab. 4.2.2-2). As the log K_{ow} increases, contamination shares do, however, shift to the particle-bonded phase. An analysis of pesticides that are relatively difficult to dissolve in water, such as DDT and Isodrin in the original sample, generally produce results below detection limits. As a result, even increased contamination may frequently not be recognized.

In accordance with the principle of precaution, chlorinated pesticides should in future be monitored both in the original sample and the suspended matter of surface waters. From the results of the analysis of suspended matter, concentrations expected in a water sample may be calculated and evaluated by FSS content. Conversion from suspended matter contents to water concentrations must be critically evaluated for pesticides subject to a low log K_{ow}, as these substances will always contain fluctuating dissolved proportions that should not be ignored.

5.4   Water-soluble herbicides

In the past, water monitoring considered the concentration of water-soluble herbicides in an original sample that had to be (centrifuged or filtered because of the method) during the preparation of samples. Methods used are established and many years of data are available for environmental evaluation. In addition to prioritary herbicides, such as Diuron and Isoproturon, numerous other pesticides are also analysed during the same analysing cycle.

For Isoproturon und Diuron, the EU has proposed the following QN for original samples (KOM 2006):

Diuron	0.2 µg/l
Isoproturon	0.3 µg/l

It is, however, not an explicit requirement that analyses must take place of an original sample. Where there is proof that a substance is nearly completely dissolved, the latter may also be analysed in the filtrate. Analyses of Isoproturon and Diuron concentrations in the original sample, as proposed by the EU, correspond to current monitoring practice. Isoproturon and Diuron are almost fully dissolved in water.

The database to be obtained in the future and the assessments of conditions derived therefrom, are fully compatible with past monitoring practice.

5.5 PCB

Polychlorinated biphenyls are not part of prioritary substances, may however, play an important role as hazardous substances specific to river environments. During past water monitoring activities, PCB contaminations were monitored in suspended matter. Representative for 209 individual substances, so-called Ballschmiter congeners were analysed. Methods used are established, and a database established over an extensive period of time is available for environmental evaluation.

20 µg/ kg (or 0,5 ng/l for an unfiltered water sample) were defined for suspended matter in surface waters as a national quality standard for Ballschmiter congeners. PCBs in surface waters are almost exclusively bonded to suspended matter or accumulated in fatty tissue of biota.

The above results confirm that qualified monitoring of PCBs by analyzing suspended matter concentrations of surface waters should be carried out. Based on analyses of suspended matter, concentrations expected in an original sample may be calculated and evaluated from FSS volumes.

It is not recommended to change analyses to the original sample. In the unfiltered water sample (original sample), PCBs cannot be regularly quantified and evaluated, even in the case of known water contamination. In addition, the bases for reliable detection of contamination do not exist. Results to be expected are not compatible with the results of past water monitoring.

There is currently no requirement for changing analyses to original samples as the draft of the affiliated Directive (KOM 2006) does not contain any EU-wide QN for PCBs in the original sample.

6. Summary

33 substances or groups of substances subject to a high ecotoxicological risk potential were included as "prioritary substances" in Appendix X of the Water Framework Directive and EU-wide quality standards were defined for the "good condition" of surface water to be maintained. There are plans to monitor organic pollutants in original samples and metals in filtered water samples.

The objective of the project was to examine the distribution of priority **metals, PAHs, chlorinated pesticides, water-soluble herbicides** and (non-priority**) PCBs** throughout the dissolved and particular phase. In addition, the influence of sampling and sample preparation on monitoring results for new EU-wide matrixes to be examined was tested under the practical conditions of routine water monitoring.

The results of the project implemented on five surface waters subject to different levels of contamination, may be regarded as representative for clearly anthropogenically contaminated surface waters in densely populated and industrialized catchment areas in Central Europe.

Prioritary metals: Binding quality standards for the dissolved phase were only suggested for prioritary metals by the EU. All other metals are evaluated based on current national quality standards for original samples. Consequently, parallel determination of metal concentrations in a filtrate and the original sample or a change of the national QN will be required.

For monitoring dissolved prioritary metals, "in-situ" filtration of water samples under standardised conditions immediately after sampling is recommended, as in particular in the case of samples subject to high FSS contents, significant losses may occur within a short time due to adsorption on sample container surface.

As an analysis of the filtrate does not provide the information required for calculating the total contamination load, the original sample must always be analysed for this purpose. When using modern analysing methods (e.g. ICP-MS), numerous other metals subject to national QN may be analysed for original samples.

The results of the project confirm that no satisfactory forecasts for concentrations in other matrixes (filtered samples, suspended matter) may be derived from metal concentrations in a matrix (e.g. original sample). Future evaluations of the conditions of

surface waters to be carried out in line with EU regulations will therefore deviate significantly from an initial inventory in compliance with WFD, based on analyses of suspended matter or original sample tests.

For metals, the dissolved concentration shares of which regularly are below detection limits (e.g. mercury), regional differences in contamination and time-related contamination trends cannot be recognized and evaluated.

Results confirm the dependence of dissolved heavy metal shares underlying on chemical/physical conditions of surface waters. Consequently, the volume and condition of suspended matter in surface waters (particle size composition, TOC content), pH value, DOC and concentrations of Na, K, Ca and Mg, should also be incorporated in a qualified evaluation of existing dissolved prioritary heavy metals.

The evaluation of an extensive data collective shows that monitoring of the QN for lead, nickel and mercury could already be carried out for a large section of monitoring stations, based on the analysis of original samples. In order to continue previous observations of the development of contamination, future monitoring should, where possible, focus on the analysis of original samples.

PAHs: In an unfiltered water sample (original sample) only low-condensed PAHs (naphthalene, methyl naphthalene, phenanthrene, fluoranthene) may be detected. Higher-condensed PAHs are not fully determined with increasing log K_{ow}, so that even higher contamination leves can not be detected.

Qualified monitoring of PAH contamination may be carried out by improved matching of the matrix to be examined for respective characteristics of the substances. For average and highly condensed PAHs, the analysis of concentrations in the suspended matter of surface water will be of advantage, whilst low condensed PAHs should be analysed in the original sample.

chlorinated pesticides: As test results were regularly below detection limits, no distribution of chlorinated pesticides to the dissolved and particulate phase could be derived from results. According to the precautionary principle, future monitoring of chlorinated pesticides should be carried out both on the original sample and the suspended matter of surface waters. From analyses of suspended matter, concentration

of pesticides to be anticipated in the original sample for pesticides may be calculated by means of higher log K_{ow}.

Water soluble herbicides (Diuron und Isoproturon): The evaluation of Isoproturon and Diuron concentrations in original samples, as suggested by the EU, corresponds to current research practices. Databases to be produced in the future and evaluations of conditions derived therefrom, are fully compatible with past monitoring practices.

PCBs: Non-prioritary polychlorinated biphenyles are also relevant contaminants, specific to river areas. Qualified monitoring of PCBs should be carried out by analysing concentrations in the suspended matter of surface waters. Concentrations to be expected in the original sample may be calculated and evaluated. Changing of analyses to the original sample is not recommended.

7. References

1. ARGE ELBE(2000) Multielementanalysen von Wasserproben der Elbe und ausgewählter Nebenflüsse - Längsprofilbeprobung vom September 1997 - 2000,   Arbeits-gemeinschaft für die Reinhaltung der Elbe, in-house publication, Hamburg

2. ARGE ELBE (1998) Verteilung von organischen Kontaminanten zwischen wässriger und partikulärer Phase in der Elbe und der Deutschen Bucht, Arbeitsgemeinschaft für die Reinhaltung der Elbe, in-house publication, Hamburg

3. Böhm,E.; Hillenbrand,T.; Marscheider-Weidemann,F. (2002) Ermittlung der Quellen für die prioritären Stoffe nach Artikel 16 der Wasserrahmenrichtlinie und Abschätzung ihrer Eintragsmengen in die Gewässer in Deutschland. UBA-Forschungsbericht 200 28 234

4. Busch,D.; Lucker,T.; Cetinkaya,M.; Schirmer,M. (1995) Bioverfügbarkeit und Biomonitoring von Schwermetallen und schwerflüchtigen chlorverbindungen in der Weser. Limno-logie aktuell Bd.6, Gustav Fischer Verlag, Stuttgart, 93-107

5. Busch,D.; Lucker,T.; Wosniok,W. (1996): Effects of changing salt concentrations and other physical-chemical parameters on bioavailability and bioaccumulation of heavy metals in exposed Dreissena polymorpha (PALLAS, 1771). Limnologica 28 (3), 263-274.

6. Busch,D.; Büther;H.; Rahm,H. Ostermann,K. (2001) Emscher-PLUS, Projekt zur Langzeit-Untersuchung des Sanierungserfolges, Staatliches Umweltamt Herten, in-house publication

7. Carpenter,J.H.; Hugget,R.J. (1984): Meaningfull chemical measurements in the marine environment - transition metals. In: WHITE,H.H. (ed): Concepts in marine pollution measurements. Maryland Sea Grant College.

8. Chlup,M. (2004) Synthese und Analytik von Alkylaromaten (PAH), thesis, University of Ulm, September 2004

9. DIN EN ISO 10304-1, 1995-04 issue, Wasserbeschaffenheit - Bestimmung der gelösten Anionen Fluorid, Chlorid, Nitrit, Orthophosphat, Bromid, Nitrat und Sulfat mittels Io-nenchromatographie - Teil 1: Verfahren für gering belastete Wässer (ISO 10304-1:1992); German version EN ISO 10304-1:1995

10. DIN ISO 10694, 1996-08 issue, Bodenbeschaffenheit - Bestimmung von organischem Koh-lenstoff und Gesamtkohlenstoff nach trockener Verbrennung (Elementaranalyse) (ISO 10694:1995)

11. DIN EN ISO 11885, 1998-04 issue, Wasserbeschaffenheit - Bestimmung von 33 Elementen durch induktiv gekoppelte Plasma-Atom-Emissionsspektrometrie (ISO 11885:1996); German version EN ISO 11885:1997

12. DIN EN 13346, 2001-04 issue, Charakterisierung von Schlämmen - Bestimmung von Spurenelementen und Phosphor - Extraktionsverfahren mit Königswasser; German version EN 13346:2000

13. DIN EN 13506, 2002-04 issue, Wasserbeschaffenheit - Bestimmung von Quecksilber mittels Atomfluoreszenzspektrometrie; German version EN 13506:2001

14. DIN EN 1483, 1997-08 issue, Wasserbeschaffenheit - Bestimmung von Quecksilber; German version EN 1483:1997

15. DIN EN 1484, 1997-08 issue, Wasseranalytik - Anleitungen zur Bestimmung des gesamten organischen Kohlenstoffs (TOC) und des gelösten organischen Kohlenstoffs (DOC); German version EN 1484-1997

16. DIN EN ISO 15587-2, 2002-07 issue, Wasserbeschaffenheit - Aufschluss für die Bestimmung ausgewählter Elemente in Wasser - Teil 2: Salpetersäure-Aufschluss (ISO 15587-2:2002); German version EN ISO 15587-2:2002

17. DIN EN ISO/IEC 17025, 2005-08 issue, Allgemeine Anforderungen an die Kompetenz von Prüf- und Kalibrierlaboratorien (ISO/IEC 17025:2005); Deutsche und Englische Fassung EN ISO/IEC 17025:2005.

18. DIN EN ISO 17294-2, 2005-02 issue, Wasserbeschaffenheit - Anwendung der induktiv gekoppelten Plasma-Massenspektrometrie (ICP-MS) - Teil 2: Bestimmung von 62 Elementen (ISO 17294-2:2003); German version EN ISO 17294-2:2004.

19. DIN EN ISO 17993, März 2004, Wasserbeschaffenheit – Bestimmung von 15 polycyclischen aromatischen Kohlenwasserstoffen (PAH) in Wasser durch HPLC mit Fluoreszenzdetektion nach Flüssig-Flüssig-Extraktion (ISO 17993:2002); German version EN ISO 17993: 2003.

20. DIN 32645, 1994-05 issue, Chemische Analytik; Nachweis-, Erfassungs- und Bestimmungsgrenze; Ermittlung unter Wiederholbedingungen; Begriffe, Verfahren, Auswertung.

21. DIN 38402-51, 1986-05 issue, Deutsche Einheitsverfahren zur Wasser-, Abwasser und Schlammuntersuchung; Allgemeine Angaben (Gruppe A); Kalibrierung von Analysenverfahren, Auswertung von Analysenergebnissen und lineare Kalibrierfunktionen für die Bestimmung von Verfahrenskenngrößen (A 51).

22. DIN 38407-2, Februar 1993, Gaschromatographische Bestimmung von schwerflüchtigen Halogenkohlenwasserstoffen (F2).

23. DIN 38407-3, Juli 1998, Gaschromatographische Bestimmung von polychlorierten Biphenylen (F3).

24. DIN 38409-2, 1987-03 issue, Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung; Summarische Wirkungs- und Stoffkenngrößen (Gruppe H); Bestimmung der abfiltrierbaren Stoffe und des Glührückstandes (H 2).

25. DIN 38414-20, Januar 1996, Bestimmung von 6 polychlorierten Biphenylen (S20).

26. DIN 38414-23, Februar 2002, Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung Schlamm und Sedimente (Gruppe S), Teil 23: Bestimmung von 15 polycyclischen aromatischen Kohlenwasserstoffen (PAH) durch Hochleistungs-Flüssigkeitschromatographie (HPLC) und Fluoreszenzdetektion (S23).

27. ISO 5667-17, 2000-07 issue, Wasserbeschaffenheit - Probennahme - Teil 17: Anleitung zur Probennahme suspendierter Sedimente.

28. DIN EN ISO 6468, 1997-02 issue, Wasserbeschaffenheit - Bestimmung ausgewählter chlorinsektizide, Polychlorbiphenyle und Chlorbenzole - Gaschromatographisches Verfahren nach Flüssig-Flüssig-Extraktion (ISO 6468:1996); German version EN ISO 6468:1996.

29. Förstner,U. & Patcheneelam,S.R. (1976): Bindung und Mobilisation von Schwermetallen in fluviatilen Sedimenten. Chemiker-Zeitung 100 (2): 49-57.

30. Förstner,U. & Salomons,W. (1984): Mobilisierung von Schwermetallen bei Wechselwirkungen mit Sedimenten. In: MERIAN,E. (Hrsg.) Metalle in der Umwelt. Verlag Chemie, Weinheim, 171-179.

31. Föstner,U., Calmano,W. & Schroer,J. (1985): Verteilung von Spurenmetallen zwischen Lösung und Feststoffen - Aktuelle Fragen der Gewässergüte-Praxis an die Sedimentforschung. Vom Wasser 64: 1-16

32. GKSS (1997) Erfassung und Beurteilung der Belastung der Elbe mit Schadstoffen, Teilprojekt 2: Schwermetalle – Schwermetallspezies. GKSS-Forschungszentrum Geesthacht GmbH.

33. Koch, R. (1995) Umweltchemikalien, 3. Auflage, VCH, Weinheim

34.   KOM (2006) Proposal for a Directive of the European Parliament and of the Council on environmental quality standards and pollution control in the field of water policy and amending Directive 2000/60/EC; 2005, Entwurf der Tochterrichtline zur EU-WFD.

35.   LAWA-AQS-Merkblatt P-8/4 (1997) Probenahme von Schwebstoffen und Sedimenten; Erich Schmitt Verlag, Berlin

36.   LUA NRW (2000) – 30 Jahre Biologische Gewässerüberwachung in NRW, Sonderbericht, LUA NRW, in-house publication

37.   Merian, E. (1991) Metals and their compounds in the environment, VCH Verlagsgesellschaft mbH, 1991

38.   Müller,M.; Storm,U.; Storm,A. (1997): Reihung gewässerrelevanter, gefährlicher Stoffe aufgrund ihrer Exposition und Wirkung für 1993/94 UBA-Texte 40/97

39.   Pohl,C. (1997) Trace metals (Cu, Pb, Zn, Cd, Al, Li, Fe, Mn, Ni, Co) in marine suspended particulate matter: an international ICES intercomparison exercise, Springer-Verlag, 1997

40.   Rippen, G.(1987): Handbuch Umweltchemikalien. Stoffdaten – Prüfverfahren – Vorschriften. 2. Auflage, Landsberg: ecomed, Loseblattsammlung, 1987

41.   Schmitt, D. (2002) Charakterisierung der Bindung von Metallionen an natürliche organische Substanzen und deren Auswirkungen auf Adsorption und Transport, Dissertation Universität Karlsruhe, Fak. f. Chemieingenieurwesen und Verfahrenstechnik

42.   Wachs,B. (1994): Limnotoxizität und Ökobewertung der Schwermetalle sowie entsprechende Qualitätsziele zum Schutz aquatischer Ökosysteme, Münchener Beiträge zur Abwasser-, Fischerei- und Flußbiologie vol. 48, 425-486, Oldenbourg Verlag, München

43.   Yabutani,T.; Mouril,F.; Itoh,A.; Haraguchi,H. (2001)   Multielement Monitoring for Dissolved and Acid-soluble Concentrations of Trace Metals in Surface Seawater along the Ferry Track between Osaka and Okinawa as Investigated by ICP-MS, Analytical Sciences Vol. 17, March 2001

8. Annex

Tab. Annex 1: Summary of sampling

Monitoring station	Starting date	Duration	Volume of suspended matter (g)	Centrifuged water volume (l)	Centrifuge
Wupper/Opladen	26.04.2005	48 h	866	52800	mob. c.
	30.05.2005	21 h 35 min.	> 500	23738	mob. c.**'
	28.06.2005	24 h	378	26400	mob. c.
	13.07.2005	24 h	266	24000	mob. c.
	06.09.2005	23 h 5 min.	313	23050	mob. c.
	21.09.2005	35 h 50 min.	414	39413	mob. c.
	24.10.2005	24 h 40 min.	1811	24925	mob. c.
	21.11.2005	23 h 45 min.	293	24013	mob. c.
	19.12.2005	23 h	376	23177	mob. c.
	23.01.2006	24 h	243	24326	mob. c.
	14.02.2006	26 h 15 min.	281	26506	mob. c.
	13.03.2006	23 h	388	23223	mob. c.
Lippe/Wesel	**09.05.2005**	24 h	700	21600	Max Prüss
	05.07.2005	22 h	542	22000	mob. c.
	18.08.2005	22 h 25 min.	403	20175	mob. c.
	05.09.2005	49 h	680	49000	Max Prüss
	05.10.2005	5h 30 min.	91	5500	mob. c.
	17.10.2005	23 h 30 min.	364	20633	mob. c.
	02.11.2005	23 h 20 min.	430	19693	mob. c.
	28.11.2005	23 h 35 min.	578	21246	mob. c.
	09.01.2006	23 h 35 min.	394	21007	mob. c.
	06.02.2006	23 h 20 min.	346	20708	mob. c.
	28.02.2006	24 h	840	21600	Max Prüss
Emscher/Dinslaken	10.05.2005	24 h	425	24000	mob. c.
	15.06.2005	5 h	100	7500	mob. c.
	04.07.2005	20 h	> 500	20000	mob. c.**'
	30.08.2005	22 h 10 min.	255	22100	mob. c.
	19.09.2005	24 h	340	24000	mob. c.
	12.10.2005	23 h	277	20918	mob. c.
	07.11.2005	26 h 25 min.	570	26020	mob. c.
	13.12.2005	25 h 15 min.	413	25073	mob. c.
	10.01.2006	24 h 45 min.	373	24515	mob. c.
	07.02.2006	25 h 35 min.	635	24531	mob. c.
	15.03.2006	23 h 15 min.	396	21143	mob. c.

Tab. Annex 1: contd. Summary of sampling

Monitoring station	Starting date	Duration	Volume of suspended matter (g)	Centrifuged water volume (l)	Centrifuge
Rhine/Bad Honnef	10.05.2005	24 h	> 500	24000	stat. c.
	07.06.2005	48 h	> 500	48000	stat. c.
	05.07.2005	50 h 30 min.	> 500	50500	stat. c.
	02.08.2005	48 h 30 min.	> 500	48500	stat. c.
	30.08.2005	24 h 30 min.	2598	24500	stat. c.
	27.09.2005	50 h 20 min.	2357	50333	stat. c.
	25.10.2005	31 h 40 min.	743	31667	stat. c.
	22.11.2005	47 h 35 min.	830	47583	stat. c.
	20.12.2005	48 h 30 min.	1279	48500	stat. c.
	17.01.2006	71 h 45 min.	ca.1195	71750	stat. c.
	14.02.2006	50 h	ca.920	50000	stat. c.
	14.03.2006	22 h	1083	22000	stat. c.
Rhine/Bimmen	11.05.2005	24 h	> 500	24000	stat. c.
	08.06.2005	20 h	> 500	20000	stat. c.
	06.07.2005	19 h	832	19000	stat. c.
	03.08.2005	20 h 30 min.	325	20500	stat. c.
	31.08.2005	20 h	1600	20000	stat. c.
	28.09.2005	20 h	652	20000	stat. c.
	26.10.2005	20 h	801	20000	stat. c.
	23.11.2005	20 h	577	20000	stat. c.
	21.12.2005	20 h 30 min.	701	20000	stat. c.
	18.01.2006	19 h 45 min.	715	19750	stat. c.
	15.02.2006	20 h 30 min.	681	20500	stat. c.
	15.03.2006	20 h	1353	20000	stat. c.
Erft/Eppinghoven	23.05.2005	20 h 30 min.	700	18450	Max Prüss
	15.06.2005	19 h	650	17100	Max Prüss
	18.07.2005	20 h	700	18000	Max Prüss
	08.08.2005	20 h	680	18000	Max Prüss
	12.09.2005	21 h	740	18900	Max Prüss
	26.09.2005	21 h	680	18900	Max Prüss
	20.12.2005	22 h 45 min.	740	20475	Max Prüss
	23.01.2006	21 h 40 min.	740	19500	Max Prüss
	06.03.2006	22 h	1140	19800	Max Prüss

mob. c. : mobile centrifuge; mob. Z ** mob. centrifuge, autom. deactivation due to fault;   Max Prüss use of sampling vessel;   stat. c.: stationary centrifuge of water monitoring station