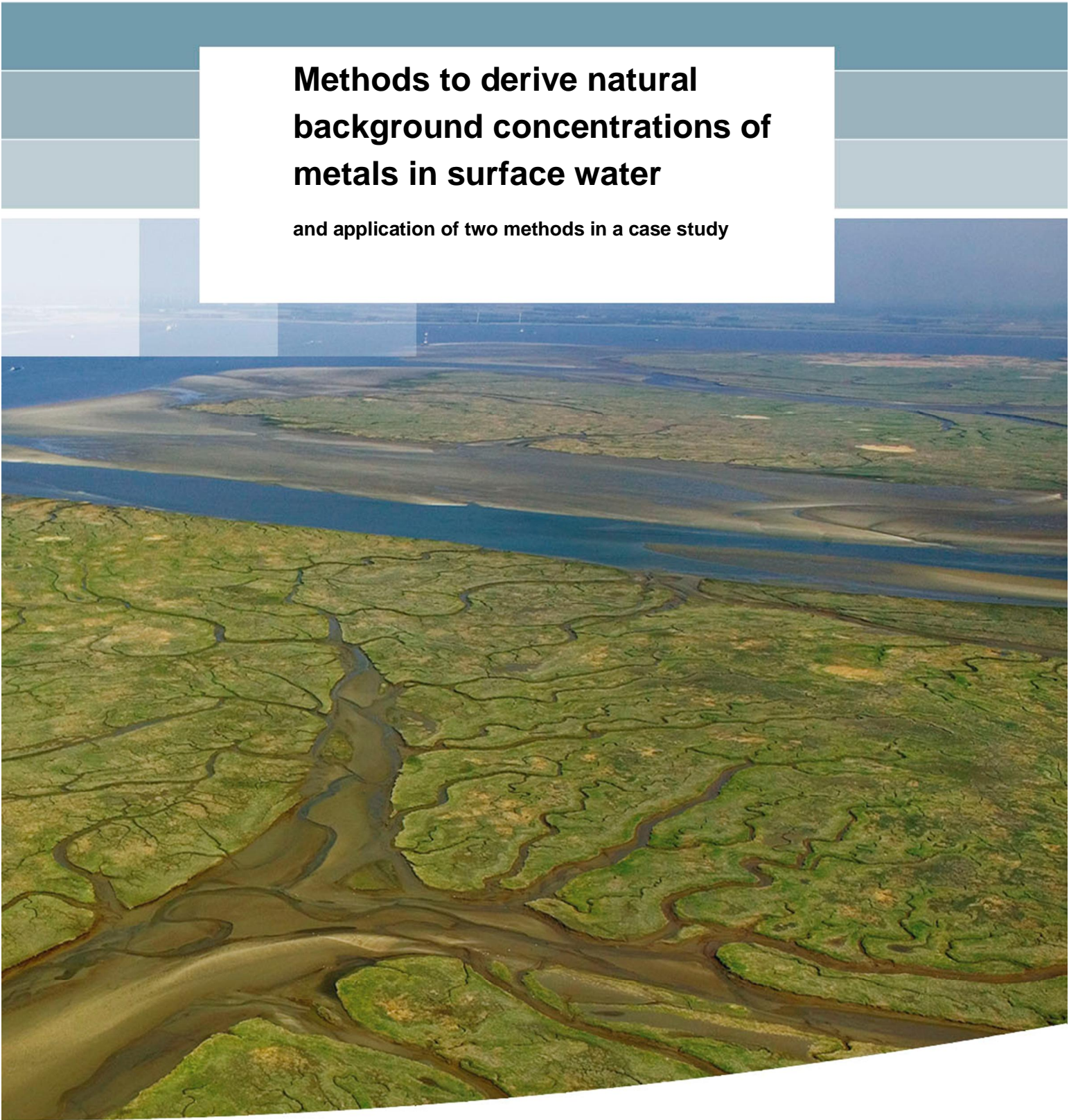


**Methods to derive natural
background concentrations of
metals in surface water**

and application of two methods in a case study



Methods to derive natural background concentrations of metals in surface water

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1206111-005

Title

Methods to derive natural background concentrations of metals in surface water

Client	Project	Reference	Pages
Waterdienst	1206111-005	1206111-005-BGS-0006-vj	67

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Osté, L.A., J. Klein, and G.J. Zwolsman, 2011. Inventory and evaluation of methods to derive natural background concentrations of trace metals in surface water, and application of two methods in a case study. Deltares report 1206111.005, Utrecht.

Summary

The Water Framework Directive (WFD) allows member states to correct monitoring data of trace metals for natural background concentrations. Background concentrations for Dutch surface waters are available for As, Ba, Be, Cd, Cr, Co, Cu, Pb, Hg, methyl-Hg, Mo, Ni, Se, Tl, Sn, V, and Zn. These concentrations, derived according to the clean streams approach, are published in the 4th National Water Plan (NW4, 1998). Background concentrations are also required for Ag, B, Co, Cs, Gd, La, Li, Sb, U, and Y. Several methods have been proposed to derive (natural) background concentrations of trace metals, ranging from scientific to pragmatic. Now that background concentrations for trace metals may be taken into account under the WFD, the question arises which method(s) should be chosen to assess these background concentrations.

The current background concentrations as recorded in the Dutch National water Plan (NW4, 1998) are not reliable. Total concentrations in pristine water in NW Europe measured in the eighties of the 20th century were transferred to the Netherlands. Equilibrium partitioning was used to calculate dissolved background concentrations. It is definitely time to update the method and the values, but can the available methods really improve the current values?

This report makes an inventory of six available methods to determine background concentrations in surface water:

- Clean streams approach
- Erosion model
- Sediment approach
- Stable summer levels
- Origin of surface water
- Monitoring data

Based on the assessments and discussions in an expert group, three methods are proposed for further evaluation: 1) the clean streams approach (based on measurements in relatively undisturbed aquatic systems); 2) the sediment approach (based on the composition of unburdened sediments and equilibrium partitioning); 3) the origin of surface water (based on measurements of the composition of the surface water's source). The monitoring data approach (a percentile of the monitoring data) can be used as an independent method, but is also used as a quality control for other methods.

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These methods are not applicable in all situations. Four types of aquatic systems were distinguished. Different conditions require different approaches to derive background concentrations:

- Open sea and oceans
- Estuaries and coastal water (influenced by river water)
- Large (transboundary) rivers
- Smaller inland streams

In the open sea, outside the area of river influence (i.e. salinity around 35), the clean streams approach is useful since (almost) unburdened sites of this type exist. Possibilities to obtain data in unburdened environments are metal concentrations found in open ocean waters or concentrations from the middle of the North Sea.

In estuaries and coastal areas significantly influenced by fresh (river) water, the natural background concentration would depend on the natural composition of both fresh and sea water. Salinity is a useful indicator to quantify the contribution of salt and fresh water backgrounds.

The recommended method to derive background concentrations for large rivers in the Netherlands is the use of unburdened sediments. Sediment can be dated accurately, so it is possible to derive naturally occurring metal concentrations. The alternative is to adopt the approach for soils: sub surface data combined with a baseline model. Once the background concentration in sediments has been determined, the recalculation from total metal contents to dissolved concentrations in surface water (by equilibrium partitioning) remains a critical point due to the uncertainty of this method. The uncertainty can be demonstrated by using a distributed K_p , resulting in a distributed background concentration. The case study in the river Rhine revealed that this method is feasible for a considerable number of elements. New sediment samples have to be collected if background concentrations are needed for additional metals, but this requires a limited amount of work.

Groundwater is the most important source in many Dutch regional aquatic systems, so their natural composition may be based on the natural composition of groundwater. The method to derive background concentrations in groundwater can be adopted from the Groundwater Directive. The number of elements for which groundwater backgrounds can be derived depends on the available groundwater data. The case study in Noord-Brabant showed that the method to determine a background concentration in groundwater requires more study. At the moment the groundwater approach can not be used and the monitoring data approach is recommended.

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The monitoring data approach is always part of the procedure to derive background concentrations in surface water. The 10 percentile value (P10) can be taken as an ambient background concentration. As a basic quality control, the obtained background concentrations of a particular method need to be compared with actual measured concentrations in the field. If the derived background concentration exceeds the P10 of the measured concentration (to be specified), the background concentration has to be rejected. In case the proposed background concentration is rejected, the P10 according to the monitoring data is taken as the background concentration.

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Preface

This is not the first report on background concentrations. We gratefully used earlier studies in this field, particularly Zuurdeeg et al. (1992), Laane et al. (1992), Van Tilborg (2002), and the Working group VEM (2004). They did a lot of useful preliminary work.

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1 Introduction

The primary goal of the Water Framework Directive (WFD) is to achieve a good ecological and chemical status of surface waters in all member states. To that purpose, water quality standards have been issued, either by the Commission (for priority substances), or by the member states themselves (for other relevant substances). These standards have been implemented in Dutch legislation. Standards for Priority substances were published in the Quality Standards and Monitoring Decree (in Dutch: Bkmw; Ministry of VROM, 2009) and the standards for other relevant substances were published in the Monitoring Regulation (in Dutch: Ministeriële Regeling Monitoring (Rm); Ministry of VROM, 2010).

In case of non-compliance with the standard, member states are allowed to take account of natural background concentrations or bioavailability. That is the reason why background concentrations for relevant substances (e.g. trace metals) need to be derived. Another reason to derive background concentrations relates to the regulation practice of point sources. The increase of a discharge plus background concentration is compared to the standards.

The WFD allows a correction for natural background concentrations only for metals, though several organic contaminants also have a natural origin (e.g. PAHs). The WFD does not demand the derivation of background concentrations. Each country can decide to do so for itself.

In support of water policy developments in The Netherlands, The Dutch Ministry of Infrastructure and Environment has launched an inventory on methods to derive natural backgrounds for trace metals. The following questions are leading in the project:

1. For which metals are (national) background concentrations available and how were they derived? (Chapter 2).
2. For which metals are background concentrations needed and in which water systems (distinction between river basins/water bodies)? (Chapter 2).
3. What methods are available to derive background levels for trace metals? (Chapter 3).
4. What are the criteria for the 'ideal' method to derive background concentrations? (Chapter 3)
5. To what extent do the available methods meet these criteria? (Chapter 3).
6. Which method(s) to determine background concentrations can be recommended? (Chapter 4).

This study will primarily focus on methods, and will not determine the background concentration of individual substances.

2 Available and currently used background concentrations

2.1 A short history of background concentrations in surface water in The Netherlands

In the mid-seventies, the issue of natural background concentration was first raised. Schuiling (1974) and, a number of years later, Van der Weijden and Middelburg (1989) developed the so-called erosion model to estimate natural background concentrations. At that time, the question was primarily scientific: how to distinguish between natural and anthropogenic (pollution) sources?

In the nineties, the added risk approach (ARA) was proposed. In this approach the maximum permissible addition (MPA) of metals and other naturally occurring substances is defined as the concentration that may be added to the background concentration (Cb). The maximum permissible concentration (MPC) is thus defined by:

$$\text{MPC} = \text{MPA} + \text{Cb}$$

From that moment, the Cb was not only of interest to scientists, but also to policy makers. Background concentrations were derived by Crommentuijn et al. (1997) and formally implemented by The Ministry of Housing, Spatial Planning and the Environment (Ministry of VROM, 1999). Crommentuijn et al. (1997) adopted the clean streams approach presented by Zuurdeeg et al. (1992), and added two additional aspects to the method: they used a mean instead of a 90-percentile, and they recalculated total concentrations in water to dissolved concentration in water (the calculation method is described in paragraph 3.1.1), using a nationwide partition coefficient for each metal. They used a mean for total background concentrations in surface water (table 35a in Zuurdeeg et al, 1992), and they recalculated total concentrations in water to dissolved concentration in water (the calculation method is described in paragraph 3.1.1), using a nationwide partition coefficient for each metal.

In the nineties, the accuracy and the principle of background concentrations gave rise to a sharp debate between scientists, policy makers, industry representatives and other stakeholders. The working group VEM (2004), under the authority of VROM-INS, published a review on existing methods to derive background concentrations for trace metals. They preferred the sediment approach (see 3.3). However, this advice did not lead to modification of Dutch water policy with regard to the background concentrations for trace metals. Indeed, the formal (policy-based) background concentrations for trace metals in Dutch surface water have remained the same since 1999.

Under the WFD Common Implementation Strategy, an Expert-Group on Environmental Quality Standards (EQS) was initiated in 2007, to produce guidance on establishment of the EQSs. Currently, the Technical guidance for deriving environmental quality standards (EC, 2011) is available, which includes the following text (p.64):

The natural background concentration is determined by mineral and biological factors. A major contribution to the background concentration will be from weathering of surface geology and any groundwater spring inputs. Therefore, a 'global' natural background level will normally not be meaningful because of the great variation between different regions. In freshwater, the preferred procedure for assigning a 'natural' background will usually be to determine the concentrations in springs and/or in water bodies in 'pristine' areas in the given region, e.g. headwaters. Other possibilities are:

- To measure concentrations in deep groundwater. In some cases, however, the concentration of the metal may be higher in the groundwater than in the surface water, e.g. because of the groundwater's contact with deep lying mineral rocks or soils and subsequent dilution by rain.
- To gather information from national or international databases, such as the FOREGS Geological Baseline Programme (<http://weppi.gtk.fi/publ/foregsatlas/index.php>).
- Geological modelling, to estimate the contribution from erosion.
- To estimate the concentration in the water from natural background concentrations found in the sediment by means of equilibrium partitioning models.

In practice, the input data needed to determine background concentrations in pristine areas by modelling may be inadequate to estimate a reliable value. An alternative pragmatic approach in these cases is to take the 10th percentile dissolved metal concentration of all the monitoring data available for the water body or region (after removing sample results with elevated concentrations from known point source discharges or pollution events). If this technique is used, some interpolation of the distribution of values is needed from the laboratory's reporting limit (the 'less than' value) and zero.

Use of percentiles in this report

The Guidance (EC, 2011) mentions a 10th percentile of all data as a background concentration, but this is an arbitrary number. Why not a 5th percentile? However, in this example, the value should be in the lower range of the data. There is no fundamental difference between a 5th and 10th percentile, but there is an essential difference between a 10th and a 90th percentile. To increase the readability, three levels of percentiles are used in this report:

- a 10th percentile indicating a value in the lower range of a dataset
- a 50th percentile indicating a median value of a dataset
- a 90th percentile indicating a value in the higher range of a dataset

The member states are free to choose a method to determine background concentrations. Only a limited number of European member states has been active to derive background concentrations. The UK used the pragmatic approach by using the 10th percentile (Peters et al., 2010). The activities in other countries have been limited to regional technical studies (e.g. Greif and Klemm, 2010).

Because the standards for metals are defined as dissolved concentrations, the background concentrations should be defined as **dissolved natural background concentrations** as well. An update of the current background concentrations should not be limited to existing metal backgrounds, but should also include other relevant metals for which no background concentrations are available to date. Paragraph 2.2 describes the current background concentrations used in Dutch water policy; paragraph 2.3 lists other relevant metals for which a background concentration is required.

2.2 Is it possible to derive a dissolved natural background concentration?

Paragraph 2.1 starts describing the scientific challenge to distinguish the natural and anthropogenic part of metal concentrations. The approach was very much focused on a total mass balance: the total load of a river consisted of erosion and anthropogenic loads.

The WFD focuses on the reactive concentrations of metals: the dissolved concentration (as long as the analysis of freely dissolved metals is quite complicated).

The dissolved concentration is, like the total concentrations, a result of natural and anthropogenic contributions, but the proportion of both 'sources' may be completely different,

because the speciation is different. In that view, it is conceptually very difficult to distinguish dissolved natural background concentrations in anthropogenically influenced surface waters. It might be possible only in pristine (unburdened) water bodies.

Another complication is the fact that dissolved metal concentrations vary in time and place. Seasonal and spatial variation in DOC and living organisms may influence the background concentrations due to binding/uptake of metals (e.g. Stolwijk et al., 2000, Verschoor et al., 2011). Spatial variation is also caused by differences in the original rock formations, the pathways to the surface water, but also by the proportion of different water sources (rain, groundwater, melting water, upstream river water).

All methods that will be presented in this report have to deal with these complications, and therefore we expect that each method will have considerable limitations.

2.3 Currently available background concentrations

Table 2.1 shows the official background concentrations in the Netherlands for fresh and marine waters¹. These values are based on the clean streams approach of Zuurdeeg et al. (1992), and were published first by Crommentuijn et al. (1997), then rounded in the Dutch National water Plan (NW4, 1998).

It should be emphasised here that Crommentuijn et al. (1997) recalculated the dissolved metal background concentration from the total metal background concentration taken from Zuurdeeg et al. (1992). This approach was taken because the background concentrations for dissolved metals which were also reported by Zuurdeeg et al. (1992) were considered to be less reliable. The dissolved background concentrations were calculated using a nationwide partition coefficient for each metal (taken from van der Kooij et al., 1991) and assuming a suspended matter concentration of 30 mg/l, typical of the Rhine River SPM in the Netherlands, according to the following equation:

$$C_b(\text{dissolved}) = C_b(\text{total}) / (K_p * S)$$

in which:

$C_b(\text{dissolved})$	= dissolved background concentration in $\mu\text{g/l}$
$C_b(\text{total})$	= total background concentration in $\mu\text{g/l}$
K_p	= partition coefficient in l/g^2
S	= concentration suspended matter in g/l^3

Table 2.1: Natural background concentrations (C_b) used in Dutch water policy (NW4, 1998)

Element	C_b (fresh water) Total ($\mu\text{g/l}$)	C_b (fresh water) Dissolved ($\mu\text{g/l}$)	C_b (marine water) Dissolved ($\mu\text{g/l}$)
Antimony (Sb)	0.3	0.3	
Arsenic (As)	1.0	0.8	
Barium (Ba)	76	73	

- ¹ Fresh water and inland water are similarly used in this report. Marine waters include both coastal and sea water. Coastal water is the part of the marine waters influenced by fresh water (river outflow). No specific attention is paid to transitional waters (estuaries).
- The partition coefficient is often expressed in l/kg . To convert from l/kg into l/g , the value should be divided by 1000.
- The suspended matter concentration is often expressed in mg/l . To convert from mg/l into g/l , the value should be divided by 1000.

Beryllium (Be)	0.02	0.02	
Cadmium (Cd)	0.4	0.08	0.03
Chromium (Cr)	1.6	0.2	
Cobalt (Co)	0.2	0.2	
Copper (Cu)	1.1	0.4	0.3
Lead (Pb)	3.1	0.2	0.02
Mercury (Hg)	0.06	0.01	0.003
Methyl Mercury	0.06	0.01	
Molybdenum (Mo)	1.4	1.4	
Nickel (Ni)	4.1	3.3	
Selenium (Se)	0.04	0.04	
Thallium (Tl)	0.04	0.04	
Tin(Sn)	0.002	0.0002	
Vanadium (V)	1	0.8	
Zinc (Zn)	12	2.8	0.4

2.4 Which metals require background concentrations?

Background concentrations can be required for a number of reasons:

- Natural backgrounds need to be derived for metals which exceed water quality standards.
- When granting a discharge permit for waste water containing trace metals, background concentrations play a role in the assessment of the discharge.
- Existing background values (Table 2.1) can be updated when another method for assessment of background is adopted, or when new data become available.

(non)compliance with water quality standards

The Ministry of Infrastructure and Environment (Min.I&M) provided a frequency table (see Table 2.2) comprising for each substance the number of water bodies (of the total 724 inland water bodies) that does not comply with current water quality standards (Bkmw/MR), The database was compiled in 2008.

Table 2.2 : Number of non-compliances with the Bkwm/RM-standards for relevant metals in Dutch inland surface waters (724 water bodies) based on an inventory of RWS (Hannie Maas, pers. communication). The table only show the compliance with the AA-EQS, MPC or MPA; not with the MAC-EQS.

Metal	Bkmw/Rm standards Inland water bodies (µg/l)	Bkmw/Rm standards Transitional/coastal water (µg/l)	Number of data (n _{max} = 724)	Number of exceedings	Exceedance occurring in:
Ag	0.08 (MPA)	1.2 (MPA)	71	0	
As	32 (MPC)	32 (MPC)	427	0	
B	650 (MPA-dissolved)	650 (MPA-dissolved)	206	2	Main water system
Ba	9.3 (AA-EQS) 148 (MAC-EQS)	n.a.	5	2	Main water system (1x); Water board Fryslan (1x)
Be	0.0092 (AA-EQS) 0.813 (MAC-EQS)	n.a.	n.a.		
Cd	0.08* (AA-EQS) 0.45* (MAC-EQS)	0.2 (AA-EQS) 0.45* (MAC-EQS)	602	52	Water Board Aa en Maas (28x) and five other water boards
Cr	3.4 (AA-EQS)	n.a.	461	2	Water board Delfland (2x)
Co	0.089 (AA-EQS) 1.36 (MAC-EQS)	n.a.	59	34	Main water system (33x); Water Board Fryslan (1x)
Cu	3.8 (MPC)	3.8 (MPC)	682	431	Main water system and all water boards except Regge & Dinkel
Hg	0.05** (AA-EQS) 0.07 (MAC-EQS)	0.05** (AA-EQS) 0.07 (MAC-EQS)	494	24	Water board Hollandse Delta (18x); Water board Dommel (4x), Water board Regge & Dinkel (2x)
Pb	7.2 (AA-EQS)	7.2 (AA-EQS)	628	0	
Mo	136 (AA-EQS) 340 (MAC-EQS)	n.a.	177	1	Canal Ghent-Terneuzen (1x)
Ni	20 (AA-EQS)	20 (AA-EQS)	599	1	Water Board Peel & Maasvallei
Sb	7.2 (MPC)	7.2 (MPC)	225	0	
Se	0.052 (AA-EQS) 24.6 (MAC-EQS)	2.6 (MAC-EQS)	n.a.		
Sn	0.6 (AA-EQS) 36 (MAC-EQS)	n.a.	168	0	
Te	100 (MPA)	100 (MPA)	207	0	
Ti	20 (MPA)	20 (MPA)	207	0	
Tl	0.013 (AA-EQS) 0.76 (MAC-EQS)	0.34 (MAC-EQS)	74	29	Main water system (29x)
U	1 (MPA)	1 (MPA)	183	2	Main water system (2x)
V	5.1 (MPC)	5.1 (MPC)	196	8	Main water system (4x); Water board Fryslan (4x)
Zn	7.8 (AA-EQS) 15.6 (MAC-EQS)	3 (AA-EQS) n.a.	677	278	Main water system and many water boards

MPA = Maximum permissible addition: the standard is defined as a dissolved concentration; the local background concentration should be added to the standard.

MPC = Maximum permissible concentration (see paragraph 2.1): the standard is defined as a dissolved concentration and includes the national background concentration. Maximum Permissible Concentrations (MPC) were checked for compliance with current water quality standards (NW4, 1998) after recalculation of the

(total metal) results to standard water containing 30 mg suspended matter per liter (using a K_p value for each metal).

AA-EQS = Annual Average – Environmental Quality Standard. The measured values may be corrected for the natural background concentration and for bioavailability before compliance checking.

MAC-EQS = Maximum acceptable concentration - Environmental Quality Standard. The measured values may be corrected for the natural background concentration and for bioavailability before compliance checking.

n.a. = not available

* depends on hardness

** EQS does not account for bioaccumulation of methyl mercury

Table 2.2 shows that a number of metals have been measured less frequently than other metals (Ba, Co, Ag, Tl) or not at all (Be, Se). However, Tl and Co seem to exceed the standards frequently while for Ba, 2 out of 5 measurements exceed the standards. Other conclusions which can be drawn from Table 2.2:

- Cu and Zn exceed the standards most often; Cd, Hg, and V to a lesser extent;
- B, Cr, Mo, Ni, and U exceed the standards occasionally;
- Ag, As, Pb, Sb, Sn, Te, and Tl always meet the standards.

In most of the coastal water bodies, only Cu and Zn have been measured in addition to the priority substances. An extended set of metals has been measured in the Western Scheldt, the Nieuwe Maas/Oude Maas, the Nieuwe Waterweg incl. Hartel-, Caland-, Beerkanaal, and Haringvliet-West. Roughly, the same metals exceed the standards as in the inland water bodies.

A few elements exceed the standards in specific regions or water types: Cd is a problem in the sandy areas in the Southern part of Holland, Co and Tl are a problem in the large rivers. Just the water boards Hollandse Delta and Schieland en de Krimpenerwaard (Tl) measured these elements. They report full compliance with the standards. Hg seems to be a (limited) problem in regional waters and not in the large rivers.

Substances without a current background concentration, that exceed the standard one or more times, are B and U. Van Hoorn (2009) also reports Ag to be a substance of interest, but the information supplied by RWS shows compliance with the standard.

Relevant metals for granting permits

When granting a permit, the responsible water agency (either RWS or a water board) will apply the added risk approach and therefore background concentrations are needed. The following metals were mentioned in a report on granting permits (Rob Berbee, pers. Comm.):

- Rare earth elements, for example La and Y
- metals present in hospital waste, such as Cs, Gd
- Li

From the criteria formulated in the beginning of paragraph 2.4, it can be concluded that the following metals potentially require a (new) background concentration:

- **Existing background values: As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se, Sb, Sn, Tl, V, Zn**
- **Exceeding the standards: Ag, B, U,**
- **permits: Cs, Gd, La, Li, Y.**

3 Methods to derive natural background concentrations

This chapter aims to give a description of different existing methods to derive natural background concentrations in surface water and seawater. For every method the following points will be described successively:

- Short description of the method;
- The available data (data and models);
- Modifications of the method. For certain methods other authors made modifications to improve the method or to make it more applicable;
- Finally, the methods are evaluated based on the following criteria:
 - o Natural background: the extent to which the method produces a real natural background. Three categories are distinguished:
 - The geochemical background: weathering and dissolution of naturally present metals
 - The 'present-day' background: geochemical background plus atmospheric deposition and antropogenically induced geochemical processes, e.g. NO₃ induced dissolution of pyrite including the metals in pyrite.
 - Ambient background concentrations; minimally contaminated aquatic systems
 - o Data: the type, representativeness in time and space, availability and analytical accuracy of the data (detection limit and contamination issues, etc.);
 - o Methodological uncertainty: the uncertainty of different steps in the derivation method; seasonal variability
 - o Available elements: the number of elements that can be addressed without substantial additional work;
 - o Regional differentiation: the possibility to differentiate between river basins and water types. This can for example be based on environmental characteristics like the pH, DOC and presence of pyrite in the underground;

A general condition is that the results of the method should be consistency with field data: no method should result in background concentrations higher than truly observed dissolved metal concentrations.

3.1 Clean streams approach

3.1.1 Fresh water

Description

This method was developed and described by Zuurdeeg et al. (1992). The principle of this method is that the water quality of the (head)waters in relatively unpolluted European regions is used for the derivation of natural background levels in areas with comparable geology and topography. Basic checks for nitrate and major ions are carried out in order to validate the assumption that the streams are relatively undisturbed. Zuurdeeg et al. (1992) then assumed that water quality of small (apparently pristine) streams in the North European Lowlands is a fair measure for natural background levels of trace metals in The Netherlands.

To derive natural background levels Zuurdeeg et al. (1992) followed the steps written below:

- To collect worldwide data they started with an extensive literature study, aiming to only select locations with pristine water. For different trace elements they collected 'recent' analytical results in fresh, relatively unpolluted and filtered surface water.

- They collected data from Northern Europe from institutes in different countries. To assure that the metal data obtained are representative of clean streams they used a number of selection criteria:
 - o The use of general water quality classification systems, often based on dissolved oxygen;
 - o Local knowledge of the responsible water manager or other specialists on water quality;
 - o Information from reports or publications;
 - o Information on geographical (e.g. the presence of industry) and geological characteristics of the sample location;
 - o Auxiliary measurements of nitrate, sulphate and chloride in the water samples.
- Based on major element concentrations (Na, K, Ca, Mg), the water type was assessed and coupled to the landscape. The trace metal concentration was found to vary with the major element concentration and thus with the type of water. Analyses were statistically clustered on major elements, and subsequently the corresponding metal concentrations were calculated.
- They correlated the interpreted water types and the Dutch surface water.
- They determined natural metal concentrations that could not be coupled to a specific water type. For these elements only an average for the whole of The Netherlands was calculated.
- Finally, only the dataset of the Northern European Lowlands was used for the characterization of the water types because of the different composition compared to the rest of the world. For the elements that were not measured in the Northern European Lowlands, the world dataset was used to get an indication of the natural background level in The Netherlands.
- The P90 of the dataset was chosen to guarantee that 90% of the natural waters would match a compliance check.

Available data

An important step of this method is the data collection. Zuurdeeg et al. (1992) did this in two ways:

- Worldwide dataset. Analyses of water quality of “natural” surface waters in international literature are collected. Only the data of locations with ‘clear’ water and filtered (0.45 μ) samples is used. For some elements there is not much data. For references see Zuurdeeg et al. (1992).
- Northern European Lowland dataset. Data is collected from the Northern European countries The Netherlands, Germany, Belgium, France, Poland, Denmark and Russia. The data selection is based on clear, natural water and geographical and geological characteristics. For references see Zuurdeeg et al. (1992).

This work resulted in natural background levels for the following compounds: As, Sb, Ba, Be, Cd, Cr, Co, Cu, Hg, Pb, Mo, Ni, Se, Tl, Sn, V, Zn. They derived total metal concentrations for fresh water. From the results, the dissolved background concentrations in The Netherlands were calculated as described in paragraph 2.3.

A recent example of the clean streams approach can be found in Greif & Klemm (2010), who attempted to derive regional natural background concentrations for trace metals and arsenic for the Erzgebirge/Vogtland area in Germany. Samples from sites believed to be clearly influenced by anthropogenic activities were discarded from the data sets. The decision was based on knowledge about anthropogenic activities, geochemical characteristics (upstream rivers), and sometimes on deviating EC of pH.

It appeared that, although it is desirable to define background concentrations on a water body level, this was not possible for the study area due to the high sample density necessary for a sound statistical underpinning. The authors state that the P50 value always represents the lower limit for the characterization of the natural background concentration and can be used in lithologically homogeneous areas with low mineralization rates. The P90 value could, in the view of the authors, be used for deriving natural background concentrations in lithologically and highly mineralogical inhomogeneous areas.

Modifications of the method

Different researchers have used the clean streams approach or have compared this method with other methods to derive natural background levels.

Van den Hoop et al. (1995) used the clean streams approach for surface water, based on the dataset of *Zuurdeeg et al. (1992)*. However, they selected the mean of the dataset for each metal instead of the 90-percentile. They did so because they argued that there still is anthropogenic influence in the dataset of *Zuurdeeg et al. (1992)*, despite the fact that they characterized their water samples as “clean”. If that holds true, the 90-percentile is very likely to result in overestimation of the natural background level.

Laane et al. (1992) analysed reference data for river water from *Zuurdeeg et al. (1992)* and from *Bewers & Yeats (1989)*. They recommended taking the data of *Bewers & Yeats (1989)* as a freshwater background reference because of the matching of these data with river Rhine background values established by expert judgement of the Institute for Inland Water Management and Waste Water Treatment (RIZA) and comparable concentrations in rivers in southern Sweden. For metals not considered by *Bewers & Yeats (1989)*, *Laane et al. (1992)* recommended using the values of *Zuurdeeg*.

Crommentuijn et al. (1997), like *Van den Hoop (1995)*, also used the dataset of *Zuurdeeg et al. (1992)*, taking mean values instead of 90-percentile values (except for tin). However, whilst *van den Hoop* only reported total metal backgrounds, *Crommentuijn* went one step further by converting total metal concentrations to dissolved concentrations. To do so, they used a nationwide partition coefficient for each metal derived from a dataset for the years 1983-1986 (*Van der Kooij et al., 1991*) and a suspended matter concentration of 30 mg/l (details are given in paragraph 2.2). Of course, this introduces methodological uncertainty with respect to the representativeness of the K_p used (see further discussion in paragraph 3.3).

Assessment

The assessment of the clean streams approach on different criteria is shown in Table 3.1.

Table 3.1 : Assessment of the clean streams approach on different criteria for fresh water (+ = advantage, – = disadvantage).

+ or -	Assessment
<i>Natural background</i>	
+	Aims to yield a geochemical background concentration, although it is not completely certain that the (alleged) clean streams are truly pristine. The use of a mean can be regarded as an implicit correction for some anthropogenic influence
-	Some diffuse anthropogenic influence can not be excluded (atmospheric deposition, land use)
<i>Data</i>	
+	Real measured values are used instead of calculated values
-	There is a lot of data on total concentrations available from different sources, but very few on dissolved concentration
-	The availability of dissolved metal concentrations is poor, though data availability is growing now. The use of old datasets (< 1985-1990), when the analytical quality control for dissolved metals was highly questionable, may cause significant errors

-	Difficult to get a database of pristine waters and besides that the selection of the undisturbed data is subjective and different for different data sets
-	By using different datasets from different countries, different research aims and different periods (1978-1990), the dataset is not really consistent because of the use of different analytical methods, different detection limits, and, most of all, different concern for contamination issues
-	When using data of the Northern European Lowlands or worldwide data, we can not be sure that this data is representative for surface water in The Netherlands
<i>Methodological uncertainty</i>	
+	If representative pristine waters can be found, direct measurement data of natural background concentrations are available
±	Dissolved concentrations vary within the seasons
-	It is difficult to judge whether pristine headwaters (in a large area) are representative for all Dutch waters
-	If dissolved concentrations are calculated from total concentrations measured, the choice of the K_p introduces a significant uncertainty (see also Table 3.5)
<i>Available elements</i>	
+	This method can in principle be used for many different metals and trace elements.
-	If existing databases are used, the number of available elements is restricted by the metals in the database of the clean waters.
<i>Regional differentiation</i>	
+ / -	In principle, each pristine water body is indicative for the downstream area. Mostly, a number of different waters are combined to derive a background concentration for a large area (e.g. North west Europe). Then regional differentiation is impossible.

3.1.2 Open sea and ocean water

Description

Like for fresh water, also for seawater it is possible to use pristine water as a reference to derive natural background levels. Pristine ocean water (from the Atlantic Ocean) can be used to derive natural background levels for coastal waters like the North Sea. This method is mentioned in both Laane et al. (1992) and EC (2011).

Laane et al. (1992) reported the range and mean of background dissolved trace metals in off-shore sea water, based on a survey of data reported for the north-east Atlantic Ocean and the Norwegian Sea. However, it is not clear which criteria Laane et al. (1992) used to select the different references for the different trace metals. Laane et al. (1992) recognized that it is unlikely that metal concentrations in the Atlantic Ocean represent true natural background values unaffected by human activities, as the impact of atmospheric pollution cannot be ruled out.

In the document of OSPAR (2005), which is fully based on Laane et al. (1992; personal communication Remi Laane). However the values are not exactly the same as is shown in table 3.2. Ranges of background concentrations of dissolved trace metals in specific regions of the Convention area are also given in table 3.2

Table 3.2: Ranges of background concentrations of dissolved trace metals [ng/L] in specific regions of the Convention area (derivation method is unknown).

Element	Southern North sea OSPAR, 2005 ng/l	Northern North sea OSPAR, 2005 ng/l	Atlantic Ocean OSPAR, 2005 ng/l	Atlantic Ocean Laane et al., 1992 ng/l
As				1400 +/-100
Cd	9-12	8-25	5-25	4-9
Cu	140-360	50-90	50-100	70 +/-13
Co				3,5
Cr			90-120	160 +/-30
Fe		200-600	25-150	
Hg		0,2-0,5	0,1-0,4	0,5
Mn		60-150	10-25	
Ni	180-260	200-250	160-250	140
Pb	10-17	10-20	5-20	33 +/-15
Sb				140 +/-7
Se			2-20	
Ti				13 +/-2
V	900-1050	1250-1450	1250-1450	1660
U		3000-3500	3000-3500	
Zn	170-280	250-450	30-200	130

Modifications

Van den Hoop (1995) reported ranges of background concentrations of dissolved metals in the North Sea from *Van Eck et al. (1985)* and from the Atlantic Ocean (*Laane et al., 1992*). *Van den Hoop (1995)* used the data of *Van Eck (1985)* even though these values were obtained in the early eighties. The basis for this decision is not given. He recommends that new measurements are necessary to derive more reliable estimations of background concentrations for the Dutch marine environment.

An alternative for Dutch waters is using measurements taken 70 km out of the North Sea coastline, which has been routinely sampled within the Dutch water quality monitoring programme. At 70 km from the coastline there is 'real' sea water (salinity of ca. 35 PSU), coming from the Atlantic Ocean mainly through the English Channel. The concentrations of dissolved metals (Cd, Cu, Zn) were all found to be very low (*Zwolsman, 1999*) and the measurements are analytically reliable. These values can be used as upper limits for the natural trace metal background in sea water.

Available data

Both *Laane et al. (1992)* and *EC (2011)* provided references that can be used:

- *Middelburg et al. (1988)*
- *Hydes & Kremling (1993)*
- *Fileman & Harper (1989)*
- *Flegal & Patterson (1985)*
- *Danielsson et al. (1985)*
- *Landing et al. (1995)*
- the UK National Marine Monitoring Programme 2004
<http://www.jncc.gov.uk/pdf/nmmp2ndreport.pdf>;

Assessment

The assessment of the clean streams approach for seawater on the different criteria is shown in Table 3.3.

Table 3.3 : assessment of the clean streams approach on different criteria for seawater (+ = advantage, – = disadvantage).

+ or -	Assessment
<i>Natural background</i>	
+	Yields a geochemical background concentration
<i>Data</i>	
+	Real measured values are used instead of calculated values
+	There is data available from different sources
-	Difficult to get a database of pristine waters because metal concentrations in the Atlantic Ocean are still affected by human activities, for example by atmospheric pollution, so some diffuse anthropogenic influence can not be excluded
-	Data obtained from other areas of the water system might not be representative for Dutch coastal waters.
<i>Methodological uncertainty</i>	
	Seasonal variation can be observed due to uptake by and adsorption to phytoplankton
<i>Available elements</i>	
+	This method can be used for many different metals and trace elements
-	Depending on available datasets, in which the list of trace elements is incomplete
<i>Regional differentiation</i>	
-	Not relevant for seawater. One background value should suffice for the entire open North Sea

3.2 The erosion model

Description

The first attempt to define the natural load of the river Rhine by analysing the erosion in the catchment area was published by Schuiling (1974). Schuiling started from the assumption that, on a geological time scale, a steady state will exist between erosion, transport through rivers and the formation of oceanic deposits. If no large deposition areas are present in the river basin, the average erosion together with the average composition of the eroded material, will determine the average concentration of metals present in the river. For the hinterland of the river Rhine, composition data are known with respect to both igneous and carbonate rock. An erosion rate of 4 cm/1000 year was calculated. Together with the average composition of the bed rock this led to a yearly estimated load for the river Rhine of 1.040.000 kg Cu, 960.000 kg Zn, 2.800 kg Cd, 320.000 kg Pb and 1.060.000 kg Ni. In combination with the river flow, the average natural background concentrations (total metal) can be derived.

Available data

Accurate data on the solid matter load of the river are needed, not only the amount, but also the origin and the natural background in the original rocks.

Modifications of this method

Van der Weijden & Middelburg (1989) improved the erosion model. Based on recent and historical data on the chemistry of the Rhine, one can estimate the natural levels of the major element load of the river. This natural load is derived from denudation of various rock types in the drainage basin. The main elements are used to estimate the contribution of aluminosilicate rocks and of limestones to the total denudation. Data for trace element contents of common rocks are available in geochemical tables. This then allows one to estimate the natural trace metal load of the river, which can be converted to the background concentration (total metal) through division by the average river flow.

Assessment

The assessment of the erosion model on different criteria is shown in Table 3.4.

Table 3.4 : Assessment of the erosion model on different criteria (+ = advantage, – = disadvantage).

+ or -	Assessment
<i>Natural background</i>	
+	Yields a geochemical background concentration for total metals
-	This method yields the total metal concentration; the dissolved amount has to be estimated by equilibrium partitioning as done by Crommentijn et al. (1997)
-	No account is made of the contribution by natural atmospheric deposition (e.g. from volcanism, forest fires and desert storms). However, this contribution is unlikely to be significant.
<i>Data</i>	
±	Availability of data on rock composition and erosion rates for specific river basins can be limited (but not for the Rhine basin)
-	Compositional differences of suspended matter between different areas within the catchment
<i>Methodological uncertainty</i>	
-	The division of the particulate metal load into SPM transport and bed load may introduce further uncertainty. Bed load transport of trace metals is usually not determined.
-	Errors in the data/interpretation can be raised by the elemental composition variation of eroding rocks and minerals, as well as their contribution to the total weathering rate in the catchment area.
-	Focuses on the total load, which is transported by the river. Recalculation to dissolved concentrations according to equilibrium partitioning may lead to errors as the K_p values have to be estimated from present-day metal distributions in the river
<i>Available elements</i>	
±	Depends on the elemental analysis in representative rocks. Van der Weijden and Middelburg (1989) derived background concentrations for Cr, Mn, Co, Ni, Cu, Zn, Cd, and Pb
<i>Regional differentiation</i>	
+	With this method background concentrations in individual river basins can be derived

3.3 Background concentration based on composition of unburdened sediments

Description

Van den Berg & Zwolsman (2000) proposed this method, which is based on the measured partition of the trace metals over the water and solid (suspension) phase, combined with measured contents of trace metals in pre industrial deposits. The method is used to derive natural background concentrations of trace metals in the river Rhine (at Lobith).

The partition coefficient (K_p) is defined as follows: $K_p = C_s/C_d$

In which:

C_s = trace metal content in solid phase (suspended matter) [mg/kg]

C_d = dissolved trace metal concentration in the water phase [$\mu\text{g/l}$]

The K_p -value has the unit l/g^4 .

The natural background level can then be calculated as: $AC_d = AC_s/K_p$

In which:

AC_d = background level of dissolved metal in the water phase [$\mu\text{g/l}$]

AC_s = background level of metal in solid phase (suspended matter) [mg/kg]

The critical point in this approach is the value of K_p . It is common knowledge that the K_p will vary as a function of the river water chemistry (pH, DOC, hardness etc.). These parameters vary for each location, but also have a seasonal trend. Figure 3.1 shows the seasonal trend in K_d from ca. 120 in the spring and summer and around 80 in autumn and winter.

4. The partition coefficient is often expressed in l/kg . To convert from l/kg into l/g , the value should be divided by 1000.

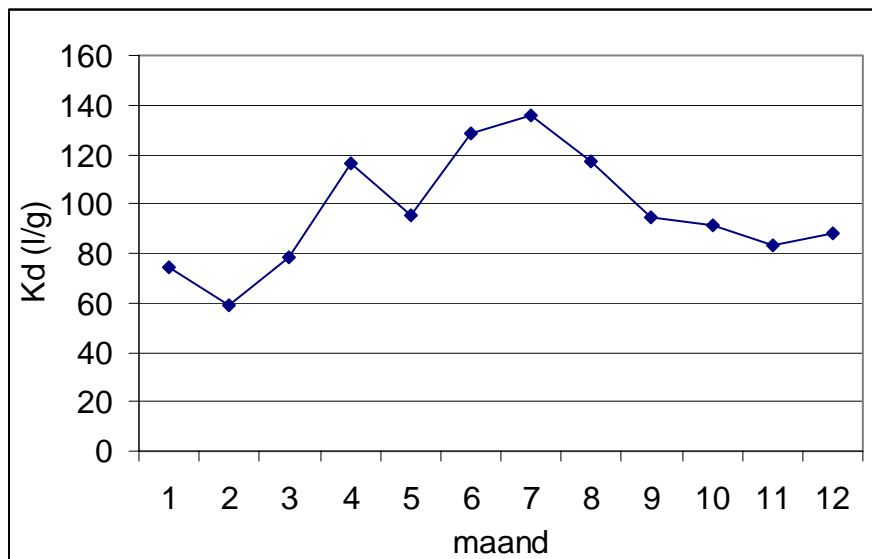


Figure 3.1 Seasonal variation of the K_d for Zn at Lobith monitoring station over the period 2003-2012.

Another factor is the mineralogy of the suspended matter. It can be argued that the K_p in pristine conditions will be higher than under present-day (moderately polluted) conditions, because only the strongest adsorption sites of the suspended matter will be occupied in pristine conditions. This means that the dissolved metal background calculated with this method may be somewhat overestimated. In the study of Van den Berg & Zwolsman (2000) the partition coefficients are calculated as median values of the period 1992-1998. The natural background in suspension is based on the trace metal contents in the fine fraction (< 20 μ m) of non-contaminated sediment (pre industrial radiodated deposits in floodplains). Because of the similarities of the rocks between the catchments of the Rhine and the Meuse, Van den Berg & Zwolsman state that the derived background levels can also be used as a first estimate for the Meuse. However, several references might provide more information of the Meuse catchment (e.g. Van den Berg and Van Wijngaarden, 2000; Van Os, 2001). In specific areas, e.g. streams draining ancient mine deposits (e.g. the Geul River), site-specific backgrounds have to be estimated, using sediment data and local K_p values from that river system.

Equilibrium partitioning is not always the dominating process, particularly for elements that precipitate at very low concentrations. This should be taken into account in the conversion from total to dissolved concentration.

Available data

The partition coefficients in this study for the Rhine were derived from measurements of dissolved metals and the metal content of riverine suspended matter at station Lobith in the period of 1992-1998. For every metal, the median K_p was used. The natural background level of the suspended matter was assumed to be identical to the composition of the fine fraction (< 20 μ m) of non-contaminated sediment as reported by the IRC (International Rhine Commission, 1993) based on a large number of publications. Van den Berg and Zwolsman (2000) derived background concentrations for Cd, Cr, Cu, Hg, Ni, Pb, and Zn. However, sediment background data are also available for As, Ba, Co, Ga, La, Nb, Rb, Sr, V, Ti, and Zr (pers.comm. G.J. Zwolsman).

Van Os *et al.* (2001) used the same method, but used other input data. They interpreted the TNO/NITG database containing analyses of deposited sediment in ancient layers. They concluded that there are two regions in which the metal contents of old sediment cores differ significantly: large rivers and estuaries. In their study they calculated natural lead, copper and zinc contents in different catchments. The derived concentrations are somewhat higher than the concentrations used by Van den Berg & Zwolsman (2000).

Modifications of this method

Different researchers have used this method or have compared this method with other methods to derive natural background levels.

Working group VEM (2004) used this method to derive background concentrations for Cu and Zn with a correction for the DOC content in the different water types identified in their study: large rivers, large and small lakes and canals/ small streams and ditches..

Recently, Zwolsman modified the unburdened sediment method by considering not the median partition coefficient in the calculation of the dissolved metal concentration, but to use a frequency distribution of partition coefficients based on time series of dissolved and particulate (SPM) metal concentrations in a given river. Since the dissolved metal background concentration is calculated from the unburdened sediment composition divided by the partition coefficient, this approach leads to a range of background concentrations for a given metal. For instance, Figure 3.2 shows the background concentration of dissolved Zn in the Rhine River, based on measurements of the dissolved and particulate metal concentrations in the period 1990-2009. The background concentration is presented for the 5-95 percentile range, in order to correct for outliers in the K_p at the low or high edge of the K_p distribution (due to e.g. detection limit problems or contamination). If the median background is chosen from this frequency distribution, this approach leads to the same result as the original sediment approach.

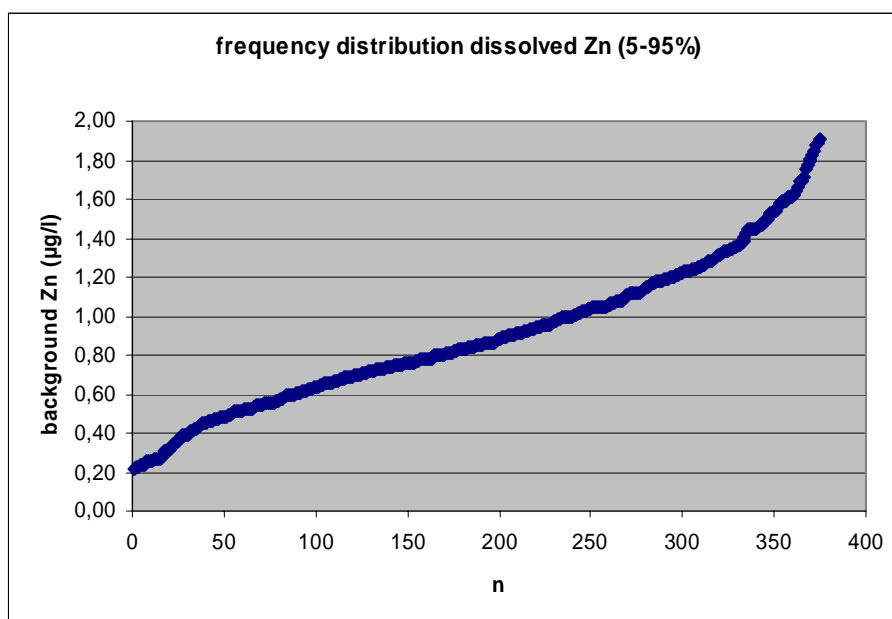


Figure 3.2 Frequency distribution of the dissolved Zn background in the Rhine River based on a dataset for dissolved and particulate Zn in the period 1990-2009.

Assessment

The assessment of the background concentration based on the sediment composition on different criteria is shown in Table 3.5.

Table 3.5 : Assessment of the background concentration based on unburdened sediment composition on different criteria (+ = advantage, - = disadvantage).

+ or -	Assessment
<i>Natural background</i>	
+	In principle, this method yields a geochemical background concentration for dissolved trace metals, by transformation of a natural background concentration in sediment
-	Questionable whether
<i>Data</i>	
+	A lot of undisturbed sediment data is available from different publications, and these data have been thoroughly reviewed by an expert panel on behalf of the International Rhine Commission (IRC, 1993), but also the fluvial sub-surface data used to compose the geochemical atlas of the Netherlands can be used by applying a geochemical baseline model.
<i>Methodological uncertainty</i>	
-	The crucial factor in this approach is the partition coefficient (K_p). Van den Berg & Zwolsman (2000) assumed K_p 's from the period 1992-1998 to be representative of natural K_p 's for calculating the background concentration. Under natural conditions, the availability of metals is probably lower (since only the strongest adsorption sites of the SPM will be occupied), which might lead to a higher K_p . This means that the approach of Van den Berg and Zwolsman (2000) yields the upper limit of the natural background concentration.
-	For metals a high variation in K_p is reported, due to various environmental factors (ionic strength, pH, type of organic matter, temperature etc.). In addition, the method assumes full equilibrium between the solid phase and surface water concentration, which might be questionable
<i>Available elements</i>	
+	Depending on the available data, the method is applicable to all metals for which unburdened sediment composition and partition coefficients are known. Van den Berg and Zwolsman (2000) derived background concentrations for Cd, Cr, Cu, Hg, Ni, Pb, Zn. However, data are available to derive also backgrounds for dissolved As, Ba, Co, Ga, La, Nb, Rb, Sr, V, Ti, and Zr.
<i>Regional differentiation</i>	
+	The background concentration can be calculated for different catchments, based on catchment-specific data (sediment composition, K_p). The correction for the DOC content, as proposed by the Working group VEM, also allows to derive different background levels for different water types.

3.4 Stable summer levels as ambient background concentration

Description

Van Tilborg (2002) reviewed surface water measurement data (in the period of 1995-1999), which revealed the existence of a stable summer concentration for total metals, identical for most surface water types except large rivers and lakes. This summer level was found to be independent of the winter concentrations. Streams with a high winter concentration for total metals were found to reach low summer concentrations of the same level as streams with relatively low winter values. He concluded that the dynamic water systems find sufficient stabilizing forces to reach their summer equilibrium level. These stable summer levels can be regarded as indicative for an ambient background total metal concentration as long as they are not substantially contaminated.

Van Tilborg (2002) based his conclusion on total concentrations in water including suspended matter. The differences in summer and winter concentrations may very likely be explained by differences in suspended matter concentration and associated total metal levels between summer and winter. However, the assumption that small rivers have a base flow predominantly consisting of groundwater from less contaminated deeper layers has been confirmed by several investigations (Rozemeijer, 2010; Klein et al., 2008).

During wet periods, the contribution of more contaminated shallow ground water is larger. This approach does not apply to aquatic systems that are influenced by inlet water or in areas with base flow from the upper layers (South Limburg).

If interpreted in this way, the method comes close to the method based on the origin of surface water (paragraph 3.6).

Assessment

The assessment of the method of the stable summer level on different criteria is shown in Table 3.6. The method as proposed by Van Tilborg has not been proved for dissolved concentrations. Further development to a calibrated/validated method based on dissolved concentrations requires a considerable amount of work.

Table 3.6 : Assessment of the method of the stable summer level on different criteria (+ = advantage, - = disadvantage).

+ or -	Assessment
<i>Natural background</i>	
-	The stable summer level for total metals is the ambient background concentration, that can still be anthropogenically influenced. It has not been sufficiently argued why this stable summer level should represent a natural background level for trace metals.
<i>Data</i>	
±	At this moment a limited number of data for dissolved metal concentrations is available, on the longer term the data availability should not be a problem
<i>Methodological uncertainty</i>	
-	The current analysis was performed on total metal concentrations in water. The (alleged) stable summer level should be proven again for dissolved concentrations
<i>Available elements</i>	
+	All elements that are measured frequently
<i>Regional differentiation</i>	
±	Only valid for small waters, further differentiation is possible when data is available

3.5 Monitoring data approach

3.5.1 Fresh water: UK method

Description

The description of this method is based on a document of the Environment Agency (Peters et al., 2010). In the UK they use a monitoring data approach to estimate ambient background concentrations (ABCs) by using a low percentile (e.g. 5 or 10) of the distribution of monitoring data of dissolved metals for a specific WFD hydrometric area. According to the authors, the derived ABCs are relatively conservative values. This based on the fact that the percentile is low, but they do not give a scientific explanation that a low percentile is mostly below the natural background concentration.

Peters et al. (2010) estimated ABCs for As, Cu, Fe, Mn, Ni and Zn in freshwaters that are relevant for use at Water Framework Directive spatial scales. They derived the ABCs by performing the following steps:

- In the data obvious outliers and pollution incidents are removed;
- Determining the 5 or 10 percentile of the distribution of monitoring data for a metal for a specific hydrometric area;
- Considering groundwater data in hydrometric areas in which there are insufficient surface water monitoring data;

- Using expert judgment to recommend situations in which 'read across' from other hydrometric areas may be reasonable, based on geology or proximity. Peters et al. (2010) mentioned some points of attention when using this method:
- Dealing with limits of detection (LOD). Peters et al. advised to take the LOD as reported value or halve the LOD. The half of the LOD is seen as slightly more precautionary.
- Availability of the data. Peters initially estimate ABCs for those hydrometric areas where there are at least as many samples available as there are water bodies in the area. On average there should ideally be a minimum of 5 monitoring data for each water body in a hydrometric area. Peters et al. (2010) recommended that datasets with less than 50 data points should not be included for derivation of ABCs, unless they are from a hydrometric area with less than 10 water bodies. This should ensure that there are adequate numbers of data for the derivation of ABCs in large hydrometric areas, without penalising small hydrometric areas. There are some options available in the absence of adequate data to derive an ABC:
 - o Pool data across several adjacent hydrometric areas. These need to have broadly comparable geology, land use and hydromorphology;
 - o Adopt an ABC from an adjacent hydrometric area;
 - o Derive a reasonable worst case UK ABC for use in cases where neither of the above options is viable. This might be based on a low percentile of the whole UK data, or on a statistical data treatment of the derived ABCs (e.g. the mean of all derived ABCs). This can be verified against other monitoring data for the UK, such as FOREGS database.
- Use of total metal concentrations to derive dissolved metal concentrations. The proposed EQS for Zn is set on the basis of dissolved concentrations, whereas the current statutory EQS for Zn is set on the basis of total concentrations. As a result, there are very limited monitoring data for dissolved Zn available in some regions of the UK. Background concentrations need to be expressed in the same form as the quality standard, so they need to be derived for dissolved Zn (and other metals). Peters et al. (2010) did not recommend the estimation of dissolved metal concentrations from measured total concentrations. Any efforts to derive ABCs for dissolved metal from total metal concentrations will be subject to considerable uncertainty (at least 3 times greater than for ABCs derived from dissolved metal data).
- Seasonal variability. The dissolved concentration, particularly for essential elements, can vary throughout the year due to uptake/adsorption and elimination/desorption. The database to derive a background concentration should contain data that are evenly distributed over the year, because the WFD compliance check is also based on 12 measurements in a year.

Data availability

- A data collection (fact sheets) of the 92 elements occurring in nature (fresh and marine water), based on literature, is presented by *Reiman & Caritat (1998)*. The data is collected from all over the world. The amount of underlying data depends on the research that had been done on a specific element. This book gives a nice general overview of the elements, and might give some background information, particularly for metals that are not measured very often.
- The FOREGS (Forum of European Geological Surveys) database (<http://www.gtk.fi/publ/foregsatlas/>) is a European database of data from different compartments. The main aim of this database is to provide high quality, multi-purpose environmental geochemical baseline data for Europe. A global geochemical reference baseline for more than 60 determinants in a range of media for environmental and other applications is established.

The main objectives of this European survey were: 1) to apply standardised methods of sampling, chemical analysis and data management to prepare a geochemical baseline across Europe; and 2) to use this reference network to level national baseline datasets. Samples of stream water, stream sediment and three types of soil (organic top layer, minerogenic top and sub soil) have been collected. Selecting of the sample sites of stream water was done as follows:

- The land surface was divided into 160km x 160km cells (GTN grid cells);
- In each of the GTN cells five points were randomly selected;
- The randomly selected points were used to select the five nearest small drainage basins of <math><100 \text{ km}^2</math> in the area. Here sample sites for stream water (filtered and unfiltered) had to be prepared.

Assessment

The assessment of the monitoring data approach for fresh water on different criteria is shown in Table 3.7.

Table 3.7 : Assessment of the monitoring data approach for fresh water on different criteria (+ = advantage, – = disadvantage).

+ or -	Assessment
<i>Natural background</i>	
-	This method is a monitoring data approach to derive a natural background concentrations: the Ambient Background Concentration is not based on real measured data of background levels, but is derived as a 10 percentile. It is not at all sure if this is a 'real' natural background level, it can be underestimated or overestimated.
<i>Data</i>	
+	At this moment a limited number of data for dissolved metal concentrations is available, on the longer term data availability should not be a problem
<i>Methodological uncertainty</i>	
±	Using this method is a relatively easy and robust way to derive background concentrations, but the extent to which these concentrations represent the true natural background is highly uncertain.
<i>Available elements</i>	
+	The method can be applied for all metals for which (dissolved) monitoring data are available
<i>Regional differentiation</i>	
+	With this method it is relatively easy to derive background concentrations for different water types/bodies

3.5.2 Transitional and coastal waters

Description

Transitional and coastal waters contain both seawater and freshwater. The speciation of metals is influenced by salt levels, particularly by a change of dissolved organic carbon or the formation of dissolved metal chloride complexes. Figure 3.3 shows three possibilities: an increased mobility (addition), a decreased mobility (removal) or unchanged mobility (conservative). Several methods to derive background concentrations in estuaries have been suggested.

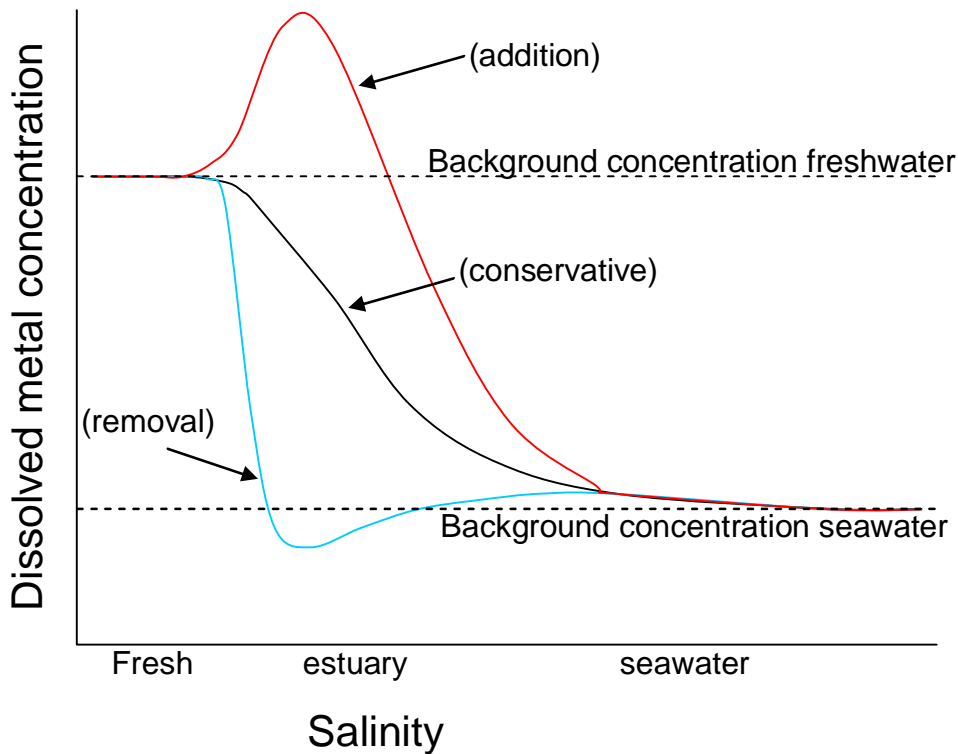


Figure 3.3 Potential effects on dissolved metal concentrations in estuaries due to a changing salinity

The exact figures of metals showing addition or removal in Figure 3.3 need to be calculated with advanced speciation models that account for organic and inorganic metal complexes. The remainder of the paragraph focuses on conservative metals. The EC (2011) proposed a monitoring data approach for the derivation of natural background levels in coastal waters based on conservative behaviour of metals. Their method is shown in Figure 3.4.

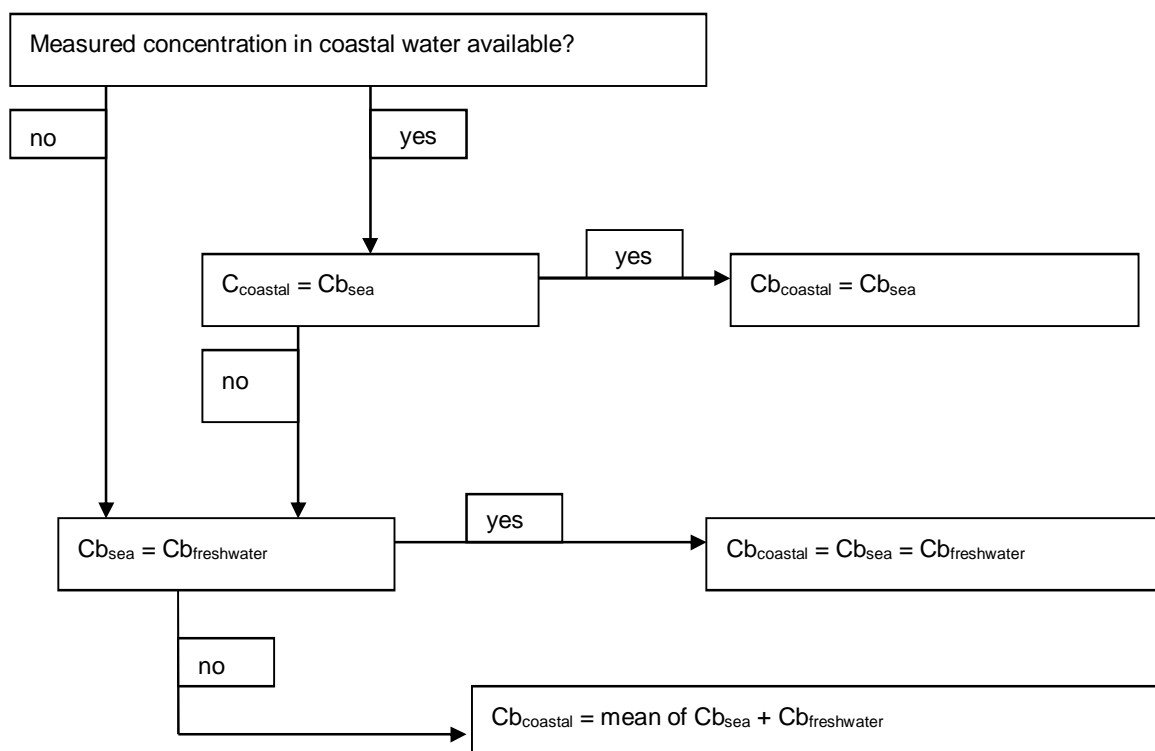


Figure 3.4: Determining the natural background concentration of a metal in coastal waters; $C_{coastal}$ = concentration measured in coastal water, $Cb_{coastal}$ = natural background concentration in coastal water, Cb_{sea} = natural background concentration at sea, $Cb_{freshwater}$ = natural background concentration in freshwater; concentrations refer to the dissolved metal.

As a starting point, the dissolved metal concentration in the coastal water is compared with the natural background concentration at sea (Cb_{sea}). If these values are equal, then the $Cb_{coastal}$ for the coastal water is set equal to the Cb_{sea} . If there are no measurements in the coastal water or if the concentration is greater than Cb_{sea} then the Cb in freshwater and at sea are compared. If they are the same, it will be reasonable to set the Cb in estuaries and coastal waters equal to those in freshwater and at sea (except for reactive metals such as Cd and Cs, which are mobilised within the estuary). If the $Cb_{freshwater}$ is different from Cb_{sea} , which will usually be the case, the mean of the two values may be used for coastal waters, assuming that coastal water is a 1:1 mixture of freshwater and seawater and that the reactivity of metals does not change going from fresh to salt water. If the $Cb_{coastal}$ values derived as above create no problems in relation to measured concentrations and compliance, then no further refinement will be necessary. Alternatively, the $Cb_{coastal}$ can be derived as the 10th percentile of concentrations measured in coastal waters draining only relatively uncontaminated areas.

A major point of criticism is that coastal waters are usually dominated by sea water rather than river water (except for very large rivers). For instance, the salinity of near-coastal waters in the Netherlands (2 km off the coast) is usually around 30 practical salinity units (PSU), implying a seawater contribution of 85% (Zwolsman, 1999). The remaining 15% is mainly river water from the Rhine (and, to a much smaller extent, from the Scheldt and the Meuse).

This means that a mean of river water and sea water background concentrations is not applicable; rather the background for coastal waters would be calculated from the respective contributions of sea water and river water (to be inferred from coastal water salinity) and the background concentrations in each of the “end members”. The resulting background concentration in transitional water can be described by:

$$C_{b_{transitional}} = \frac{[salinity]}{35} * C_{b_{sea}} + \left(1 - \frac{[salinity]}{35}\right) * C_{b_{fresh}}$$

In which:

- $C_{b_{transitional}}$ = background concentration at transitional water sampling station (µg/l)
- $C_{b_{sea}}$ = background concentration in seawater (µg/l)
- $C_{b_{fresh}}$ = background concentration in fresh (river) water (µg/l)
- salinity = salinity at the transitional water sampling station (PSU)

An alternative that accounts for removal or addition in estuaries is based upon the heuristic procedure proposed by Reimann et al. (2005) and Reimann & Garrett (2005). The heuristic method is based upon graphical inspection and using statistical and geographical representations, in which they prefer to take the box plot inner fences and [median±2MAD⁵] to estimate the background range. Some preselection of data takes place by removing data from river catchments with more than 10% outliers.

Tueros et al. (2008) used this method to determine background levels of dissolved trace metals in estuarine and coastal waters of Basque Country. Tueros et al. (2008) distinguished the data from in the Basque coastal waters in 6 categories, from fresh water (<0,5 PSU) to euhaline littoral (>30 PSU). Indeed some variation between the categories was observed. As and Cu seem rather conservative (continuous increase/decrease), whereas Ni, Pb and Zn show a slight increase in the transitional zone.

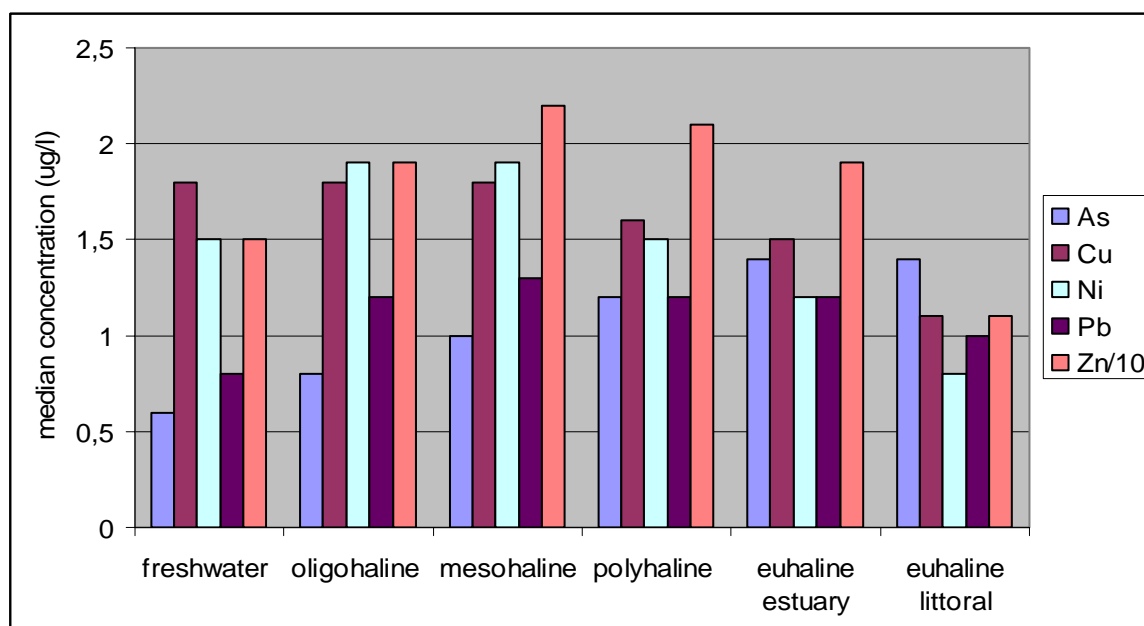


Figure 3.5 Median metal concentrations in different zones in Basque waters as determined by Tueros et al., 2008.

5. MAD = median absolute deviation.

The effect of addition in transitional waters is probably most distinct for metals that form strong complexes with chloride, such as Cd, and Cs. The heuristic method of Reimann et al. (2005) is appropriate for these metals as well. If no data is available, chloride complexes can easily be calculated by speciation calculations.

Available data

- Laane (1992)
- Landing et al. (1995)
- the UK National Marine Monitoring Programme 2004
<http://www.jncc.gov.uk/pdf/nmmp2ndreport.pdf>;

Assessment

The assessment of the monitoring data approach for transitional waters on different criteria is shown in Table 3.8.

Table 3.8 : Assessment of the heuristic approach by Reimann et al. (1995) for coastal and transitional waters on different criteria (+ = advantage, - = disadvantage).

+ or -	Assessment
<i>Natural background</i>	
-	In principle, an ambient background concentration is derived. However, the value might approach a geochemical background concentration if the data fit into a geochemical background concentration in seawater and freshwater (see Figure 3.3).
<i>Data</i>	
±	Data in different zones (varying salinity) need to be available
<i>Methodological uncertainty</i>	
±	The accuracy of the measurements determines the accuracy of the background concentrations
<i>Available elements</i>	
+	This method can be used for many different metals and trace elements
<i>Regional differentiation</i>	
n.a.	No Regional differentiation along the Dutch coast possible

n.a. = not applicable

3.6 Origin of surface water: natural background level based on ground water background concentrations

Description

In the previous paragraphs we looked at estimates of the natural background level in the surface water itself. We can also have another starting point that is the origin of the surface water. Many surface waters in the Netherlands are strongly affected by the interaction with soils, groundwater, and sediments. In these systems, the background concentration in surface water is highly influenced by the background concentration in groundwater.

The method for deriving the background concentration in groundwater described in Verweij et al. (2007), has been updated recently (De Nijs et al., 2011). The report of The Nijs et al. (2011) leaves a number of decisions, particularly the exact percentiles of the data, to policy makers. This decision has not been made yet.

Available data

Van den Brink et al. (2007) derived background concentrations in groundwater for Ba, As, Cu, Zn, Cr, Cd, Pb, Ni, and Al. Fraters et al. (2001) also mentioned background concentrations in groundwater for: Sb, Be, Co, Mo, Se, Tl, Sn, and V, suggesting that they had sufficient data to derive background concentrations.

Assessment

The assessment of the 'origin of surface water' approach on different criteria is shown in Table 3.9.

Table 3.9 : Assessment of the 'origin of surface water' approach on different criteria (+ = advantage, – = disadvantage).

+ or -	Assessment
<i>Natural background</i>	
±	The character of the background concentration depends on the method from another compartment (groundwater). The current method for groundwater aims to derive a geochemical background concentration, because anthropogenically affected samples are discarded. Furthermore, the method does not account for possible changes in concentration during transport from deeper groundwater to surface water.
<i>Data</i>	
±	Data are available from groundwater monitoring, but not all areas in the Netherlands have detection limits that are low enough.
<i>Methodological uncertainty</i>	
-	No attention to chemical behaviour of several metals during transport from groundwater to surface water.
<i>Available elements</i>	
±	The number of elements monitored in groundwater is limited but can be extended.
<i>Regional differentiation</i>	
+	Regional differentiation per groundwater body is possible

4 First selection of methods

4.1 Methods and different aquatic systems

National background concentrations are available for As, Ba, Be, Cd, Cr, Co, Cu, Pb, Hg, methyl-Hg, Mo, Ni, Se, Tl, Sn, V, and Zn. They were published in the 4th National Water Plan (NW4, 1998) and were derived according to the clean streams approach, using equilibrium partitioning to convert total metal concentrations to dissolved metal concentrations. Additional background concentrations are needed for a second tier compliance check under the WFD or for granting a waste water discharge permit. New background concentrations are required for at least Ag, B, Co, Cs, Gd, La, Li, Sb, U, and Y. If new background concentrations are derived with another method, it might be useful to evaluate the current background concentrations.

Six methods have been evaluated in chapter **Error! Reference source not found.**:

- clean streams approach for fresh and marine waters;
- erosion model;
- sediment approach;
- stable summer levels;
- monitoring data methods based on actual measurements;
- origin of surface water.

Six criteria had been formulated for each method, some of them are scientific (natural background, uncertainty), other are practical (data, elements, Regional differentiation).

An important observation in Table 4.1 is that all methods score \pm or $-$ with respect to uncertainty. This is predominantly caused by one or more assumptions in all methods, e.g.: translation from pristine (head) waters to downstream water or other river basins, the reliability of the Kd to calculate dissolved concentrations from contents in soil or suspended matter, processes at the sediment – water interface, etc. It is impossible within this study to quantify the uncertainty, but it is a serious limitation in deriving new background concentrations. On the other hand, the current dissolved background concentrations also have serious limitations: they are based on very old (probably inaccurate) data, they are based on total concentrations in surface water and converted to dissolved concentrations by using Kd-values and standardized amounts of suspended matter.

Table 4.1 Summarizing table for evaluation of the methods

method	1. Natural background	2. data	3. uncertainty	4. elements	5. Regional differentiation
Clean stream	+	-*	\pm	\pm	-
Erosion	-	\pm	-	\pm	-
Sediment	+	+	-	+	+
Stable summer levels	-	+	-	+	\pm
Origin of water	\pm	\pm	-	\pm	+
Monitoring data	-	+	\pm	+	+

* depends on the area; pristine waters might be found in marine areas.

Not all criteria are of the same importance. The WFD focuses on natural dissolved background concentrations (criterion 1 in Table 4.1), indicating that only the clean stream approach, the sediment approach and the origin of surface water approach may be acceptable. However, the Technical guidance for deriving environmental quality standards (EC, 2011) allows methods deriving ambient background concentrations as an alternative. The monitoring data method based on actual measurements, which has the maximum score on criteria 2, 4, and 5, is be regarded as an acceptable fall-back alternative.

The result of the first selection step (determination of the real natural background concentration and a pragmatic fall-back alternative) implies that the erosion model, and the stable summer levels approach are rejected. The method based on stable summer levels does not produce real natural background concentrations. Further development of the method is required to investigate whether this method also yields stable summer concentrations for dissolved trace metals and to what extent these concentrations can be regarded as natural background concentrations. The erosion model focuses on natural concentrations, but basically on metals associated with the rock composition of the catchment area. The WFD requires dissolved concentrations. That means that the concentrations calculated using the erosion model should be converted to dissolved concentrations. It is more reliable to use measured data of (historic) suspended matter composition and to convert this to a dissolved metal concentration.

Three methods thus remain: the clean streams approach, the sediment approach, and the origin of surface water. These methods are not applicable in all situations. Four types of aquatic systems are distinguished, that need different approaches to derive background concentrations:

- open sea and ocean water;
- transitional waters (influenced by river water);
- large (transboundary) rivers;
- smaller inland waters.

4.2 Selection of methods for four different aquatic systems

Open sea and ocean water

The clean streams approach is useful since (almost) unburdened sites of this type exist (open ocean environment). The discussion that remains is which parts of the sea might be considered as representative for undisturbed water along the Dutch coast. There are roughly two possibilities: concentrations from open ocean waters or concentrations from parts of the North sea that are not significantly influenced by human activities (except deposition) and river inflow.

Transitional waters (influenced by river water)

In estuaries and coastal areas significantly influenced by fresh (river) water, the natural background concentration should vary between the composition of natural sea water and natural river water, except for those metals which are mobilised to the dissolved phase within estuaries. The salinity determines the contribution of sea water and fresh water. The background concentration is based on a weighted average of these two.

Large (transboundary) rivers

Different (natural) processes have influenced the river water when it arrives in the Netherlands, so the background concentration resulting from Swiss rocks only is not very appropriate. The clean streams approach is a good option if comparable large clean rivers

can be found. Zuurdeeg (1992) used upstream areas in the North European Lowlands and the surrounding areas as a reference. The large rivers in the Netherlands are downstream sections, and the natural background concentrations are the result of many sources and (solid-solution) processes. Moreover, the Zuurdeeg dataset should be replaced by unburdened dissolved concentrations, which requires the collection of a large amount of international data. The use of historic (uncontaminated) sediments is recommended as an indicator for large rivers in the Netherlands, because the method aims to derive real natural background concentrations. Van den Berg and Zwolsman (2000) derived background concentrations for Cd, Cr, Cu, Hg, Ni, Pb, Zn. However, data are available to derive also As, Ba, Co, and V. The use of K_p -values, based on the national monitoring dataset (total content in suspended solids / dissolved concentration in water) is the best option possible at the moment. For those elements for which undisturbed sediment concentrations are unknown, it should suffice to sample a number of sediment cores in the river basin. The locations should have a long (dating back to 1800 at least) and relatively undisturbed deposition history (these sites are known along the Rhine river from previous sampling campaigns). The cores need to be dated to check whether the sediment is pre industrial. Furthermore, the grain size distribution needs to be more or less similar compared to fresh sediments. The sediment analyses can be converted to dissolved background concentrations using equilibrium partitioning.

Small inland waters

Groundwater is the most important source for many Dutch regional aquatic systems. Two types of groundwater have to be distinguished: deep (ancient) groundwater and superficial groundwater which is prone to pollution due to soil leaching (fertilizers, manure, etc.) The latter is very important in the western part (polders) of the Netherlands. Streams in the higher part of The Netherlands are fed by both deep and superficial groundwater. However, the superficial groundwater is often polluted, and therefore not suitable to derive background concentrations. The method to derive background concentrations can be adopted from the Groundwater Directive (Appendix A), with the remark that final decisions for this method have not been made yet. Background concentrations in groundwater are available for Ba, As, Cu, Zn, Cr, Cd, Pb, Ni, and Al.

An elementary point of quality control is that no method should result in “natural background concentrations” higher than dissolved metal concentrations truly measured in the field. For instance, nearly all measurements of dissolved Cd in the Rhine river are well below the “natural concentration” of 0.08 µg/l proposed by Crommentuijn et al. (1997). Clearly, this natural background is chosen inappropriately. Therefore, it is recommended that for all methods the obtained background values need to be compared with measured concentrations. In moderately polluted waters, it is clear that the background concentration should fall in the lower region of the measurements. If this turns out to be not the case, this is a strong indication that the background value has to be adjusted.

If the background concentration resulting from the proposed method is rejected, or if the proposed method requires a disproportionate amount of work, the monitoring data method can be regarded as a fall-back option. A percentile of the measurements (to be determined later) will be adopted as the background concentration.

5 Case studies for fresh water systems

The methods in chapter 4 have been selected on a theoretical basis. The next step is to carry out a case study with these methods to determine whether they result in realistic natural background concentrations. In this project, we elaborated the two methods that are recommended for freshwater systems: 1) the sediment approach, and 2) the origin of surface water approach (ground water).

5.1 The sediment approach for the river Rhine

The principle of this method is described in paragraph 3.3. The river Rhine is the largest river in the Netherlands and it has been extensively studied. The available data were sufficient to apply the sediment approach to this river. Details of the case study Rhine can be found in Appendix B. The approach (5.1.1) and the results (5.1.2) are presented in this chapter.

5.1.1 Approach

Figure 5.1 shows the steps to derive a background concentration based on the original content in unburdened sediment. The essential, and critical, step is the conversion of metal contents in sediments into dissolved concentrations in water by using a K_p -value. The other steps are to prevent that 'unburdened sediments' provide higher concentrations than the recently measured values in sediment/water.

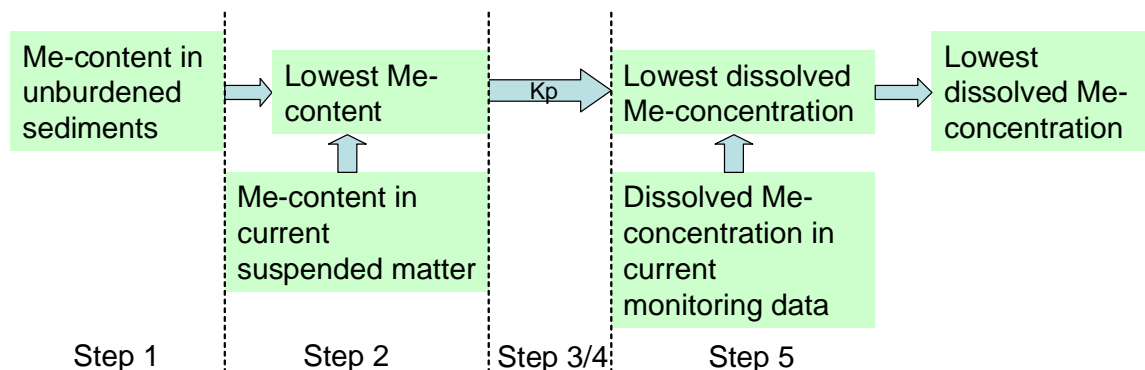


Figure 5.1 Principle of the sediment approach in 5 steps.

Step1: Determine the total content of a metal in unburdened sediment (which is assumed to be the background concentration in sediments).

The first approach is to find data or sample sediment sections dating back to the 16th–17th century (or earlier). It is crucial to note that:

- the K_p for suspended matter will be used. This requires that the sediment composition is comparable to recent suspended matter with respect to size distribution and organic matter;
- the analytical technique to determine the concentrations in sediment and in recent suspended matter should be comparable. Data collected by different analytical techniques need to be corrected. If this is impossible, the data should be excluded;
- the concentrations should be expressed in similar units, e.g. mg/kg dry matter or mg/kg fine fraction (<63 μm);

- it is necessary to check how often values are below the detection limit. This can affect the 10 percentiles, and, if many data are below the detection limit, also higher percentiles. Generally, 0.5 x detection limit is taken if the value is < detection limit.

It is difficult to prescribe a particular number of cores. The ICPR used 2 cores to derive natural background concentrations in sediment. Additional data were found (see Appendix B), but these data roughly confirmed the background concentrations derived by the ICPR.

A second approach to determine the background concentration in sediments has been performed by Spijker et al. (2008). They derived geochemical background concentrations in Dutch sub-soils including fluvial clays using geochemical baseline models. The geochemical background was determined by regression equations based on the %-Al₂O₃. The %-Al₂O₃ in Dutch fluvial clays (sub soils) ranged from 2.4% to 19%. To determine background concentrations in surface water, we need one value instead of an equation. To derive one geochemical background concentration in sediments requires an assumption about the %-Al₂O₃. This should be the same %-Al₂O₃ as in suspended matter. However, the %-Al₂O₃ in suspended matter is not measured in monitoring programmes. Spijker derived a relationship between the clay fraction < 2 µm and %-Al₂O₃. The median clay fraction in suspended matter is 37%, which corresponds to 14% Al₂O₃.

Step 2: The background concentrations in sediment (step 1) should be lower than the 10-percentile of the metal concentrations in recent suspended matter, because the recent suspended matter is largely influenced by anthropogenic loads for most metals. The natural background concentration must be a lower percentile of the whole distribution⁶.

Concentrations in suspended matter have been measured quite regularly, but not always. An alternative approach to determine metal concentrations in suspended matter is to use total metal concentrations, dissolved metal concentrations, and concentrations of suspended matter in water. The metal concentration in suspended matter can be calculated by:

$$C_{SPM} = \frac{(C_{total} - C_{diss})}{SPM}$$

In which:

C _{SPM} =	trace metal content in solid phase (suspended matter) [mg/kg]
C _{total} =	total concentration of trace metals in the water phase [mg/l]
C _{diss} =	dissolved trace metal concentration in the water phase [mg/l]
SPM =	concentration of suspended matter in the water phase [kg/l]

However, this approach may lead to large errors for metals that are predominantly (>90%) present in the dissolved phase, because in that case C_{total} will be close to C_{diss}.

Step 3: Determine partition coefficients using (monitoring) samples in which both metal contents in suspended matter and dissolved metal concentrations in surface water have been measured.

$$K_p = C_{SPM} / C_{diss}$$

In which:

C _{SPM} =	trace metal content in solid phase (suspended matter) [mg/kg]
C _{diss} =	dissolved trace metal concentration in the water phase [µg/l]

6. The 10-percentile is a proposal. It is a policy decision to set the exact percentile.

Step 3 results in a range of K_p -values and can be presented in a distribution graph (Figure 5.2). As in step 1, also in step 3 the number of data below the detection/reporting limit requires attention.

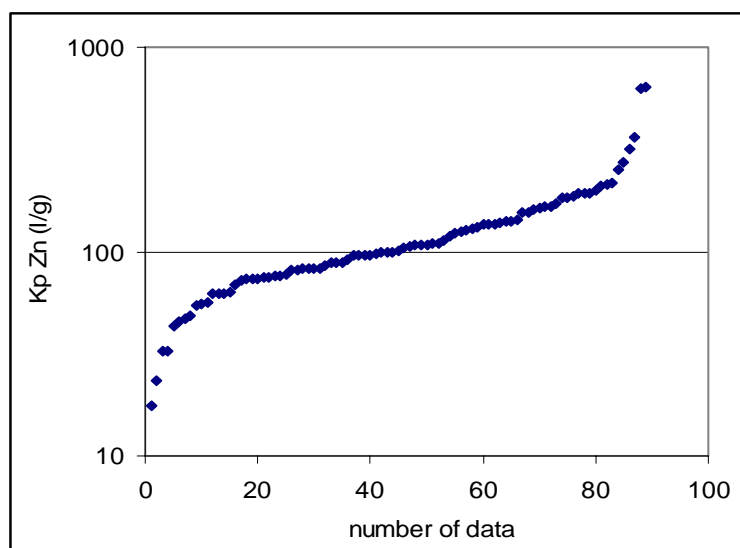


Figure 5.2 Distribution of K_p for Zn based on the monitoring data in Lobith (NL)

Step 4: Convert the total content obtained in step 1 to a dissolved concentration by using a partition coefficient (step 3). The natural background level can then be calculated as:

$$BC_{\text{diss}} = BC_{\text{sed}} / K_p$$

In which:

BC_{diss} = background level of dissolved metal in the water phase [$\mu\text{g/l}$]

BC_{sed} = background level of a metal in sediment = the level of a metal in unburdened sediments [$\mu\text{g/g}$]

K_p = the partition coefficient (l/g)

It is possible to take into account the variability of the K_p and the uncertainty of the method to estimate it. This will lead to a possible range of BC_{diss} values (Figure 3.2). We recommend to calculate and report at least the BC_{diss} values based on the median, the P10 and P90 values of the K_p .

Step 5: compare the calculated BC_{diss} with the 10-percentile of the measured dissolved concentrations⁷. Choose the lowest value of these two.

5.1.2 Results for the river Rhine

Step 1: total content of a metal in pre industrial sediment

Based on the available field studies (ICPR, 1993; Förstner and Müller, 1974), an expert panel of the International Commission on Protection of the Rhine (ICPR) proposed background concentrations for trace metals in fine-grained Rhine sediments (< 20 μm fraction).

7. This step is valid if the actual concentration in surface water is largely influenced by anthropogenic loads, which holds for most metals.

This was done for a limited number of elements. In this study, additional information (Salomons & De Groot, 1978; Hakstege et al., 1993) has been used to derive background concentrations for other available metals.

The alternative method, based on a baseline model in fluvial clays (Spijker et al, 2008) is also presented in Table 5.1. The background is based on 14%-Al₂O₃. If these values are compared to the metal contents in pre industrial sediment cores (data copied from Table 5.1), the BC-14%- Al₂O₃ is slightly higher for most substances. Because of the higher number of data and the statistical foundation, the values derived by Spijker et al. (2008) are preferred to the ICPR cores.

Step 2: Metal contents in unburdened sediment (step 1) versus concentrations in recent suspended matter.

The proposed natural backgrounds for sediments/suspended matter, based on step 1 and 2, are listed in Table 5.1. If a BC-14%- Al₂O₃ is available, this value is compared to the P10 suspended matter. The lowest value is proposed as final BC sediment. If a BC-14%- Al₂O₃ is not available, the contents in the ICPR-research are adopted and compared to the P10.

The contents in unburdened sediments as determined in step 1 are lower than the P10 for Cd, Cu, Hg, Ni, Pb, and Zn, but not for Cr, and V. Values are almost equal for As, Sn, and Co and a comparison is impossible for Ba, Be, and Sb due to a lack of data.

Table 5.1 Background concentrations Rhine sediment, based on the lowest concentration in unburdened sediments or in recent suspended matter (2nd column), and background concentrations in fluvial clays based on 14% Al₂O₃ (see paragraph 5.1.1) according to Spijker et al. (2008).

	Content in pre Industrial sediment (mg/kg)	BC-14%-Al ₂ O ₃ (Spijker et al., 2008) (mg/kg)	P10 suspended matter Lobith 2001-2010 (mg/kg)	Final value BC sediment (mg/kg)
As	12*	16	13	13
Ba	140**	450		450
Be		2,5		2,5
Cd	0.3***	0.3	0.61	0.3
Co	15**		14	14
Cr	80***	101	64	64
Cu	20***	24	52	24
Hg	0.2***		0.32	0.2
Ni	30***	54	40	40
Pb	25***	26	55	26
Sb		0.8		0.8
Sn		3.2	3.4	3.2
V		102	49	49
Zn	100***	93	316	93

* Salomons & De Groot, 1978

** ICPR, 1993; Förstner and Müller, 1974

*** ICPR, 1994

Step 3: Determine partition coefficients

Partition coefficients were obtained from the metal concentrations in SPM and dissolved metal concentration.

Three different data sources have been used to obtain K_p -values for all metals. First of all, the regular monitoring data of Lobith Ponton for the period 2001-2010 have been used. Because of varying detection limits (and surprisingly higher limits in recent years), two K_p -values for Cd are presented. Next to the period 2001-2010, also a K_p -value is calculated using monitoring data with lower detection limits (1996-1998).

If metals are not available in the regular monitoring, the K_p was based on project data from 2004-2005 collected also at Lobith Ponton (Schrap et al., 2008). The chosen K_p (final) is selected using the preference order: (1) Lobith, 2001-2010, (2) Lobith 2004-2005, (3) literature.

Table 5.2 K_p -values based on monitoring data from 2001-2010 at Lobith, based on monitoring data or literature, Ranges represent the 10-percentile to 90-percentile.

	K_p final (l/g)		Source
	Median	range	
As	18	12-24	Lobith, 2001-2010
Ba	10	4-25	Allison & Allison, 2005
Be	0.9		Normen voor waterbeheer, 2000
Cd	55	24-91	Lobith, 2001-2010
Cd	310	83-515	Lobith, 1996-1998
Co	118	81-161	Lobith, 2004-2005
Cr	280	112-410	Lobith, 2001-2010
Cu	35	24-51	Lobith, 2001-2010
Hg	920	250-1764	Lobith, 2001-2010
Ni	39	30-85	Lobith, 2001-2010
Pb	1360	605-2400	Lobith, 2001-2010
Sb	4		Normen voor waterbeheer, 2000
Sn	372		Normen voor waterbeheer, 2000
V	55	37-66	Lobith, 2004-2005
Zn	106	63-195	Lobith, 2001-2010

Step 4: Convert the total content into a dissolved concentration.

Table 5.3 shows that the newly derived median background concentrations for Ba, Cd, Hg, Ni, Pb, and Zn are considerably lower than the currently used background concentrations (by a factor of 3 to 45). The differences are relatively small for other metals.

Table 5.3 Background concentrations in sediment/SPM, the selected partition coefficients, and the resulting dissolved background concentration in surface water. The column at the right side shows the current background concentrations (copied from Table 2.1). Ranges represent the 10-percentile to 90-percentile.

	BC_{sed} ($\mu\text{g/g}$)	K_p final (l/g)		BC_{diss} ($\mu\text{g/l}$) median	BC_{diss} ($\mu\text{g/l}$) range	BC_{diss} ($\mu\text{g/l}$) Current
		Median	range			
As	13	18	12-24	0.7	0.5-1.1	0.8
Ba	450	10	4-25	45	18-112	73
Be	2,5	0.9		2.8		0.02
Cd	0.3	55	24-91	0.005	0.003-0.013	0.08
Cd*	0.3	310	83-515	0.001	0.0005-0.0036	0.08
Co	14	118	81-161	0.12	0.09-0.17	0.2
Cr	64	280	112-410	0.23	0.16-0.57	0.2
Cu	24	35	24-51	0.7	0.47-1.0	0.4

Hg	0.2	920	250-1764	0.0002	0.00011-0.0013	0.01
Ni	40	39	30-85	1.0	0.47-1.3	3.3
Pb	26	1360	605-2400	0.019	0.011-0.043	0.2
Sb	0.8	4		0.22		0.3
Sn	3.2	372		0.0086		0.0002
V	49	55	37-66	0.89	0.63-1.3	0.8
Zn	93	106	63-195	0.88	0.48-1.5	2.8

* BC for Cd calculated with a higher K_p due to lower detection limit in the period 1996-1998

Step 5: compare the calculated BC_{diss} with the 10-percentile of the measured dissolved concentrations.

In Table 5.4 the proposed BCs are compared with the P10 of the monitoring data of dissolved metals at Lobith. Most derived BCs are below or equal to the P10.

Table 5.4 The derived background concentrations as shown in Table 5.3 compared with the P10 of the monitoring data from 2001-2010 at Lobith. The 4th column shows the proposed BC, being the lowest value of these two. The last column shows the current BC; values in red indicate that the new value is at least 50% lower, in green means that the new value is at least 50% higher.

	BC (median)	P10 (ug/l)	Proposed BC (ug/l)	BC_{diss} (µg/l) current
As	0.7	0.79	0.7	0.8
Ba	45	68	45	73
Be	2.8	-	2.8	
Cd	0.005	<0.05	0.005	0.08
Cd*	0.001	<0.05	0.001	0.08
Co	0.12	0.10	0.10	0.2
Cr	0.23	<0.5	0.23	0.2
Cu	0.7	1.7	0.7	0.4
Hg	0.0002	<0.001	0.0002	0.01
Ni	1.0	0.6	0.6	3.3
Pb	0.019	<0.1	0.019	0.2
Sb	0.22	0.23	0.22	
Sn	0.0086	<0.1	0.0086	
V	0.89	0.91	0.89	0.8
Zn	0.88	2.1	0.88	2.8

* see Table 5.3

5.1.3 Conclusions

If background concentrations for additional elements should be determined, data of unburdened sediment, monitoring data of dissolved metals and K_p -values need to be available. Based on currently available data of the river Rhine, background concentrations could be derived for As, Ba, Cd, Co, Cr, Cu, Hg, Ni, Pb, V, and Zn.

For most metals, the proposed background concentrations in this report are lower than or (approximately) equal to the current background concentrations derived by Crommentuijn et al. (1997).

5.2 Regional waters with surface water originating from ground water.

Many regional surface waters in the Netherlands are strongly affected by the interaction with soils and sediments. In such cases, the background concentration in groundwater should be an appropriate basis for surface water quality assuming that no major natural changes occur during transport from groundwater to surface water, which might not be true for all metals. An updated approach to derive natural background levels in groundwater was published in 2011 (De Nijs et al., 2011, Appendix A).

The background concentrations of groundwater are derived for the province of Noord-Brabant and compared with concentrations in surface water in the Water boards of Aa & Maas and De Dommel. Details can be found in Appendix C. The approach (5.1.1) and the results are presented in this report (5.1.2).

5.2.1 Approach

Step 1: Derive a background concentration for all relevant metals in groundwater using the procedure described by De Nijs et al. (2011). This requires a groundwater monitoring network in which many metals are measured. More important, they should be measured accurately. State-of-the-art equipment is required to measure sufficiently low concentrations.

The most important steps to derive background concentrations for groundwater are (see Appendix A):

1. Use all measurement data:
 - a. for which chloride is measured;
 - b. with a length of the filter between 1 and 5 meters;
 - c. at all depths;
 - d. independent of monitoring frequency.
2. Half of the detection limit is taken if values are below the detection limit.
3. Calculate the median per filter.
4. Separate the fresh and the brackish/salt water bodies (fresh is < 200 mg Cl/l).
5. Check the modality of the data on basis of the cumulative probability plot. A uni-modal distribution is expected if all data is unburdened. If the data is not uni-modal, the data has to be split in two (or more) uni-modal distributions. Dependent on the substance a pre-selection rule can be defined to remove anthropogenic influenced data from the dataset.
6. Derive the background concentration on the basis of the non-anthropogenic influenced data⁸:
 - a. The 50-percentile
 - b. The lower limit of the 95%-confidence level of the 90-percentile
 - c. The 90-percentile
 - d. The lower limit of the 95%-confidence level of the 95-percentile
 - e. The 95-percentile

Step 2: Compare the derived background concentrations for groundwater with the P10-percentile of surface water monitoring data⁹. Choose the lowest value.

5.2.2 Results

Step 1: groundwater data

8. The exact value is still to be decided.

9. The 10-percentile is a proposal. It is a management decision to specify the exact value. Furthermore, this step is valid if the concentration in recent suspended matter is largely influenced by anthropogenic loads, which holds for most metals.

Two different monitoring networks were used in this study:

- National monitoring network groundwater quality (LMG);
- Provincial monitoring network groundwater quality (PMG).

In the province of Noord-Brabant, the LMG contains 75 piezometers with 75 different filters with different depths. Data from 1980 to 2008 is used. The PMG includes 48 different piezometers with 132 different filters. Data are available for: As, B, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Se, Sn, Sr, Tl, V and Zn. Ag, and Sb were measured only 15 or 16 times. The background concentration will be derived for these metals, but the results have a high uncertainty.

The selection of the data resulted in a removal of 9 filters due to a chloride concentration above 200 mg/l. The low number of brackish/salt filters lead to the decision to remove these 9 filters in stead of deriving a background concentration for brackish/salt water. It was difficult to evaluate the probability plots, also because De Nijs et al. (2011) do not give clear criteria when the probability plot is bimodal. Cadmium (Figure 5.3) seems to have a bimodal distribution, which is caused by the detection limit.

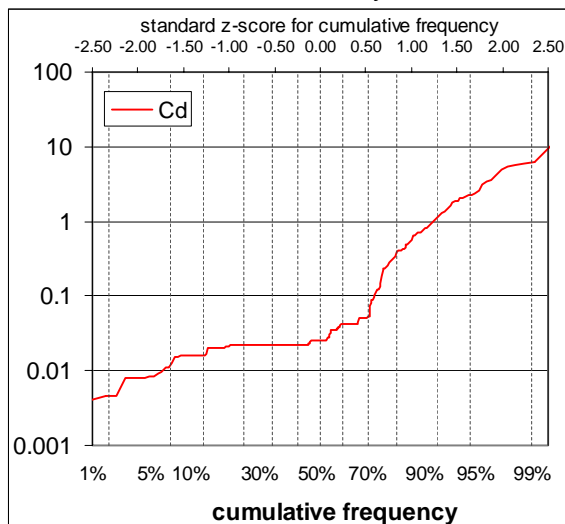


Figure 5.3 Probability plot for Cd.

Additional research revealed that the depth of the filter affected the values. We removed the data collected in filters 1 and 2, and used only the data from the (deeper) filters 3 and 4.

Other probability plots are presented in Appendix C. Although more graphs could be interpreted as a bi-modal probability plot, it is difficult to define exact criteria. Except for Cd, we did not remove any data from the groundwater dataset for this reason. The P50, P90, and P95 in groundwater were calculated. The results are shown in Table 5.5.

Step 2: Comparison of proposed background concentration in groundwater with surface water data.

The metals available in groundwater (step 1) were all measured in surface water by Water board De Dommel, and partly by Water board Aa en Maas (Cd, Cr, Cu, Ni, Pb, Zn). Only measurements of filtrated samples from 2005 till 2011 are selected. Table 5.5 presents the P10 of the surface water data. Though there is some variation between the values, differences are small and not systematic. Table 5.5 also shows that the detection limits for surface water are always higher than those for groundwater.

Table 5.5 For the different metals the 50-, 90-percentile in groundwater in the province of Noord-Brabant and the 10-percentile in surface water in Water boards De Dommel and Aa en Maas.

	Groundwater				Surface water: De Dommel (after filtration)			Surface water: Aa en Maas (after filtration)		
	n	P50	P90	Detection limit	n	P10	Detection limit	n	P10	Detection limit
As		0.88	7.5	0.1-5	144	2	4			
B		17	70		471	19	10			
Ba		51	124	0.23	608	17	1			
Cd		0.02	0.04	0.003-0.1	4506	0.05**	0.01-0.4	1968	0.05**	0.1
Co		0.69	34	0.08-0.3	669	0.5**	0.1-1			
Cr		0.52	2.08	0.05-1	4467	0.25*	0.5-2	1911	0.25**	0.5
Cu		0.56	8.4	0.1-10	4493	1	0.1-3	1920	1.1	1
Mo		0.08	0.40	0.002-0.6	614	1	1-2			
Ni		1.3	74.4	0.001-0.52	4530	1.8	0.5-2	1968	2.1	0.5-1.5
Pb		0.31	2.01	0.08	4506	0.1*	0.1-3	1968	0.1*	0.1-1.5
Sb		0.05	0.13		144	2.5*	5			
Se		0.19	0.74	0.05-5	671	0.25*	0.5-5			
Sn		0.01	0.04	0.005-5	144	2.5*	5			
Sr		140	337	0.03-0.1	471	95	-			
Tl		0.01	0.10	0.001-0.07	527	0.25	0.1-0.5			
V		0.63	2.57	0.07-3	144	1*	2			
Zn		5	193	0.0002-0.12	4492	3.4	3-5	1920	2.5*	3-5

* P10-value definitely affected by the detection limit (Appendix C)

** P10-value possibly affected by the detection limit (appendix C).

If the groundwater data represents true undisturbed measurements, the P90 is an appropriate choice, because most of the data should be lower than the proposed background concentration. However, if the P90 in (undisturbed) groundwater is compared to the P10 in (disturbed) surface water, only Mo, Sb, Sn, and Tl show lower P90-concentrations in groundwater than in P10-concentrations surface water. If the median (P50) values in groundwater are compared to the P10 in surface water, also Cd, Cu, Se, Tl, and V have a lower concentration in groundwater. However, the detection limits in surface water provide considerable uncertainty.

The groundwater database seems to contain some pollution for a number of elements. Therefore, the P50 (and not the P90) is taken as the natural background concentration in groundwater. As for all methods, the proposed background concentration based on the P50-groundwater should not exceed the P10 in surface water. Table 5.6 reveals that most values are in the same order of magnitude as the current background concentrations.

Table 5.6 Proposed background concentrations for regional waters in the area of De Dommel and Aa en Maas (BC_{diss}) and current (National) background concentrations (BC_{diss} current). In red means that the new value is at least 50% lower, in green means that the new value is at least 50% higher.

	BC_{diss} ($\mu\text{g/l}$) De Dommel		BC_{diss} ($\mu\text{g/l}$) Aa en Maas		BC_{diss} ($\mu\text{g/l}$) current
As	0.88	gw			0.8
B	17	gw			-

Ba	17	sw			73
Cd	0.02	gw	0.02	gw	0.08
Co	0.5	sw			0.2
Cr	0.25	sw	0.25	sw	0.2
Cu	0.56	gw	0.56	gw	0.4
Mo	0.08	gw			1.4
Ni	1.3	gw	1.3	gw	3.3
Pb	0.1	sw	0.1	sw	0.2
Sb	0.05	gw			0.3
Se	0.19	gw			0.04
Sn	0.01	gw			0.0002
Sr	87	sw			-
Tl	0.01	gw			0.04
V	0.63	gw			0.8
Zn	3.4	sw	2.5	sw	2.8

Gw = background concentration based on P50 in groundwater

Sw = background concentration based on P10 in surface water

5.2.3 Discussions and conclusions

Background concentrations can be derived only for elements that are measured regularly and accurately (i.e. low concentrations) in groundwater and surface water. The groundwater data in Noord-Brabant have low detection limits and are suitable for this approach¹⁰. The P10 values in the surface water data of De Dommel and Aa en Maas are often influenced by detection limits.

The number of elements taken into account is limited by the number of elements measured in groundwater. Background concentrations, based on the lowest value of the P50 in groundwater and the P10 in surface water, could be derived for 17 elements. However, the relatively high detection limits in surface water provide considerable uncertainty.

This study also reveals that even with the detection problems in surface water, the P90 (but also the P50) in groundwater is often higher than the P10 in surface water. A number of explanations can be raised:

- Fate and transport: changes in chemistry during transport from (deep) groundwater to surface water may change the mobility, particularly for redox-sensitive metals, like As, or metals that precipitate under oxic conditions (iron/manganese).
- Processes in surface water, e.g. adsorption to sediment and suspended matter or uptake by biota.
- Change in DOC-concentrations (and metals bound to DOC)
- Anthropogenically affected groundwater. A gradient in depth could be demonstrated for Cd, but we expect the presence of such a gradient also for Zn and Cu in Noord-Brabant. The guidance for derivations of background concentrations in groundwater does not define exactly whether a probability plot has a bi-modal distribution.
- Chemical processes in deeper groundwater may cause higher Ni concentrations in deep groundwater, whereas surface water is often supplied by shallow groundwater.
- Dilution with rain water.

10. The detection limits of the Provincial Monitoring network Groundwater (PMG) Noord-Brabant are very low compared to many other PMGs.

- Low anthropogenic influence. If there is no anthropogenic load, the distribution of the concentrations in groundwater and surface water may be equal for elements. Comparison of a P50-groundwater with a P10-surface water is not appropriate in that case. This might be true for B, Ba, and Co.

6 Conclusions and recommendations

6.1 Conclusions

The current background concentrations as recorded in the Dutch National water Plan (NW4, 1998) are not reliable. Total concentrations in pristine water in NW Europe measured in the eighties of the 20th century were transferred to the Netherlands. Equilibrium partitioning was used to calculate dissolved background concentrations. It is definitely time to update the method and the values.

Six methods to derive background concentrations in surface waters were identified: the clean streams approach, the erosion model, the sediment approach, stable summer levels, monitoring data approach based on field measurement, the origin of surface water.

Three methods are proposed for further evaluation:

- 1 the clean streams approach (based on measurements in relatively undisturbed aquatic systems);
- 2 the sediment approach (based on the composition of unburdened sediments and equilibrium partitioning);
- 3 the origin of surface water (based on measurements of the composition of the surface water's source).

The monitoring data approach can be seen as a fall-back option as well as a basic quality control for all methods. The obtained background concentrations need to be compared with actual measured concentrations in the field. If the derived background concentration exceeds the P10 of measured concentrations, the background concentration is rejected.

The selected methods can not be applied in all water systems. Four types of aquatic systems were distinguished. They need different approaches to derive background concentrations:

- Open sea and oceans
- estuaries and coastal water
- large (transboundary) rivers
- smaller inland streams

Two methods, both suitable for fresh water, are worked out in a case study: the sediment approach for the river Rhine, and the origin of surface water for regional waters in the south of the Netherlands.

The sediment method is applied to the river Rhine. Both data of unburdened sediment and monitoring data of dissolved metals and metals adsorbed to SPM need to be available. Based on currently available data of the river Rhine, median background concentrations ($\mu\text{g/l}$) were listed in Table 6.1. No values could be derived for Ag, B, Be, Cs, Gd, La, Li, Mo, Sb, Se, Sn, U, Tl, and Y, due to a lack of unburdened sediment data or K_p -values at Lobith. For most metals the proposed background concentrations in this report are lower than the current background concentrations derived by Crommentuijn et al. (1997). New sediment samples have to be collected if background concentrations are needed for additional metals, but this requires a limited amount of work.

The origin of surface water method (groundwater) is applied to the regional waters in Noord-Brabant. Based on the P50 in (undisturbed) groundwater, and checked with the P10 in surface water, background concentrations ($\mu\text{g/l}$) are presented in Table 6.1.

Background concentration could not be derived for Ag, Be, Hg, Cs, Gd, La, Li, U, and Y, due to a lack of ground water quality data. Most values are in the same order of magnitude as the current background concentrations derived by Crommentuijn et al. (1997). The detection limits of the surface water data were often not low enough to derive a reliable P10 in surface water. This problem might be solved if better equipment is used for analyses.

It requires a lot of work to collect reliable groundwater quality data to derive background concentrations for the missing elements. P50 or P90-values in groundwater (assumed to be undisturbed) are often higher than P10 values in (disturbed) surface water. Various reasons are mentioned in this report. We conclude that the step from groundwater to surface water is too complicated to 'copy' background concentrations in groundwater directly to surface water.

Table 6.1 Proposed and current background concentrations (BC) in µg/l

Element	Proposed BC Rhine cf sediment approach	Proposed BC De Dommel cf groundwater approach	Proposed BC Aa en Maas cf groundwater approach	Current BC (Crommentuijn, 1997)
As	0.7	0.88		0.8
B		17		-
Ba	45	17		73
Cd	0.005	0.02	0.02	0.08
Co	0.10	0.5		0.2
Cr	0.23	0.25	0.25	0.2
Cu	0.7	0.56	0.56	0.4
Mo		0.08		1.4
Hg	0.0002			
Ni	0.6	1.3	1.3	3.3
Pb	0.019	0.1	0.1	0.2
Sb		0.05		0.3
Se		0.19		0.04
Sn		0.01		0.0002
Sr		87		-
Tl		0.01		0.04
V	0.89	0.63		0.8
Zn	0.88	3.4	2.5	2.8

6.2 Recommendations

This report shows that all available methods to determine background concentrations have serious limitations, and (until now) experts do not agree which method should be adopted to derive a new set of background concentrations. Taking into account all comments and remarks, we recommend the following activities to extend and improve the dissolved background concentrations in surface water.

The clean streams approach for open sea and ocean water needs additional data for metals such as B, U, and Ag. Concentrations for these metals in ocean water are probably available in the international literature, whereas RWS might have measurements in the North Sea for a broader range of metals. It is important to calculate an annual average in which all months have an equal distribution.

The preferred method in the rivers Rhine, Meuse, Scheldt and Ems is to analyse unburdened sediments and calculate the concentration in water by equilibrium partitioning, using a river-specific K_p for each metal. Dated sediment cores are available for the river Rhine for a considerable number of elements, but another possibility is to use subsoil data of fluvial clays combined with a chemical baseline model. The resulting background concentrations should not exceed the P10 of actual monitoring data. The P10 of actual measurements can also be used if there are no sediment data available. The derived background concentrations for the Rhine can be used as a first estimate for the other large Dutch rivers, however it is recommended to derive background concentrations for each river system. To obtain background concentrations for other rivers, it is necessary to collect additional data of undisturbed sediment.

The background concentration in transitional waters can be calculated if the background concentration in seawater and river water is available. This is easy if a metal behaves conservatively, but for metals that form organic or inorganic metal complexes (see Figure 3.3), such as Cd and Cs, speciation calculations and validation can improve the quality of the background concentration in brackish water.

The case-study in Noord-Brabant reveals that the method to determine a background concentration in groundwater requires more study. Moreover, the relationship between groundwater and surface water is quite complicated. At the moment the groundwater approach can not be used and the monitoring data approach is recommended.

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A Natural background levels in other compartments

Natural background levels for groundwater

To derive background concentrations for groundwater De Nijs et al. (2011) is followed. The most important steps to derive background concentrations for groundwater are:

1. Use all good useful measurement data in the groundwater monitoring network:
 - f. For which chloride is measured;
 - g. With a length of the filter between 1 and 5 meters;
 - h. Do not select on the depth of the filter or on the filter that is most measured.
 - i. Values less than the detection limit are given half of the actual value.
2. Calculate the median per filter.
3. Calculate the background concentration for the fresh and the brakish/salt water bodies.
4. Check the modality of the data on basis of the cumulative probability plot. If the data is not uni-modal, the data has to be split in two (or more) uni-modal distributions. Dependent on the substance a pre-selection rule can be defined to remove anthropogenic influenced data from the dataset.
5. Derive the background concentration on the basis of the non-anthropogenic influenced data:
 - j. The 50-percentile
 - k. The lower limit of the 95%-confidence level of the 90-percentile
 - l. The 90-percentile
 - m. The lower limit of the 95%-confidence level of the 95-percentile
 - n. The 95-percentile

Background concentrations rainwater

Rain water contributes directly to surface water. The question is if we have to take natural background levels of rain water to derive natural background levels of surface water or that it is enough to take current rainwater concentrations.

In The Netherlands a national network to monitor the rainwater composition exists. The measurements are executed every 4 weeks on 15 stations. The measured substances are hydronium/hydrocarbonate, sodium, potassium, calcium, magnesium, fluoride, chloride, nitrate, sulphate, phosphate EC, pH, arsenic, cadmium, chromium, cobalt, copper, lead, nickel, iron, vanadium and zinc. The latest report of this network is published by Stolk (2001).

Background concentrations in soils

In the study of Spijker et al. (2008) empirical relations are used to estimate the natural background levels of trace metals, arsenic and antimony in soils.

There is a natural relation between bulk chemical and trace element composition of the minerals (for example between aluminium and nickel, chromium and lead). The idea behind this is that the concentration of a bulk element is not easily anthropogenically influenced and the deviation from the natural concentration is small. Having the natural ratio, one can estimate the natural background level of a trace metal with the help of the bulk element concentration. For 12 elements baseline models are derived, based on a robust regression technique. They call this concept the 'geochemical baseline'.

Soil samples from the C horizon are used to derive the natural ratio between aluminium and the trace elements.

A disadvantage of this method is that the model is only suitable for soils with a mineral composition. For peat soils, a different model has to be used.

This model can not be used for surface water, because in surface water there will be no fixed relation between bulk elements and trace elements.

B Case study river Rhine: the unburdened sediment method (contribution KWR)



Background concentrations of trace metals in the Rhine river

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Watercycle Research Institute



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1 Introduction

The primary goal of the Water Framework Directive (WFD) is to achieve a good ecological and chemical status of surface waters in all the member states. To that purpose, water quality standards have been issued, either by the Commission (for the priority substances), or by the member states themselves (for other relevant substances). These standards have been implemented in Dutch legislation (in Dutch: Besluit kwaliteitseisen en monitoring water, 2009; Ministeriële Regeling monitoring, 2010).

In case of non-compliance with the standard, member states are allowed to take natural background concentrations and/or bioavailability into account. However, the WFD does not provide strict regulation pertaining to the derivation of background concentrations. Each member state can decide to do so for itself.

Under the WFD Common Implementation Strategy, an Expert Group on Environmental Quality Standards (EQS) was initiated in 2007, to produce guidance on establishment of the EQSs. Currently, a draft Technical guidance for deriving environmental quality standards (Paya Perez et al., 2010) is available, which includes the following text:

In fresh water, the preferred procedure for assigning a 'natural' background will usually be to determine the concentrations in springs and/or in water bodies in 'pristine' areas in the given region, e.g. headwaters. Other possibilities are:

- *To measure concentrations in deep groundwater. In some cases, however, the concentration of the metal may be higher in the groundwater than in the surface water, e.g. because of the groundwater's contact with deep mineral rocks or soils and subsequent dilution by rain.*
- *To gather information from national or international databases, such as the FOREGS Geological Baseline Programme (<http://www.gsf.fi/foregs/geochem>).*
- *Geological modelling, to estimate the contribution from erosion.*
- *To estimate the concentration in the water from natural background concentrations found in the sediment by means of equilibrium partitioning models.*

In practice, the input data needed to determine background concentrations in pristine areas by modelling may be inadequate to estimate a reliable value. An alternative pragmatic approach in these cases is to take the 10th percentile dissolved metal concentration of all the monitoring data available for the water body or region (after removing sample results with elevated concentrations from known point source discharges or pollution events).

For this reason, the Netherlands Water Agency (RWS-Waterdienst) has launched a research project on methods to derive natural backgrounds for trace metals (Osté et al., 2011). One of the promising methods identified by that study will be elaborated here. The purpose of our study is to derive natural background concentrations for dissolved trace metals in the Rhine river, based on the composition of pre-industrial sediments and equilibrium partitioning. This approach is equivalent to the fourth method identified by the WFD Expert Group on Environmental Quality Standards.

2 Approach

Ten years ago, Van den Berg & Zwolsman (2000) proposed a method to estimate natural background concentrations of dissolved trace metals in surface water, based on the partition of metals over the water and solid (suspended matter) phase, combined with measured contents of trace metals in pre-industrial sediments. The method was used to derive natural background concentrations of dissolved Cd, Cr, Cu, Hg, Ni, Pb, and Zn in the river Rhine (at the Dutch-German border station Lobith). The method can be outlined as follows.

The partition coefficient (K_p) is defined as: $K_p = C_s/C_d$

In which:

C_s = trace metal content in solid phase (suspended matter) [$\mu\text{g/g}$]

C_d = dissolved trace metal concentration in the water phase [$\mu\text{g/l}$]

The K_p -value has the unit l/g.

The natural background concentration can be calculated as: $BC_d = BC_s/K_p$

In which:

BC_d = background concentration of dissolved metal in the water phase [$\mu\text{g/l}$]

BC_s = background concentration of metal in the suspended matter [$\mu\text{g/g}$]

The natural background in the suspended matter is based on the trace metal content of the fine-grained fraction ($< 20 \mu\text{m}$) of non-contaminated (pre-industrial) sediment. These particulate backgrounds can be derived from radiodated sediment cores or floodplain sediments deposited in pre-industrial times (i.e., before 1800 AD).

The critical point in this approach is the choice of K_p . It is common knowledge that K_p will vary as a function of river water chemistry (pH, DOC, hardness etc.) and the composition of the suspended matter. However, it can be argued that the K_p in pristine conditions will be higher than under present-day (i.e. polluted) conditions, because only the strongest adsorption sites of the suspended matter will be occupied in pristine conditions. This means that the dissolved metal background calculated by this method may be overestimated to some extent.

Although there may be valid criticism on the equilibrium partitioning concept, it should be emphasized that this concept is applied in Dutch water management policy for over 20 years. For instance, equilibrium partitioning has been applied to derive standards for sediment quality in the Netherlands, based on a uniform (nation-wide) K_p value for each metal (Van der Kooij et al., 1991). The concept could be improved, however, by using specific K_p values for individual river systems, as done in this study.

If suspended matter composition is not available, the K_p can be estimated from measurements of total metal (C_t), dissolved metal (C_d) and suspended matter concentration (SPM), as follows:

$$K_p = [(C_t - C_d) / (\text{SPM})] / C_d$$

However, this approach may lead to large errors for metals that are predominantly ($>90\%$) present in the dissolved phase, because in that case C_t will lie close to C_d .

3 Trace metal concentrations in the Rhine river (2001-2010)

3.1 Particulate metal concentrations

An overview of the particulate metal concentrations of the Rhine river at station Lobith is presented in Table 1. Suspended matter samples were taken biweekly using centrifugation and analysed for particulate metals by ICP-AES after *aqua regia* destruction in a closed teflon bomb placed in a microwave oven. The dataset comprises a 10-year period (2001-2010) and consists of 250-260 records for each metal, except for As (analysed monthly) for which there were 144 records. In general, particulate metal levels were above the reporting limits (RL), except for Cd (4% of the measurements < RL).

Table 1. Trace metal content of Rhine suspended matter (station Lobith). Statistics for the years 2001-2010.

	As µg/g	Cd µg/g	Cr µg/g	Cu µg/g	Hg µg/g	Ni µg/g	Pb µg/g	Zn µg/g
n	144	261	256	249	261	255	259	261
n < RL*	1	11	0	0	0	0	0	0
2-perc	10	<0.10	58	45	0.24	34	46	262
5-perc	12	0.23	61	50	0.28	38	49	290
10-perc	13	0.61	64	52	0.32	40	55	316
50-perc	18	1.50	76	71	0.53	46	73	428
90-perc	23	2.47	99	102	0.94	55	118	597
95-perc	24	3.00	104	110	1.20	58	137	658

* RL = Reporting Limit

3.2 Dissolved metal concentrations

Dissolved metals at station Lobith were analysed after filtration (0.45 µm) by ICP-MS taking all the necessary precautions to avoid contamination of the samples. Results for the period 2001-2010 are shown in Table 2. In general, dissolved As, Cu, Ni and Zn are well above the reporting limits, which are 0.1 µg/l for As, Cu and Ni, and 0.5-1 µg/l for Zn. However, the vast majority of the records of dissolved Cd (90%), Cr (72%), Hg (73%), and Pb (70%) were below the reporting limit in the period considered. This means that the median value of the dissolved metal concentration cannot precisely be determined for these metals.

Table 2. Dissolved metal concentrations of the Rhine river (station Lobith). Statistics for the years 2001-2010.

	As* µg/l	Cd µg/l	Cr µg/l	Cu µg/l	Hg µg/l	Ni µg/l	Pb µg/l	Zn µg/l
n	157	257	257	259	255	257	259	259
n < RL	0	231	185	1	186	8	180	8
5-perc	0.7	<0.05	<0.5	1.6	<0.001	0.3	<0.1	1.2
10-perc	0.8	<0.05	<0.5	1.7	<0.001	0.6	<0.1	2.1
50-perc	1.0	<0.05	<0.5	2.0	<0.001	1.2	<0.1	4.2
90-perc	1.3	0.050	0.7	2.9	0.002	1.6	0.11	8.2
95-perc	1.4	0.052	1.1	3.2	0.003	1.8	0.21	9.3

* As measured from 2005-2010

However, it should be noted that the reporting limits have changed over time. For instance, the reporting limit for dissolved Cd in the nineties (except in 1995) was five times lower than it is nowadays (for reasons unknown). For dissolved Cr and Pb, but not for Hg, the reporting limits were also lower in previous years (see Table 3). Therefore, we also calculated dissolved metal concentrations for the periods when reporting levels were sufficiently low to allow meaningful measurements, i.e. 1996-1998 (Cd) and 1999-2003 (Cr and Pb). The results are shown in Table 4..

Table 3. Reporting limits for dissolved Cd, Cr, Hg and Pb ($\mu\text{g/l}$)

Period	Cd	Cr	Hg	Pb
1990-1994	0.01	0.1	0.01	0.1
1995	0.04	0.1	0.003	0.9
1996-1998	0.01	0.01	0.001	0.1
1999-2000	0.05	0.01	0.001	0.05
2001-2003	0.05	0.05	0.001	0.05
2004-2010	0.05	0.5	0.001	0.1

Table 4. Best estimation of dissolved Cd, Cr, and Pb concentrations in the Rhine river (station Lobith).

period	Cd ($\mu\text{g/l}$)		Cr ($\mu\text{g/l}$)		Pb ($\mu\text{g/l}$)	
	1996-1998	2001-2010	1999-2003	2001-2010	1999-2003	2001-2010
n	72	257	129	259	129	259
n < RL*	55	231	15	1	50	180
5 perc	< 0.01	<0.05	<0.05	<0.5	<0.05	<0.1
10 perc	< 0.01	<0.05	<0.05	<0.5	<0.05	<0.1
50 perc	< 0.01	<0.05	0.3	<0.5	0.06	<0.1
90 perc	0.02	0.050	1.0	0.7	0.20	0.11
95 perc	0.03	0.052	1.3	1.1	0.30	0.21

* RL = Reporting Limit

3.3 Partition coefficients

Partition coefficients (K_p 's) were calculated for the period 2001-2010 as $K_p = C_p / C_d$. In the calculation of individual K_p 's, dissolved metal concentrations below the reporting limit were considered to be half the reporting limit (highly relevant for Cd, Cr, Hg, and Pb; see Table 2). The resulting set of partition coefficients is shown in Table 5.

Table 5. Partition coefficients for trace metals in the Rhine river. Statistics for the years 2001-2010. Dissolved metal concentrations below the detection limit were considered to be half the detection limit.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
n	79	230	225	220	229	224	230	232
K_p (l/g)								
5-perc	11	9	78	21	150	26	490	54
10-perc	12	24	112	24	250	30	605	63
50-perc	18	55	280	35	920	39	1360	106
90-perc	24	91	410	51	1764	85	2400	195
95-perc	28	100	1283	87	2200	202	2914	371

As mentioned before, variability in K_p values is to be expected because of its dependence on water column chemistry (e.g. pH, hardness) and composition (mineralogy) of the suspended matter. However, the variability in K_p 's appears to be rather limited for As, Cu, Ni and Zn; i.e. for metals of which (almost) all the dissolved concentrations lie above the reporting limit. The

variability in Kp for these metals, defined here as the ratio 90-percentile/10 percentile, varies within a factor of 2 (As, Cu) to 3 (Ni, Zn). For Cd, Cr, and Pb, Kp varies within a factor of 4 and for Hg Kp varies within a factor of 7.

Partition coefficients for Cd, Cr, Hg, and Pb may be biased for the period 2001-2010 because of the large number of dissolved metal concentrations being under the reporting limit. Therefore, we have also calculated partition coefficients for Cd, Cr, and Pb for the period when reporting limits were sufficiently low to allow reliable dissolved metal measurements (Table 4). Most of the dissolved Cd measurements (78%) in the period selected were below the reporting limit, however. For dissolved Cr (17% < RL) and dissolved Pb (37% < RL), this was not the case. In the Kp calculation, dissolved metal concentrations < RL were assumed to be equal to 0,5 x RL. The resulting Kp's are shown in Table 6.

Table 6. Best estimation of partition coefficients of Cd, Cr, and Pb in the Rhine (Lobith).

	Cd (µg/l)	Cr (µg/l)	Pb (µg/l)
period	1996-1998	1999-2003	1999-2003
n	63	119	120
Kp (l/g)			
5 perc	66	72	253
10 perc	83	83	570
50 perc	310	241	1510
90 perc	515	2401	3332
95 perc	573	3472	3530

Based on the median values, the Kp for Cr and Pb in the period 1999-2003 appears to be similar to that in the period 2001-2010 (cf. Tables 5 and 6). However, for Cd the Kp appears to be much higher, i.e. 310 l/g (1996-1998) instead of 55 l/g (2001-2010).

3.4 Non-conventional metals

In the year 2005, a sampling campaign was executed in Dutch surface waters in order to assess the concentration of (amongst others) non-conventional trace metals. In this campaign, Co and V, but not Ba, were measured in the dissolved phase and in the suspended matter. The results for station Lobith are summarized in Table 7.

Table 7. Dissolved and particulate Co and V concentrations and Kp values at station Lobith (2005).

	Co (µg/l)	Co (µg/g)	Kp Co (l/g)	V (µg/l)	V (µg/g)	Kp V (l/g)
n	19	19	19	19	19	19
5-perc	0,09	13,2	78	0,90	47	36
10-perc	0,10	14,0	81	0,91	49	37
50-perc	0,14	15,9	118	1,04	56	55
90-perc	0,21	18,0	161	1,36	64	66

For Ba, measurements in the dissolved phase are available at station Lobith for the year 2010 only (n = 26). The 10-90 percentile range amounts to 68-105 µg/l; the median concentration is 82 µg/l. Measurements of Ba in the suspended matter are not available, however. Therefore, the Kp for Ba was taken from a comprehensive EPA review on partition coefficients in surface waters. The Kp ranges from 4-25 l/g, with a median value of 10 l/g (Allison & Allison, 2005).

4 Background concentrations of pre-industrial Rhine sediments

4.1 Field data

In 1993, the International Commission for the Protection of the Rhine (IKSR) published a report on the composition of pre-industrial Rhine sediment. In Table 8, the composition of a sediment core of the Rhine taken near Dusseldorf is presented, with four sediment sections dating back to the 16th-17th century. It is crucial to note that the sediment composition refers to the < 63 µm fraction of the sediments, i.e. the silt and clay fraction. Therefore, it may reasonably be assumed that the sediments have a grain size (distribution) comparable to average suspended matter of the Rhine. Another sediment core, taken at Cologne, was described by Förstner and Müller (1974). The composition of the pre-industrial part of this sediment core is also shown in Table 8.

Table 8: Composition of pre-industrial aquatic sediments (< 63 µm) of the Rhine river (Dusseldorf, Cologne)

		Sediment sections from the 16 th – 17 th century (Dusseldorf) ¹				Pre-industrial sediments (Cologne) ²
		0-10 cm	10-20 cm	20-30 cm	30-40 cm	
Al	%	2.78	2.97	3.65	3.39	-
Fe	%	2.91	3.06	3.18	3.17	3.23
Ca	%	4.92	4.20	4.93	5.67	-
Ba	µg/g	141	142	155	138	-
Cd	µg/g	1.4	1.7	1.1	0.9	0.3
Co	µg/g	12.5	13.5	16.4	16.0	16
Cr	µg/g	46	46	50	49	47
Cu	µg/g	25	36	34	37	51
Hg	µg/g	-	-	-	-	0.2
Ni	µg/g	40	46	44	42	46
Pb	µg/g	25	86	39	41	30
Zn	µg/g	92	207	126	120	115

1. (IKSR, 1993)

2. Förstner and Müller (1974).

Salomons & De Groot (1978) studied background concentrations of trace metals in soils from polders along the Rhine river which were reclaimed in 1788 and in the 15th-16th century. They applied a grain size correction on the results in order to derive background concentrations for standard sediments (grain-size 50% < 16 µm). Their results are shown in Table 9. In general, these results compare very well to the results of Förstner and Müller (1974) and IKSR (1993), although differences can be observed for Cd (high in IKSR dataset) and Cr (high in polders).

Table 9: Trace metal concentrations in standard sediments (50% < 16 µm) from Rhine polders reclaimed in 1788 and the 15th-16th century (Salomons & De Groot, 1978).

Age	As µg/g	Cd µg/g	Cr µg/g	Cu µg/g	Hg µg/g	Ni µg/g	Pb µg/g	Zn µg/g
1788	12.2	0.5	77	21	0.14	33	31	93
15th-16th century	12.5	0.3	89	25	0.21	39	29	100

Hakstege et al. (1993) studied the geochemistry of Holocene clays from the Rhine and Meuse Rivers. They studied sediment sections from cores taken from river floodplains, going back as far as the Roman and Middle Bronze Ages. A summary of their results is presented in Table 10. Sediment composition was measured by X-ray fluorescence which yields total metal content, contrary to more conventional methods based on strong acid digestion (e.g. nitric acid, *aqua regia*) which only yield the reactive metal fraction. This reactive fraction is on the order of 40-60% for Al, 60-80% for Fe, and 60-100% for trace metals, depending on the metal (Cr and Ni on the lower edge, Cd, Cu, Pb, and Zn on the higher edge; Zwolsman et al., 1996).

Table 10. Average composition of Holocene floodplain sediments of the Rhine (Hakstege et al., 1993).

Location	Deest	Zoelen	Arnhem	Lobith
Samples (n)	24	45	46	21
Fraction < 10 µm (%)	72 ± 15	62 ± 11	39 ± 9	45 ± 10
Al (%)	8.94 ± 1.64	7.73 ± 1.16	5.61 ± 0.58	6.09 ± 0.85
Fe (%)	4.42 ± 1.16	3.85 ± 0.86	2.73 ± 0.50	2.99 ± 0.54
Ca (%)	0.76 ± 0.26	3.77 ± 3.14	7.12 ± 1.64	4.91 ± 1.32
Ba (µg/g)	405 ± 65	335 ± 43	294 ± 95	290 ± 26
Cr (µg/g)	72 ± 12	62 ± 10	51 ± 21	53 ± 8
Ni (µg/g)	52 ± 13	39 ± 10	35 ± 13	31 ± 10
Pb (µg/g)	56 ± 16	46 ± 20	51 ± 51	39 ± 6
V (µg/g)	89 ± 18	76 ± 12	57 ± 9	65 ± 13
Zn (µg/g)	93 ± 28	78 ± 59	114 ± 228	51 ± 14

4.2 Background concentrations of trace metals in suspended matter

Based on the available field studies (i.e., Tables 8 and 9), an expert panel of the IKSr proposed background concentrations for trace metals in fine-grained Rhine sediments (< 20 µm fraction), as well as in suspended matter (IKSR, 1993; 1994). In Table 11, these backgrounds are compared to the present-day composition of suspended matter of the Rhine river (taken from Table 1).

Table 11. Background concentrations of trace metals in suspended matter of the Rhine river (IKSR, 1994), compared with the 5- and 10-percentile concentration found in recent suspended matter of the Rhine.

	Cd µg/g	Cr µg/g	Cu µg/g	Hg µg/g	Ni µg/g	Pb µg/g	Zn µg/g
Background (IKSR)	0.30	80	20	0.20	30	25	100
SPM, 5-percentile	0.23	61	50	0.28	38	49	290
SPM, 10-percentile	0.61	64	52	0.32	40	55	316

In principle, background concentrations for trace metals in suspended matter should be lower than the concentrations measured in recent samples, even at the lower edge of the distribution. This appears to be the case for Cu, Hg, Ni, Pb, and Zn, but not for Cd and Cr (Table 11). Based on Table 11, we propose natural backgrounds of 0.2 µg/g for Cd and 60 µg/g for Cr.

For As, we propose a background concentration of 12 µg/g, based on the soil composition of pre-industrial Rhine polders (Table 9) and confirmed by the 5-percentile composition of recent suspended matter (Table 1). Natural backgrounds for Ba and Co in the suspended matter can be estimated at 140 µg/g and 15 µg/g, respectively, based on the composition of fine-grained pre-industrial Rhine sediments (Table 8). However, the natural background of Ba is uncertain because of the much higher Ba concentrations found in Holocene floodplain deposits (Table 10). The natural background of V in floodplain deposits (Table 10) would be estimated at 70 µg/g. However, the actual V concentration measured in the suspended matter is lower (see Table 7). Based on table 7, we suggest a background of 50 µg/g for V in suspended matter.

5 Calculation of dissolved background concentrations

5.1 Dissolved metal backgrounds based on equilibrium partitioning
Background concentrations for dissolved trace metals were calculated as described in chapter 2. Input for the calculations are the partition coefficients and the natural background of each metal in the suspended matter, which are given in chapters 3 and 4, respectively. The results of the calculations are summarized in Table 12. For the partition coefficient, we used the range from 10-percentile to 90-percentile (if available), as well as the median value.

Table 12. Calculation of natural background concentrations for dissolved trace metals in the Rhine river. Ranges are indicated based on the 10-percentile to 90-percentile variation in the partition coefficient.

	Background SPM (µg/g)	Background SPM based on	Kp (l/g)		Background (dis.)	
			median	range	median	range
As	12	Pre-industrial sediments; Table 9	18	12-24	0.67 µg/l	0.50-1.0
Ba	140	Pre-industrial sediments; Table 8	10	4-25	14 µg/l	6-35
Cd	0.2	Adapted IKSR estimate; Table 11	55	24-91	3.6 ng/l	2.2-8.3
Co	15	Pre-industrial sediments; Table 8	118	81-161	0.13 µg/l	0.09-0.19
Cr	60	Adapted IKSR estimate; Table 11	280	112-410	0.21 µg/l	0.15-0.54
Cu	20	IKSR (1994); Table 11	35	24-51	0.57 µg/l	0.39-0.83
Hg	0.2	IKSR (1994); Table 11	920	250-1764	0.22 ng/l	0.11-0.80
Ni	30	IKSR (1994); Table 11	39	30-85	0.77 µg/l	0.35-1.0
Pb	25	IKSR (1994); Table 11	1360	605-2400	0.018 µg/l	0.01-0.04
V	50	10-percentile SPM; Table 7	55	37-66	0,91 µg/l	0.76-1,35
Zn	100	IKSR (1994); Table 11	106	63-195	0,94 µg/l	0.51-1.59

5.2 Comparison of background concentrations with field data

An elementary point of quality control is that “natural background concentrations” cannot be higher than dissolved metal concentrations truly measured in the Rhine river today (since the river is not in pristine condition). We have made this comparison in Table 13. For dissolved As, Cu, and Zn, the proposed background concentration is indeed lower than the 10-percentile of the field measurements. This means that the proposed background concentrations can be used as a basis to derive water quality standards. For dissolved Cd, Cr, Hg, and Pb, the proposed background concentration may be lower than the 10-percentile of the field measurements, but this cannot be concluded unambiguously since the 10-percentile lies under the reporting limit. For dissolved Ni, the proposed background concentration is higher than the 10-percentile of the field measurements. Therefore, we propose to define a pragmatic background for dissolved Ni, based on the 10-percentile of the measurements at Lobith (2001-2010), i.e. 0.60 µg/l.

Table 13. Comparison of (median) background concentrations for dissolved trace metals in the Rhine river with field measurements (station Lobith). Statistics for the years 2001-2010.

	As µg/l	Cd µg/l	Cr µg/l	Cu µg/l	Hg µg/l	Ni µg/l	Pb µg/l	Zn µg/l
Background concentration	0.67	0.0036	0.21	0.57	0.0002	0.77	0.018	0.94
5-perc	0.71	<0.05	<0.5	1.6	<0.001	0.30	<0.1	1.2
10-perc	0.79	<0.05	<0.5	1.7	<0.001	0.60	<0.1	2.1

The proposed background concentration for dissolved Ba (14 µg/l; Table 12) lies well below the 10-percentile of the measurements at station Lobith (68 µg/l) and is therefore considered to be valid. The proposed background concentration of dissolved Co (0.13 µg/l) is somewhat higher than the 10-percentile of the measurements (0.10 µg/l; Table 7) and is therefore adjusted to 0.10 µg/l. The proposed background concentration of V (0.91 µg/l) is identical to the 10-percentile of the field measurements (Table 7).

5.3 Proposal for dissolved background concentrations

In Table 14, the final selection of background concentrations for dissolved trace metals in the Rhine is presented. The outcome of the equilibrium partitioning method (see chapter 2) was considered to be valid if the resulting background concentrations turned out to be lower than the 10-percentile of the field measurements. This was the case for As, Ba, Cd, Cr, Cu, Hg, Pb, V, and Zn. If the calculated background concentration was higher than the 10-percentile of the field data, we selected the latter value in order to derive a pragmatic background (Co and Ni).

Table 14. Proposed background concentrations of dissolved trace metals in the Rhine river.

	Background concentration	Background based on	Reference
As	0.67 µg/l	Equilibrium partitioning	Table 12
Ba	14 µg/l	Equilibrium partitioning	Table 12
Cd	3.6 ng/l	Equilibrium partitioning	Table 12
Co	0.10 µg/l	10-percentile field data	Table 7
Cr	0.21 µg/l	Equilibrium partitioning	Table 12
Cu	0.57 µg/l	Equilibrium partitioning	Table 12
Hg	0.22 ng/l	Equilibrium partitioning	Table 12
Ni	0.60 µg/l	10-percentile field data	Table 13
Pb	0.018 µg/l	Equilibrium partitioning	Table 12
V	0.91 µg/l	Equilibrium partitioning	Table 12
Zn	0,94 µg/l	Equilibrium partitioning	Table 12

6 References

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C Case study regional waters in Noord-Brabant: the origin of surface water (groundwater)

C Natural background levels surface water based on groundwater background concentrations

C.1 Description

The natural background level in the surface water can be estimated from the surface water itself, but we can also have another starting point, namely the origin of the surface water. This approach might be particularly in aquatic systems that are fed by groundwater.

Many surface waters in the Netherlands are strongly affected by the interaction with soils and sediments. Then, groundwater quality is the basis for surface water quality. A European accepted method is available to derive natural background levels in groundwater bodies Van den Brink et al. (2007). In 2011 a new approach to derive natural background levels in groundwater is published (De Nijs et al., 2011).

The assumption that small rivers have a base flow predominantly consisting of groundwater from less contaminated deeper layers has been confirmed by several investigations (Rozemeijer, 2010; Klein et al., 2008). During wet periods, the contribution of more contaminated shallow groundwater is larger. This approach does not apply to aquatic systems that are influenced by inlet water or in areas with base flow from the upper layers (South Limburg).

A point of attention is that changes in groundwater composition and metal concentrations can occur near the sediment-water interface due to e.g. redox transitions and adsorption reactions, which is not accounted for by this method.

As case-study the background concentrations of groundwater are derived for the province of Noord-Brabant and compared with concentrations in surface water in the waterboards of Aa & Maas and De Dommel.

C.2 Approach

C.2.1 Used datasets

Groundwater

To derive background concentrations in the groundwater, two different monitoring networks are used to derive data from:

- National monitoring network groundwater quality (LMG);
- Provincial monitoring network groundwater quality (PMG).

In the province of Noord-Brabant the LMG contains 75 observation wells with 219 different filters with different depths. Data from 1980 till 2008 is used. The PMG includes 48 different observation wells with 132 different filters in the province of Noord-Brabant (see **Error! Reference source not found.**). Data from 1991 till 2009 were selected in the PMG. Most filters have a depth between 10 and 25 meters below surface. The filters in the monitoring networks are yearly sampled and analyzed.

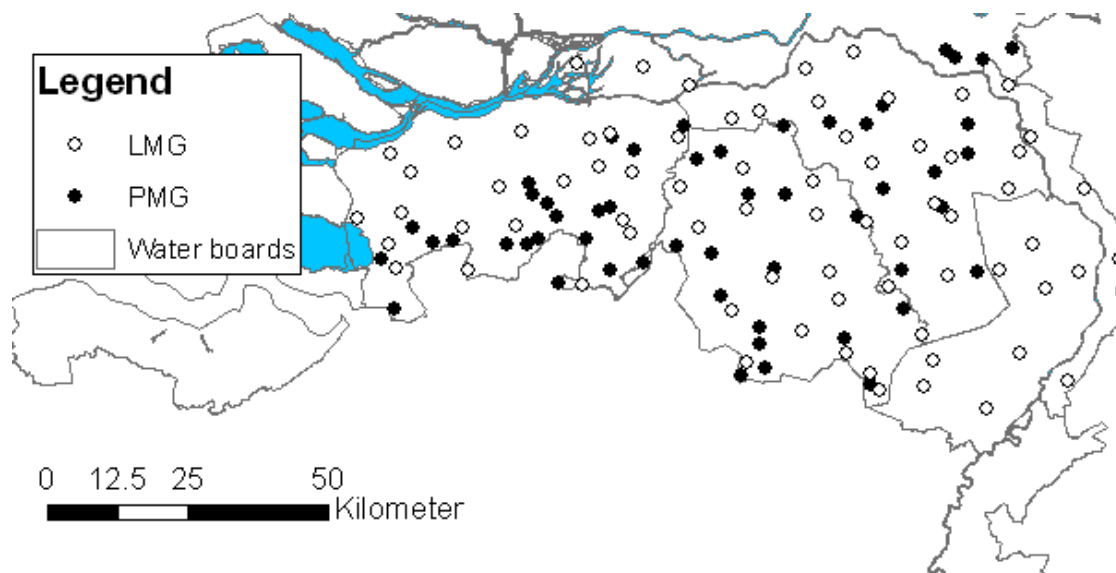


Figure C1. Locations of the piezometers of the LMG en PMG in the province of Noord-Brabant.

The following table (see Table) summarizes the measured metals in groundwater in the two different monitoring networks and in the surface water in the Waterboards of Aa & Maas and De Dommel (see paragraph surface water).

For the province of Noord-Brabant background concentrations in groundwater can be derived for the metals: As, B, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, Sn, Sr, Tl, V and Zn were measured more than 20 times. Only 15 or 16 values are available for Ag, Br and Sb. The background concentration will be derived for these metals, but the results have a high uncertainty.

Surface water

The surface water datasets of Waterboard Aa & Maas and Waterboard De Dommel are used. In the datasets only measurements of filtrated samples from 2005 till 2011 are

selected. In table C1 the metals that are measured are shown. Table C1 shows that Waterboard De Dommel measures more metals than Waterboard Aa & Maas. Besides this, some metals have a lot of values below the detection limit. For Waterboard De Dommel enough data are available for B, Ba, Cd, Co, Cr, Cu, Ni, Pb, Sr and Zn. For the metals As, Br, Mo, Sb, Se, Sn, Tl and V more than half the values is below the detection limit, which requires attention when comparing these values with the values in the groundwater.

For Waterboard Aa & Maas Cr, Cu, Ni, and Zn can be used for evaluation. Over 50% of the data are below the detection limit for Br, Cd and Pb.

Table C1: Availability of metals in groundwater (PMG/LMG) and surface water (Waterboards De Dommel and Aa & Maas). A grey colour means that a background concentration is determined in this study

Metal	PMG Noord-Brabant	LMG Noord-Brabant	SW De Dommel	SW Aa & Maas
Ag	No	Yes, but not often (15 times)	No	No
As	Yes	Yes	Yes*	No
B	No	Yes	Yes	No
Ba	Yes	Yes	Yes	No
Be	No	No	No	No
Br	No	Yes, but not often (16 times)	Yes*	Yes*
Cd	Yes	Yes	Yes	Yes*
Co	Yes	Yes	Yes	No
Cr	Yes	Yes	Yes	Yes
Cu	Yes	Yes	Yes	Yes
Hg	No	No	No	No
Mo	Yes	No	Yes*	No
Ni	Yes	Yes	Yes	Yes
Pb	Yes	Yes	Yes	Yes*
Sb	No	Yes, but not often (16 times)	Yes*	No
Se	Yes	No	Yes*	No
Sn	Yes	No	Yes*	No
Sr	Yes	Yes	Yes	No
Te	No	No	No	No
Ti	No	No	No	No
Tl	Yes	No	Yes*	No
U	No	No	No	No
V	Yes	Yes	Yes*	No
Zn	Yes	Yes	Yes	Yes

* Over 50% of the data are below the detection limit.

C.2.2 Data handling

Derive background concentrations for groundwater

To derive background concentrations for groundwater De Nijs et al. (2011) is followed. The most important steps to derive background concentrations for groundwater are:

1. Use all good useful measurement data:
 - a. For which chloride is measured;
 - b. With a length of the filter between 1 and 5 meters;
 - c. Do not select on the depth of the filter or on the filter that is most measured.
 - d. Values less than the detection limit are given half of the actual value.
2. Calculate the median per filter.
3. Calculate the background concentration for the fresh and the brakish/salt water bodies.
4. Check the modality of the data on basis of the cumulative probability plot. If the data is not uni-modal, the data has to be split in two (or more) uni-modal distributions. Dependent on the substance a pre-selection rule can be defined to remove anthropogenic influenced data from the dataset.
5. Derive the background concentration on the basis of the non-anthropogenic influenced data:
 - a. The 50-percentile
 - b. The lower limit of the 95%-confidence level of the 90-percentile
 - c. The 90-percentile
 - d. The lower limit of the 95%-confidence level of the 95-percentile
 - e. The 95-percentile

The detection limit in the data of the PMG and the LMG are presented below. Detection limits in the network are relatively low.

Table C.1: Detection limits in the provincial monitoring network groundwater in Noord-Brabant.

Metal	Detection limit groundwater (PMG) (ug/l)
As	0.1 - 5
B	
Ba	0.23 - 0.23
Cd	0.0003 - 0.1
Co	0.08 - 0.3
Cr	0.05 - 1
Cu	0.1 - 10
Mo	0.002 - 0.6
Ni	0.001 - 0.52
Pb	0.08 - 0.08
Sb	
Se	0.05 - 5
Sn	0.005 - 5
Sr	0.03 - 0.1
Tl	0.001 - 0.07
V	0.07 - 3
Zn	0.0002 - 0.12

The above-described steps are followed. According to step 3 nine filters have a chloride concentration above 200 mg/l. It is useless to calculate a separate background concentration for the brakish/salt water body because nine measurements are too few to calculate a background concentration from. Therefore, these nine filters are removed from the dataset.

According to step 4 the modality of the different metals is checked with the help of probability plots. At the end of this appendix the probability plots for the different metals are presented.

It is not really clear from De Nijs et al. (2011) at what point you have to say that the data is anthropogenic influenced. When a plot is bi-modal, will this say that the second distribution consists of anthropogenic influenced locations? It was difficult to evaluate the probability plots, also because De Nijs et al. (2011) do not give clear criteria when the probability plot is bimodal. Cadmium (figure C2) seems to have a bimodal distribution. This is mainly caused by the detection limits.

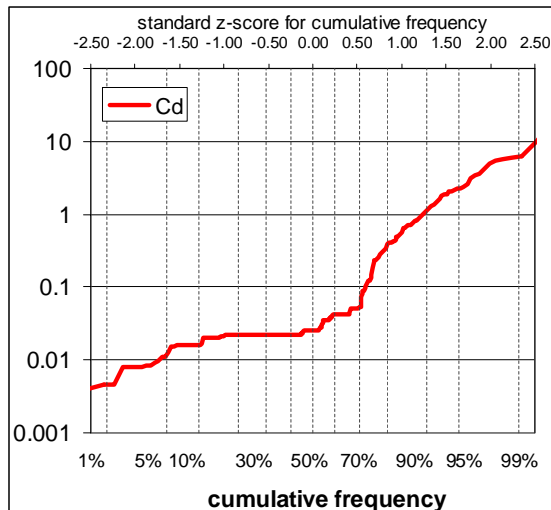


Figure C2 Probability plot for Cd.

Additional research revealed that the depth of the filter affected the values. We removed the data collected in filters 1 and 2, and used only the data from the (deeper) filters 3 and 4.

Although more graphs could be interpreted as a bi-modal probability plot, it is difficult to define exact criteria. Except for Cd, we did not remove any data from the groundwater dataset for this reason. There were no substances with an obvious bi-modal distribution, so we did not remove any data from the groundwater dataset for this reason. Only a check is performed to look if high values of more substances occur in the same location. A few times two or three substances have an exceptionally high concentration in one filter. To limit the amount of work (it is no more than a case-study), we did not calculate the lower limit of the 95%-confidence level of the 90- and 95-percentile, but only the 50-, 90- en 95-percentile of the groundwater data.

1.1.1.2 Derive concentrations in surface water

Table C3 shows the number of measurements in the surface water of Waterboard Aa & Maas and De Dommel for the period 2005 till 2011. In addition, the number of values below the detection limit and the detection limit itself are presented in table C3.

Table C3 Number of measurements and the number of values below the detection limit in the surface water of Waterboard Aa & Maas and De Dommel for the period 2005 till 2011.

Metal	Surface water Aa & Maas			Surface water De Dommel		
	Number of values	From which <dl	Detection limit (ug/l)	Number of values	From which <dl	Detection limit (ug/l)
As	-			144	138	4
B	-			471	8	10
Ba	-			608	4	1
Cd	1968	1575	0.1	4506	2457	0.01-0.4
Co	-			669	69	0.1-1
Cr	1911	827	0.5	4467	2706	0.5-2
Cu	1920	150	1	4493	506	1-3
Mo	-			614	369	1-2
Ni	1968	26	0.5-1.5	4530	288	0.5-2
Pb	1968	1141	0.1-1.5	4506	3502	0.1-3
Sb	-			144	140	5
Se	-			671	400	0.5-5
Sn	-			144	105	5
Sr	-			471	0	-
Tl	-			527	399	0.1-0.5
V	-			144	139	2
Zn	1920	404	3-5	4492	419	3-5

Values that are less than the detection limit are recalculated to 0.5 times the detection limit.

1.2 Results

1.2.1 Groundwater

The 50-, 90- and 95-percentile of the groundwater data are presented in the table below. For the most metals the P90 and P95 are much higher than the P50. Therefore, it makes a lot of difference which value to take as background concentration.

Table C4: 50-, 90- and 95-percentile for the different metals in groundwater in the province of Noord-Brabant.

Metals	P50	P90	P95
Ag (µg/l)	0.01	0.04	0.05
As (µg/l)	0.88	7.50	11.77
B (µg/l)	16.8	69.5	123.0
Ba (µg/l)	51.0	123.8	159.3
Cd (µg/l)	0.02	0.04	0.25
Co (µg/l)	0.69	34.33	74.55
Cr (µg/l)	0.52	2.08	2.64
Cu (µg/l)	0.56	8.45	14.92
Mo (µg/l)	0.08	0.40	0.52
Ni (µg/l)	1.3	74.4	134.6
Pb (µg/l)	0.31	2.01	3.34
Sb (µg/l)	0.05	0.13	0.45
Se (µg/l)	0.19	0.74	0.97
Sn (µg/l)	0.01	0.04	0.09
Sr (µg/l)	140	337	414

Tl (µg/l)	0.01	0.10	0.17
V (µg/l)	0.63	2.57	4.40
Zn (µg/l)	5.0	193.3	438.0

1.2.2 Surface water

The 5-, 10- and 50-percentile of the surface water data in Waterboard Aa & Maas and De Dommel are presented in the table below for the different metals.

Tabel C5: 5-, 10- and 50-percentile for the dissolved metals in surface water (µg/l) in Waterboard Aa & Maas and De Dommel (µg/l).

Metals	Surface water: AA & Maas After filtration			Surface water: De Dommel After filtration		
	P5	P10	P50	P5	P10	P50
As (µg/l)				2	2	2
B (µg/l)				16	19	44
Ba (µg/l)				11.55	17	33
Cd (µg/l)	0.05	0.05	0.05	0.05	0.05	0.05
Co (µg/l)				0.5	0.5	3.1
Cr (µg/l)	0.25	0.25	0.58	0.25	0.25	0.25
Cu (µg/l)	0.5	1.1	2.3	0.5	1	2.2
Mo (µg/l)				1	1	1
Ni (µg/l)	1.6	2.1	5.5	0.75	1.8	8.6
Pb (µg/l)	0.1	0.1	0.26	0.1	0.1	0.75
Sb (µg/l)				2.5	2.5	2.5
Se (µg/l)				0.25	0.25	1
Sn (µg/l)				2.5	2.5	2.5
Sr (µg/l)				87	95	120
Tl (µg/l)				0.05	0.25	0.25
V (µg/l)				1	1	1
Zn (µg/l)	2.5	2.5	13	1.5	3.4	29

1.3 Comparison of background concentrations for groundwater with concentrations in surface water

In table C6 the values from the groundwater and the surface water are presented together in one table.

Tabel C6: For the different metals the 50-, 90- and 95-percentile in groundwater in the province of Noord-Brabant and the 5-, 10- and 50-percentile in surface water in Waterboard Aa & Maas and De Dommel (µg/l).

	Groundwater			Surface water: Aa en Maas			Surface water: De Dommel		
	P50	P90	P95	P5	P10	P50	P5	P10	P50
As	0.88	7.5	11.8				2	2	2
B	17	70	123				16	19	44
Ba	51	124	159				11.55	17	33
Cd	0.02	0.04	0.25	0.05	0.05	0.05	0.05	0.05	0.05
Co	0.69	34	75				0.5	0.5	3.1
Cr	0.52	2.08	2.64	0.25	0.25	0.58	0.25	0.25	0.25

Cu	0.56	8.4	14.9	0.5	1.1	2.3	0.5	1	2.2
Mo	0.08	0.40	0.52				1	1	1
Ni	1.3	74.4	134.6	1.6	2.1	5.5	0.75	1.8	8.6
Pb	0.31	2.01	3.34	0.1	0.1	0.26	0.1	0.1	0.75
Sb	0.05	0.13	0.45				2.5	2.5	2.5
Se	0.19	0.74	0.97				0.25	0.25	1
Sn	0.01	0.04	0.09				2.5	2.5	2.5
Sr	140	337	414				87	95	120
Tl	0.01	0.10	0.17				0.05	0.25	0.25
V	0.63	2.57	4.40				1	1	1
Zn	5	193	438	2.5	2.5	13	1.5	3.4	29

In Table C7 and C8 the differences between the groundwater and the surface water are described. In **Error! Reference source not found.** a comparison is made between the P90 and P95 of the groundwater with the P5, P10 and P50 of the surface water and in **Error! Reference source not found.** a comparison is made between the P50 of the groundwater with the P5, P10 and P50 of the surface water.

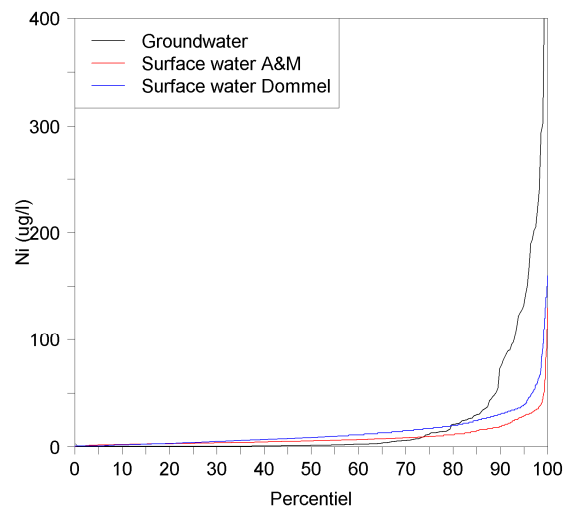
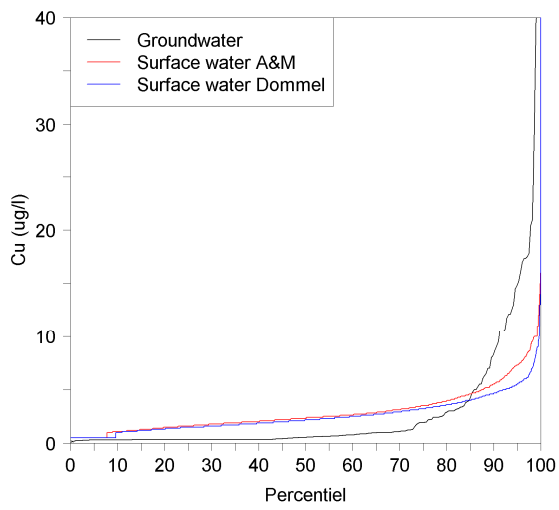
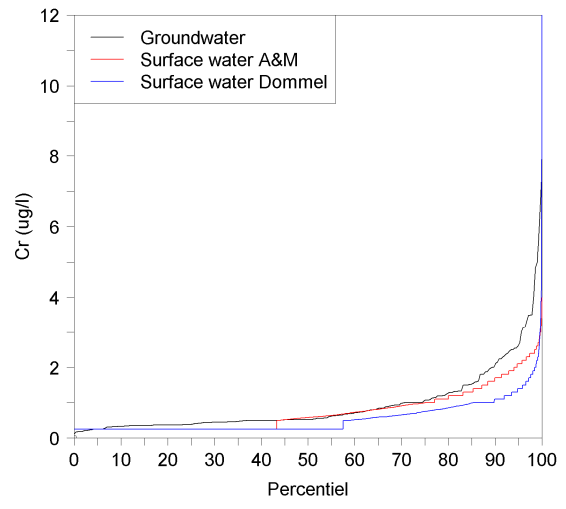
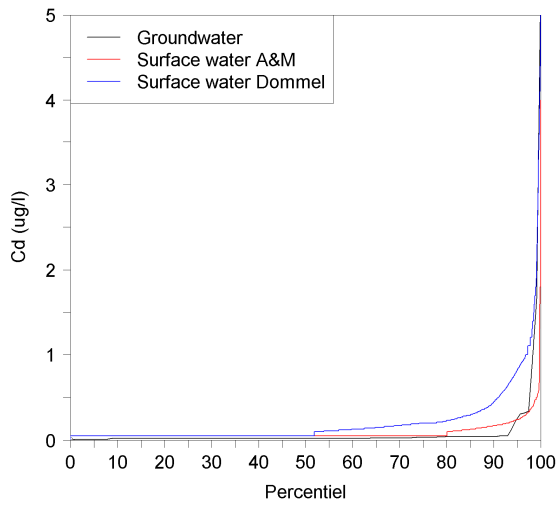
Table C7: Comparison P90 and P95 of the groundwater with the P5, P10 and P50 of the surface water (sw = surface water and gw = groundwater).

	Aa en Maas	Dommel
As	-	P90 and P95 gw much higher than P10 and P50 sw,
B	-	P90 and P95 gw much higher than P10 and P50 sw
Ba	-	P50, P90 and P95 gw much higher than P10 and P50 sw
Br	sw influenced by detection limit and gw higher than sw	sw influenced by detection limit and gw higher than sw
Cd	sw influenced by detection limit and gw higher than sw	gw higher than sw
Co	-	gw higher than sw
Cr	gw higher than sw	gw higher than sw
Cu	gw higher than sw	gw higher than sw
Fe	gw higher than sw	gw higher than sw
Mn	gw higher than sw	gw higher than sw
Mo	-	sw influenced by detection limit
Ni	gw higher than sw	gw higher than sw
Pb	gw higher than sw	gw higher than sw
Sb	-	sw influenced by detection limit
Se	-	more or less same order
Sn	-	sw influenced by detection limit
Sr	-	gw higher than sw
Tl	-	sw influenced by detection limit
V	-	sw influenced by detection limit and gw higher than sw
Zn	gw higher than sw	gw higher than sw

Table C8: Comparison of the P50 of the groundwater with the P5, P10 and P50 of the surface water (sw = surface water and gw = groundwater).

	Aa en Maas	Dommel
As	-	P50 gw higher than P5 sw but lower than P10 and P50
B	-	P50 gw higher than P5 sw but lower than P10 and P50
Ba	-	P50 gw higher than P5, P10 and P50 sw
Br	sw influenced by detection limit and gw higher than sw	sw influenced by detection limit and gw higher than sw
Cd	sw influenced by detection limit and gw higher than sw	P50 gw lower than P5, P10 and P50 sw
Co	-	P50 gw somewhat higher than P5 and P10 sw but lower than P50
Cr	P50 gw somewhat higher than P5 and P10 sw but lower than P50	P50 gw somewhat higher than P5 and P10 sw but lower than P50
Cu	P50 gw somewhat higher than P5 sw but lower than P10 and P50	P50 gw lower than P5, P10 and P50 sw
Fe	P50 gw higher than P5, P10 and P50 sw	P50 gw higher than P5, P10 and P50 sw
Mn	P50 gw higher than P5, P10 and P50 sw	P50 gw higher than P5, P10 and P50 sw
Mo	-	sw influenced by detection limit
Ni	P50 gw higher than P5 sw but lower than P10 and P50	P50 gw higher than P5 sw but lower than P10 and P50
Pb	P50 gw higher than P5 and P10 sw but lower than P50	P50 gw somewhat higher than P5 sw but lower than P10 and P50
Sb	-	sw influenced by detection limit
Se	-	P50 gw lower than P5, P10 and P50 sw
Sn	-	sw influenced by detection limit
Sr	-	P50 gw higher than P5, P10 and P50 sw
Tl	-	sw influenced by detection limit
V	-	sw influenced by detection limit
Zn	P50 gw higher than P5 and P10 sw but lower than P50	P50 gw higher than P5 sw but lower than P10 and P50

To give a better view of the differences in concentrations between groundwater and surface water, frequency contribution plots are made of the metals Cd, Cr, Cu, Ni, Pb and Zn (see figure C3).



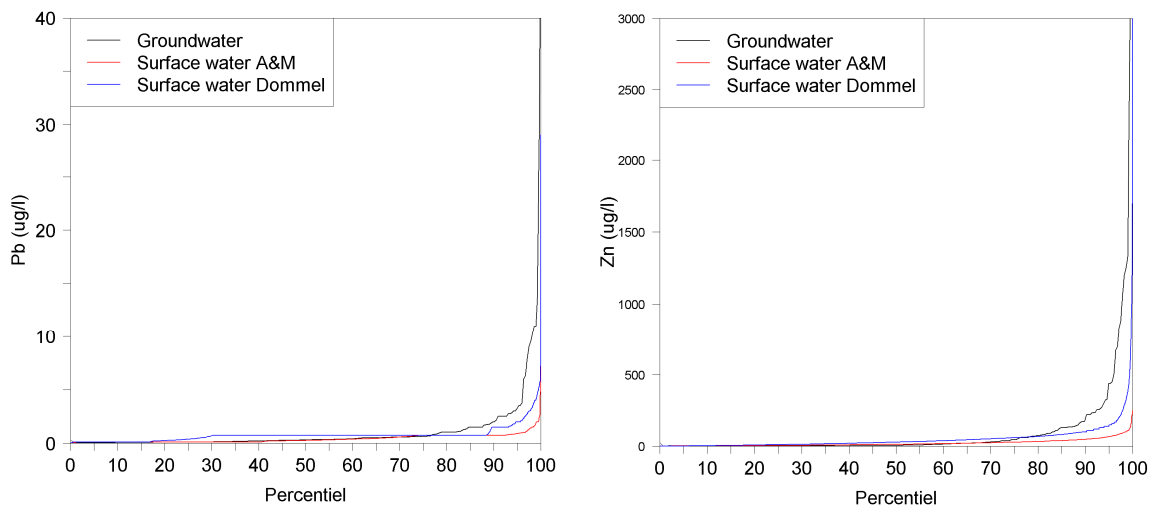


Figure C3: Frequency contribution plots for the metals cadmium, copper, chromium, nickel, lead and zinc.

It is shown in the frequency contribution plots that concentrations in groundwater and surface water are in the same order. The plots also demonstrate that it makes a lot of difference which percentile to take as a background concentration for groundwater. The P90 and P95 are mostly in the tail of the distribution so they result in high values that are much higher than the P5 and P10 and most of the times higher than the P50 of the surface water. From this it can be concluded that the P50 of the groundwater might be a good background concentration for groundwater. This value can be used as a background level for surface water for the following metals: As, Cd, Co, Cr, Cu, Ni, Pb, Se and Zn. For Ba, Br, Fe, Mn, Sr the P50 of the groundwater can not be used as background level for the surface water because the P50 of the groundwater is higher than the P50 of the surface water. For the metals Mo, Sb, Sn, Tl and V nothing can be concluded because most of the values in the surface water are below the detection limit.

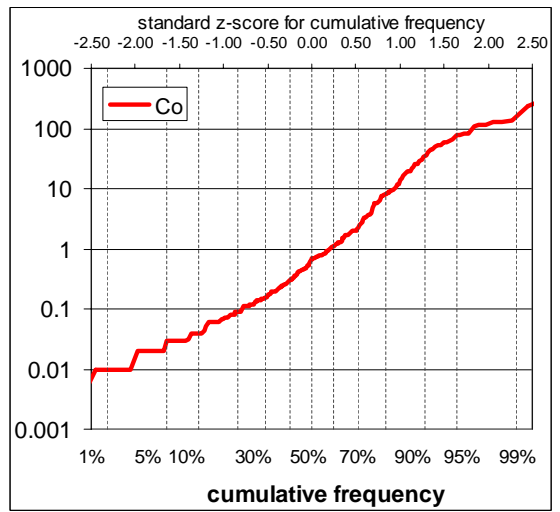
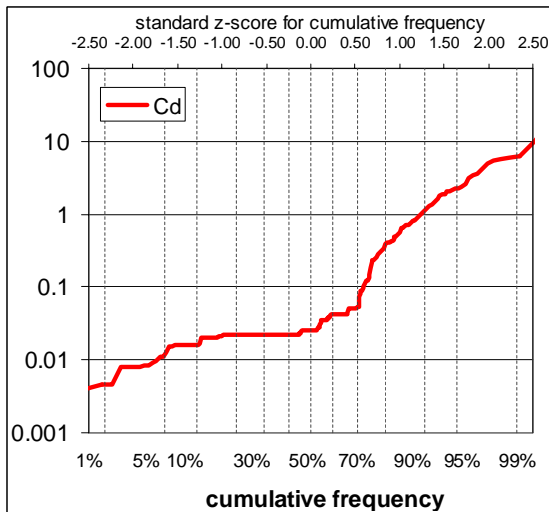
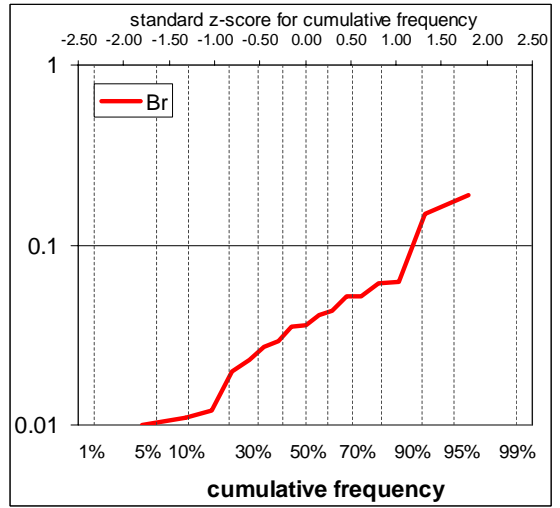
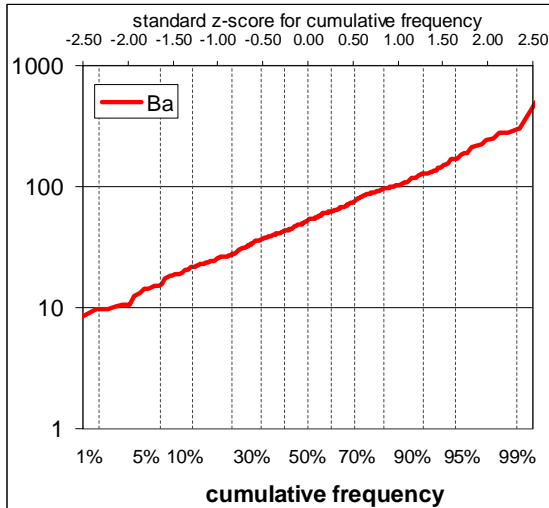
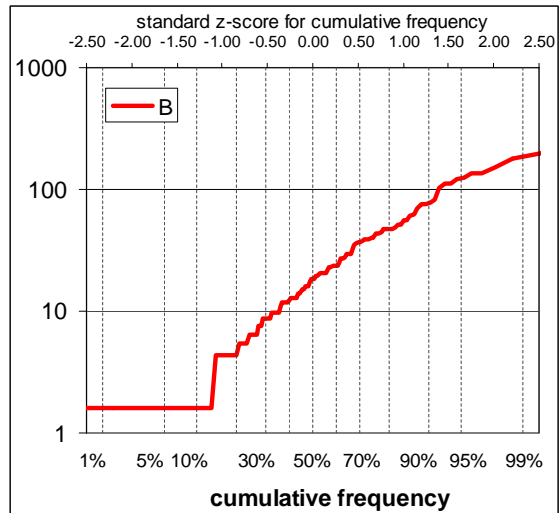
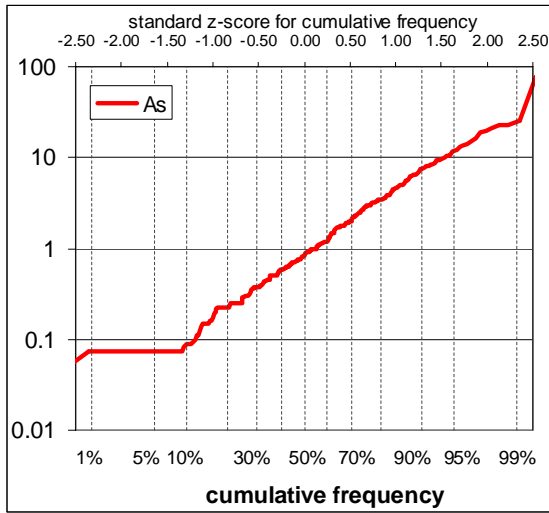
Taking this into account the conclusions per metal are shown in the table below.

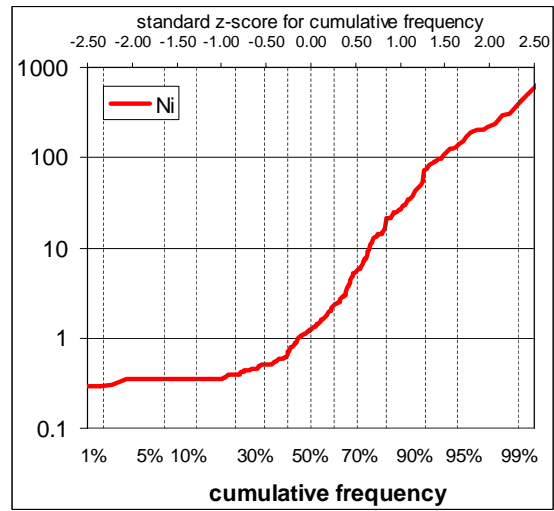
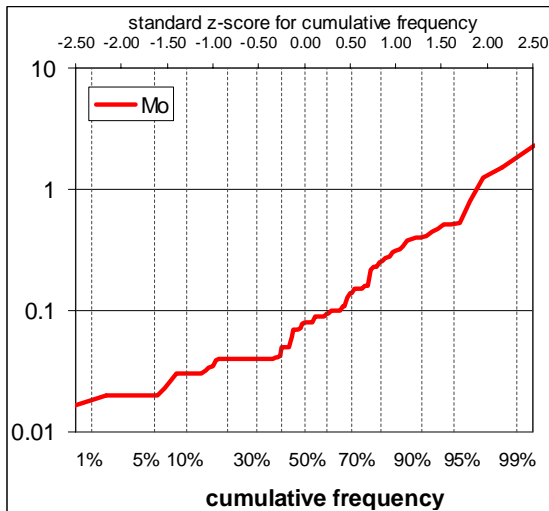
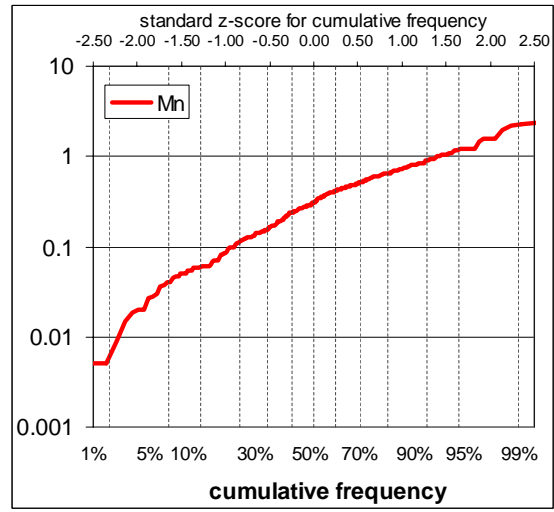
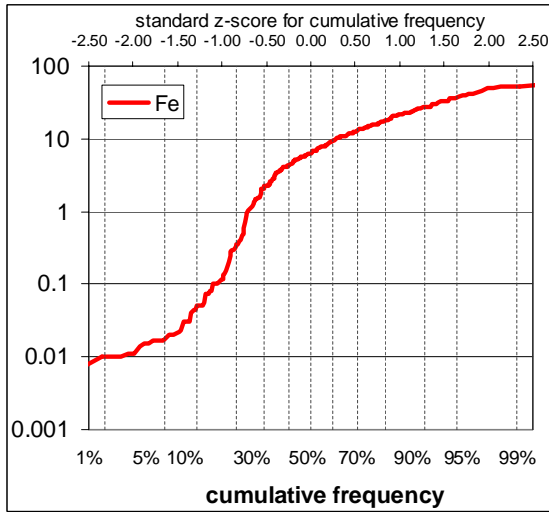
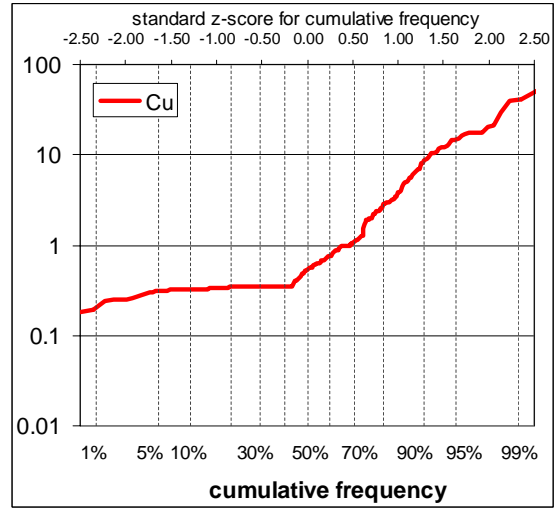
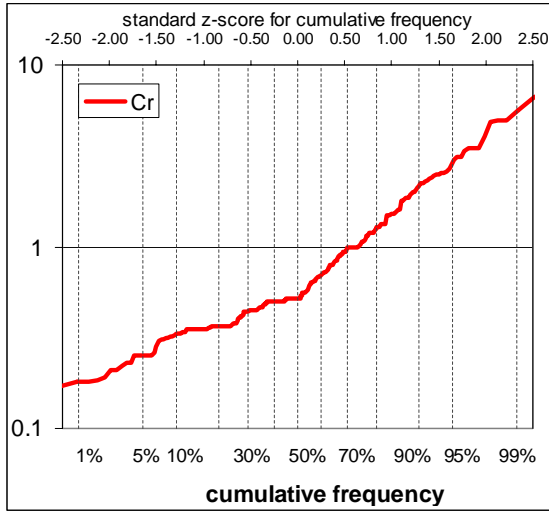
Table C9 Proposed background levels for different metals in surface water and reasons why this method is not usable for some metals.

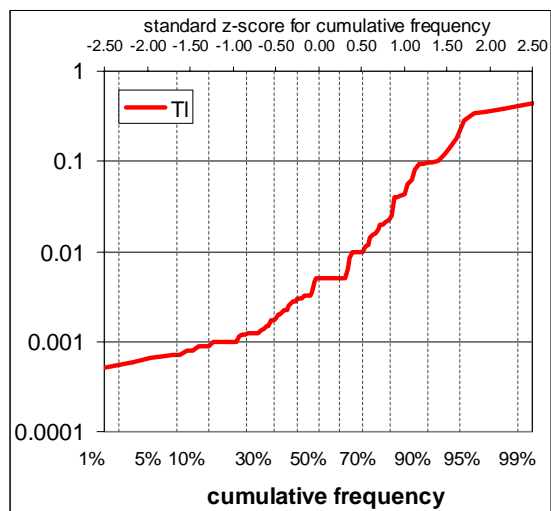
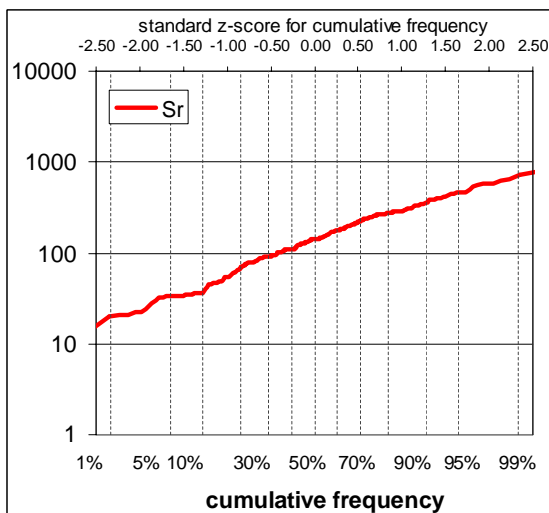
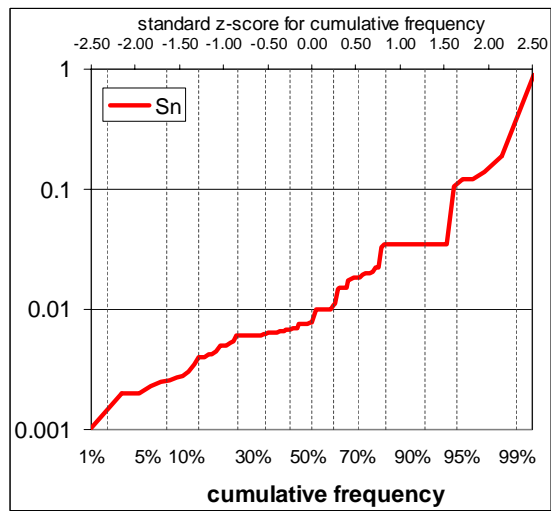
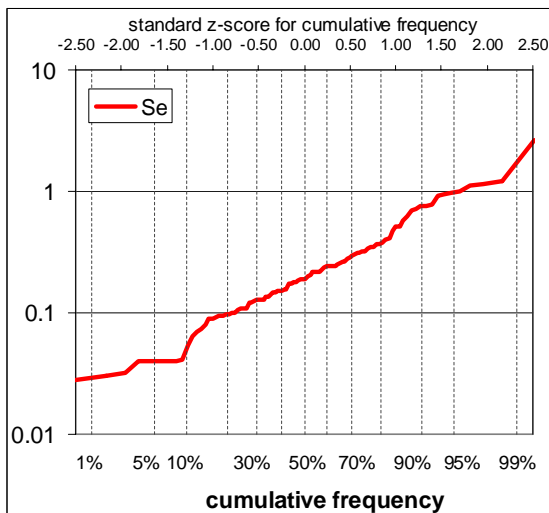
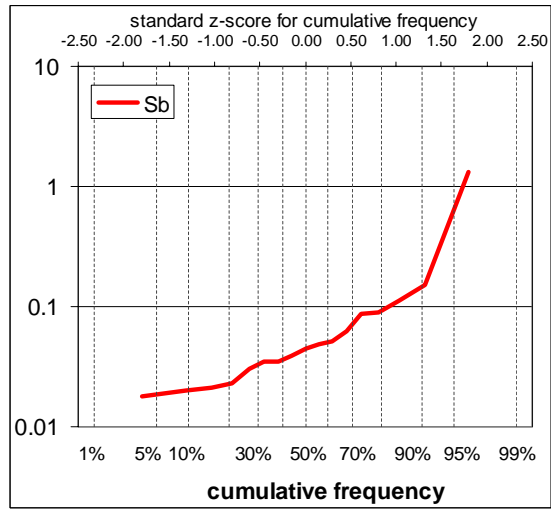
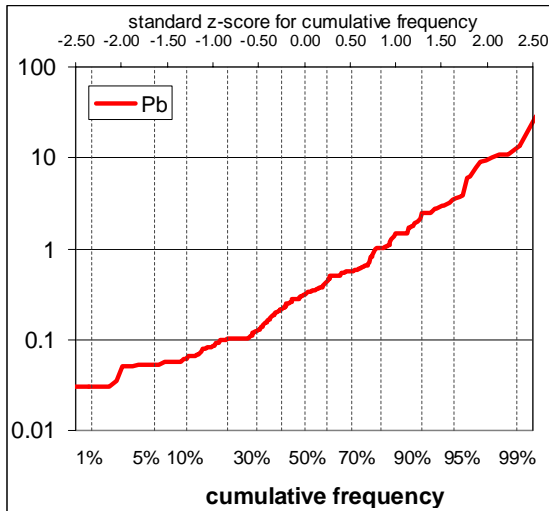
	BC _{diss} (µg/l) De Dommel		BC _{diss} (µg/l) Aa en Maas		BC _{diss} (µg/l) current
As	0.88	gw			0.8
B	16	sw			-
Ba	12	sw			73
Cd	0.02	gw	0.02	gw	0.08
Co	0.5	sw			0.2
Cr	0.25	sw	0.25	sw	0.2
Cu	0.5	sw	0.5	sw	0.4
Mo	0.08	gw			1.4
Ni	0.75	sw	1.3	gw	3.3
Pb	0.31	sw	0.31	sw	0.2
Sb	0.05	gw			0.3
Se	0.19	gw			0.04

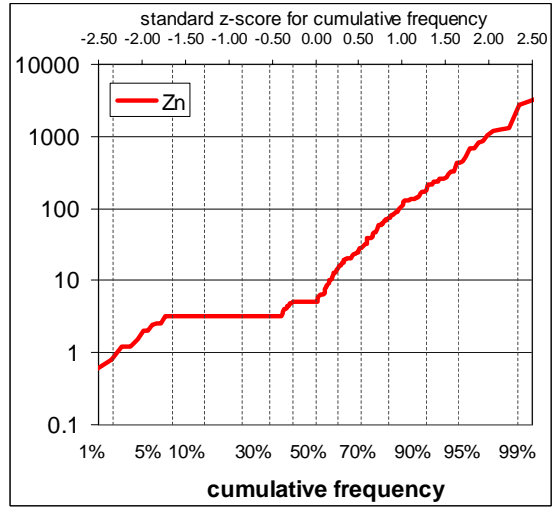
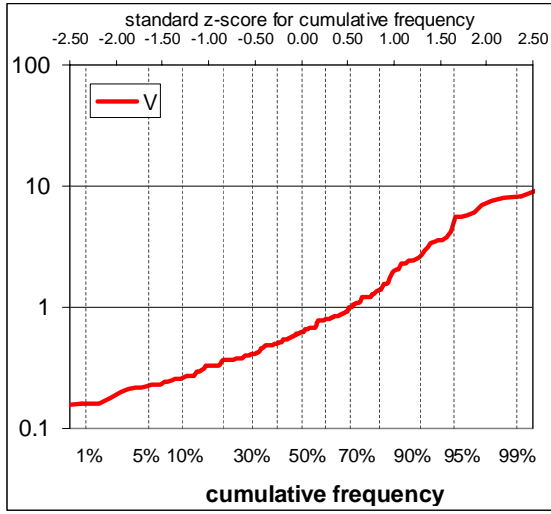
Sn	0.01	gw			0.0002
Sr	87	sw			-
Tl	0.01	gw			0.04
V	0.63	gw			0.8
Zn	1.5	sw	2.5	sw	2.8

Probability plots









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