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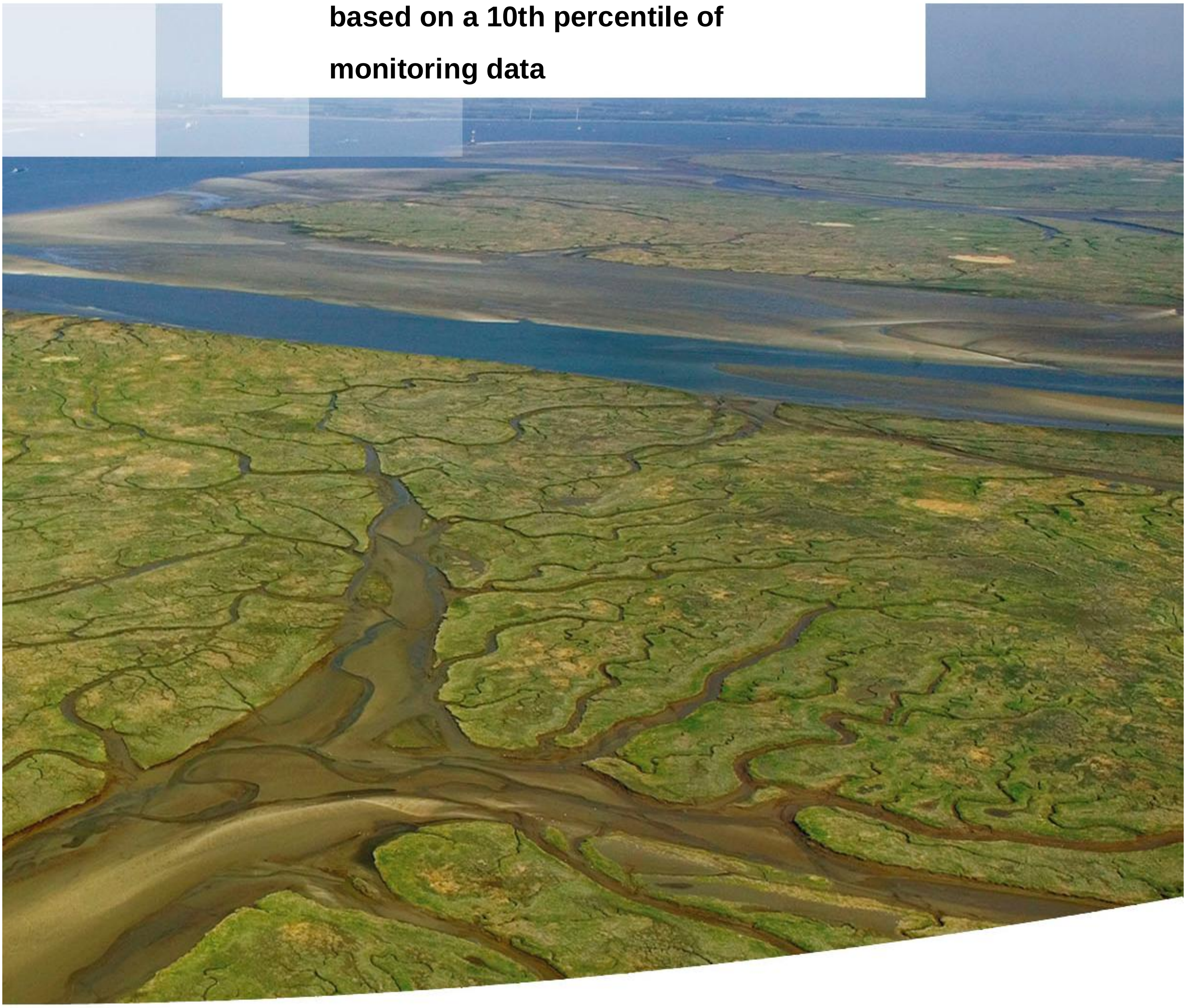
Derivation of dissolved background concentrations in Dutch surface water based on a 10th percentile of monitoring data



Derivation of dissolved background concentrations in Dutch surface water based on a 10th percentile of monitoring data

Leonard Osté

1206111-005

Title

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Client	**Project**	**Reference**	**Pages**
Rijkswaterstaat Waterdienst	1206111-005	1206111-005-BGS-0005	34

Keywords

Background concentration, metals, WFD, environmental quality standards.

Summary

Dissolved background concentrations were derived for fresh water and marine waters. Based on an inventory of methods to derive dissolved background concentrations (Oste et al., 2012), the monitoring data approach was used to determine the dissolved background concentration. The monitoring data approach means that a 10th percentile of all monitoring data is considered as an ambient background concentration. The table below shows background concentrations derived in this study as well as the existing background concentrations as published in the 4th National Waterplan (Ministry of Traffic and Water management, 1998).

Element (µg/l)	Derived BC Inland surface waters, this study	Existing BC Inland surface waters, NW4 1998	Derived BC Other surface waters, This study	Existing BC Other surface waters, NW4 1998
As	0.5	0.8	0.62	-
B	26	-	3000	-
Ba	20	73	8.9	-
Be	-	0.02	-	-
Cd	0.005	0.08	0.020	0.03
Co	0.14	0.2	-	-
Cr	-	0.2	-	-
Cs	0.03	-	-	-
Cu	0.5	0.4	0.40	0.3
Li	3.5	-	120	-
Mo	0.5	1.4	8.8	-
Hg-inorg.	-	0.01	-	0.003
Hg-org	-	0.01	-	-
Ni	1.2	3.3	0.25	
Pb	-	0.2	-	0.02
Rb	2.3	-	88	-
Sb	-	0.3	0.14*	-
Se	0.2	0.04	0.059*	-
Sn	-	0.0002	0.025	-
Sr	110	-	-	-
Tl	0.01	0.04	-	-
U	0.33	-	2.7	-
V	0.5	0.8	1.1	-
Zn	0.7	2.8	0.15	0.4

* values based on <100 data

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Rijkswaterstaat Waterdienst	1206111-005	1206111-005-BGS-0005	34

The report also presents the derived BCs for other elements that already have an official dissolved background concentration.

Reference
Oste, L.A. 2013. Derivation of dissolved background concentrations in Dutch surface water based on a 10th percentile of monitoring data. Deltares-report 1206111.005-2. Deltares Utrecht, The Netherlands

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1 Introduction

Environmental Quality Standards (EQS) are listed in the Priority Substances Directive (PSD) (EC, 2008), a ‘Daughter’ Directive of the Water Framework Directive (WFD) (EC, 2000). According to Annex I, Part B.3 of the PSD, Member States may, when assessing the monitoring results against the EQS, take into account:

a. natural background concentrations for metals and their compounds, if they prevent compliance with the EQS value; and
b. hardness, pH or other water quality parameters that affect the bioavailability of metals.

This report focuses on aspect a, the derivation of dissolved background concentrations.

Dissolved background concentrations are available for 17 elements in Dutch inland surface waters, and for only 5 metals in marine waters (Table 1.1). The Water Framework Directive (WFD) allows member states to correct monitoring data of trace metals for natural background concentrations. With respect to WFD compliance checking, and discharge permits, the Dutch water managers do not only wish background concentrations for the elements listed in Table 1.1, but also for Ag, B, Cs, Gd, La, Li, Sb, U, and Y.

Table 1.1: Dissolved background concentrations (Cb) used in Dutch water policy (NW4, 1998)

Element	**Cb (fresh water) Dissolved (µg/l)**	**Cb (marine water) Dissolved (µg/l)**
Antimony (Sb)	0.3	
Arsenic (As)	0.8	
Barium (Ba)	73	
Beryllium (Be)	0.02	
Cadmium (Cd)	0.08	0.03
Chromium (Cr)	0.2	
Cobalt (Co)	0.2	
Copper (Cu)	0.4	0.3
Lead (Pb)	0.2	0.02
Mercury (Hg)	0.01	0.003
Methyl Mercury	0.01	
Molybdenum (Mo)	1.4	
Nickel (Ni)	3.3	
Selenium (Se)	0.04	
Thallium (Tl)	0.04	
Tin(Sn)	0.0002	
Vanadium (V)	0.8	
Zinc (Zn)	2.8	0.4

The concentrations in table 1.1, published in the 4th National Water Plan (Ministry of traffic and water management, 1998), were derived according to the ‘clean streams’ approach. 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 unburdened regions represents the background levels of areas with comparable geology and topography. Zuurdeeg et al. (1992) assumed that water quality of streams in the North European Lowlands can be adopted as a natural background level of trace metals in The Netherlands. However, Zuurdeeg et al. (1992) only derived total background concentrations, because they did not have sufficient data to derive dissolved concentrations. Crommentuijn et al. (1997) converted the total metal concentrations to dissolved concentrations by using a nationwide partition coefficient and a suspended matter concentration of 30 mg/l. Obviously, this introduces a methodological uncertainty: both K_p-values and suspended matter concentrations can vary strongly. Moreover, the Zuurdeeg database did not contain the necessary data to derive values for additional metals.

Osté et al. (2012) made an inventory of the available methods to determine dissolved background concentrations in surface water. They listed 6 methods, but concluded that only 3 methods are potentially useful to implement: 1) the clean streams approach (only for marine waters): the background concentration is equal to the measured concentration in representative (almost) undisturbed surface waters, 2) the sediment approach: the metal concentration of unburdened sediments is transferred to a concentration in water using equilibrium partitioning and 3) the monitoring data approach: a low (10th)percentile of recent monitoring data is used as the background concentration.

However, also the three selected methods have serious limitations, and (until now) experts have not agreed which method should be adopted to derive a new set of dissolved background concentrations. If there is no decisive argument from a scientific point of view for choosing one particular method, the Ministry of Infrastructure and Environment (IenM) decided that the monitoring data approach to extend the list of dissolved background concentrations in Dutch inland surface waters had a number of practical advantages (e.g. data availability, number of elements, recent analytical methods). The P10 was chosen as a low percentile. The P10 was also mentioned in the Technical guidance for deriving environmental quality standards (EC, 2011, p.64), and adopted by the UK (Peters et al., 2010).

Marine waters are also affected by pollution, but the dilution results in a very low addition per m^3 in open seas. Osté et al. (2012) stated that monitoring data at the monitoring locations > 70 km out of the coast may be used to calculate a dissolved background concentration according to the clean streams approach. However, the Dutch monitoring program does not measure dissolved metal concentrations at these locations. There are probably more international data available in unburdened North Sea areas, but they are not easily accessible. Locations closer to the coast have been used in this study to derive background concentrations for marine waters. These locations are more influenced by river inflow, and for that reason a lower percentile of the database was used (P10), which is essentially the monitoring data approach.

The uncertainty which percentile is the best estimate for the natural background concentration is the critical point of this approach. The ‘right’ percentile may vary per element. Particularly, for elements with a relatively low anthropogenic load, a low percentile may be too conservative. However, in this study the P10 is chosen for all elements.

In this report, dissolved background concentrations for all available metals in fresh water and marine water are derived according to the monitoring data approach. All available monitoring data are used in this approach.

2 The monitoring data approach

The monitoring data approach has been elaborated for the hydrometric areas[1] in the UK by Peters et al., (2012). The approach uses recent monitoring data. For the Dutch approach, the database should meet the following criteria:

- ✓ Only measured dissolved metal concentrations (filtrated through a 0.45 µm filter) should be used, which is a standard procedure for WFD monitoring.
- ✓ The period of the data collection ranges from 2000-2012. A shorter period may be used if clear trends are registered, but it should at least cover a period of 3 years.
- ✓ The database is checked whether it contains only fresh water or salt water data. The chloride concentration of fresh water should be less than 500 µg/l. The salinity of salt water should be at least 25 PSU.
- ✓ The monitoring data used for derivation of the background concentration should be distributed evenly over the year, because of seasonal effects. We also looked at seasonal concentrations differences, but this did not lead to modifications in the method. Appendix A gives additional information on this issue.
- ✓ Data below the limit of detection (LOD) count for 0.5 x LOD[2].

Please note that it is very important to check the quality of the database before starting the determination of the background concentration. E.g. check whether one name and unit is used for all substances or whether values 0 and <0 represent real values.

If the listed criteria have been processed, there are two conditions before a background concentration can be derived. First of all, the minimum number of data for a metal is 100. Secondly, the percentage of data below the LOD is important. Figure 2.1 shows how the LOD affects the P10. The left graph shows a metal without values smaller than the LOD. The P10 is 25 µg/l. The middle graph shows the same metal with 25% of the values below the LOD. The P10 of this database is 17.5 µg/l, which is slightly lower than the 'real' P10. If the metal has an ideal normal distribution, the lack of real values results in a more conservative value. However, this compensates for the uncertainty of the distribution in the lower range. The right graph of Figure 2.1 shows that the P10 is 42.5 µg/l at 75% of the values < LOD. The relative deviation of the 'real' P10 depends on the steepness of the line.

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[1] *Hydrometric Areas are either integral river catchments having one or more outlets to the sea or tidal estuary, or, for convenience, they may include several contiguous river catchments having topographical similarity with separate tidal outlets.*

[2] *Peters et al (2012) prefer this method to the extrapolation method*

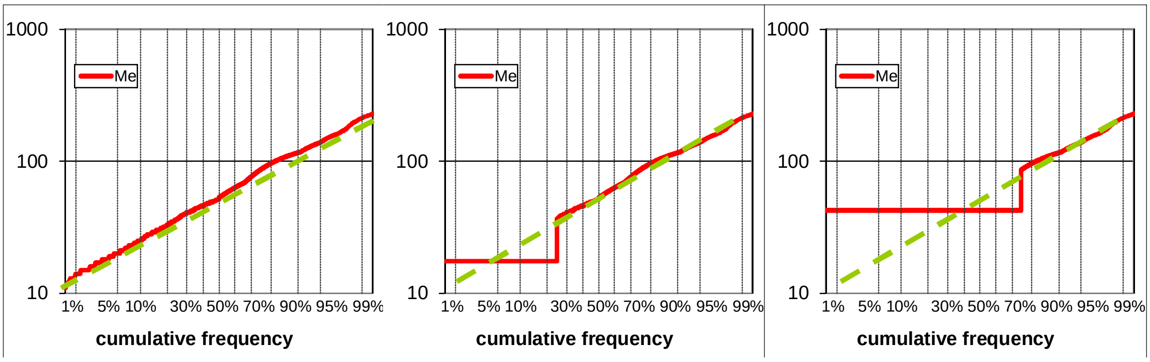

Figure 2.1 Result of taking the P10 depending on the percentage of values < LOD. The red line represents (an ideal) dataset in which the data below the LOD were halved. The green dashed line extrapolates the data above the LOD assuming a normal distribution.

Based on Figure 2.1 we decided that the P10 is chosen as a background concentration, if the percentage of data < LOD is not more than 25%. No background concentration is derived if more than 75% of the data is below the LOD. In the range between 25 and 75% we check the distribution of the data. Based on a qualitative assessment a background concentration is determined or not.

3 Derivation of dissolved background concentrations for metals in Dutch fresh waters

3.1 Data

Monitoring of fresh waters in the Netherlands is conducted by Rijkswaterstaat (large rivers), by regional water authorities, and by drinking water companies that use surface water to produce drinking water. The monitoring data were kindly provided by the Rijkswaterstaat - Helpdesk Water for data of the large rivers, lakes, estuaries and coast, and the InformatieHuis Water (IHW) supplying data of regional monitoring and drinking water companies. Both RWS and IHW have their own quality assurance standards. Deltares did not perform an additional quality check. All data were combined to one database for inland waters. The properties of the database are described in the remainder of this paragraph:

- The database only contained filtrated samples in µg/l in the period of 2005-2011.
- The Rijkswaterstaat locations Beerkanaal and Maassluis were excluded, because average chloride-concentrations exceed 500 mg/l. This also applies for 34 locations in regional waters.
- 630 regional data were removed, because they were recorded as 0 or <0. It was unclear whether these numbers represent measured values.
- Figure 3.1 shows differences between the months, but no strong seasonal variation (summer vs. winter) in the monitoring frequency.
- The data recorded as “<” were halved.

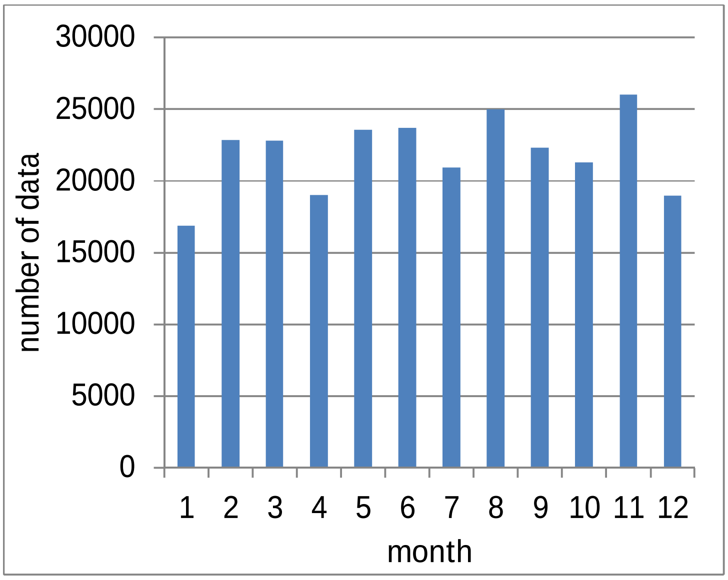

Figure 3.1 Distribution of the data within the year.

The final database contained more than 250,000 data, most of them measured by regional water authorities (Table 3.1).

Table 3.1 Number of data from different water managers.

Total number of data:	**263,449**
State water authority (Rijkswaterstaat)	37,308
Regional water authorities:	209,528
Drinking water companies & unknown	16,613

The distribution over the years is shown in Table 3.2. The number of data has increased each year until 2010. The number of data was reduced in 2011 with 40%.

Table 3.2 Number of data for each year

Jaar	Number of data
2005	8,966
2006	11,929
2007	29,112
2008	41,828
2009	49,655
2010	87,652
2011	34,307
Total	263,449

Approximately 30% was measured in the Meuse basin, whereas 65% originated from the Rhine (Table 3.3).

Table 3.3 Number of data for each river basin

River basin	Number of data
Meuse	105,934
Rhine-mid	28,090
Rhine-north	2,500
Rhine-east	31,662
Rhine-west	80,921
Scheldt*	5,944
Unknown	8,398
Total	263,449

* Regional data provided by regional water authority Scheldestromen

Also the geographic distribution within the Netherlands was checked. Figure 3.2 shows that that database does not contain any data of three water authorities in the North of the country: Noorderzijlvest, Hunze en Aa's, and Reest and Wieden, explaining the low number of data for Rhine-north. Also the density varies. The main reasons are 1) the amount of surface water and 2) the fraction of surface water that belongs to the WFD waterbodies. However, the general view is that most of the Netherlands is represented in the database.

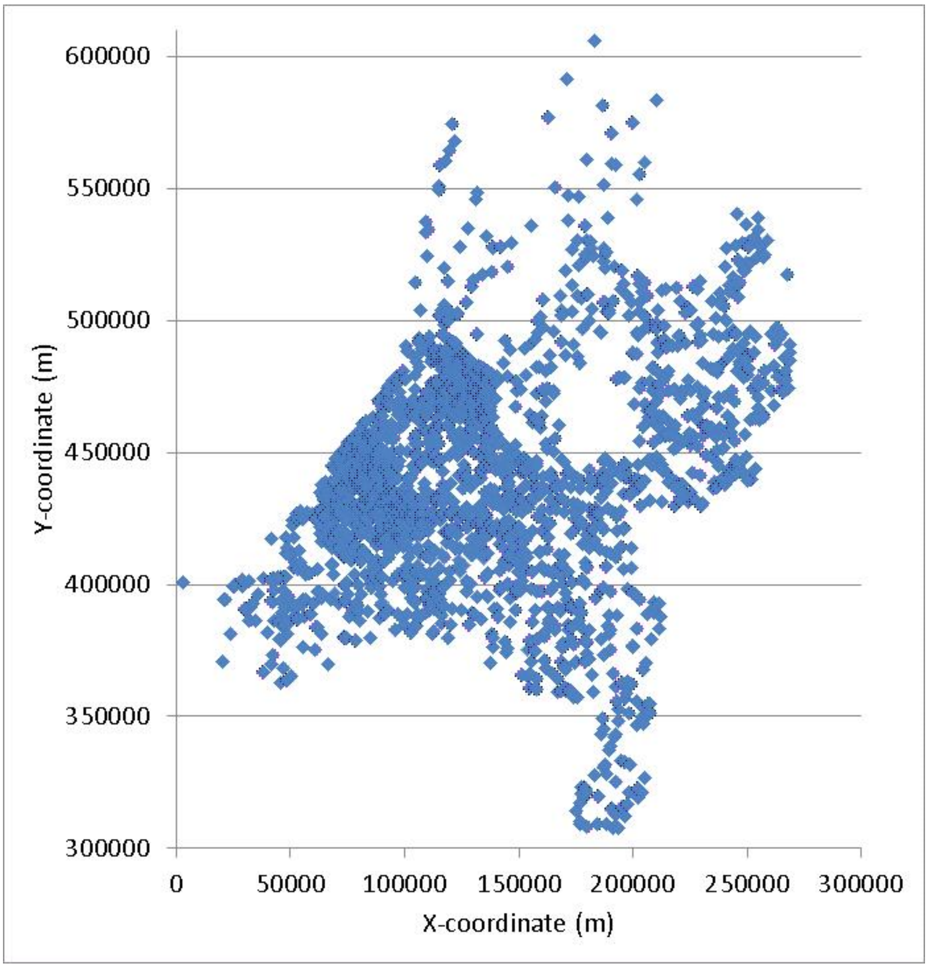

Figure 3.2 Geographical distribution of the database for freshwater

The large number of sampling points, as shown in Figure 3.2, applies for Cd, Cr, Cu, Ni, and Pb. As is only absent in the provinces of Fryslân and North-Holland. Another group of metals was measured less frequently, but is reasonably distributed over the whole country (Ba, Be, Co, Hg, Mo, Sb, Sn, Sr, Tl, and V). Figure 3.3 shows an example for Tl. The remaining elements show a poor distribution: B, Cs, Li, Rb, Se, and U. However, all elements have been measured in at least 3 areas. Figure 3.3 shows an example for locations where B was measured.

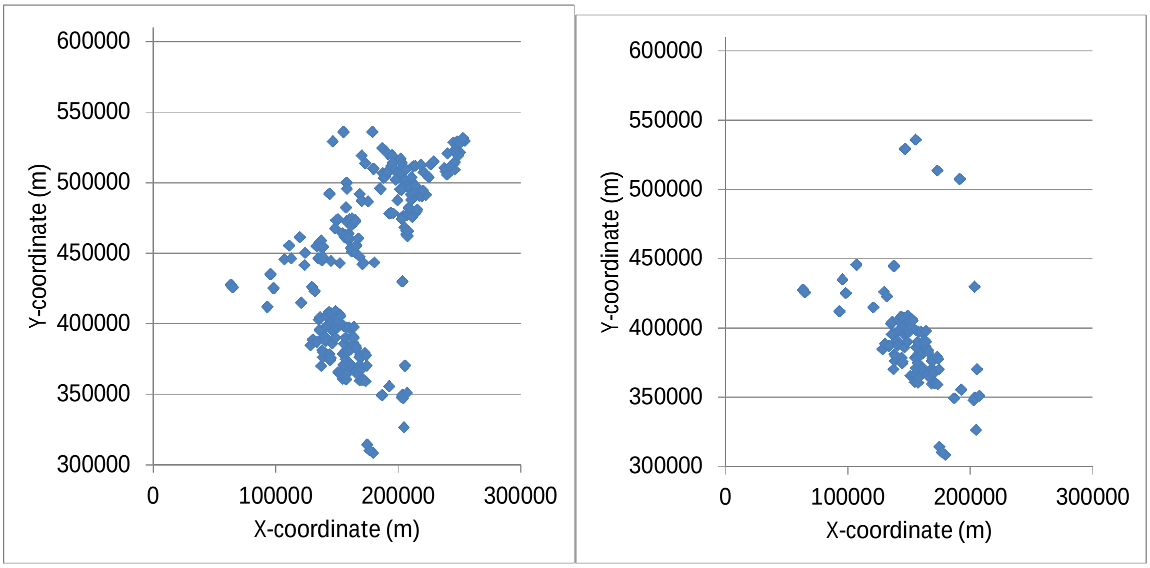

Figure 3.3 Geographical distribution of the database for Tl (left) and B (right).

Although differences were observed for each individual metal, a rough division in three groups is shown in Table 3.4.

Table 3.4 The distribution over the Netherlands in three categories.

Well distributed	**Moderately distributed**	**Poorly distributed**
Cd, Cr, Cu, Ni, Pb, Zn. As (not in Fryslan/ North-Holland)	Ba, Be, Co, Hg, Mo, Sb, Sn, Sr, Tl, and V	B, Cs, Li, Rb, Se, and U

3.2 Results

Table 3.5 shows the number of data for all water managers in the Netherlands. Gd, La, Y are not monitored by the Dutch water managers, and therefore not included in tables and figures.

Table 3.5 Number of data, number of data below the LOD, and percentage of data below the LOD (% lower than 25 in green, between 25 and 75 in yellow, and above 75 in red).

Element	n	n "<"	% "<"
Ag	2806	2794	100
As	5279	1506	29
B	2111	16	1
Ba	2994	9	0
Be	1814	1700	94
Cd	19037	11037	58
Co	4134	1723	42
Cr	16020	10629	66
Cs	807	155	19
Cu	18847	2970	16
Hg	8209	6718	82

Element	n	n "<"	% "<"
Li	1276	292	23
Mo	3814	1625	43
Ni	25477	2021	8
Pb	18614	13751	74
Rb	807		0
Sb	3083	2847	92
Se	1296	637	49
Sn	3229	2984	92
Sr	1878		0
Te	3288	2813	86
Ti	1604	1475	92
Tl	3445	1849	54
U	1699	56	3
V	3303	1434	43
Zn	23110	6968	30

Table 3.5 shows that no dissolved background concentrations will be derived for Ag, Be, Hg, Sb, Sn, Te, and Ti, because too many data are below the LOD. However, there is at least some information what the maximum value could be[3]. The P10 presented in Table 3.6 was based on all values in the database, without multiplying the “<” values by 0.5. The results are presented in Table 3.6.

Table 3.6 Elements without a dissolved background concentration. The dissolved background concentration is lower than this value.

Element	P10 is less than (µg/l)
Ag	0.1
Be	0.05
Hg	0.001
Sb	0.5
Sn	0.05
Te	0.1
Ti	1

Table 3.5 reveals that it is possible to derive a dissolved background concentration for: B, Ba, Cs, Cu, Li, Ni, Rb, Sr and U. The proposed dissolved background concentrations for these elements are listed in Table 3.7.

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[3] *This value might help water managers to get an idea whether the background concentration might ‘solve’ their problem. If the AA-concentration after correction by the value presented in Table 3.6 still exceeds the standard, water managers have to take action.*

Table 3.7 Proposed dissolved background concentrations for inland water in the Netherlands for substances having more than 100 data, and less than 25% below the LOD.

Element	dissolved background concentration (µg/l)
B	26
Ba	20
Cs	0.03
Cu	0.5
Li	3.5
Ni	1.2
Rb	2.3
Sr	110
U	0.33

For 10 remaining elements, we investigated the distribution of the data. Appendix B shows the probability plots. If the data is log normally distributed, the data form a straight line in a probability plot. If reliable data is missing in the low concentration range, the P10 can be estimated by extrapolation of the line, as shown for Zn in Figure 3.4. Ideally, the values below the LOD are reported in the lower percentiles (this is the case in the left graph in Figure 3.4), but the figures in appendix B reveal a number of plateaus for many elements indicating that the LOD also plays a role in the higher concentration range (right graph in Figure 3.4). The reason is that the analyses had been carried out in different laboratories for various water managers.

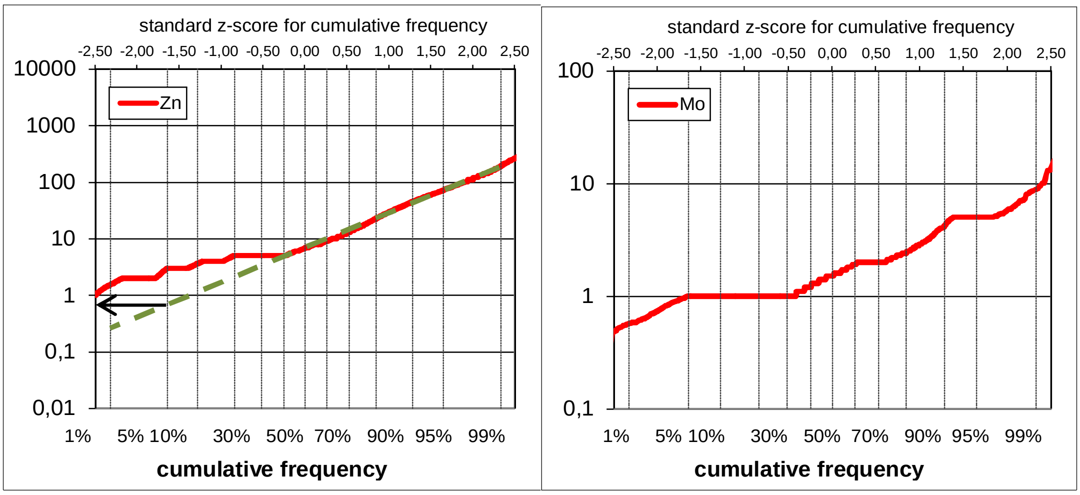

Figure 3.4 Two probability plots. The left graph for Zn shows a straight line that deviates for lower concentrations due to detection limits. Assuming a normal distribution also in the lower concentration range the P10 is indicated by the arrow (ca. 0.7 µg/l). The right graph for Mo shows detection problems at different levels, even around the P95 (values <5µg/l).

It appeared that extrapolation was only for Zn a reliable method to determine the dissolved background concentration. For most metals the method to halve values below the LOD was a reasonable choice, assuming that the data were normally distributed in the range below the LOD. No background concentrations have been determined for Cr and Pb, because the distribution did not show enough coherence to derive a 10th percentile. It is at least certain that the background concentration is less than the values in Table 3.9. More information on the decision to determine a dissolved background concentration is shown in appendix B.

Table 3.8 Proposed dissolved background concentrations in inland waters for the elements showing 25 to 75% of the data below the LOD.

Element	dissolved background concentration (µg/l)	Remarks
As	0.5	P10 is close to the range that can be measured
Cd	0.005	Extrapolation and P10 result in the same value
Co	0.14	LOD problems only in higher range
Mo	0.5	P10 is close to the range that can be measured
Se	0.2	P10 is within the range that can be analysed
Tl	0.01	P10 is close to the range that can be measured
V	0.5	P10 is within the range that can be analysed
Zn	0.7	Extrapolation is very reliable for Zn

Table 3.9 Elements having 25 to 75% of the data below the LOD, without a dissolved background concentration in inland waters. The background concentration is lower than the value presented in this table.

Element	dissolved background concentration less than (µg/l)	Remarks
Cr	0.5	Extrapolation and P10 differ considerably, P10 without correction LOD is presented
Pb	0.12	Extrapolation is impossible. P10 without correction LOD is presented

4 Derivation of dissolved background concentrations for metals in Dutch marine water systems

4.1 Data

Monitoring of coastal and marine waters in the Netherlands is conducted by the national water authority (Rijkswaterstaat). As mentioned in chapter 1, the locations > 70 km out of the Dutch coast did not contain any data of filtrated samples, so the monitoring data approach was used using 5 locations nearer to the coast:

- Goeree 6 km out of the coast
- Noordwijk 10 km out of the coast
- Rottumerplaat 3 km out of the coast
- Schouwen 10 km out of the coast
- Terschelling 10 km out of the coast.

Referring to the criteria in chapter 2:

- The database only contained filtrated samples in µg/l in the period of 2005-2011.
- The salinity is 31.5 ± 1.5, indicating that there is some influence of fresh water at these locations. That is why the data monitoring approach is used instead of the clean streams approach. No data were removed because the salinity.
- The database did not contain values<0.
- There was no seasonal variation in the monitoring frequency (Figure 4.1).
- The data recorded as “<” were halved.

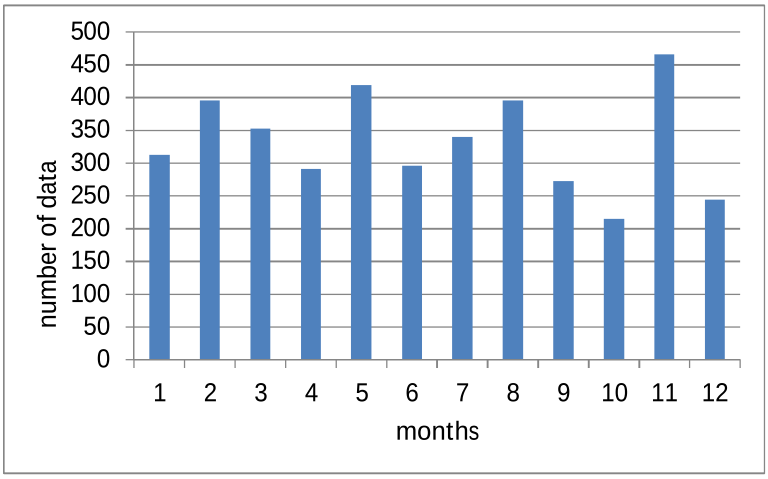

Figure 4.1 Distribution of the data within the year.

The final database contained 4,000 data, the variation in monitoring frequency is limited (Table 4.1).

Table 4.1 Number of data from different water managers.

Total number of data:	**4001**
GOERE6	814
NOORDWK10	866
ROTTMPT3	750
SCHOUWN10	814
TERSLG10	757

The distribution over the years at the selected locations is shown in Table 3.2. Monitoring of filtrated samples started in 2007, the number of parameters was increased in 2009, and the frequency was increased to 12 times a year in 2010. The number of data has increased each year. For this study, it would be useful to monitor the locations further out of the coast.

Table 4.2 Number of data for each year

Jaar	Number of data
2005	0
2006	0
2007	341
2008	402
2009	707
2010	1226
2011	1325
Total	4001

4.2 Results

Table 4.3 shows the number of data for all water managers in the Netherlands.

Table 4.3 Number of data, number of data below the LOD, and percentage of data below the LOD (% lower than 25 in green, between 25 and 75 in yellow, and above 75 in red).

Element	n	n "<"	% "<"
Ag	128	128	100
As	258	0	0
B	128	0	0
Ba	128	0	0
Be	125	79	63
Cd	281	83	30
Co	53	35	66
Cr	128	128	100
Cu	281	38	14
Hg	251	219	87
Li	128	0	0
Mo	128	0	0
Ni	281	31	11
Pb	281	260	93
Rb	128	0	0
Sb	53	2	4

Element	n	n "<"	% "<"
Se	69	0	0
Sn	128	86	67
Te	123	108	88
Ti	128	127	99
Tl	128	128	100
U	128		0
V	128	2	2
Zn	281	111	40

Table 4.3 shows that the number of data is insufficient for Co, Sb, and Se, whereas the number data above the LOD is insufficient for Ag, Cr, Hg, Pb, Te, Ti, and Tl. No background concentrations will be derived for the red coloured cells in Table 4.3. Also for Co we will not determine a dissolved background concentration, because both the number data as well as the number of values below the LOD is 'yellow', indicating that the most stringent criterion is not passed.

The elements with sufficient data, but with more than 75% of the data below the LOD, there is at least information what the maximum background concentration could be[3]. The current P10 (which is a "<" value) is presented in Table 4.4. The reason to present these values is to exclude that taking into account the background concentration may 'solve' the problem.

Table 4.4 Element without a dissolved background concentration. The dissolved background concentration is lower than the value presented in this table.

Element	P10 less than (µg/l)
Ag	0.05
Cr	0.5
Hg	0.0005
Pb	0.1
Te	1
Ti	1
Tl	0.05

Table 4.3 reveals that: As, B, Ba, Cu, Li, Mo, Ni, Rb, U, and V meet all criteria (green). The proposed dissolved background concentrations for these elements are listed in Table 4.5.

Table 4.5 Proposed dissolved background concentrations marine water in the Netherlands for substances having more than 100 data, and less than 20% below the LOD.

Element	dissolved background concentration (µg/l)
As	0.62
B	3000
Ba	8.9
Cu	0.40
Li	120
Mo	8.8
Ni	0.25
Rb	88
U	2.7
V	1.1

For 6 remaining elements, we investigated the distribution of the data, because the database contains less than 100 data or 25-75% of the data is below the LOD. Appendix C shows the probability plots. The interpretation of the probability plots is described in paragraph 3.2. For 5 metals, the data distribution shows that is was possible to estimate a P10 value. No background concentrations was determined for Be.

Table 4.6 Proposed dissolved background concentrations in inland waters for the elements showing 25 to 75% of the data below the LOD.

Element	dissolved background concentration (µg/l)	Remarks
Cd	0.020	P10 is taken
Sb	0.14	<100 data (53), but almost no <LODs and reliable distribution and P10 → indicative value
Se	0.059	<100 data (69), but no <LODs and reliable distribution and P10 → indicative value
Sn	0.025	P10 very close to the range that can be analysed
Zn	0.15	P10 and extrapolation have considerable uncertainty, but produce almost the same background concentration. P10 method used.

Table 4.7 Elements showing 25 to 75% of the data below the LOD, without a dissolved background concentration in inland waters. The background concentration is lower than the value presented in this table.

Element	**dissolved background concentration less than (µg/l)**	**Remarks**
Be	0.1	Extrapolation is impossible. P10 without correction LOD is presented.

The newly derived values were compared with measurements reported in the unburdened parts of the North Sea. Figure 4.2 shows the variation for a number of commonly measured elements. We conclude that the dissolved background concentrations derived in this study fit well within the range of other measurements. We assume that the values derived for other metals, that are less frequently measured, will also give a reasonable estimate of the dissolved background concentration.

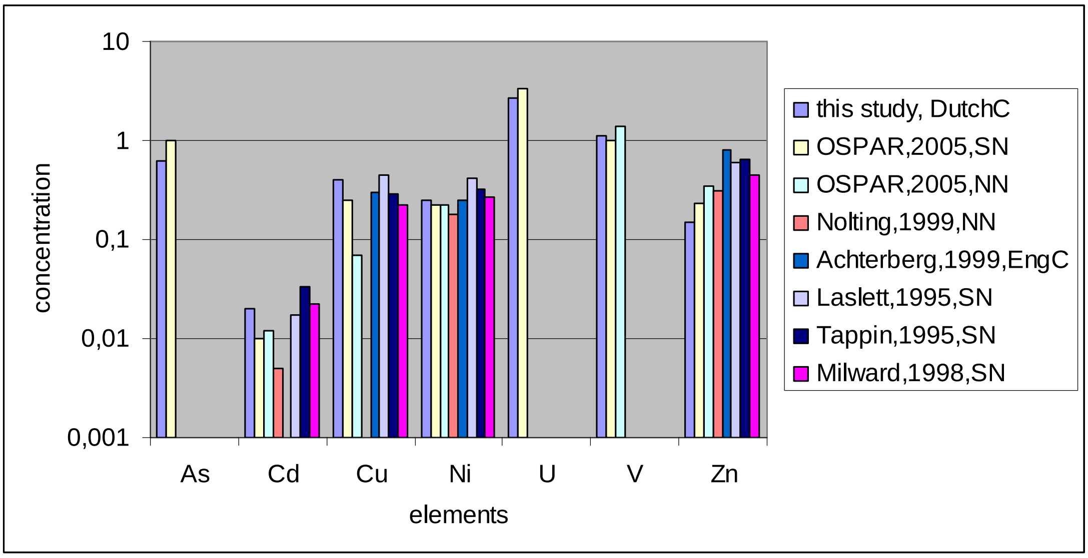

Figure 4.2 Dissolved background concentrations (in µg/l) for several elements determined in this study compared with other measurements in the North Sea. SN=Southern North Sea, NN=Northern North Sea, EngC=English Coast, DutchC=Dutch Coast. For coastal zone measurements we used a P10 or baseline values, for measurements at open sea we used the P50 or the mean value.

5 Method to calculate dissolved background concentrations in Dutch transitional water

Transitional and coastal waters contain both seawater and river water. 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 5.1 shows three possibilities: an increased mobility (addition), a decreased mobility (removal) or unchanged mobility (mixing). Several methods to derive dissolved background concentrations in estuaries have been suggested.

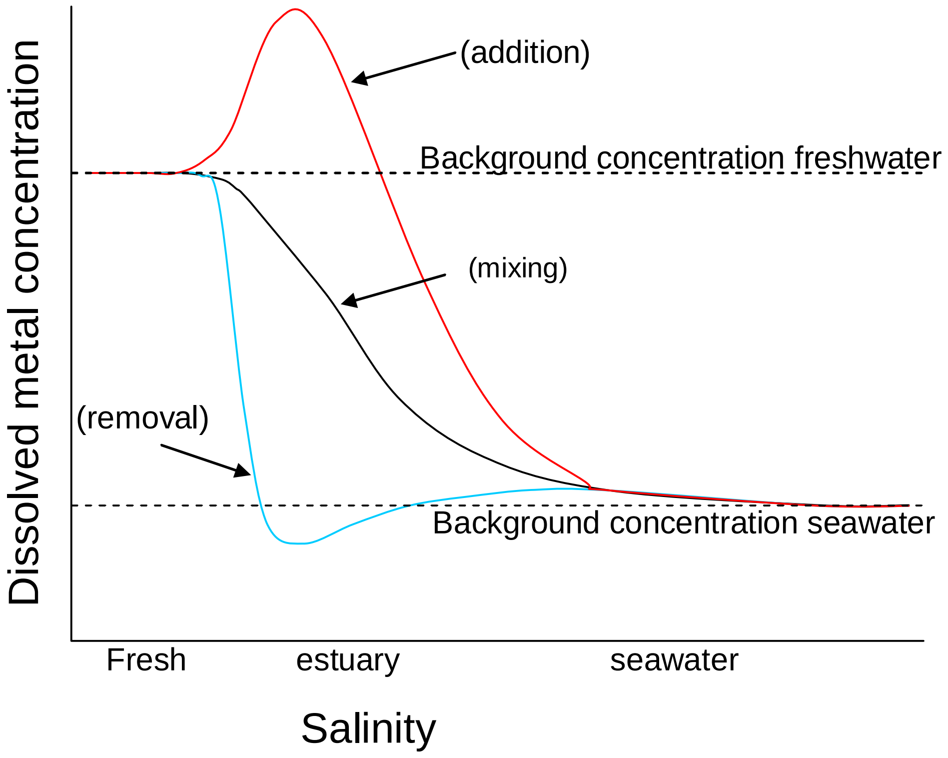

Figure 5.1 Potential effects on dissolved metal concentrations in estuaries due to a changing salinity.

The exact figures of metals showing addition or removal in Figure 5.1 need to be calculated with chemical speciation models that account for organic and inorganic metal complexes. Different processes can change the speciation of dissolved metal concentrations:

- A change in DOC-concentrations at increasing salt concentrations. At higher salt concentrations DOC can coagulate into particulate organic carbon, which is filtered out. This results in a decreased background concentration (removal in Figure 5.1), and is particularly relevant for metals with a high affinity for DOC (Cu, Pb, U, and to a lesser extent: Zn and Cd).
- A change of pH: decrease by nitrification or increase due to CO_2 degassing. A net pH increase is observed in the Scheldt estuary (Hoffman et al., 2009), which influences the sorption to organic matter and formation of hydroxide complexes.

- A change in inorganic metal complexes mainly with chloride and sulphate (e.g. Cd, Pb). The free metal concentration is more or less stable, but the dissolved concentration increases (addition in Figure 5.1).

It is possible to calculate the composition of species by speciation modelling, but the question is how the background concentration is determined in relation to the background concentrations in fresh and salt water which are simply based on total dissolved concentrations after filtration. Therefore, the generic method to derive background concentrations in transitional waters is based on mixing behaviour (Figure 5.1). Only the mixing of seawater and river water determines the background concentration in the transitional zone, neglecting the chemical processes. Under these conditions, the resulting dissolved background concentration in transitional water can be described by:

$$Cb_{transitional} = \frac{[salinity]}{35} * Cb_{sea} + \left(1 - \frac{[salinity]}{35}\right) * Cb_{fresh} \qquad [5.1]$$

In which:

$Cb_{transitional}$ = dissolved background concentration at transitional water sampling station (µg/l)

$Cb_{sea.}$ = dissolved background concentration in seawater (µg/l)

$Cb_{fresh.}$ = dissolved background concentration in fresh (river) water (µg/l)

salinity = salinity at the transitional water sampling station (PSU).

Equation 5.1 requires the salinity at the location in transitional water, regularly measured, and both the background concentration in fresh water and in open sea. This is possible for As, B, Ba, Cd, Cu, Li, Mo, Hg-inorg., Ni, Pb, Rb, Sb, Se, Sn, U, V, and Zn (see also tables 6.1 and 6.2).

Because of the variation in salinity the background concentration need to be determined for each data point individually. Compliance checking should be done by equation 5.2:

$$AA_{Me} = \sum_{1}^{n} (C_{Me,transitional} - Cb_{Me,transitional}) / n$$

In which:

AA_{Me} = Annual average that is checked with the AA-EQS

$C_{Me,transitional}$ = measured concentration at transitional water sampling station (µg/l)

$Cb_{Me,transitional}$ = dissolved background concentration at transitional water sampling station (µg/l) as calculated by equation 5.1

n = number of measurements within a year.

6 Resulting values for fresh waters and marine waters.

6.1 Inland water

The dissolved background concentrations derived in this study are listed in Table 6.1. However, there are already background concentrations available for a large number of elements in fresh water. New values are added in the table for B, Cs, Li, Rb, and Sr. It appeared to be impossible to derive new values for Ag, Gd, La, and Y, because the number of data (above the LOD) was insufficient.

Table 6.1 Dissolved background concentrations in this study and the existing dissolved background concentrations in fresh water. Red indicated that the newly derived values are at least a factor of 2 lower; Values in green indicate that the newly derived are at least a factor of 2 higher.

Element	Derived BC This study (µg/l)	Existing BC NW4 1998 (µg/l)
Ag	-	-
As	0.5	0.8
B	26	-
Ba	20	73
Be	-	0.02
Cd	0.005	0.08
Co	0.14	0.2
Cr	-	0.2
Cs	0.03	-
Cu	0.5	0.4
Gd	-	-
La	-	-
Li	3.5	-
Mo	0.5	1.4
Hg-inorg.	-	0.01
Hg-org	-	0.01
Ni	1.2	3.3
Pb	-	0.2
Rb	2.3	-
Sb	-	0.3
Se	0.2	0.04
Sn	-	0.0002
Sr	110	-
Tl	0.01	0.04
U	0.33	-
V	0.5	0.8
Y	-	-
Zn	0.7	2.8

6.2 Marine water

Dissolved background concentrations in marine water are available for only 5 metals. The dissolved background concentrations derived in this study show limited differences with existing values, only for V more than a factor of 2 (Table 6.2). It appeared to be impossible to derive new values for Ag, Be, Co, Cr, Cs, Gd, La, Tl and Y.

Table 6.2 Dissolved background concentrations in this study and the existing dissolved background concentrations in salt water. Red indicated that the newly derived values are at least a factor of 2 lower; Values in green indicate that the newly derived are at least a factor of 2 higher.

Element	Derived BC This study (µg/l)	Existing BC NW4 1998 (µg/l)
Ag	-	-
As	0.62	-
B	3000	-
Ba	8.9	-
Be	-[$]	-
Cd	0.020	0.03
Co	-	-
Cr	-	-
Cs	-	-
Cu	0.40	0.3
Gd	-	-
La	-	-
Li	120	-
Mo	8.8	-
Hg-inorg.	-	0.003
Hg-org	-	-
Ni	0.25	
Pb	-	0.02
Rb	88	-
Sb	0.14*	-
Se	0.059*	-
Sn	0.025	-
Sr	-	-
Tl	-	-
U	2.7	-
V	1.1	-
Y	-	-
Zn	0.15	0.4

[$] 0.05 µg/l might be used as an indicative value

* values based on <100 data

7 Recommendations

The limit of detection is often the limiting factor to derive a background concentration. For most elements, this is not caused by analytical possibilities but by the acceptance of higher LODs by water managers. Higher LODs do not cause a problem for compliance checking in most cases (LOD is below the standard), but problems rise if information on a lower concentration level is needed (e.g. trends, background concentrations). Water managers should look very carefully to the detection limits they accept.

Several elements show a poor geographic distribution, because they were only measured by a few water managers. This is the case for B, Cs, Li, Rb, Se, and U. It might be useful for other water managers to extend the monitoring with these metals. It does not cost much more to extend the number of elements measured by ICP-MS. The same applies for elements that are not measured at all at the moment. Gd, La, Y are interesting with respect to permits, but there might be more elements that are interesting to measure.

No dissolved concentrations were measured at the Dutch monitoring sites far from the coast (> 70 km). Additional monitoring at these sites is recommended, but there are probably more international data available in unburdened North Sea areas. The Informatiehuis Marien may facilitate the cooperation with other North Sea countries to improve the accessibility of international North Sea data.

8 References

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A Seasonal trends

A.1 If seasonal trends are recorded

It is regularly reported that the summer concentrations for (essential) metals are lower compared to winter concentrations. The lowest data (below P10) may be the result of just summer concentrations. AA-concentrations are used for compliance checking. This might justify that the background concentration should be based on annual average concentrations per location per year.

This has been elaborated for zinc, which shows a clear seasonal trend (figure A1). The same trend could be seen for the median value. The general approach would be to take the P10 of all measurements in fresh water in the Netherlands: 2.0 µg/l. The alternative approach requires calculating the annual average per location per year. The P10 of these average values is 2.5 µg/l. This is different, but compared to the average concentration, it is a small difference. Apparently, the variance between locations and years is very large compared to the seasonal trends.

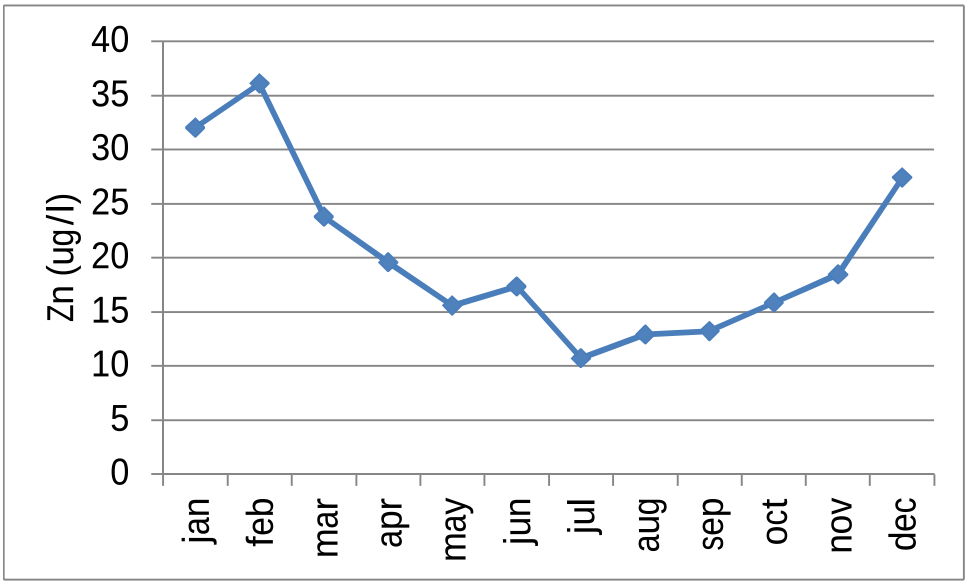


Figure A1 Variation within the year for the average dissolved Zn-concentration in the national database (all years and all locations were separated per month).

Table A1 shows an overview for various metals. Figure A2 shows the lines for the groups with summer or a winter low. Essential elements like Cu, Ni, and Zn show indeed a lower concentration during summer, but also Cd shows lower concentrations in the summer period. The elements having a winter low are mainly anions. Figure A3 shows the elements without seasonal trends.

Table A1 Seasonal trends for various metals based on graphs of the averaged values per month.

Trends	**Metals**
Summer low	Cd, Cu, Ni, Zn
Winter low	As, B, Mo, Rb, V.
No differences	Ba, Co, Cs, Li, Se, Sr, Tl, U.

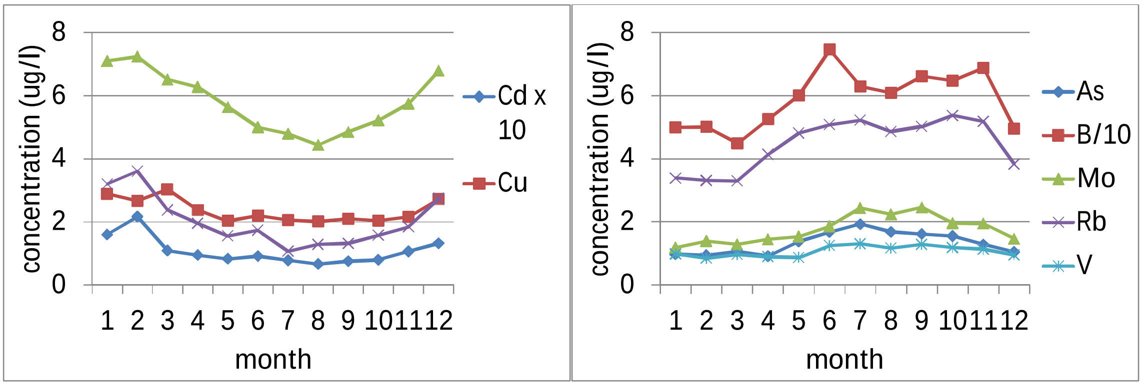


Figure A2 Seasonal variation for various elements in the national database (data were only separated per month).

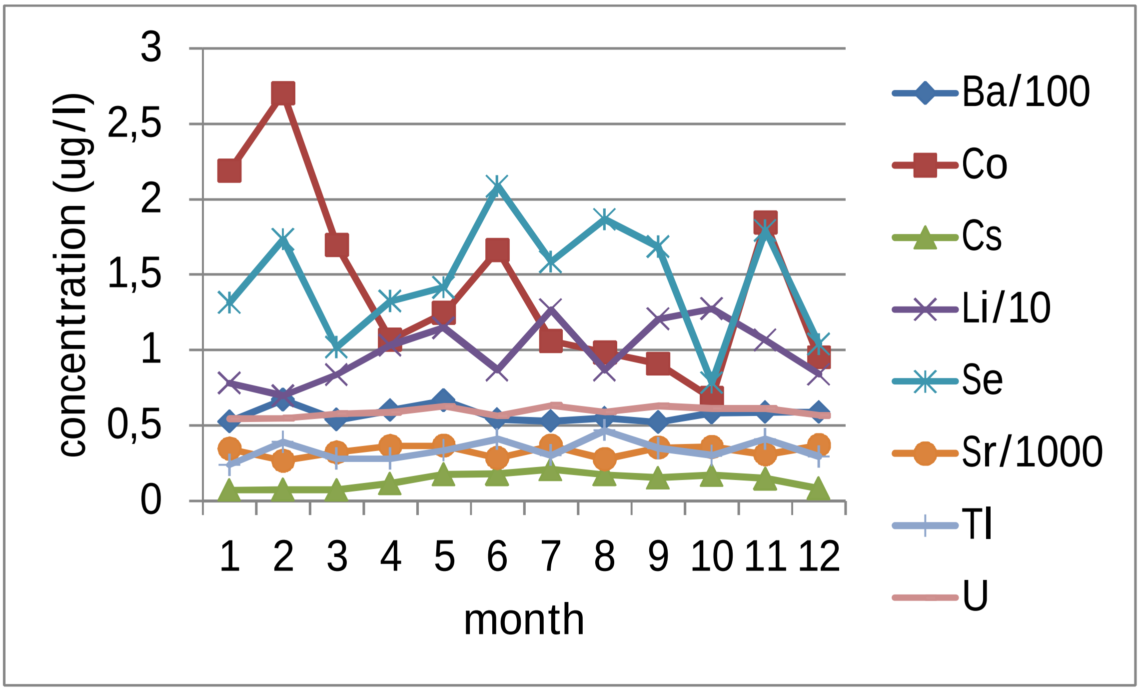
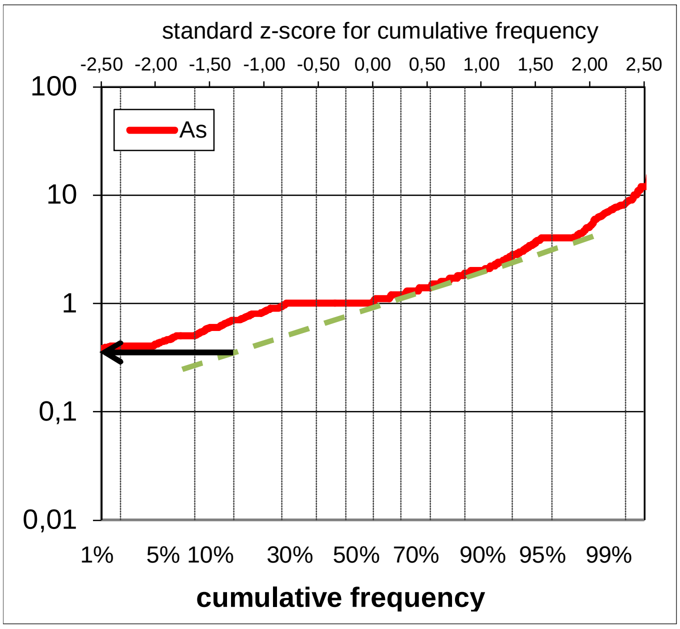


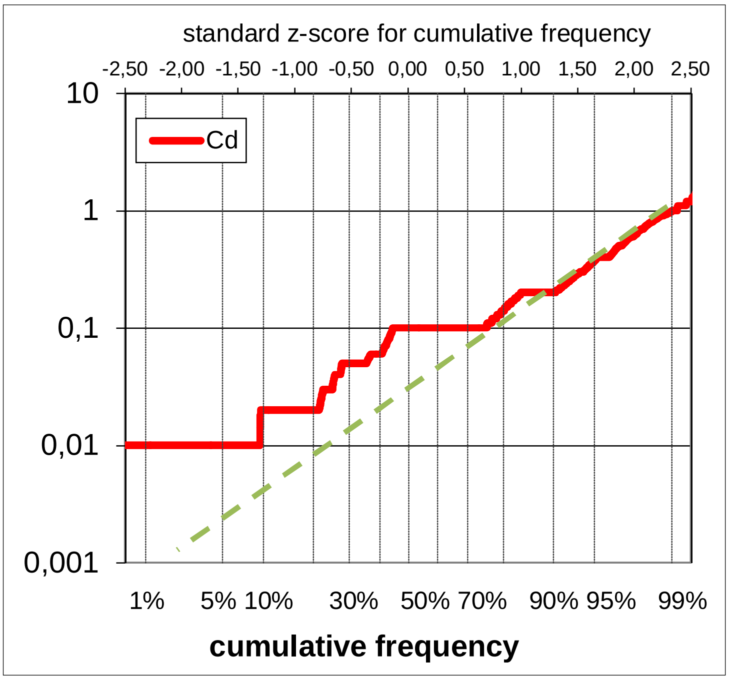
Figure A3 Seasonal variation for various elements in the national database (data were only separated per month).

B Probability plots for inland waters

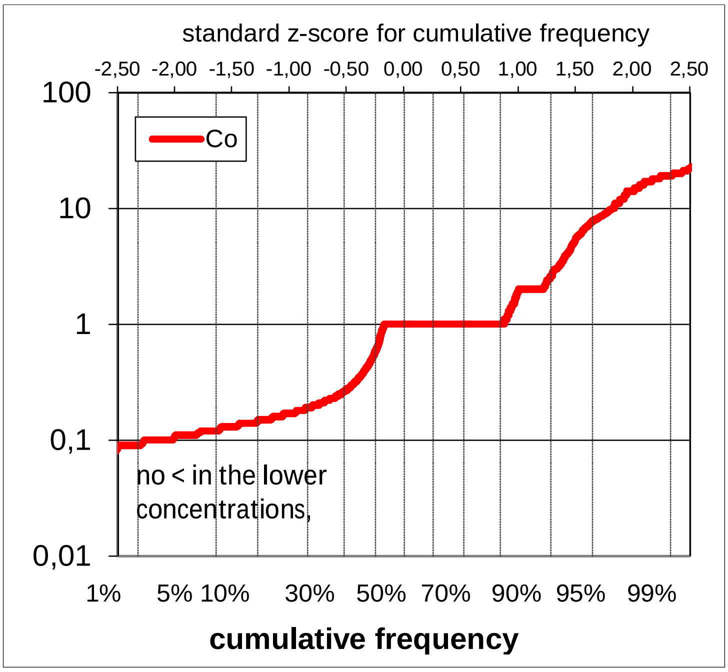
General assessment: if there are plateaus in the graph due to a high LOD, these plateaus represent values somewhere in the range left of the plateau. If the values would have been measured properly, the slope of the line would be less steep. Drawing a line trough the data would thus result in an underestimation of the P10. Besides the extrapolation also the 0.5xLOD-method (all values below the LOD are counted as 0.5xLOD) is used. This value can not be read from the graphs, because the LOD themselves are used in the graphs.



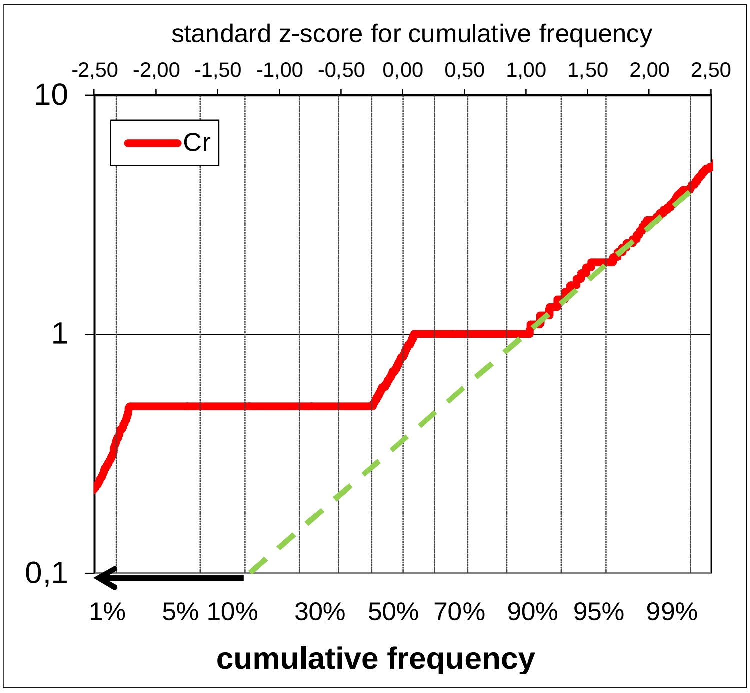
Extrapolation: 0.3 µg/l,
P10 in data (0.5 x LOD-method): 0.5 µg/l. The P10 is within the range that can be analysed.
Proposed: 0.5 µg/l



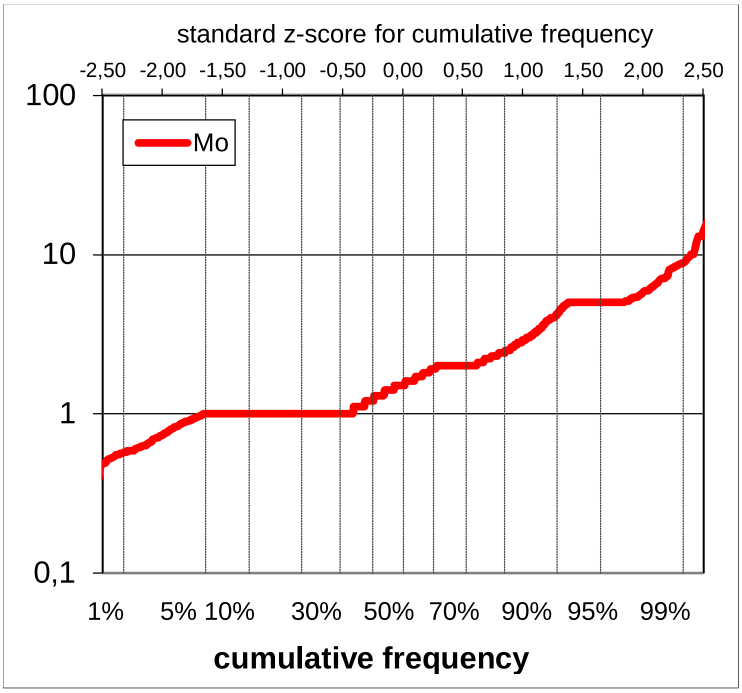
Extrapolation: 0.005 µg/l,
P10 in data (0.5 x LOD-method): 0.005 µg/l
Proposed: 0.005 µg/l, both methods result in the same value.



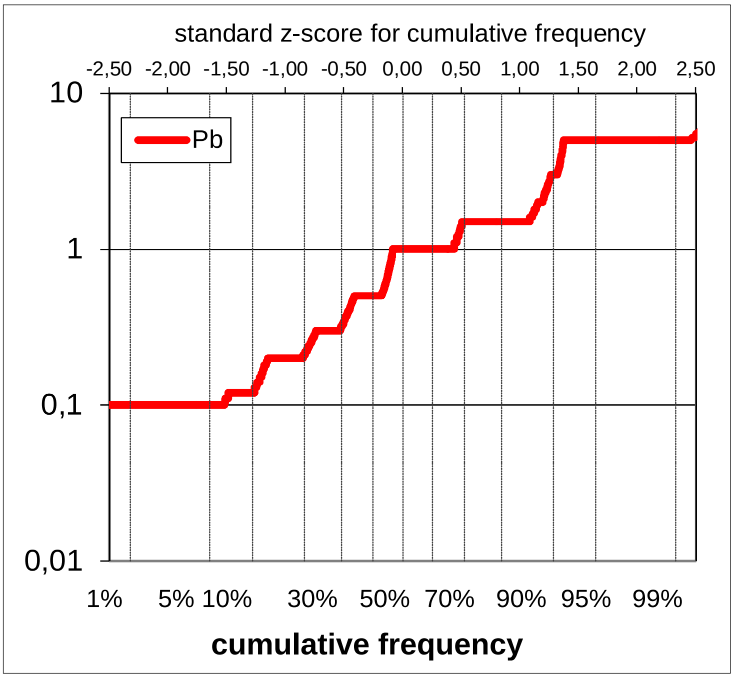
Extrapolation: impossible, data is not normally distributed
P10 in data (0.5 x LOD-method): 0.14 µg/l. The P10 is within the range that can be analysed.
Proposed: 0.14 µg/l



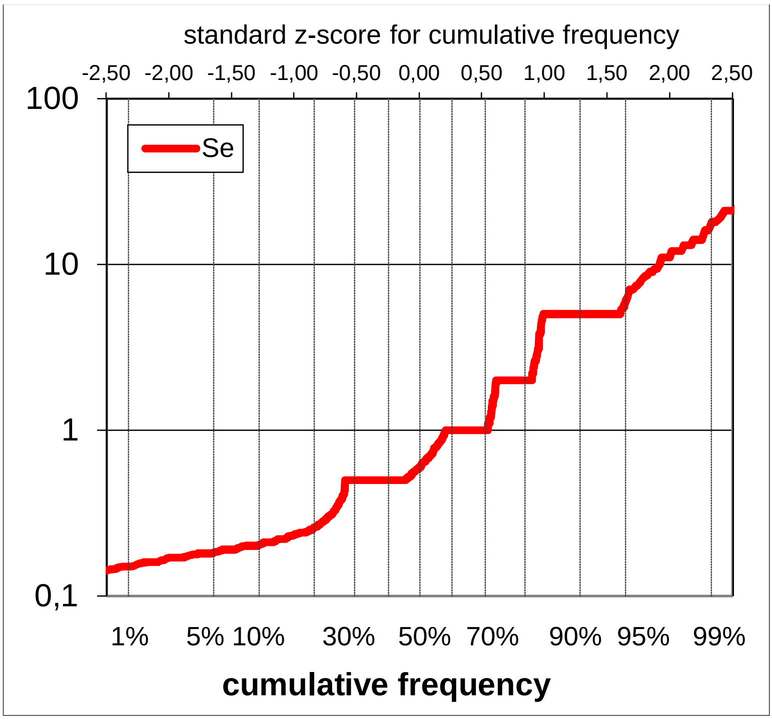
Extrapolation: 0.1 µg/l
P10 in data (0.5 x LOD-method): 0.25 µg/l
Proposed: no background concentration.



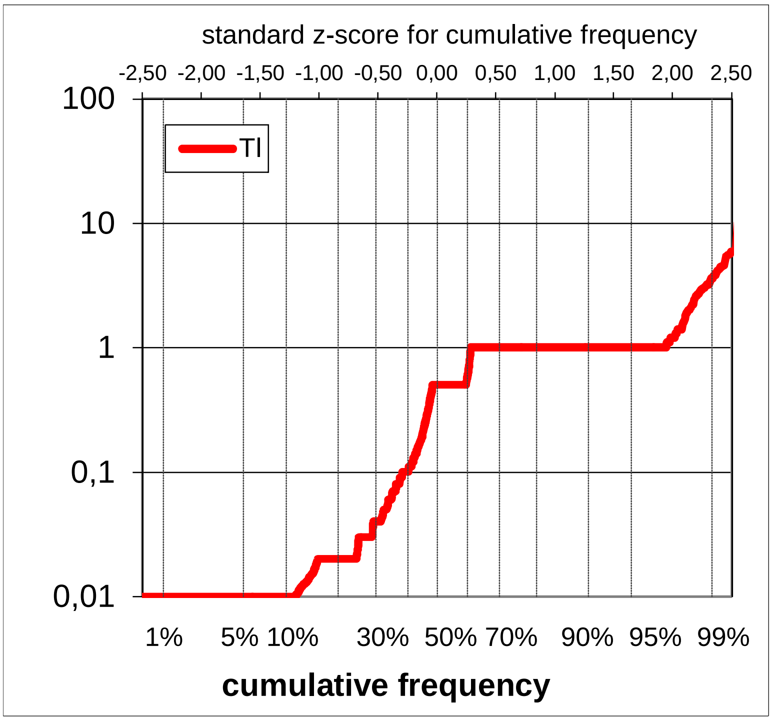
Extrapolation: impossible,
P10 in data (0.5 x LOD-method): 0.5 µg/l
Proposed: 0.5 µg/l.



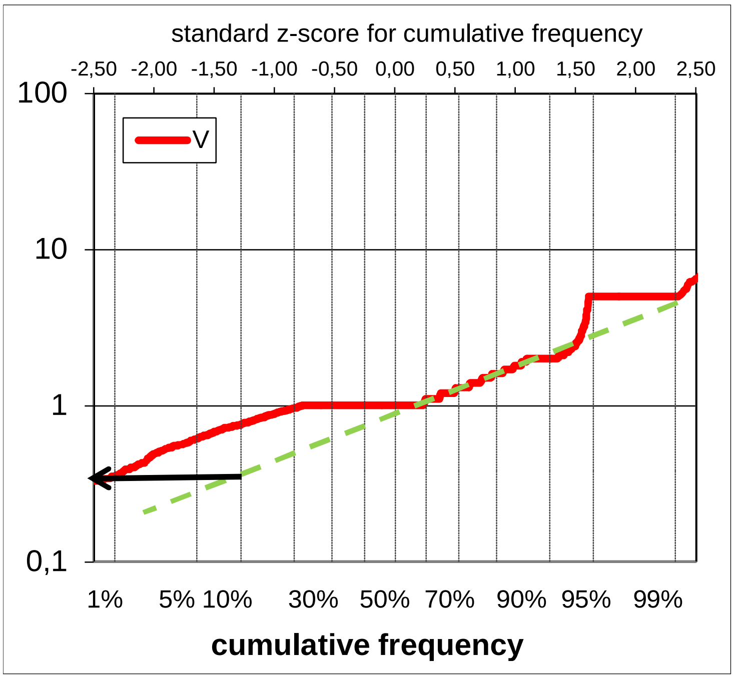
Extrapolation: impossible,
P10 in data (0.5 x LOD-method): 0.1 µg/l
Proposed: no background concentration.



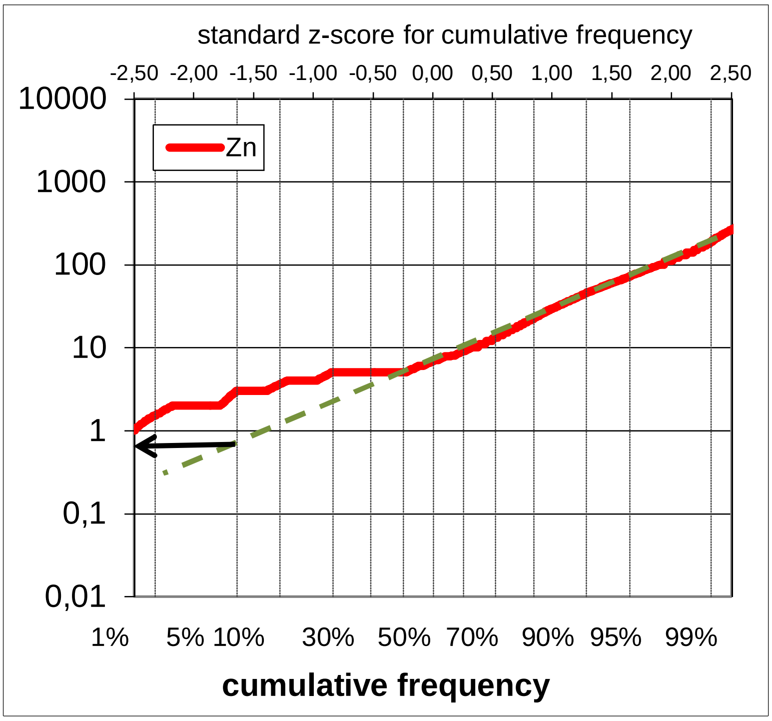
Extrapolation: impossible,
P10 in data (0.5 x LOD-method): 0.2 µg/l. The P10 is within the range that can be analysed.
Proposed: 0.2 µg/l.



Extrapolation: impossible,
P10 in data (0.5 x LOD-method): 0.01 µg/l.
Proposed: 0.01 µg/l



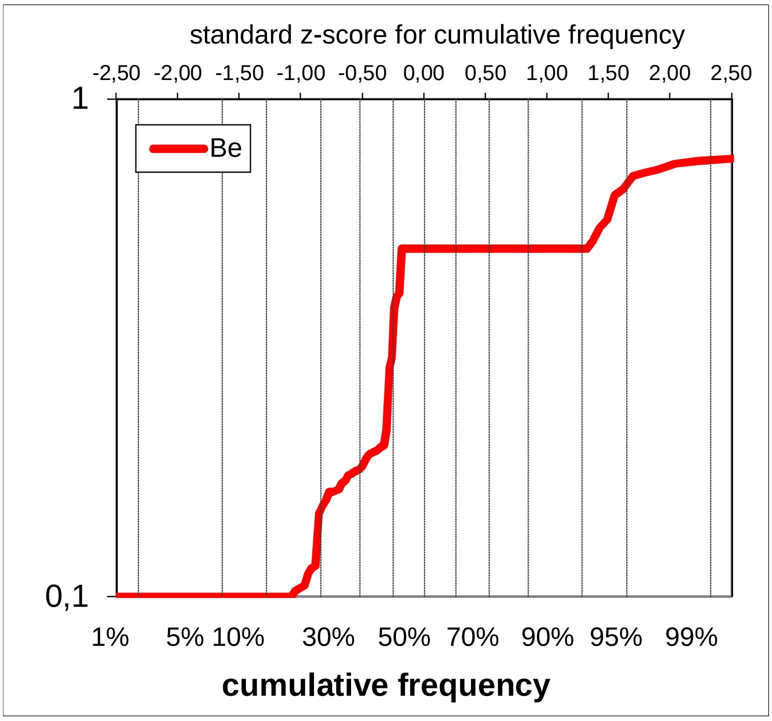
Extrapolation: 0,35 µg/l
P10 in data (0.5 x LOD-method): 0.5 µg/l. The P10 is within the range that can be analysed.
Proposed: 0.5 µg/l.



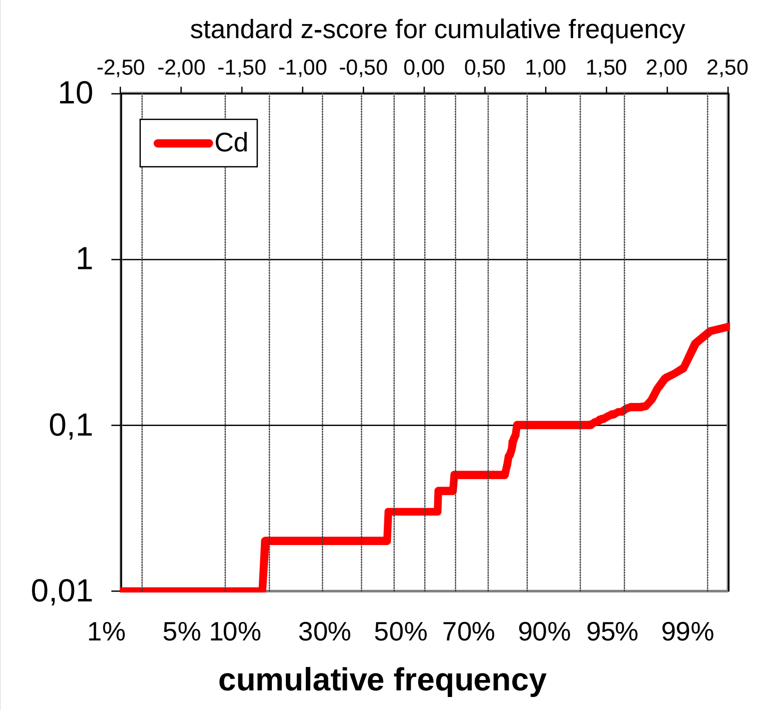
Extrapolation: 0,7 µg/l
P10 in data (0.5 x LOD-method): 2 µg/l.
Proposed: 0.7 µg/l.

C Probability plots for marine waters

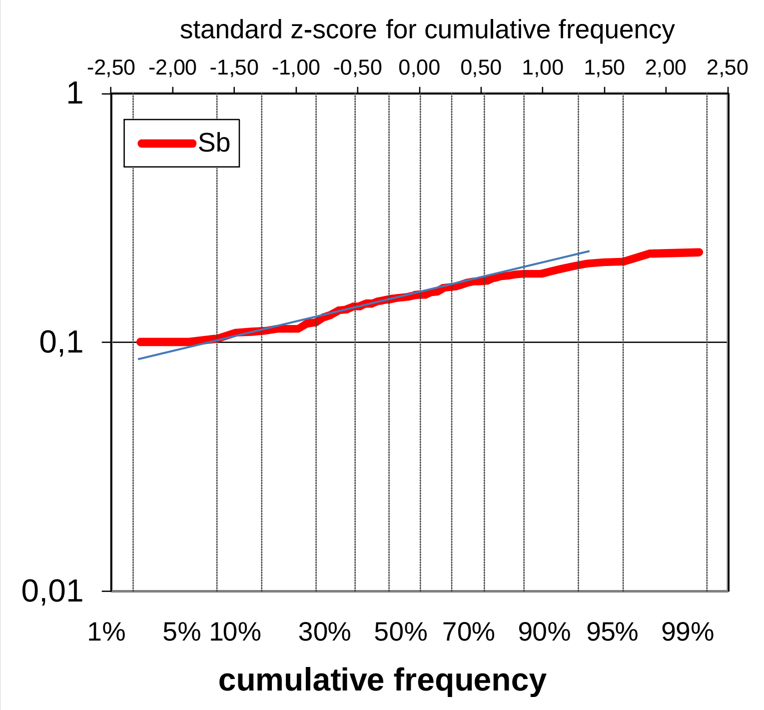
General assessment: if there are plateaus in the graph due to high LOD, these plateaus represent values somewhere in the range left of the plateau. If the values would have been measured properly, the slope of the line would be less steep. Drawing a line trough the data would thus result in an underestimation of the P10. Besides the extrapolation also the 0.5xLOD-method (all values below the LOD are counted as 0.5xLOD) is used. This value can not be read from the graphs, because the LOD themselves are used in the graphs.



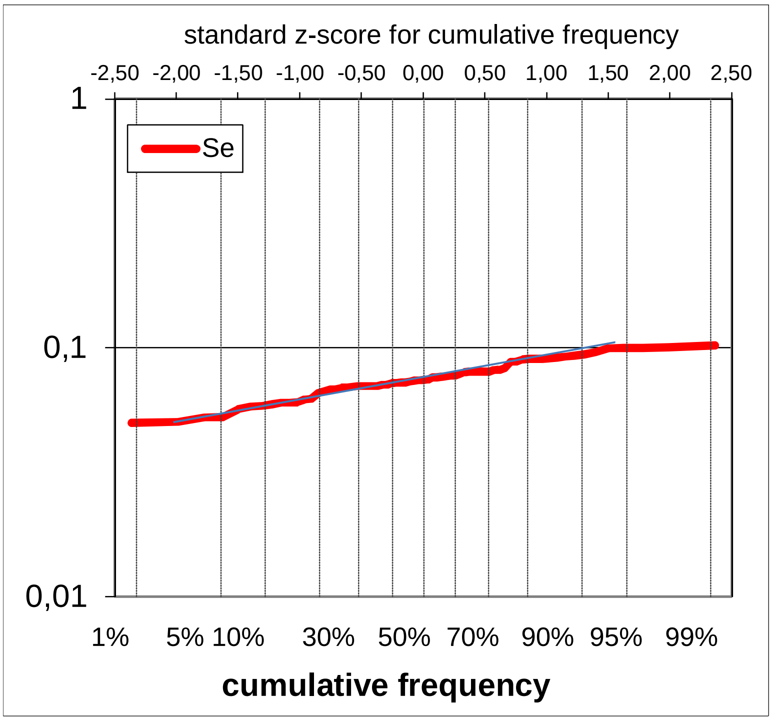
Extrapolation: impossible
P10 in data (0.5 x LOD-method): 0.05 µg/l.
Proposed: no background concentration.



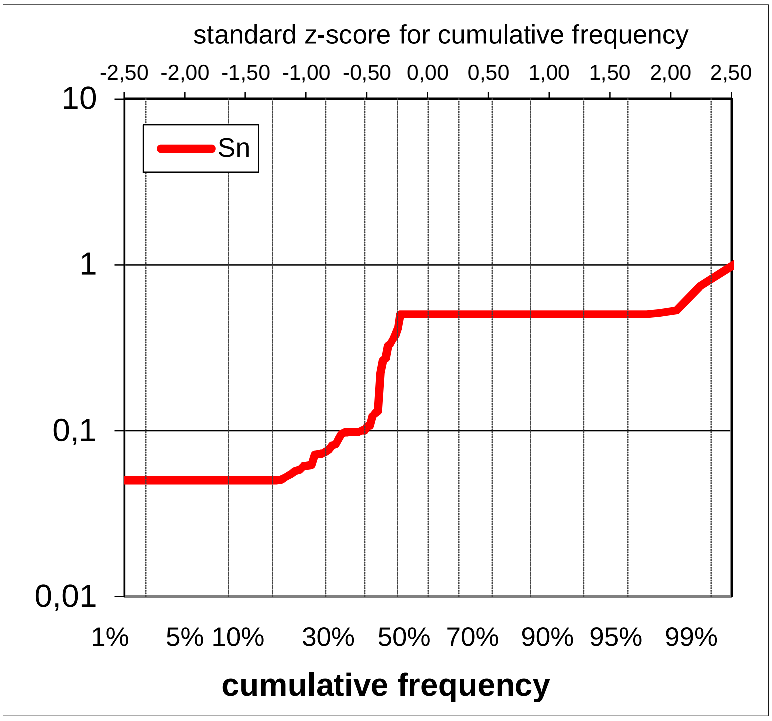
Extrapolation: impossible
P10 in data (0.5 x LOD-method): 0.02 µg/l.
Proposed: 0.02 µg/l.



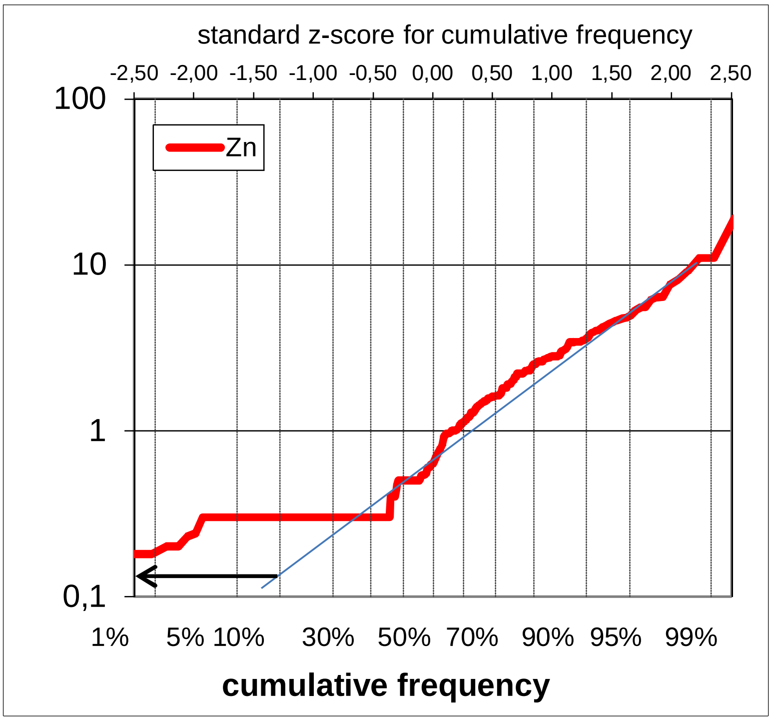
Extrapolation: 0.1µg/l.
P10 in data (0.5 x LOD-method): 0.11 µg/l.
Proposed: 0.11 µg/l.



Extrapolation: 0.058 µg/l.
P10 in data (0.5 x LOD-method): 0.059 µg/l.
Proposed: 0.059 µg/l.



Extrapolation: impossible
P10 in data (0.5 x LOD-method): 0.025 µg/l.
Proposed: 0.025 µg/l.



Extrapolation: 0.12 µg/l, but questionable whether the data is normally distributed
P10 in data (0.5 x LOD-method): 0.15 µg/l.
Proposed: 0.15 µg/l.