

RIJKSINSTITUUT VOOR VOLKSGEZONDHEID EN MILIEU  
BILTHOVEN

Rapport nr. 719101018

**Een conceptuele basis voor het omgaan met  
risicogrenzen en achtergrondgehalten bij het  
afleiden van milieukwaliteitsdoelstellingen**

W.J.G.M. Peijnenburg, M.A.G.T. v.d. Hoop,  
D. v.d. Meent en J. Struijs

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## WOORD VOORAF

Dit rapport is het resultaat van een uitgebreide schriftelijke en mondelinge consultatie van een groot aantal deskundigen binnen de voor de vraagstelling relevante onderzoeksgebieden. Wij zijn alle betrokken deskundigen dankbaar voor de kostbare tijd en energie die zij bereid waren te spenderen aan brainstormsessies, interviews, telefoontjes en workshops.

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## SAMENVATTING

Van nature aanwezige stoffen kunnen voorkomen in concentraties die hoger liggen dan de huidige risiconiveau's. Vanuit beleidsoogpunt zou er, zelfs in de natuurlijke situatie, sprake zijn van een risico voor het desbetreffende ecosysteem: voor een beperkt aantal zware metalen blijkt zelfs de concentratie die behoort bij het maximaal toelaatbare risiconiveau onder het natuurlijke achtergrondniveau te liggen. Deze constatering was aanleiding voor een inventariserend onderzoek met als vraagstelling: "Hoe kan op wetenschappelijk verantwoorde wijze bij het afleiden van milieukwaliteitsdoelstellingen voor zware metalen rekening gehouden worden met de achtergrondgehaltes van deze van nature voorkomende stoffen én met verschillen in beschikbaarheid van deze verbindingen voor opname door organismen?".

Om deze vraag te beantwoorden is een uitgebreid inventariserend onderzoek gestart, waarbij consultatie van experts op het gebied van (hydro-)geochemie, aquatische en terrestrische chemie en (eco-)toxicologie, centraal stond. Deze consultaties hebben geleid tot twee voorstellen voor methodes om de bovenstaande vraag aan te vatten: zogenaamde "concentratielimitatie" en "effect-limitatie". De onderzoeksbegeleidingsgroep van het project "Integrale Normstelling Stoffen" heeft besloten om de methode van effect-limitatie toe te passen voor het afleiden van risicogrenzen voor zware metalen. De onderbouwing van de methode van effect-limitatie is uitgewerkt in een wetenschappelijke publikatie.

In dit rapport wordt verslag gedaan van de wijze waarop de methode van effect-limitatie tot stand is gekomen. De wetenschappelijke publikatie waarin de methode van effect-limitatie wordt uitgewerkt, is integraal opgenomen.

## ABSTRACT

In some cases natural background concentration of heavy metals exceed the present environmental quality objectives, and thus may pose a risk to the ecosystem of interest: for a limited number of metals the background levels even exceed the maximum permissible concentration. This observation led us to initiate an inventorizing study among a number of experts, aimed at deriving new, scientifically based, methods for incorporating both natural background concentrations of heavy metals and the availability of heavy metals for uptake by organisms, into the environmental quality objectives.

Two proposals for new, scientifically sound, methods for deriving environmental quality objectives incorporating background concentrations and availability, resulted from the consultations of the experts: the so-called methods of "effect-addition" or "effect-limitation" versus "concentration-addition" of concentration-limitation".

The method of effect-limitation was preferred by the advisory board of the project "Integrale Normstelling Stoffen" and will be applied to derive new quality objective for heavy metals. The method of effect-limitation is described in a scientific publication.

In this report an overview is given of the approach that was followed to answer the questions raised. The scientific publication resulting from the consultations is included.

## 1 INLEIDING

Van nature aanwezige stoffen kunnen voorkomen in concentraties die hoger liggen dan de huidige risiconiveau's. Vanuit beleidsoogpunt zou er, zelfs in de natuurlijke situatie, sprake zijn van een risico voor het desbetreffende ecosysteem. Daartegenover staat dat deze stoffen in verschillende concentraties voorkomen en daarmee bijdragen aan de natuurlijke variatie. Mogelijk is er sprake van effecten op organismen, maar uitgaande van de wens om de natuurlijke variatie in stand te houden, kunnen deze (mogelijk regulerende) effecten gewenst zijn. Deze tegenstelling is voor DGM aanleiding geweest om een inventariserend onderzoek te initiëren, waarin getracht wordt een structurele oplossing voor dit beleidsmatige 'probleem' aan te dragen.

De problematiek kan worden verduidelijkt middels onderstaande tabel, waarin voor een aantal zware metalen een vergelijking is gemaakt tussen de concentratie behorende bij het verwaarloosbare risiconiveau,  $C_{VRwater}$ , voor oppervlaktewater en het achtergrondgehalte,  $C_{AGwater}$ , in dit systeem. In een aantal gevallen ligt zelfs de concentratie die behoort bij het maximaal toelaatbaar risiconiveau,  $C_{MTRwater}$ , onder het achtergrondniveau (ervan uitgaande dat  $C_{MTR} = C_{VR} * 100$ ).

Tabel 1.1: Achtergrondgehaltes ( $C_{AGwater}$ ) en concentraties behorende bij het verwaarloosbaar risiconiveau ( $C_{VRwater}$ ) voor een aantal zware metalen in oppervlaktewater [MILBOWA, 1991].

element	$C_{VRwater}$ (mg/L)	$C_{AGwater}$ (mg/L)
cadmium	0.0016	0.01
zink	0.016	2
nikkel	0.014	7
kwik	0.0001	0.003
lood	0.02	0.2
chroom	0.02	0.5
koper	0.017	1
arsen	0.086	4

Bij het inventariserend onderzoek stond consultatie van een aantal deskundigen op de relevante vakgebieden centraal.

Deze consultatie heeft in een aantal stappen plaatsgevonden:

- 1 - Op basis van de resultaten van een in februari gehouden brainstormsessie, waaraan werd deelgenomen door vertegenwoordigers van VROM/DGM en RIVM, is een korte notitie opgesteld. In deze notitie was de vraagstelling verwoord alsmede de aan de te consulteren experts voor te leggen vragen.
- 2 - Vervolgens is een aantal experts op het gebied van (hydro-)geochemie en aquatische en terrestrische chemie en (eco-)toxicologie, geselecteerd en elk van deze experts is een interview afgenumen aan de hand van de vragen verwoord in de onder 1 genoemde notitie.

- 3 - De meningen en suggesties van de geconsulteerde experts zijn geïntegreerd en verwoord in een tweede notitie.
- 4 - Vervolgens is een workshop georganiseerd waarin de experts in de gelegenheid werden gesteld om hetgeen verwoord is in de laatstgenoemde notitie van commentaar te voorzien. Daarnaast werden de experts in de gelegenheid gesteld om schriftelijk commentaar te leveren.
- 5 - Alle op- en aanmerkingen, suggesties en adviezen zijn door de auteurs van voorliggend rapport verzameld en geïntegreerd tot een aantal aanbevelingen.
- 6 - Als eindresultaat van de hierboven onder de punten 1 - 5 uitgevoerde acties zijn door de auteurs van het voorliggend rapport een tweetal modificaties uitgewerkt voor het afleiden van MTR-waarden voor metalen: "effect-additie" versus "concentratie-additie", ook wel respectievelijk "effect-limitatie" en "concentratie-limitatie" genoemd. Vervolgens is binnen de onderzoeksbegeleidingsgroep van het project "Integrale Normstelling Stoffen" de beleidsmatige keuze gemaakt om, ondanks gesignaleerde kennislijnen, de methode van effect-limitatie toe te passen voor het afleiden van risicogrenzen voor zware metalen, rekening houdend met natuurlijke achtergrondgehaltes en verschillen in beschikbaarheid.

De modificatie gebaseerd op effect-limitatie is verder uitgewerkt in een wetenschappelijke publicatie. Deze publicatie is als hoofdstuk 2 in dit rapport opgenomen. In een binnenkort te verschijnen RIVM-rapport [T. Crommentuijn, M.D. Polder and E. van de Plassche, maximum permissible and negligible concentrations for metals -taking background concentrations into account-, rapport nummer 679101019, januari 1996] wordt de methode van effect-limitatie toegepast voor het afleiden van MTR en VR-niveaus. Hierbij worden een beperkt aantal aannames gedaan voor wat betreft de mate van beschikbaarheid van de natuurlijke achtergrondconcentraties voor de compartimenten bodem en water.

De hierboven weergegeven vraagstelling is eveneens aanleiding geweest om een literatuuronderzoek uit te voeren naar de achtergrondgehalten van zware metalen in de verschillende milieucompartimenten. De resultaten van dit onderzoek zijn beschreven in RIVM-rapport nr. 719101019 [M.A.G.T. van den Hoop, literatuurstudie naar achtergrondgehalten van zware metalen in bodem, sediment, oppervlaktewater en grondwater, augustus 1995].

## 2 ADDED RISK APPROACH TO DERIVE MAXIMUM PERMISSIBLE CONCENTRATIONS FOR HEAVY METALS: HOW TO TAKE INTO ACCOUNT THE NATURAL BACKGROUND LEVELS?

### Abstract

A unified method is presented to derive Maximum Permissible Concentrations (MPCs) of xenobiotic and naturally occurring substances. The method relies upon risk limitation expressed as the maximum fraction of all possible species that is unprotected ( $F_{U_{max}}$ ) in a component ecosystem, due to a bio-available concentration of the considered substance. For xenobiotic compounds the method simplifies to the "HC5 approach", i.e. the MPC equals the hazardous concentration at which 5 % of the species are unprotected. If the natural background of a substance is (partly) bioavailable, the related background effect, also expressed as  $F_U$ , is taken into account in deriving a MPC. Examples are given and MPCs for zinc, chromium, cadmium, copper and lead for different levels of bio-availability in water are developed.

### Introduction

Maximum Permissible Concentrations (MPCs) for toxic substances are derived on the basis of risk considerations, where "risk" usually has the meaning of the extent of an adverse effect, quantified in dimensions accordingly. In the context of environmental risk management of toxic substances, risk is expressed as "that fraction of all species that is exposed to concentrations higher than the No Observed Effect Concentration (NOEC)". This fraction has been called the "fraction unprotected", abbreviated as " $F_U$ ". Application of  $F_U$  in risk assessment requires that sufficient NOECs of different species are known, to evaluate the distribution of NOECs. In the Netherlands, the starting point for setting MPCs is to limit the fraction unprotected to 0.05 (Health Council, 1989; DGEP, 1988-1989).

Attempts to apply this methodology to metals have resulted in MPCs that were below natural background concentrations (Van de Meent et al., 1991). It was concluded that this procedure could not be applied to derive Maximum Permissible Concentrations for metals and other chemicals of natural origin, and that further research was necessary (MILBOWA, 1991). This paper reports on investigations focussed on this particular matter; it is aimed at the incorporation of natural background levels into MPCs.

It was felt that the procedure, proposed by Van de Meent (1991), the discrepancy between availability of metals in laboratory tests and field conditions is ignored. The actual effect of naturally occurring metals may be lower than expected on the basis of laboratory tests, because of the lower bioavailability under field conditions. In order to develop MPCs it is appreciable to account also for the bioavailability of natural and anthropogenic concentrations, anticipating that only the bio-available part of the total concentration may cause an effect. The natural and anthropogenic concentrations may be transformed into *background effect* and *added risk*, respectively.

A methodology for deriving MPCs on the basis of a maximum permissible addition to the background of water and soil is described. To illustrate the proposed method, it is applied to

two hypothetical metals with different ecotoxicological characteristics, but having in common that the background concentration causes a significant effect. As a second example MPCs for the metals arsenic, cadmium, chromium, copper and zinc in Dutch surface water for different levels of bioavailability are derived.

## Methods

### *Guiding principles of the proposed procedure, premises and assumptions*

Considering a toxic substance, NOECs for different species have different values. Because in principle all species are concerned, a distribution of NOEC data has to be anticipated. Such a distribution can be formulated if only a relatively small sample of NOEC data is available, characterized by the mean value ( $\alpha$ ) and the standard deviation ( $\sigma$ ) of log transformed NOECs. Van Straalen and Denneman (1989) proposed that a logistic distribution of log(NOEC) data be satisfactory (Figure 1a). The advantage of the logistic density function is that it allows the analytical evaluation of the cumulative distribution,  $F_u(x)$ , simply by integration (Figure 1b):

$$F_u(x) = \frac{1}{1 + \exp\left(\frac{\alpha - x}{\beta}\right)} \quad (1)$$

where the scale parameter  $\beta$  is equal to approximately half times  $\sigma$  ( $\beta = \sigma \sqrt{3}/\pi$ ), and  $x$  is the logarithm of the concentration. For the sake of simplicity in reasoning, it is assumed here that the log-logistic distribution function is suitable. However, every other function (e.g. (log)normal) would work equally well.  $F_u(x)$  has a value between 0 and 1.  $F_u(x)$  is the fraction of the species that have log(NOEC) values smaller than  $x$ . In this explicit form  $HC_p$ , the "hazardous concentration for  $p\%$  of the species", can easily be obtained (Van Straalen and Denneman, 1989). As stated before, in the Netherlands the maximum level of  $p$  is set to be 5, which means that  $F_{u_{max}} = 0.05$ , resulting in  $HC5$  as the Maximum Permissible Concentration.

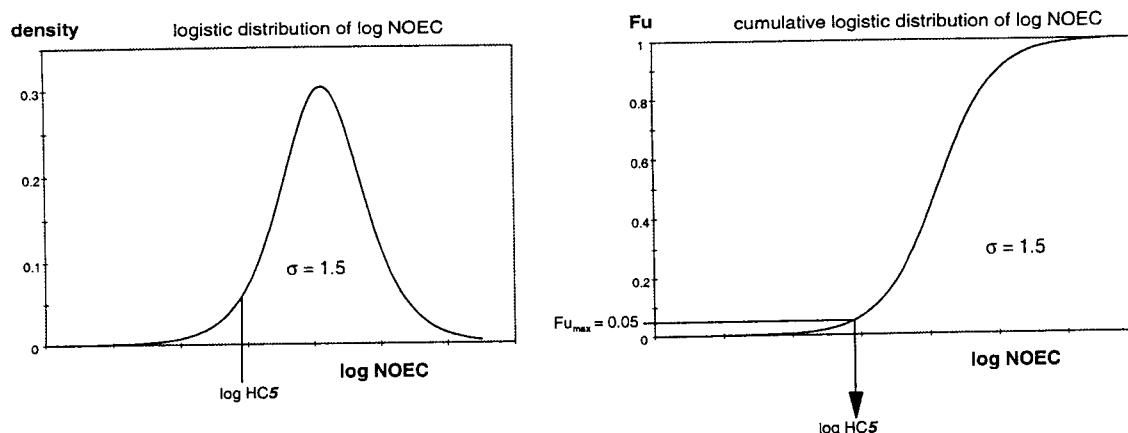


Figure 1: Logistic (left, Figure 1a) and cumulative logistic (right, Figure 1b) distribution of log NOEC data.

Naturally occurring chemicals may also impose stress. While such stressors imply risk, it is common practice to refer to their impact in terms of "effects", rather than "adverse effects". Nevertheless, such effects should similarly be quantified as  $F_u$ , the fraction unprotected. Another assumption is that no different levels of bio-availability in the natural background are distinguished. There are only two fractions of  $C_b$ : active or bio-available ( $\phi$ ) and inactive or unavailable ( $1-\phi$ ). The *bio-available fraction of the natural background concentration*,  $\phi C_b$ , indicated as "active" in Figure 2, ideally is compared with the NOEC data obtained from laboratory tests, so that  $\log(\phi C_b)$  truly ranks on the log(NOEC) axis. The corresponding *background effect*,  $F_{u_b}$ , which is the fraction of species unprotected due to this bio-available background concentration, can be simply obtained as  $F_{u_b} = F_u(\log(\phi C_b))$  according to equation 1. In this reasoning it is assumed that the laboratory NOECs pertain to 100 % availability. It is also assumed that the *unavailable* or *inactive* part of the background,  $(1-\phi) \cdot C_b$ , does not cause any effect to any of the occurring species.

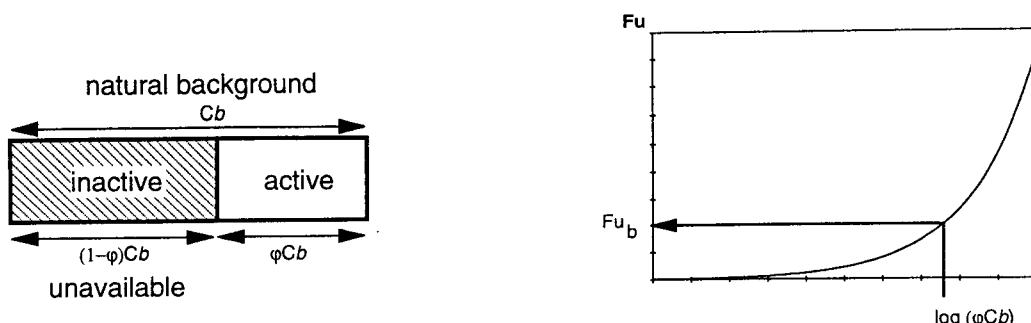


Figure 2: The active or bio-available ( $\phi$ ) and inactive or unavailable ( $1-\phi$ ) fractions of the background concentration ( $C_b$ ) and the background effect ( $F_{u_b}$ ) due to the bio-available background concentration.

We propose to relate "acceptable added risk" to a "maximum permissible addition" ( $C_a$ ) by combining 1) ecotoxicity data, 2) the effect inducing natural background concentration ( $\phi C_b$ ) and 3) the risk limit chosen by environmental policy makers as tolerable if there are no background phenomena, for example the fraction unprotected is 0.05. In the left diagram of Figure 3, the bar is extended with a maximum permissible (active) addition ( $C_a$ ) of anthropogenic origin.

MPCs relying on the proposed added risk principle, i.e.  $MPC = C_b + C_a$ , may be regarded as a general approach, whereas  $MPC = C_a$  is a special case of zero natural background levels ( $C_b = 0$ ), to be applied to derive MPCs for xenobiotic compounds.

The choice *not* to ignore natural background raises the question how to quantify such a maximum addition. By adding some calculated concentration to  $\phi C_b$  or by adding some specified fraction unprotected to  $F_{u_b}$ ? In the right diagram of Figure 3 the two possibilities of adding an ecotoxicological parameter to some natural background level, are visualized:

- Deriving the maximum permissible addition ( $C_a$ ) by *effect limitation*. A specified addition of effect to the natural background effect is allowed. Subsequently, this effect addition is transformed into  $C_a$ .
- Deriving  $C_a$  by *concentration limitation*. The sum of the total background concentration and HC5 is allowed. At first glance, this possibility seems most

straightforward:

$C_a = HC5$ . No information of the background effect is required or in other words: it is not necessary to know  $\varphi$ .

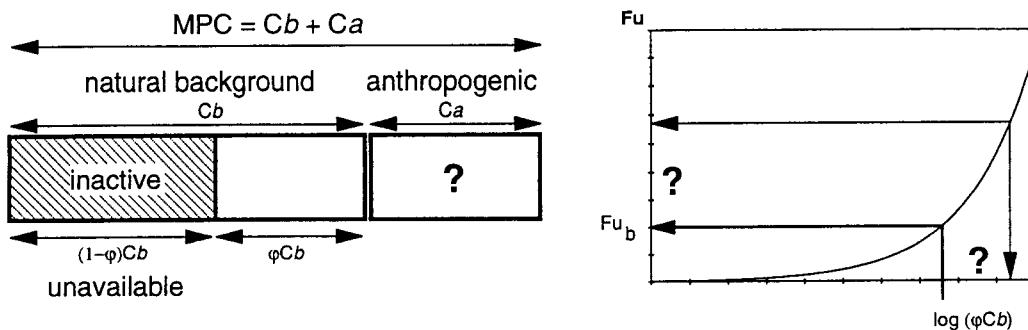


Figure 3: Possibilities for deriving a maximum permissible addition ( $C_a$ ) of anthropogenic origin to the natural background level.

It is clear that both approaches require ecotoxicity data which are summarized by  $\alpha$  and  $\sigma$ . However, we discard the concentration limitation approach as it violates accepted principles of ecotoxicological risk assessment.

#### *The Maximum Permissible Addition, $C_a$ , based on effect limitation*

The method requires that in addition to the total background concentration, also the fraction of the background that is bio-available,  $\varphi$ , be known.

Four steps are necessary to calculate  $C_a$ :

- 1) The background effect  $Fu_b = Fu(\log\varphi Cb)$  is calculated from eqn 1 as the fraction that is not fully protected due to the available background concentration  $\varphi Cb$ .
- 2) Additional effect or additional risk is defined as  $(1 - Fu_b) \cdot 0.05$ . Figure 4 indicates that "additional" means that it is put on top of the background effect,  $Fu_b$ .

The term  $(1 - Fu_b) \cdot 0.05$  contains the fraction  $(1 - Fu_b)$ , representing all species not affected by the background concentration. Of these non-affected species, being liable for risk limitation, a fraction 0.05 is considered acceptable as unprotected. The following example may clarify this: the additional risk would be lower than 0.05 as 0.05 is multiplied by a factor lower than one, i.e.  $(1 - Fu_b)$ .

- 3) The maximum permissible effect,  $Fu_{max}$ , is the sum of the background effect and this additional risk:

$$Fu_{max} = Fu_b + (1 - Fu_b) \cdot 0.05 \quad (2)$$

Without any background level,  $Fu_b = 0$ ,  $Fu_{max}$  would reduce to 0.05, meaning that 5% of all species is not fully protected as the maximum permissible effect.

4) Combining eqs 1 and 2 leads to the relationship

$$\log (\varphi Cb + Ca) = \alpha - \beta \ln \left( \frac{1 - Fu_{\max}}{Fu_{\max}} \right) \quad (3)$$

from which  $Ca$  is obtained.

These four steps: the evaluation of  $Fu(\varphi Cb)$ , defining additional effect, deriving  $Fu_{\max}$  and calculation of  $Ca$  are shown in Figure 4.

Without any background activity - if either  $\varphi$  or  $Cb$  equals zero - and with  $Fu_p$  equal to 0.05,  $\log(Ca)$  would be equal to  $\alpha - \beta \cdot \ln 19$ , a result that is identical to the logarithm of the "Hazardous Concentration for 5% of the species", also known as HC5. With  $Fu_b > 0$ , in principle there is no real limitation to  $(\varphi Cb + Ca)$  as, theoretically,  $Fu_{\max}$  may approximate 1 if there are extremely high background effects.

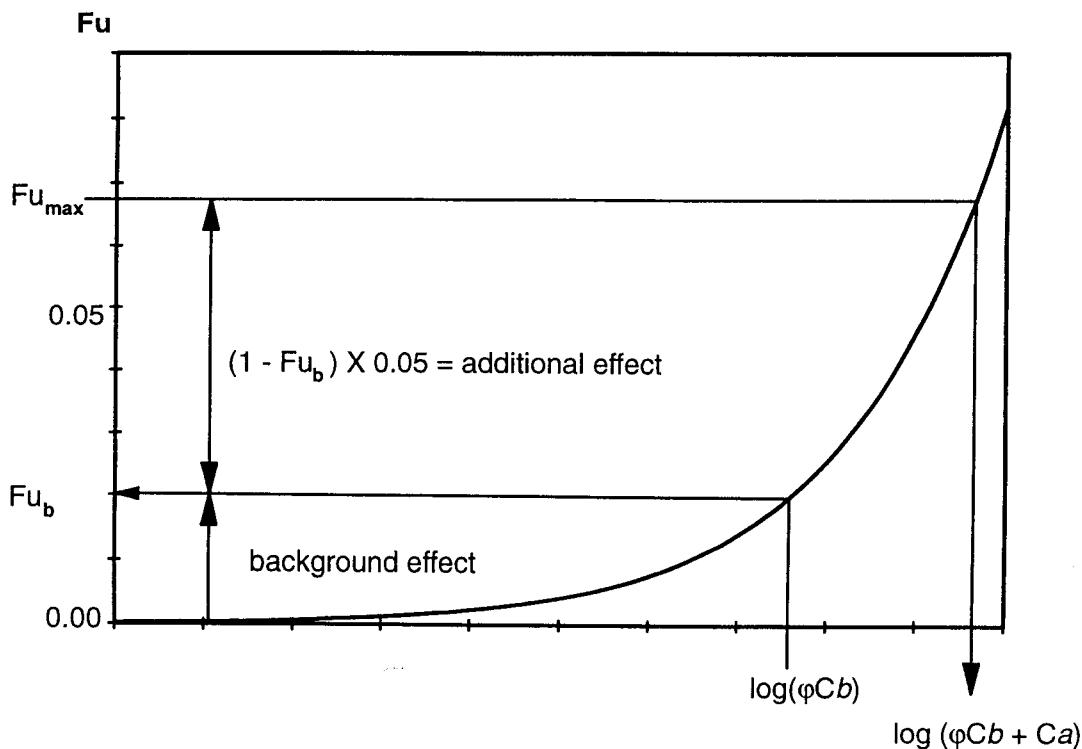


Figure 4: Calculation of the maximum permissible addition ( $Ca$ ), based on effect limitation.

*Application to water; default bio-availability: the total background is 100% active*

For the water compartment, it is usually assumed that the metals in the dissolved phase are available. Since water quality objectives are set for the dissolved phase, it is adequate to assume a value of 1 for the bio-availability  $\varphi$ , if any information other than the dissolved concentration is lacking. The background effect is calculated with eqn 1 as  $Fu_b = Fu(\varphi Cb) = Fu(Cb)$ . The maximum permissible effect,  $Fu_{\max}$ , is obtained from eqn 2. Subsequently,  $\varphi Cb + Ca$  is calculated from eqn 3, resulting in the maximum permissible addition,  $Ca$ . The maximum permissible concentration for the water compartment ( $MPC_{water}$ ) is obtained as the

sum of  $C_b$  and  $C_a$ . This is visualized in Figure 5.

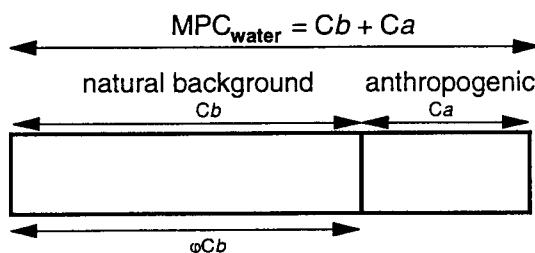


Figure 5: Maximum Permissible Concentration for the water compartment, assuming that the total background is 100 % active.

*Application to soil; default bio-availability: the total background is 0 % active*

It is often reported that the availability of non-anthropogenic metals in soil is low. Therefore, if only the total background metal content of soil can be estimated, a default bioavailability equal to zero may be justified as an educated guess. For the special case that  $\phi = 0$ , deriving  $MPC_{soil}$  is straightforward. This is shown in Figure 6, where the block representing  $\phi C_b$  is absent. The maximum permissible addition to soil,  $C_a$ , is - if  $F_{U_p}$  is agreed to be equal to 0.05 - equal to HC5. Thus HC5 can be added directly to the *total* background concentration in order to obtain  $MPC_{soil}$ .

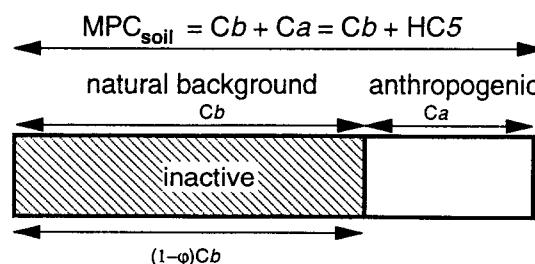


Figure 6: Maximum Permissible Concentration for the soil compartment, assuming that the total background is 0 % active.

As is stated before, the maximum permissible addition,  $C_a$ , is always equal to HC5 (or  $HC_p$ ) if either  $C_b$  or  $\phi$  is zero.

*An example: two hypothetical metals*

In the following example the method is demonstrated by evaluating two hypothetical metals, which differ in the mean ( $\alpha$ ) and the standard deviation ( $\sigma$ ) of  $\log(\text{NOEC})$ . In the following example the geochemical characteristics of these metals in a certain environmental compartment are given as total natural background concentrations - in appropriate units - and the corresponding bio-available fractions. In the right column, the ecotoxicological characteristics are given.

## EXAMPLE: TWO HYPOTHETICAL METALS

metal A	$C_b = 2.0 \cdot 10^{-3}$	$\alpha = -2.75$
	$\varphi = 0.2$	$\sigma = 0.4$
	$\varphi C_b = 4 \cdot 10^{-4}$	$\beta = 0.22$
		$HC5 = 4 \cdot 10^{-4}$

$$Fu_b = 0.05$$

$$\begin{aligned} Fu_{max} &= 0.098 \\ Ca &= 1.7 \cdot 10^{-4} \\ MPC &= 2.2 \cdot 10^{-3} \end{aligned}$$

metal B	$C_b = 5 \cdot 10^{-4}$	$\alpha = -0.80$
	$\varphi = 0.8$	$\sigma = 1.6$
	$\varphi C_b = 4 \cdot 10^{-4}$	$\beta = 0.88$
		$HC5 = 4 \cdot 10^{-4}$

$$Fu_b = 0.050$$

$$\begin{aligned} Fu_{max} &= 0.098 \\ Ca &= 1.3 \cdot 10^{-3} \\ MPC &= 1.8 \cdot 10^{-3} \end{aligned}$$

Metal A. Unless the background of metal A is entirely unavailable, its concentration might have an effect on the occurring species because  $\log C_b (= -2,7)$  is even higher than  $\alpha$ . However, the availability of  $C_b$  is only 20%. Metal A has a steep distribution of log(NOEC), given by  $\sigma = 0.4$  or  $\beta = 0.22$ . In this example it happens that the background effect,  $Fu_b$ , is calculated as 5% unprotected, which is equivalent to  $\varphi C_b = HC5$ , if the risk limit would have been set to  $Fu_p = 0.05$ . The proposed method applied to metal A, allows an anthropogenic increase of only less than 10% of the total natural background concentration.

Metal B. Although displaying a relatively low average toxicity, however, like metal A, its natural occurrence may also have a significant effect on the ecosystem. The non-anthropogenic content of metal B in the considered compartment is, on a log scale ( $\log C_b = -3.3$ ), more than two units lower than the average log(NOEC). The NOECs are rather widely distributed:  $\sigma = 1.6$ . Moreover, the bioavailability of metal B is as high as 80% and, accidentally again, these data make  $\varphi C_b$  and  $HC5$  to coincide. In this case a maximum permissible concentration is calculated which is nearly four times the total natural background concentration.

This example may seem highly coincidental as the four concentrations  $\varphi C_b(A)$ ,  $HC5(A)$  and  $\varphi C_b(B)$ ,  $HC5(B)$  all have the value  $4.0 \cdot 10^{-4}$ . An available background value approximately

equal to HC5 of a metal is, however, not so unlikely. It is a typical scenario that has led to "MPCs" below the background as has been derived previously, when the background was completely ignored. The coincidence that  $HC5(A) = HC5(B)$  has the function to illustrate how the method may produce different results, in spite of such a coincidence. In the cumulative frequency distribution of Figure 7, the metals with the different density distributions but similar HC5 have different values for  $Ca$  if derived according to the proposed method. Note that if the maximum permissible addition,  $Ca$ , would have been evaluated simply by adding HC5 to  $Cb$  - an approach we consider inappropriate - the result would have been equal for both metals.

In contrast, the effect limitation approach produces for this particular case only one value of  $F_{U_{max}}$  - however, limited to 0.098 - but different values  $Ca$ . For  $\sigma = 0.4$  the resulting MPC is more conservative than for  $\sigma = 1.6$ .

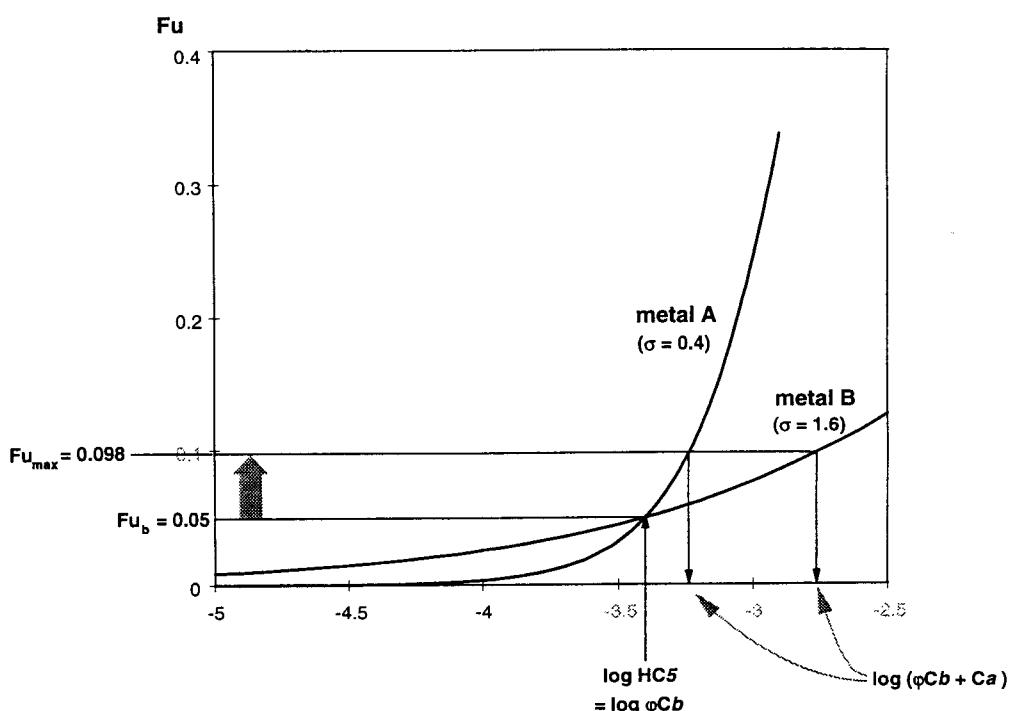


Figure 7: Calculated maximum permissible additions for two hypothetical metals A en B.

## Results and discussion

The maximum permissible concentrations of five metals in Dutch surface waters are evaluated. All the required data for the derivation of  $MPC_{water}$  are summarized in Table 2.1. These include ecotoxicological properties, characterized by  $\alpha$  and  $\sigma$  (or  $\beta$ ) as derived from Crommentuijn et al., (1996), as well as the total natural background concentrations in Dutch fresh water taken from a recent literature survey (Van den Hoop, 1995). Although not necessary for the evaluation of  $MPC_{water}$ , also HC5 is given. Note that for three metals HC5 is lower than the total background concentration. The fraction bio-available of the background levels are not yet known, therefore an estimate of MPC could be obtained from calculations, carried out for two levels of bio-availability of the total background. In Table 2.1 background effects are calculated for both 100% and 10 % bioavailability of  $Cb$ .

Table 2.1: Geochemical and ecotoxicological properties of five metals in Dutch surface waters. HC5 and C<sub>b</sub> in µg/L (dissolved); F<sub>Ub</sub> is the effect related to the natural background concentration at bioavailability 100% ( $\phi = 1$ ) and 10% ( $\phi = 0.1$ ).

metal	$\alpha$	$\sigma$	HC5	C <sub>b</sub>	F <sub>Ub</sub> ( $\phi=1$ )	F <sub>Ub</sub> ( $\phi=0.1$ )
arsenic	2.93	1.00	20.12	0.77	0.0040	0.0007
chromium	2.16	1.16	1.95	0.17	0.0098	0.0021
cadmium	1.20	1.03	0.34	0.08	0.0172	0.0030
copper	1.11	0.83	0.55	0.44	0.0408	0.0049
zinc	1.93	0.71	6.07	2.8	0.0217	0.0017

In Table 2.2 the results are given for the case  $\phi = 1$ . Values of maximum permissible additions to the background, C<sub>a</sub>, range from 0.5 (zinc) to nearly 22 (arsenic) times C<sub>b</sub>. In Table 2.3 the calculation is repeated for  $\phi = 0.1$ , leading to results that do not differ very much from Table 2.2.

Table 2.2: Proposed Maximum Permissible Concentrations (µg/L, dissolved) for five metals in Dutch surface waters taking into account the natural background concentration at bioavailability 100% ( $\phi = 1$ ).

metal	C <sub>a</sub> (µg/L, dissolved)	F <sub>U<sub>max</sub></sub>	MPC <sub>water</sub>
arsenic	21.5	0.054	22.2
chromium	2.4	0.059	2.6
cadmium	0.42	0.066	0.5
copper	0.63	0.089	1.1
zinc	5.6	0.071	8.4

Table 2.3: MPCs for five metals in Dutch surface waters taking into account the natural background concentration at bioavailability 10% ( $\phi = 0.1$ ).

metal	C <sub>a</sub> (µg/L, dissolved)	F <sub>U<sub>max</sub></sub>	MPC <sub>water</sub>
arsenic	20.4	0.051	21.4
chromium	2.1	0.052	2.2
cadmium	0.36	0.053	0.44
copper	0.57	0.055	1.0
zinc	6.0	0.052	

Toxic stress resulting from exposure to naturally occurring toxicants has an ecological function and should not be considered undesirable. It is postulated here that if natural background concentrations are partly bio-available they may cause effects that can be evaluated as the fraction unprotected,  $F_{ub}$ , from laboratory ecotoxicity data. Therefore, if background concentrations are taken into account they must be based on activity, or bio-availability, to be able to estimate the extent of the natural effect on the diversity of species in the component ecosystem. We propose to calculate these effects using the cumulative logistic distribution of  $\log(\text{NOEC})$ . It is also proposed to include the unavailable background in the Maximum Permissible Concentration as it is presumed that no effect is related to this fraction. The total background can be obtained from direct measurement or, if the anthropogenic contribution in some region is too high, from geochemical models (Van der Weijden & Middelburg, 1989). The inactive part of MPC is assumed not to contain any anthropogenic contribution as it is the product of the total background concentration and the unavailable fraction, for which, if no information exists and only for this particular purpose, tentatively the default values 1 for soil and 0 for the water compartment may be taken as satisfactory approximations.

The introduced method was developed because an already existing method for xenobiotic chemicals proved unsatisfactory. It was attempted to find a modification of the existing MPC method for xenobiotics, taking into account the background levels. The result, however, is a method which should be regarded as a *general* procedure, valid for all chemicals, naturally occurring or not. This general procedure reduces to the well-known "HC5 method" in case the natural background is zero. Example a) in Figure 8 shows that for xenobiotics,  $C_a$  is equal to HC5 and also identical to MPC. If there is a background concentration but it is 100 % unavailable, the maximum permissible addition to the background equals HC5, and MPC is simply derived as the sum of  $C_b$  and HC5, shown as example b) in Figure 8. The hazardous concentration for 5 % of the species, HC5, disappears in the expression of MPC if part of the

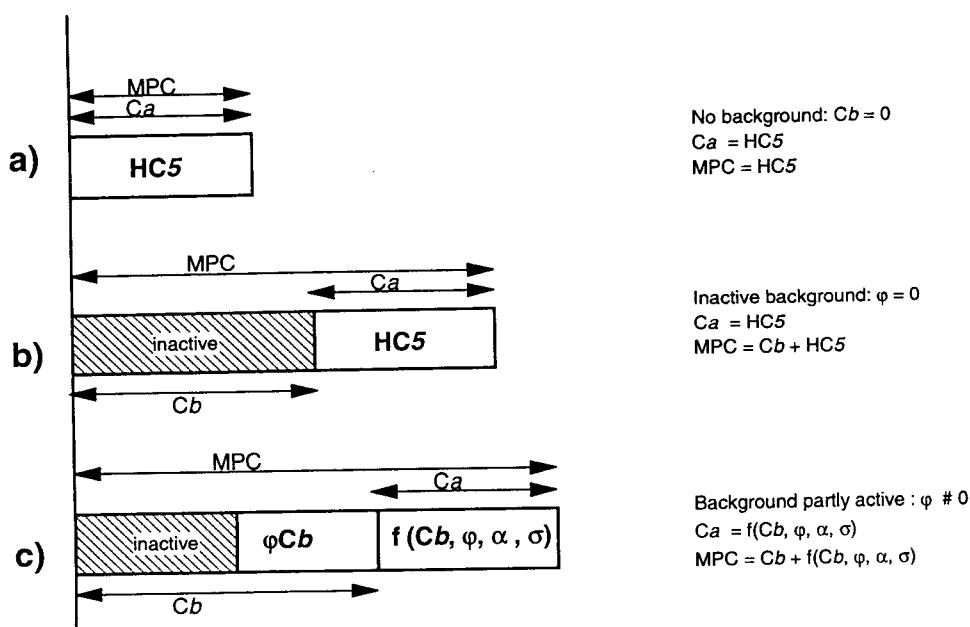


Figure 8: Results of the general procedure for deriving Maximum Permissible Concentrations of anthropogenic chemicals.

background is bio-available, shown as example c) in Figure 8. In that case the maximum permissible addition,  $Ca$ , is dependent on the total background concentration, the fraction available and the cumulative NOEC distribution curve, characterized by the average of  $\log(\text{NOEC})$  and the standard deviation. This paper offers a unified procedure for deriving MPCs, taking into account the bio-available background levels.

In the example of Figure 7 the  $\sigma$ -values represent the extremes for metals in natural environments, as for most heavy metals  $0.6 < \sigma < 1.2$  (see also Table 2.1). The effect limitation method has the advantage that, independent on  $\sigma$  and the  $\varphi Cb/HC5$  ratio, a specified fraction (for example 5%) of all species *not affected by the background* is the added risk. Thus if a high fraction is influenced by some available background - a relatively high  $\varphi Cb$  causes a significant effect  $Fu_b$  - the added risk is attenuated to a value considerably lower than 0.05 because this fraction is multiplied by a factor also significantly lower than one: the fraction  $(1 - Fu_b)$ . The maximum permissible concentration addition,  $Ca$ , then strongly depends on the steepness of the cumulative species sensitivity curve and may be rather stringent or close to  $Cb$  if  $\sigma$  is low but less stringent if  $\sigma$  is high. A low  $\sigma$  indeed is a good reason for a more stringent maximum permissible addition while in case  $\sigma$  is high it is justifiable to derive a higher  $Ca$ . In both cases deriving maximum permissible concentrations relies upon effect assessment.

Deriving MPCs according to this method has the advantage that it is genuine risk limitation and should be the preferred procedure in setting environmental quality objectives. From a practical point of view, however, it is a disadvantage that  $\varphi$  has to be known. An MPC derived according to this risk limitation method is dependent on  $\varphi$  because  $Ca$  is dependent on  $\varphi$ .

It should be emphasized here that not only Figures 5 and 6 over-simplify, but that also Figure 3 is a poor representation of reality. Generally, especially for soil, the availability of toxic substances diminishes with time, also if they are from anthropogenic origin. Although the diagram of Figure 9 would be more realistic, it still is a simplification as it does not distinguish between "old" and "recent" anthropogenic and the corresponding differences in availability. Moreover, it may have a very low applicability because for most metals such detailed information on different levels of availability is simply not known.

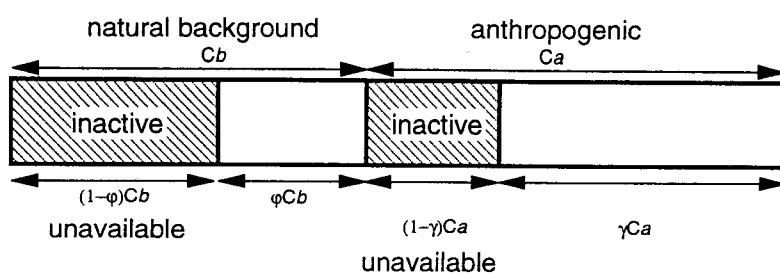


Figure 9: Illustration of differences in availability between natural background and anthropogenic concentrations.

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