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Environmental Risk Limits for Ethylene Diamine Tetra Acetic acid (EDTA)

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Abstract

In this report maximum permissible concentration (MPC) and negligible concentration (NC) in water are derived for Ethylene Diamine Tetra Acetic acid (EDTA; CAS No. 64-02-8, EINECS No. 200-573-9), based on the EU risk assessment report for this compound. The Maximum Permissible Concentration (MPC) for the water compartment is 2.2 mg/l, and the Negligible Concentration (NC) is 0.022 mg/l. Calculation of MPCs for sediment or soil is not possible due to complex speciation of EDTA.

Preface

We want to acknowledge drs. E.M. Maas from the Ministry of Housing, Spatial Planning and the Environment (VROM-DGM-SAS), dr. M.P.M. Janssen who are involved in the RIVM-project 601501 in which the work was performed.

The results as presented in this report have been discussed by the members of the 'Setting Integrated Environmental Quality Standards Advisory Group' (OZBG-ECO), who are acknowledged for their contribution. The advisory group provides a non-binding scientific comment on the final draft of a report in order to advise the steering committee of the project Setting Integrated Environmental Quality Standards (INS) on the scientific merits of the report.

Contents

Samenvatting

Voor Ethyleendiamine tetra-azijnzuur (EDTA; CAS No. 64-02-8, EINECS No. 200-573-9) is een Europese risicobeoordeling gemaakt in het kader van de beoordeling van bestaande stoffen, Eu-richtlijn 793/93. De in deze EU-beoordeling verzamelde toxiciteitsdata zijn gebruikt als basis voor de normafleiding volgens EU-richtlijnen. Daar waar er geen EU-equivalent bestaat van een norm, bijvoorbeeld voor het verwaarloosbaar risico (VR), worden de Nederlandse methoden gebruikt.

Wanneer er emissies van EDTA naar het oppervlaktewater plaatsvinden zal de stof (nieuwe) complexen vormen met de metalen die aanwezig zijn in de waterfase en het sediment. Welke vormen er zullen ontstaan en hoe snel hangt af van de aanwezige metalen en of deze metalen wel of niet gebonden zijn aan organische stof, zwevend slib of sediment. De speciatie kan niet voorspeld worden met eenvoudige equilibrium benaderingen. Door de complexvormende eigenschappen kan EDTA potentieel de natuurlijke balans van essentiële elementen verstoren. Hierdoor kan remobilisatie van zware metalen niet uitgesloten worden. De consequentie hiervan is dat het zeer moeilijk is om met voldoende zekerheid de speciatie in natuurlijke systemen te berekenen die zowel verschillende sorptiefasen kent als ook complexvormende agentia met goed en slecht gedefinieerde stabiliteitconstanten voor de elementen die van interesse zijn. Met enige voorzichtigheid kan ook geconcludeerd worden dat EDTA aanwezig is in Nederlandse rivieren in dusdanige gehaltes, dat deze een belangrijke rol kunnen spelen bij de controle van het speciatiepatroon van verschillende essentiële elementen.

Op basis van de data en methodiek in de EU-beoordeling is het Maximaal Toelaatbare Risiconiveau (MTR) voor het water compartiment 2,2 mg/l en het Verwaarloosbare Risiconiveau (VR) 0,022 mg/l. Vergelijking van de MTR met gemeten gehaltes van EDTA in de grote Nederlandse rivieren in de jaren 1997/1998 laat zien dat risico ten gevolge van EDTA toxiciteit (zonder interacties met essentiële elementen) niet waarschijnlijk is omdat geen enkele meting de MTR overschrijdt.

Voor de compartimenten sediment en bodem zijn geen toxiciteitdata beschikbaar. Berekening van de MTR's voor deze compartimenten met behulp van de equilibrium-partitie methode is niet mogelijk door de complexvormende eigenschappen van EDTA.

Summary

A European risk assessment report has been made for Ethylene Diamine Tetra Acetic acid (EDTA; CAS No. 64-02-8, EINECS No. 200-573-9) according to the EU Existing Substances Regulation 793/93. The toxicity data and methods from the EU report have been used as a scientific basis for environmental risk limits for EDTA. When no EU equivalents exist for Dutch environmental risk limits, these are derived according to national procedures.

When emitted to surface water, EDTA forms (new) complexes with the metals present in the water phase and the sediment. Which species are formed and how fast depends on the metals present and whether or not these metals are bound to organic matter, suspended matter or sediment. The speciation can not be predicted using simple equilibrium principles. As a result of the complex forming capability, EDTA could potentially disturb the natural balance of essential elements. It is concluded that remobilization of heavy metals can not be excluded. The consequence is that at present it is very difficult to calculate with enough certainty the speciation in natural systems containing various sorption phases as well complexing agents with well and poor defined stability constants for the elements of interest. Although to be taken with some care, it is concluded, that EDTA appears to be present in Dutch River systems at such levels that they play an important role in controlling the speciation pattern of various essential elements.

Based on the toxicity data and methods of the EU report, the Maximum Permissible Concentration (MPC) for the water compartment is 2.2 mg/l, whereas the Negligible Concentration (NC) is 0.022 mg/l. A comparison of measured EDTA levels in the rivers Rhine, Meuse and IJssel during the years 1997/1998 shows that risks due to EDTA toxicity alone (without interaction with essential elements) are unlikely since no measured values exceed the MPC.

For the sediment and soil compartment no toxicity data are available. Calculation of MPCs for these compartments based on the equilibrium partitioning method is not suitable for EDTA due to the complex speciation.

1.   Introduction

This report is a result in the project 'Setting Integrated Environmental Quality Standards'. In this report Environmental risk limits (ERLs) will be derived in a way, which differs from the standard procedure used in the above-mentioned project. Toxicity data for Ethylene Diamine Tetra Acetic acid (EDTA) have been collected and evaluated on a European level (EU-RAR 2003). Therefore, this report will only contain the toxicity data that have been derived in the context of the European risk assessment. However, it should be noted that EDTA is a complexing agent and not a 'standard' toxicant.

Environmental risk limits (ERLs) serve as advisory values to set environmental quality standards (EQS) by the Ministry of VROM for various policy purposes. The term EQS is used to designate all statutory and non-statutory binding standards that are used in Dutch environmental policy and Table 1 shows the correspondence between ERLs and EQSs.

Table 1. Environmental Risk Limits (ERLs) and the related Environmental Quality Standards (EQS)
that are set by the Dutch government in The Netherlands for the protection of ecosystems.
NC   Negligible Concentration
MPC   Maximum Permissible Concentration
SRC$_{eco}$ Serious Risk Concentration for the ecosystem

Description	ERL	EQS
The NC represents a value causing negligible effects to ecosystems. The NC is derived from the MPC by dividing it by 100. This factor is applied to take into account possible combined effects.	NC (for air, water, soil, groundwater and sediment)	Target Value (for air, water, soil, groundwater and sediment)
The MPC is a concentration of a substance in air, water, soil or sediment that should protect all species in ecosystems from adverse effects of that substance. A cut-off value is set at the fifth percentile if a species sensitivity distribution of NOECs is used. This is the Hazardous Concentration for 5% of the species, the HC_5^{NOEC}.	MPC (for air, water, soil, groundwater and sediment)	MPC (for air, water, sediment and air)
The SRC$_{ECO}$ is a concentration of a substance in the soil, sediment or groundwater at which functions in these compartments will be seriously affected or are threatened to be negatively affected. This is assumed to occur when 50% of the species and/or 50% of the microbial and enzymatic processes are possibly affected.	SRC$_{ECO}$ (for water, soil, groundwater and sediment)	Intervention Value (for soil, sediment and groundwater)

The various ERLs are:
- the Negligible Concentration (NC) for water, soil, groundwater, sediment and air
- the Maximum Permissible Concentration (MPC) for water, soil, groundwater sediment and air
- the Ecotoxicological Serious Risk Concentration for water, soil, groundwater and sediment (SRC_{ECO}).

Status

For EDTA (CAS No. 64-02-8, EINECS No. 200-573-9) there is a provisional EU risk assessment report available (draft version 07.02.2003). In this report environmental risk limits have been derived according to the Technical Guidance Document (ECB, 1996).

2. Methodology

The collection and screening of the literature on toxicity to derive environmental risk limits has already been done within the European frame. The method described in the Technical Guidance Document (ECB, 1996) differs from the standard procedure, that is used in the INS project. In this report, the European risk limits, 'predicted no-effect concentrations' (PNEC-values) will be converted to environmental risk limits for water, soil, and sediment if possible. Hereto, the procedure as described in the "Guidance Document on deriving Environmental Risk Limits" (Traas, 2001) will be followed.

Conversion to the Dutch situation

In the EU-RAR document PNEC's are mentioned for the different environmental compartments. In the Netherlands environmental quality standards are reported differently. For the Dutch standard water a distinction is made for 'dissolved' and 'total', for which a standard amount of 30 mg dw/l suspended matter is assumed, consisting of 20% organic matter and 40% clay. In the EU standard water consists of 15 mg/l suspended matter.

The MPCs for dissolved organic compounds in water can be recalculated to the total water phase, based on differences in the content of organic matter. The following equation is used to calculate the MPC$_{water,total}$:

$$MPC_{water,total} = MPC_{water,dissolved} (1 + K_{ppm} \times 0.001 \times 0.03)$$

With   0.001 = conversion constant [g/kg]
          0.03   = content of suspended matter (g/l) (considered the standard)
          K_{ppm} = partition coefficient suspended matter/water

K_{ppm} is calculated from the Kp sediment/water or from the K_{oc}. Suspended matter is standardised at an organic matter content of 20% (or organic carbon content of 11.72 %), twice as high as standardised soil or sediment (cf. section 4.4.3). This means that the K_{ppm} is twice as high as the Kp for sediment/water. If the K_p sediment/water is estimated from the K_{oc}, the following equation applies (cf. 4.4.2) for suspended matter as well:

$$K_{ppm} = K_{oc} * f_{oc}$$

in which:
K_{ppm} = partition coefficient for standard suspended matter [l/kg]
K_{oc} = organic carbon-normalised partition coefficient [l/kg]
foc   = fraction organic carbon (0.1172 [g oc/ g dw suspended matter])

The NC$_{water,total}$ is defined as the $_{MPCwater,total}$ /100.

3.   Ethylene Diamine Tetra Acetic Acid (EDTA)

In this chapter a summary is given of the physical- and chemical properties of H_4EDTA and Na_4EDTA (CAS No. 64-02-8, EINECS No. 200-573-9). All data are derived form BUA (1995) and in some cases more recent additional information is used.
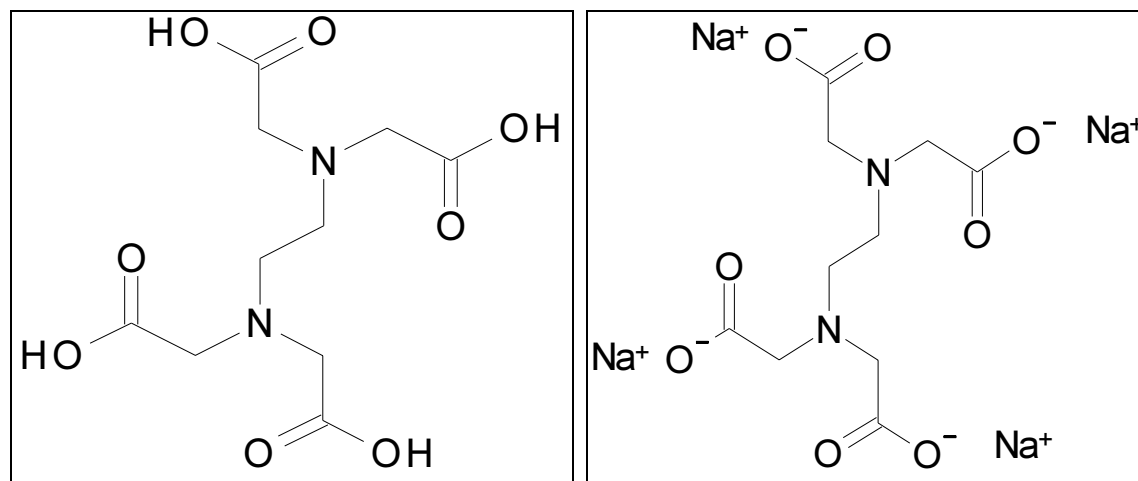
3.1   Physical- and chemical properties of EDTA

Figure 1. Structural formula of H_4EDTA (left) and Na_4EDTA (right), derived from BUA, (1995).

EDTA has six coordination sites (hexadentate ligand) for 'binding' metal ions, so called chelates, and contains four carboxylic groups (see Figure 2). The metal ions are actually surrounded by the complexing agent. EDTA forms complexes on 1:1 or 1:2 molar ratio. The active unit of EDTA is the EDTA4- anion. The concentration of this anion increases with increasing pH in aqueous solutions, due to dissociation of the various chargeable groups (see Figure 2).

In Table 2 the chemical identity and the physical- and chemical properties of EDTA are summarised. Most data are derived from BUA (1995) except for a number of calculated properties using the EPIWIN (1997) program. From the table it can be deduced that EDTA is completely miscible with water and has very low estimated log Kow values. Considering the very low Henry's constant EDTA present in the water phase will not enter the environmental compartment air in substantial quantity.
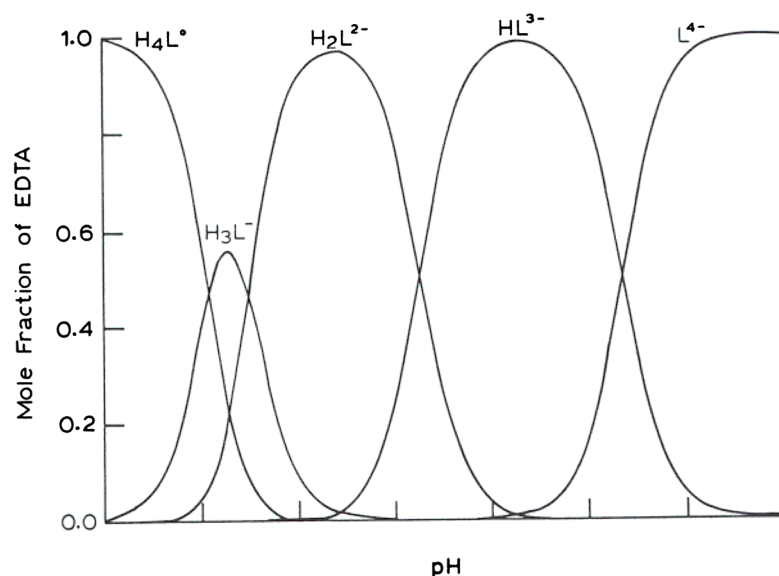
Figure 2. Distribution diagram of EDTA anion as a function of the acidity of the solution (Lindsay, 1979).

Table 2. Properties of H_4EDTA

IUPAC name	N,N'-1,2-Ethanediylbis-[N-(carboxymethyl)glycine]
Empirical formula	$C_{10}H_{16}N_2O_8$
CAS number	60-00-4
EINECS number	200-449-4
Molar mass	292.3
Water solubility	Completely miscible
Vapour pressure	$4.98*10^{-13}$ mm Hg at 25°C (EPIWIN, 1997)
Henry's constant	$1.17*10^{-23}$ atm.m^3/mol (EPIWIN, 1997)
n-Octanol/water partition coefficient[1]	Estimated -3.34 (method of Recker's)
	Estimated -5.01 (method of Hansch and Leo)
	Estimated -3.86 (EPIWIN, 1997)
pK values	1) 0.9 BUA (1995)
	2) 1.6 BUA (1995)
	3) 2.0 BUA (1995)
	4) 2.67 BUA (1995)
	5) 6.16 BUA (1995)
	6) 10.26 BUA (1995)
	Dissociation constants 5 and 6 are for the amino groups

[1] for ionic substances the partition coefficient can not be determined experimentally. According to Hansch and Leo, the partition coefficient for the undissociated free acid was calculated to be –5.01. In the EU-RAR for the exposure calculations, the lowest value accepted by EUSES (logK_{ow} –1) was used.

3.2   Use and production

The annual usage of EDTA in Western Europe from 1988 to 1994 was between 26,000 and 30,000 tonnes (BUA, 1995). Approximately 1200-1500 tonnes (1400 tonnes averaged) of EDTA were sold in the Netherlands in the same period. EDTA is utilised extensively in a

wide variety of industries (e.g. metal, rubber, leather, photographic, textile, pulp and paper, pharmaceutical, chemical and cosmetic). Generally, the complexing properties of EDTA are used to prevent undesirable effects of heavy metals. In BUA (1995) an extensive overview of EDTA, its use and applications can be found.

3.3   Discharge and concentrations of EDTA in the environment

Various analytical methods are available to analyse EDTA in water. However, most methods deal with the determination of total EDTA including charged and complexed forms. Recently, Owens et al. (2000) examined the use of capillary electrophoresis for chelate analysis and found this method to be a success in qualitative and quantitative sense. Since the method is very recent it is not yet incorporated in current monitoring programs.

Discharge of EDTA into the environment (mainly surface water) occurs via wastewater from waste water treatment plants. Approximately 5–8 % of the annual EDTA (as an ingredient of agricultural fertilisers) is discharged directly on agricultural soils (BUA, 1995).

Many data are available on measured total EDTA concentrations in the European surface- and waste water (BUA, 1995; Sillanpää, 1997). The results of these measurements are within a range of 0-62 µg/l (90th percentiles) for surface water. Higher concentrations are found for rivers and the lower values for stagnant waters. Wastewater concentrations are much higher, up to 1700 µg/l, and appear to be highly variable. The most recent 90th percentile values available are 9.8 µg/l and 19.3 µg/l for the river Rhine and 41 µg/l and 15.3 µg/l for the river Meuse (RIZA, 1997 and 1998a); (see Figure 3 up to Figure 6). These data are comparable to data for 1989 reported by Van Dijk-Looyaard et al (1990). Recently, Rozan and Benoit (1999) found maximum EDTA concentrations of about 20 µg/l for some river systems in the State of Connecticut (USA), indicating that environmental contamination with EDTA is a world wide phenomenon.

In Table 3 the basic statistics for the monitoring data presented in Figure 3 up to Figure 6 are presented. From the statistics in the table it may be concluded that measurements vary, causing relatively high standard errors of the mean.
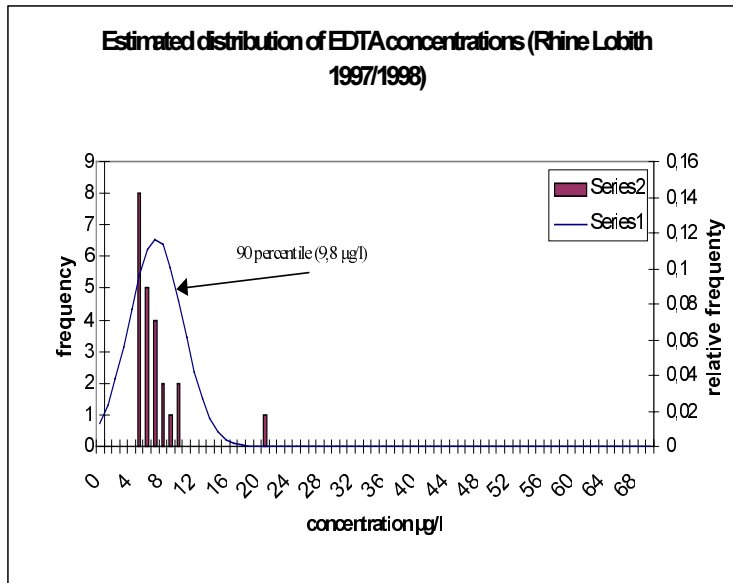
Figure 3. 90th percentile values of EDTA in the river Rhine (Lobith) in 1997/1998.
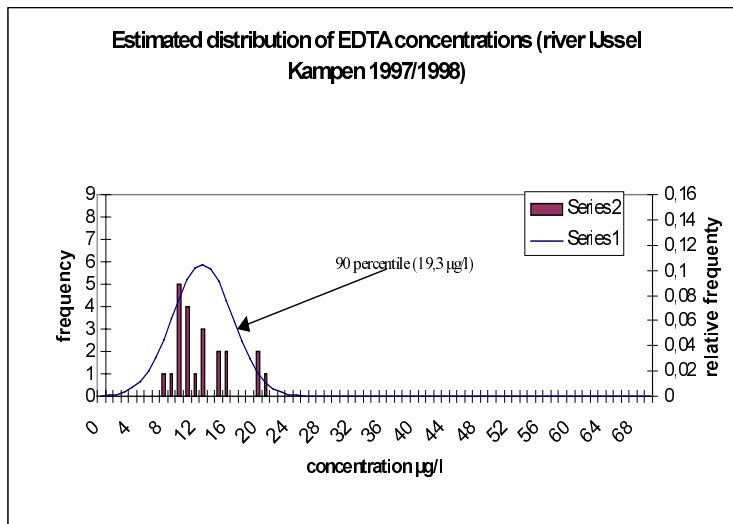

Figure 4. 90th percentile values of EDTA in the river IJssel (Kampen) in 1997/1998.
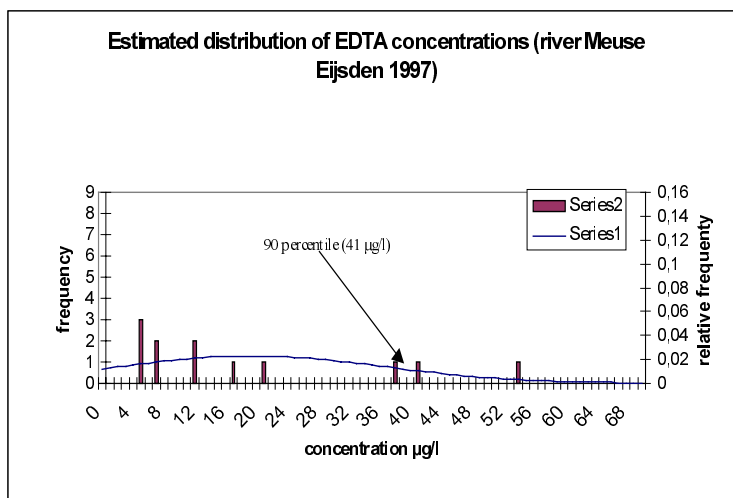

Figure 5. 90th percentile values of EDTA in the river Meuse (Eijsden) in 1997/1998.
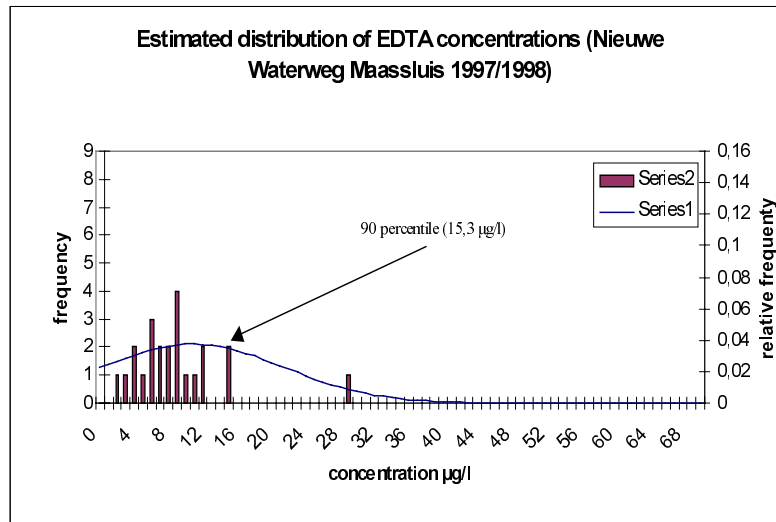
Figure 6. 90th percentile values of EDTA in the river Meuse (Maassluis) in 1997/1998.

Table 3. Statistical properties for EDTA concentrations measured in various Dutch surface waters during the period 1997-1998

	Meuse (Eijsden)	IJssel (Kampen)	Rhine (Lobith)	Meuse (Maassluis)
Mean	19.3	13.3	7.1	11.2
Standard Error	5.2	0.8	0.7	2.3
Median	12.0	12.5	6.0	8.5
Standard Deviation	17.3	3.7	3.4	11.1
Sample Variance	300	14	12	123
Range	49	12	16	52
Minimum	5	9	5	2
Maximum	54	21	21	54
Count	11	20	23	22
Confidence Level (95,0%)	11.6	1.7	1.5	4.9

The concentrations in the river Meuse are significantly (Bartlett's, $\alpha=0.05$) higher than the concentrations measured in the river Rhine (Lobith), which is probably caused by the eight times lower water debit of the river Meuse (RIZA, 1998b). The concentrations measured in the IJssel near Kampen are also significant higher than the concentrations in the river Rhine near Lobith. Since IJssel water consists solely of Rhine water, additional EDTA must be emitted to the river water in such amounts that the concentration increases. Moreover, in The Netherlands rainwater is in excess when compared to the loss caused by evaporation. The average concentration near Maassluis is not significantly different from the other three locations and is intermediate between the concentrations found for the Meuse and Rhine inlet in the Netherlands. Maassluis water is a mixture of water from various Dutch rivers, which means that concentrations will level with each other.

From the average EDTA concentrations in the Rhine and Meuse (7 µg/l and 19 µg/l), and the total water input for the same rivers (69,000 and 8,400 Million m^3 water, respectively, RIZA, 1998b), it may be concluded that a large part of the EDTA found in Dutch surface water originates from other countries in the Rhine and Meuse basin. A load of approximately 640 tons of EDTA is estimated to enter the Netherlands yearly. This tonnage is approximately half the amount sold in the Netherlands yearly (average 1400 ton/year over the years 1988-1993; BUA (1995)). Assuming that all EDTA sold in the Netherlands is emitted to the Rhine and Meuse watershed (worst-case), it is estimated that approximately 31 percent of the EDTA found in the Dutch river water originate from the other countries in the Meuse and Rhine basin.

Data on EDTA concentrations in soil are scarce. BUA (1995) cited Lübbe (1989) who estimated EDTA concentrations of 0.02-0.1 mg/kg in topsoils (arable land) after the use of trace nutrient fertilisers. The concentrations in soil (not arable land), are generally expected to be low because emissions are primarily released to surface water and EDTA has high affinity for the water phase (BUA, 1995).

No data were found on EDTA concentrations in sediments.

4.   Fate and behaviour in the environment

In this chapter the results of the literature search on; biodegradation, photo-degradation, hydrolysis, accumulation and ecotoxicology are presented. It should be noted that the results on degradation processes are not complete and present an overview of the most important data available; for MPC derivation these data are of secondary importance.

4.1   Biodegradation

EDTA complexes are found to be relatively persistent in the environment and in Wastewater Treatment Plants (BUA, 1995). Test results summarised in BUA (1995) however, show contradictory results: in most tests (activated sludge, sewage water and surface water) slow or no biodegradation was observed, whereas other tests resulted in partly or complete degradation (BUA (1995) and AKZO Nobel, unpublished data). According to Means et al. (1980) these contradictory results are most likely the result of differences in the speciation of EDTA. In general it can be stated that biodegradation depends on the presence of the right microbial populations and on other favourable conditions, such as temperature and pH. This opinion is confirmed by Nörtemann (1999) who found that EDTA is not degraded in conventional tests, but is degraded under optimal biological conditions in waste water treatment plants. Whether or not these favourable conditions occur under natural conditions remains, is at present hard to predict. The high concentrations reported in chapter 3 suggest hardly any, or very low degradation rates or a combination of high emission and degradation. The latter is expected to be most likely.

4.2   Photo-degradation and hydrolysis

Most EDTA-metal complexes are found to be relatively stable. Photo-degradation rates depend on natural conditions in the surface water. The occurrence of photo-degradation of EDTA strongly depends on the EDTA species present. Thus, laboratory test might not be directly comparable with field conditions. The set-up and conditions of most of the available photo-degradation tests are rather unrealistic when compared to surface water conditions. This makes it difficult to assess whether or not this type of degradation is of significant impact in lowering the environmental concentrations. Some authors (cited in BUA, 1995) report that photo-degradation for Fe(III)EDTA occurs to some extend in tests under artificial sunlight conditions. EDTA is resistant to hydrolysis (BUA, 1995).

4.3   Accumulation

Based on the very low calculated n-octanol/water partition coefficient (K_{ow}) of EDTA it may be expected that EDTA is not likely to accumulate in organisms. A long term accumulation test with *Lepomis macrochirus* in a flow-through system resulted in BCF values between 0.8 and 1.9 (Bishop and Maki, 1980 cited in BUA, 1995), which confirms the conclusion that EDTA is not likely to accumulate in organisms. An average BCF value of 1 is proposed in BUA (1995).

Less is known about the accumulating effects of EDTA itself. Most research has been performed on the accumulation of metals in the presence of EDTA. EDTA is known to reduce the uptake and accumulation of cadmium in laboratory tests by various organisms with 25% up to 75% (Hung, 1982; Rainbow et al., 1980; Pärt and Wikmark, 1984; Greger and Lindberg, 1986; Ray et al., 1979; Poldoski, 1980; all references cited in BUA, 1995). However, Gutiérrez-Galindo (1981) and George and Coombs (1977) found promoted adsorption of mercury and cadmium by *Mytilus edulis* in the presence of EDTA. The contradictory results give the impression that accumulation strongly depends on the conditions of the test, the species involved, the amount of EDTA present, and the metal concentrations.

4.4   Eutrophication effects

Nitrogen and phosphorus are growth-limiting elements in fresh and saltwater systems, respectively. If these elements are present in excess the growth will be limited by other essential elements present in the water phase. EDTA contains nitrogen in a relatively large amount. When mineralised or degraded this nitrogen may in potential have growth stimulating effects on algae. Hence, additional EDTA enhances growth of different species of algae in laboratory tests is summarised by Sillanpää (1997). Another EDTA related process that in potential may increase alga growth in an indirect way, is desorption of sediment bound trivalent iron ions. Trivalent iron is usually bound in sediments as inorganic phosphate salt. The binding of the trivalent iron causes remobilization of phosphate.

Although the mentioned eutrophic effects may occur, the impact on the environment is expected to be low. The first reason is that the contribution of EDTA as nitrogen source and indirect releaser of phosphate is expected to be negligible when compared to other nitrogen and phosphate inputs. The second reason is that EDTA should be mineralised to become an accessible nitrogen source for organisms, which is not the case in most environmental situations (see chapter 3).

4.5   Speciation and adsorption

Not much data are available on the adsorption of EDTA itself to sediment, particulate- and organic matter. Bowers and Huang (1986), cited in Silanpää (1997), reported that sorption of EDTA to clay minerals and sediments was negligible. Virtapohja and Alen (1999) found that a maximum of 4% (10°C) and 7% (22°C) of the initial EDTA was absorbed within 4 weeks.

To be able to quantify the speciation in the environment model calculations using the mass balance of all metals present, the partition coefficients of metals between sediment/particulate- and organic matter and the stability (affinity) constants of these metals towards EDTA, and the amount EDTA present are needed.

Gonsior et al (1997) concluded from a microcosm study that EDTA (approx. 18 µg/l) does not contribute significantly to the metal solubilisation from the sediment. This conclusion is based on observed No Observed Effect Levels for trace element solubilisation for: Ni, Co, Cu, Zn,

Cd, Fe and Pb. In this study the speciation between water and suspended matter was not taken into account because the samples were filtered. In addition, the static experiment is not comparable with rivers with low retention times. The same conclusion was drawn by Twachtmann et al. (1998) who found that remobilization of metals from the sediment in the presence of 100 µg/l EDTA had low environmental relevance. The conclusion of Twachtmann et al. (1998) however, is based on the assumption that mainly non toxic Zn is released and that EDTA use has declined and that replacement by Nitrilotriacetate (NTA) will be initiated. Contradictory results were cited in Sillanpää (1997) in which EDTA had a significant effect on the remobilization of metals from sediments. The latter results however, are based on EDTA concentrations that are much higher than the concentrations commonly found in surface water.

For Dutch River systems, with a pH varying between 7 and 8 (Buykx et al., 1999), about 75% of the carboxylic groups are dissociated, and, hence, the charged EDTA is able to complex metal ions. The total amount of metals complexed depends on the concentration of (dissociated) EDTA. For Dutch River waters, 90th percentile values were found from about 10 up to approximately 40 µg/l in the period of 1997-1998 (see paragraph 3.3.). Assuming 1:1 metal-EDTA complexes, the complexing capacity of EDTA in Dutch River waters is approximately 0.13 µmol/l. This seems to be quite significant if one considers that total complexing capacities for copper for Dutch River waters were found to vary from 0.17 to 0.43 µmol/l (Buykx et al., 1999).

Table 4. Average total concentrations of several essential elements at different locations in Dutch surface waters for 1997 (RIWA, 1997).

	Lobith	Hagesteijn	Andijk	Stellendam
Calcium (mmol l^{-1})	2.12	1.87	1.72	1.80
Magnesium (mmol l^{-1})	0.48	0.46	0.57	0.51
Iron (µmol l^{-1})	20.77	8.95	6.80	4.83
Manganese (µmol l^{-1})	1.27	0.73	0.91	1.27
Copper (µmol l^{-1})	0.08	0.11	<LOD	<LOD
Nickel (µmol l^{-1})	0.06	0.05	<LOD	0.14
Zinc (µmol l^{-1})	0.37	0.23	0.05	0.52

LOD: limit of detection

In Table 4, for 1997 average concentrations of a number of essential elements measured at various places in the River Rhine are presented. All data refer to total concentrations. Taking into account that iron will be mainly present as colloidal material the actual concentration of free iron ions is much smaller. Note that concentrations are given in moles per litre in order to compare the data with the binding capacity of EDTA and the complexing capacities of surface waters.

Total nickel and copper concentrations are mainly below the complexing capacity of EDTA or dissolved organic matter, whereas total calcium and magnesium concentrations are much higher. Hence, the sum of essential elements is much larger than the total complexing capacity of the surface water.

For mixed systems, such as river waters, the final distribution of elements over different physical-chemical forms in solution is strongly depend on the stability of the element-complex system. Element-EDTA stability constants are presented in Figure 7 (Grenthe *et al.*, 1997). The smallest value has been found for caesium, whereas the highest is reported for zirconium (note that the difference in K-value for these two complexes is more than 30 log units). Tabulated values are available in several references (Lindsay, 1979; Sillén and Martell, 1971).
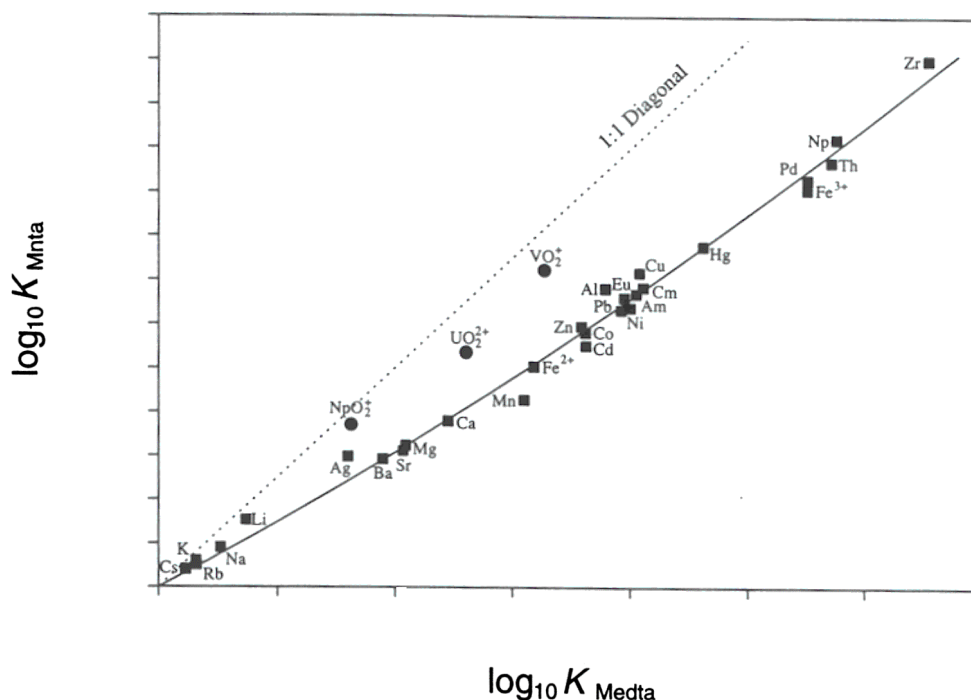

Figure 7. Stability constants for EDTA and NTA complexes, and their mutual correlation Grenthe et al. (1997).

On the basis of chemical thermodynamics, it is expected that under equilibrium conditions complexes with the highest stability will be formed. For the essential elements considered here, we get: $Fe^{3+} > Cu > Ni > Co > Zn > VO_2^+ > Fe^{2+} > Mn > Ca > Mg$. However, the actual speciation in natural water solutions is also highly dependent on the presence of other complexing agents. For the pH range and elements of interest, they consist of both small anionic, like OH^-, and large macromolecular organic ligands, like humic and fulvic acids. Stability constants for the former group of ligands are readily available (Lindsay, 1979; Sillén and Martell, 1971). Although the interaction phenomena of various elements with humic and fulvic acids are well understood in a qualitative way, it seems to be impossible to derive unique stability constants for these type of complexing ligands. Competitive behaviour of the

essential elements itself, or other cationic species present in solution will influence the speciation pattern as well depending on their actual concentration. For example, although the stability of the Ca-EDTA complex is smaller than the Zn-EDTA complex, excess of calcium over zinc concentrations in Dutch Rivers (see Table 4) will result in a different speciation pattern compared to a system without calcium. In addition, in soils and sediments other solid adsorption phases, like clay minerals, organic matter and (hydr)oxides of Si, Al, Fe and Mn, should be taken into account. On the other hand, from sorption studies of zinc onto clay minerals it was found that the amount of adsorbed zinc decreased with increasing EDTA concentration (Pickering, 1980). Hence, non-mobile elements are liberated, which might result in transport of the element.

Kinetics of the association and dissociation reactions is another aspect to consider in predicting the speciation of essential elements in natural systems. This is of particular interest if a specific constituent (e.g. an element or complexing agent) is added to the natural system, as is usually the case for industrial emissions. Hering and Morel (1989) studied the exchange reactions in a system containing Ca-EDTA and Ca humate to which copper was added. Initially, Cu was found to exchange with Ca bound to humate, because this form of binding is weaker than in case of Ca-EDTA. But with increasing time copper could displace the calcium bound EDTA, which appeared to be depending on the humate concentration. Furthermore, the less Ca in the system, the less likelihood of Cu-humate formation, and hence the more quickly Cu-EDTA will form. In Table 5 some examples of reaction rate constants of metal exchange reactions for EDTA are presented (Ritchie and Sposito (1995). Rozan and Benoit (1999) mention that introduction of Fe-EDTA to river systems may limit the Cu-EDTA complexation due to slow exchange kinetics (Xue et al., 1995).

Table 5. Examples of reaction rate constants for metal exchange reactions for EDTA Ritchie and Sposito (1995).

Complex	Metal	Rate constant
$Cd(EDTA)^{2-}$	Cu^{2+}	2.2
$Cd(EDTA)H^{-}$	Cu^{2+}	45
$Co(EDTA)^{2-}$	Cu^{2+}	15.3
$Cd(EDTA)^{2-}$	Zn^{2+}	0.23
$Ni(EDTA)^{2-}$	Zn^{2+}	$2.5*10^{-6}$
$Pb(EDTA)^{2-}$	Ni^{2+}	$2.7*10^{-2}$
$Pb(EDTA)^{2-}$	Cu^{2+}	0.89
$Zn(EDTA)^{2-}$	Cu^{2+}	19
$Zn(EDTA)^{2-}$	Ni^{2+}	$6.7*10^{-4}$

A complicating factor in determining the speciation of elements in natural surface waters is related to variations in solution composition as a consequence of seasonal variations. For example, the oxygen content is lower during the summer than during the winter, as has been shown by Zwolsman for the River Scheldt (Zwolsman, 1999). This will result in changes in redox conditions and, hence, in the speciation pattern of a number of elements. Rozan and

Benoit (1999) reported decreased dissolved organic carbon concentrations during wintertime, resulting in decreased copper complexing capacities in the same period. At constant EDTA concentrations, it is expected that this complexing agent will become more important in controlling the distribution of elements.

It has been shown in a number of dose response studies that the availability of elements for uptake by organisms is controlled by the presence of EDTA. For example, Verweij (1991) studied the effects of copper on *Scenedesmus quadricauda* in synthetic media containing EDTA as complexing agent. He concluded that at high levels of EDTA, some elements (copper, cobalt or zinc) became limiting. Comparable results were obtained by Anderson et al. (1978), who examined the growth of *Thalassiosira weissflogii* in a medium containing varies concentrations of zinc and EDTA. Due to complexation of zinc with EDTA, the growth-rate decreased. We note that the applied EDTA concentrations in these studies are usually much higher than EDTA concentrations observed under natural conditions. Lower EDTA concentrations tend to decrease the toxicity of various heavy metals due to lower bioavailability (Sillanpää and Oikari, 1996).

The total amount of essential elements in Dutch River systems exceeds the complexing capacity of the EDTA concentration. Not considering other complexing agents, this means that binding of essential elements will follow the order $Fe^{3+} > Cu > Ni > Co \sim Zn > VO_2^+ > Fe^{2+} > Mn > Ca > Mg$ based on thermodynamic data. For a complete and realistic picture, other aspects influencing the speciation pattern, such as other ligands and competitive cationic species should be taken into account. Calculations of the speciation using available software programs should be done with care, due to uncertainties in stability constants for natural organic material.

Association and dissociation rate constants of element-EDTA complexes vary in such a way that although the solution composition might be identical, the mixing order appears to be critical for the speciation pattern. The time necessary to complete the exchange reaction, i.e. to obtain equilibrium conditions, will probably exceed the residence time of the river water in the Netherlands. This conclusion is confirmed by Xue et al. (1995) who concluded that Fe^{3+}EDTA exchanges with Zn and Ca when introduced to surface water in approximately 20 days. This means that Fe^{3+}EDTA released into rivers might reach the sea unchanged. An average retention time is calculated of 11 days, using the average flow rate of the Rhine of 1.5 m/s in the Netherlands (RIZA, 1998b) and the total length of the river Rhine (1320 km). It is very likely that the average retention time of EDTA in this river is even shorter because emission occurs further downstream than the origin. It is recommended to extend the present overview with an in depth study to be able to draw more specific conclusions.

5.   Toxicity data and derivation of MPCs and NCs for water

5.1   EU(-RAR) risk assessment

In Tables 1 to 4 in Annex 2, chronic toxicity data for aquatic organisms as selected in the EU-RAR are presented. The presence of EDTA influences the bioavailability and uptake of metals. For the interpretation of toxicity tests, the complex formation properties of EDTA have to be taken into account as described in the EU-RAR (2003). A test previously selected but not considered in the EU-RAR is given in Table 5 in Annex 2.

For EDTA NOECs for four or more taxonomic groups are available. In the Netherlands, the method of Aldenberg and Jaworska (2000) would be used for deriving ERLs according to the INS protocol (Traas, 2001). However, as the data are derived from a provisional EU-RAR, the $MPC_{water, dissolved}$ will be determined using assessment factors. The assessment factors used are laid down in the Technical Guidance Document (ECB, 1996), which is developed in the framework of EU council regulation 793/93.

5.2   Derivation of ERLs for water

As mentioned earlier there is much discussion on the mechanism(s) which cause the toxicity of EDTA. The most likely mechanism is the depletion of elements as a result of the complex forming properties of EDTA. In laboratory tests elements may become exhausted but the same effect is not expected in surface water, as metals usually are present in excess over EDTA. Indirect effects are found which means that the actual toxicity of EDTA is overestimated. This means that it is possible to use these conservative results to derive a worst case MPC value. If thereupon, this MPC is much higher than the concentrations found in the environment, no direct ecotoxicological risk is expected for the aquatic environment at present. This does not mean that the presence of EDTA in the environment is of no ecological concern. Effects as disturbance of the metal balance or re-mobilisation of metals from sediments are not taken into account by the MPC value.

The aquatic toxicity data that are found for EDTA (from EU-RAR) are presented in Appendix 1. Only toxicity studies with endpoints related to survival, growth or reproduction are considered. For the interpretation of the toxicity tests, the complex formation properties of EDTA have to be taken into account. Beside Ca and Mg, test media contain a certain amount of heavy metal ions being necessary as trace nutrients. The complex forming constants of heavy metal complexes are by several orders of magnitude higher than of Ca/Mg-complexes, thus after addition of the test substance EDTA (as acid or Na-salt) the concentration of uncomplexed trace metals decreases drastically. The degree of Ca/Mg complexation is dependent on the amount of added EDTA. Uncomplexed EDTA is only present when it is present in over-stoichiometric concentrations.

The choice of the complex species being relevant for effect testing should consider their different ecotoxicological properties. Effect tests should be conducted with a complex for

which metal toxicity can be excluded. Therefore, the Ca-complex should be used as test substance for all release scenarios. Effects from complexes with a higher toxicity are caused by the dissociated metal ions and should be covered by the risk assessment of the respective metals.

In an early-life stage test on the zebrafish *Danio rerio*, the NOEC was determined to be higher than 26.8 mg/l H_4EDTA, based on analytically determined concentrations. $CaNa_2EDTA$ was used as a test substance. This test is considered to be the most relevant fish test for the MPC derivation. In a long-term test a 21 d-NOEC of 22 mg/l for reproduction could be obtained. In this test a surplus of Ca was present, thus mainly Ca-EDTA was formed in the medium being the active test substance. A standard growth inhibition test on *Scenedesmus subspicatus* resulted in an EC10 of 0.37 mg/l H_4EDTA. The effect is probably caused by nutrient deficiency, as essential metal ions like Cu, Zn and Co are largely complexed leading to drastically reduced concentrations. It could be demonstrated by Geurts and van Wijk (2001), that in a test with *Pseudokirchnerella subcapitata* with Fe(III)EDTA as active test substance following OECD 201, ECb50 and ECr50 higher than 100 mg/l were found. The NOEC based on nominal concentrations was determined to 79.4 mg/l and based on mean measured concentration to 48.4 mg/l. Therefore, the inhibition of algae growth is an artefact which is caused by the drastic increase of biomass during the test (EU-RAR, 2003).

Results of long-term tests are available for fish, daphnids and algae. The most sensitive endpoint could be found for *Daphnia magna* with a NOEC of 22 mg/l H_4EDTA. According to the TGD an assessment factor of 10 has to be used, and the calculated PNEC is equivalent to the MPC: $MPC_{water, dissolved} = 2.2$ mg/l.

In the EU-RAR a Kp_{susp} of 75 l/kg is used for exposure calculation. This is the average value between Zn- and Cu-EDTA. This would lead to a $MPC_{water, total}$ of:

$$MPC_{water, total} = 2.2 (1 + 75 \cdot 0.001 \cdot 0.03) = 2.2 \text{ mg/l}$$

where

$MPC_{water, total}$	=	environmental risk limit for 'total' water [mg/l], with standard 30 mg/l suspended matter
$MPC_{water, dissolved}$	=	environmental risk limit for 'dissolved' water [mg/l]
Kp	=	partition coefficient water/suspended matter [l/kg]
0.03	=	concentration suspended matter [mg/l]
0.001	=	recalculation factor [mg/kg]

The negligible concentration (NC) represents a value causing negligible effects to ecosystems. The NC is derived from the MPC by dividing it by 100. This assessment factor takes into account combination toxicity amongst other factors (VROM, 1989a,b).

$$NC_{water, dissolved} = 22 \text{ μg/l}$$

5.3   MPCs and NCs for soil and sediment

No ecotoxicological data were found for these environmental compartments. In the standard procedure for derivation of MPC values (De Bruijn et al., 1999) it is proposed to use the equilibrium partitioning method to calculate the MPC soil/sediment from the MPC water, if ecotoxicological soil/sediment data are lacking. For the complex forming agents such as EDTA the equilibrium partitioning is not suitable because behaviour of the compound can not be described with simple equilibrium partitioning principles. The Ep method assumes that the bio-availability and therefore the toxicity is determined by the pore water concentration in soil and sediments. This theory can not be used for EDTA as a result of the complex speciation. Therefore, the Ep-method has no relevance in calculating the MPC for EDTA for these compartments, which is confirmed by Xue et al. (1995) who also concluded that equilibrium partitioning is not suitable for EDTA due to the complex speciation. No MPCs are derived for soil and sediment.

6.   Summary of available data and conclusions

Below, an overview is presented of the ERLs (Environmental Risk Limits) and relevant physico-chemical parameters for Tetrasodium ethylenediamine tetra-acetate (EDTA), derived from the EU-RAR report.

Parameter	Value	Comments
Solubility [mg/l]	500	
Log Kow	Not determined	For ionic substances the partition coefficient can not be determined experimentally.
Koc [l/kg]	Not expected	Due to the ionic structure under environmental relevant pH conditions, no adsorption onto the organic fraction of soils or sediments is expected.
MPC_{water} [mg/l]	2.2 (Dissolved and total)	For calculation of 'total' a Kp_{susp} of 75 l/kg was used
$MPC_{sediment}$	-	Equilibrium partitioning method can not be used for this kind of substance
MPC_{soil}	-	Equilibrium partitioning method can not be used for this kind of substance
NC_{water} [mg/l]	0.022 (dissolved and total)	NC = MPC/100

Measured EDTA concentrations in the rivers Rhine, Meuse and IJssel are below 100 μg/l for the years 1997/1998. In general , higher concentrations are found for wastewater up to 1700 μg/l (Chapter 3). No risk due to EDTA toxicity alone (i.e., without interactions) is expected in Dutch surface waters in the measured range.

Chapter 4 discussed the potential interactions of EDTA with essential elements such as iron, copper and zinc. It has been shown in laboratory experiments that excess EDTA can influence the availability of essential elements, thereby limiting growth of algae. Other complicating factors are sorption and transport of metals that are mobilized by EDTA. Due to complex speciation of EDTA with competing ligands and cationic species, the exact magnitude and hence, relevance for environmental policy of these processes, was not be predicted. In depth studies can be performed using existing speciation programs (Verweij, 1991; EPA, 2000).

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89-100. Bureau Rapportenbeheer
101-110. Reserve-exemplaren

Appendix 1: Data derived from EU-RAR

Table 1: Chronic toxicity data for aquatic freshwater organisms

Species	Exposure period	Parameter	Result [mg/l]	Expressed as	Reference
Pisces:					
Danio rerio	35 d	NOEC (mortality)	>26.8	H_4EDTA	BASF (2001)
Crustaceae:					
Daphnia magna	21 d	NOEC (reproduction, mortality)	22	H_4EDTA	BASF (1996a)
Algae:					
Scenedesmus quadricauda	8 d	NOEC (growth)	8.5	H_4EDTA	Bringmann & Kuehn (1978)
Scenedesmus subspicatus	?	EC10 (growth)	0.37	H_4EDTA	BASF (1994)

Table 2: Chronic toxicity data for aquatic marine organisms

Species	Exposure period	Parameter	Result [mg/l]	Expressed as	Reference
Crustaceae:					
Penaeus stylirostris	24 h	NOEC (mortality)	96	H_4EDTA	Castille et al. (1981)
Echinodermata					
Arbacia punctulata	*	NOEC (reproduction)	20	unknown	Young & Nelson (1974)
Algae:					
Actinocyclus sp.	10 generations	NOEC (growth)	2.9	Final EDTA	Muggli & Harrison (1996)
Emiliana huxleyi	?	NOEC (growth)	2.9	Final EDTA	Muggli & Harrison (1996)

* motility of sperm is population related and is therefore supposed to be a chronic effect, although exposure time is not reported

Table 3: Chronic toxicity data for microorganisms

Species	Exposure period	Parameter	Result [mg/l]	Expressed as	Reference
Bacteria:					
Pseudomonas putida	8 d	NOEC (growth)	81	H$_4$EDTA	Bringmann & Kuehn (1976)
Cyanophyta:					
Nostoc muscorum	14 d	EC8=NOEC (growth)	9.9	H$_4$EDTA	Raizada & Rai (1985)
Mycrocystis aeruginosa	10 d	NOEC (growth)	58	H$_4$EDTA	Bringmann & Kuehn (1978)

Table 4: Chronic toxicity data for higher plants

Species	Exposure period	Parameter	Result [mg/l]	Expressed as	Reference
Macrophyta:					
Spirodela polyrhiza	10 d	NOEC (growth)	29	H$_4$EDTA	Khurana & Maheshawari (1986)

Data not mentioned in EU-RAR

Table 5: Chronic toxicity data for aquatic freshwater organisms

Species	Exposure period	Parameter	Result [mg/l]	Expressed as	Reference
Crustacea:					
Ceriodaphnia dubia	21 d	NOEC (reproduction)	7.1	unknown	Zuiderveen & Birge (1991)