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Environmental Risk Limits for Alkylphenols and Alkylphenol ethoxylates

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Abstract

Environmental Risk Limits (ERLs) have been derived for the compounds (or compound groups): nonylphenol, octylphenol 1+2 ethoxylate ($OPEO_{1+2}$), octylphenol 3-8 ethoxylate ($OPEO_{3-8}$), octylphenol >8 ethoxylate ($OPEO_{>8}$), nonylphenol 1+2 ethoxylate ($NPEO_{1+2}$), nonylphenol 3-8 ethoxylate ($NPEO_{3-8}$), nonylphenol >8 ethoxylate ($NPEO_{>8}$), carboxylated octylphenol 1+2 ethoxylate ($OPE_{1+2}C$) and carboxylated nonylphenol 1+2 ethoxylate ($NPE_{1+2}C$). Since soil and sediment toxicity data were virtually absent, nearly all ERLs for soil and sediment were calculated from ERLs for the aquatic environment using equilibrium partitioning theory. On the basis of the *in vivo* effect studies available, the derived ERLs were shown to provide protection against the endocrine effects of the compounds used. Recent measurements (1999, 2001) of nonylphenol or nonylphenol ethoxylates in rivers, estuaries and sediments in the Netherlands showed slight exceedances of the maximum permissible concentration (MPC) in a few cases.

Preface

This report is part of the project ‘Setting Integrated Environmental Quality Standards’ (RIVM-project 601501). We want to acknowledge drs. E.M. Maas and ing. M. Adams (Ministry of Housing, Spatial Planning and the Environment) and dr. M.P.M. Janssen who are involved in the RIVM-project 601501 in which the work was performed.

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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

In dit rapport zijn maximaal toelaatbaar risiconiveaus (MTR), verwaarloosbaar risiconiveaus (VR) en 'Serious Risk Concentrations' voor ecosystemen (SRC_{ECO}) afgeleid voor nonylfenol (NP), octylfenolethoxylaten (OPEO), nonylfenolethoxylaten (NPEO), gecarboxyleerd octylfenol mono- en diethoxylaat ($OPE_{1+2}C$) en gecarboxyleerd nonylfenol mono- en diethoxylaat ($NPE_{1+2}C$). De risiconiveaus zijn afgeleid met gebruik van ecotoxicologische en milieuchemische gegevens en ze geven een schatting van het potentiële risico van stoffen voor een ecosysteem. De risiconiveaus vormen de wetenschappelijke basis voor milieukwaliteitsnormen die worden vastgesteld door het ministerie van VROM. Er zijn risiconiveaus afgeleid voor de milieucompartimenten water (oppervlaktewater en grondwater), sediment en bodem. Hierbij wordt opgemerkt dat nonylfenol recent is geëvalueerd in het kader van het EU-bestaande stoffen programma. De resultaten van de EU evaluatie, inclusief de afgeleide risiconiveaus, zijn overgenomen in dit RIVM rapport. OPEO en NPEO zijn twee groepen van verbindingen. Binnen een groep is het aantal C atomen in de alkyl keten aan de fenol ring constant (C8 of C9), terwijl 'ethoxylaat' een keten van ethoxy eenheden benoemt die in lengte kan variëren (van 1 tot meer dan 100 ethoxy eenheden). Alkylfenolethoxylaten komen altijd voor in mengsels in elk van hun vele toepassingen. Voor het afleiden van risiconiveaus werden de verbindingen gegroepeerd: octylfenol 1+2 ethoxylaat ($OPEO_{1+2}$), nonylfenol 1+2 ethoxylaat ($NPEO_{1+2}$), octylfenol 3-8 ethoxylaat ($OPEO_{3-8}$), nonylfenol 3-8 ethoxylaat ($NPEO_{3-8}$), octylfenol >8 ethoxylaat ($OPEO_{>8}$) en nonylfenol >8 ethoxylaat ($NPEO_{>8}$). Bovendien werden risiconiveaus afgeleid voor $OPE_{1+2}C$ en $NPE_{1+2}C$; dit zijn degradatieproducten van octyl- en nonylfenolethoxylaten die worden gevormd in het aquatisch milieu onder natuurlijke condities.

Alkylfenolethoxylaten zijn non-ionische surfactanten. Er zijn een redelijk aantal aquatische toxiciteitsgegevens beschikbaar, die zorgvuldig moesten worden geïnterpreteerd vanwege de oppervlakte-actieve eigenschappen en omdat altijd *mengsels* van stoffen worden getest. Er zijn geen toxiciteitsgegevens beschikbaar voor sediment-organismen en nauwelijks toxiciteitsgegevens voor bodemorganismen. De risiconiveaus voor standaard NL sediment en bodem zijn voor alle stoffen afgeleid met behulp van de evenwichts-partitie methode (EqP methode). Octyl- en nonylfenolethoxylaten zijn potentiële endocriene ontregelaars. De afgeleide MTRs zijn beschermend voor deze endocriene effecten. Er moet worden opgemerkt dat deze conclusie is gebaseerd op een klein aantal relevante *in vivo* studies naar endocriene effecten. Het is daarom raadzaam om een her-evaluatie van gegevens over dit onderwerp uit te voeren indien significant meer gegevens beschikbaar zijn gekomen.

Concentraties NP, OPEO en NPEO in Nederlandse oppervlaktewateren en sedimenten overschreden het MTR in verscheidene gevallen. De meest recente metingen dateren van 2001. In het algemeen worden hogere concentraties geassocieerd met geïndustrialiseerde gebieden of met rioolwaterzuiverings-effluent. Op Europees niveau (OSPAR, EU) zijn

afspraken gemaakt om bepaalde gebruikscategoriën uit te faseren. Risicoreducerende maatregelen zijn op dit niveau echter nog niet van kracht.

De afgeleide risiconiveaus voor NP, en groeps-risiconiveaus voor OPEO, NPEO, OPEC en NPEC worden weergegeven in Tabel 1 t/m Tabel 4.

Tabel 1. ERLs voor nonylfenol voor $water_{totaal}$, $water_{opgelost}$ en grondwater.

	$WATER_{TOTAAL}$		$WATER_{OPGELOST}$		GRONDWATER	
Verbinding	VR [µg.l^{-1}]	MTR [µg.l^{-1}]	VR [µg.l^{-1}]	MTR [µg.l^{-1}]	VR [µg.l^{-1}]	MTR [µg.l^{-1}]
Nonylfenol	0,0033	0,33	0,0033	0,33	0,0033	0,33

Tabel 2. ERLs voor nonylfenol voor bodem en sediment.

	BODEM		SEDIMENT	
Verbinding	VR [µg.kg_{dw}^{-1}]	MTR [µg.kg_{dw}^{-1}]	VR [µg.kg_{dw}^{-1}]	MTR [µg.kg_{dw}^{-1}]
Nonylfenol	1,0	104	1,1	105

N.B. De bovenstaande normen zijn afgeleid op basis van een Europese risicobeoordeling, waarin geen SRC_{ECO} wordt afgeleid.

Tabel 3. ERLs voor octylfenolethoxylaten en nonylfenolethoxylaten voor $water_{totaal}$, $water_{opgelost}$ en grondwater.

	VR [µg.l^{-1}]	MTR [µg.l^{-1}]	VR [µg.l^{-1}]	MTR [µg.l^{-1}]	SRC_{ECO} [µg.l^{-1}]	VR [µg.l^{-1}]	MTR [µg.l^{-1}]	SRC_{ECO} [µg.l^{-1}]
Groep verbindingen	WATER TOTAAL		WATER OPGELOST			GRONDWATER [1]		
$OPE_{1+2}C$	0,050	5,0	0,050	5,0	500	0,050	5,0	500
$OPEO_{1+2}$	0,073	7,3	0,071	7,1	710	0,071	7,1	710
$OPEO_{3-8}$	0,018	1,8	0,018	1,8	620	0,018	1,8	620
$OPEO_{>8}$	0,021	2,1	0,021	2,1	670	0,021	2,1	670
$NPE_{1+2}C$	0,010	1,0	0,010	1,0	260	0,010	1,0	260
$NPEO_{1+2}$	0,0012	0,12	0,0011	0,11	45	0,0011	0,11	45
$NPEO_{3-8}$	0,14	14	0,13	13	410	0,13	13	410
$NPEO_{>8}$	0,10	10	0,10	10	850	0,10	10	850

[1] ERLs voor grondwater worden gelijkgesteld aan $ERL_{water,\ opgelost}$, dientengevolge zijn $VR_{grondwater}$, $MTR_{grondwater}$ en $SRC_{ECOgrondwater}$ ook gebaseerd op 'opgeloste' concentraties.

Tabel 4. ERLs voor octylfenolethoxylaten en nonylfenolethoxylaten voor bodem en sediment.

	VR [mg.kg^{-1}]	MTR [mg.kg^{-1}]	SRC_{ECO} [mg.kg^{-1}]	VR [mg.kg^{-1}]	MTR [mg.kg^{-1}]	SRC_{ECO} [mg.kg^{-1}]
Groep verbindingen	BODEM			SEDIMENT		
$OPE_{1+2}C$	0,0040	0,40	40	0,0040	0,40	40
$OPEO_{1+2}$	0,036	3,6	360	0,036	3,6	360
$OPEO_{3-8}$	0,0045	0,45	150	0,0045	0,45	150
$OPEO_{>8}$	0,0023	0,23	72	0,0023	0,23	72
$NPE_{1+2}C$	0,0015	0,15	38	0,0015	0,15	38
$NPEO_{1+2}$	0,0015	0,15	61	0,0015	0,15	61
$NPEO_{3-8}$	0,045	4,5	270	0,087	8,7	270
$NPEO_{>8}$	0,029	2,9	250	0,029	2,9	250

Summary

In this report Maximum Permissible Concentrations (MPCs), Negligible Concentrations (NCs) and Serious Risk Concentrations for the ecosystem (SRC_{ECO}) have been derived for nonylphenol (NP), octylphenol ethoxylates (OPEO), nonylphenol ethoxylates (NPEO), carboxylated octylphenol mono- and diethoxylate ($OPE_{1+2}C$) and carboxylated nonylphenol mono- and diethoxylate ($NPE_{1+2}C$). The ERLs have been derived using data on ecotoxicology and environmental chemistry, and represent the potential risk of the substances to the ecosystem. They are the scientific basis for Environmental Quality Standards (EQSs) set by the Ministry of VROM. Environmental Risk Limits (ERLs) were derived for the compartments water (surface water and groundwater), sediment and soil. It is noted that nonylphenol has recently been evaluated within the framework of the EU-program on existing substances. The results of the EU evaluation, including derived ERLs, have been adopted in this RIVM report. OPEO and NPEO are two groups of compounds. Within a group the number of C-atoms in the alkyl chain attached to phenol is constant (either C8 or C9) while 'ethoxylate' designates a chain of ethoxy units that can have varying lengths (1 to over 100 ethoxy units). Alkylphenol ethoxylates always occur in mixtures in any of their various applications. Compounds were grouped for ERL derivation: octylphenol 1+2 ethoxylate ($OPEO_{1+2}$), nonylphenol 1+2 ethoxylate ($NPEO_{1+2}$), octylphenol 3-8 ethoxylate ($OPEO_{3-8}$), nonylphenol 3-8 ethoxylate ($NPEO_{3-8}$), octylphenol >8 ethoxylate ($OPEO_{>8}$) and nonylphenol >8 ethoxylate ($NPEO_{>8}$). In addition, ERLs were derived for $OPE_{1+2}C$ and $NPE_{1+2}C$, which are degradation products of octyl- and nonylphenol ethoxylates, formed in the aqueous environment under natural conditions.

Alkylphenol ethoxylates are non-ionic surfactants. There are a reasonable number of aquatic toxicity data available, that should be interpreted carefully care because of surface-active properties and because always *mixtures* are tested. No sediment toxicity data and very few soil toxicity data were available. Hence, for all compounds the equilibrium partitioning method (EqP-method) was used to derive the ERLs for standard Dutch soil and sediment. Octyl- and nonylphenol ethoxylates are potential endocrine disrupters. The derived MPCs are protective for these endocrine effects. It should be noted that this conclusion is based on a small number of *in vivo* studies on endocrine effects; it is therefore advisable to re-evaluate data on this subject when substantially more toxicity information has become available.

Concentrations of NP, OPEO and NPEO in Dutch surface waters and sediments exceeded the MPC in several instances. The most recent measurements used dated from 2001. In general, higher concentrations are associated with industrialised areas or sewage treatment effluent. Agreements at European level (OSPAR, EU) to phase out certain uses have been made, however risk reduction measures have not yet been issued at this level.

The derived ERLs for NP and the group-ERLs for OPEO, NPEO, OPEC and NPEC are shown in Table 1 to Table 4.

Table 1. ERLs for nonylphenol for $water_{total}$, $water_{dissolved}$ and groundwater.

	$WATER_{TOTAL}$		$WATER_{DISSOLVED}$		GROUNDWATER	
Compound	NC [µg.l^{-1}]	MPC [µg.l^{-1}]	NC [µg.l^{-1}]	MPC [µg.l^{-1}]	NC [µg.l^{-1}]	MPC [µg.l^{-1}]
Nonylphenol	0.0033	0.33	0.0033	0.33	0.0033	0.33

Table 2. ERLs for nonylphenol for soil and sediment.

	SOIL		SEDIMENT	
Compound	NC [µg.kg_{dw}^{-1}]	MPC [µg.kg_{dw}^{-1}]	NC [µg.kg_{dw}^{-1}]	MPC [µg.kg_{dw}^{-1}]
Nonylphenol	1.0	104	1.1	105

N.B. The above mentioned ERLs were based on a European risk assessment in which the SRC_{ECO} is not derived.

Table 3. ERLs for octylphenol ethoxylates and nonylphenol ethoxylates for $water_{total}$, $water_{dissolved}$ and groundwater.

	NC [µg.l^{-1}]	MPC [µg.l^{-1}]	NC [µg.l^{-1}]	MPC [µg.l^{-1}]	SRC_{ECO} [µg.l^{-1}]	NC [µg.l^{-1}]	MPC [$^{µg.l^{-1}}$]	SRC_{ECO} [µg.l^{-1}]
Compound class	WATER TOTAL		WATER DISSOLVED			GROUNDWATER [1]		
$OPE_{1+2}C$	0.050	5.0	0.050	5.0	500	0.050	5.0	500
$OPEO_{1+2}$	0.073	7.3	0.071	7.1	710	0.071	7.1	710
$OPEO_{3-8}$	0.018	1.8	0.018	1.8	620	0.018	1.8	620
$OPEO_{>8}$	0.021	2.1	0.021	2.1	670	0.021	2.1	670
$NPE_{1+2}C$	0.010	1.0	0.010	1.0	260	0.010	1.0	260
$NPEO_{1+2}$	0.0012	0.12	0.0011	0.11	45	0.0011	0.11	45
$NPEO_{3-8}$	0.14	14	0.13	13	410	0.13	13	410
$NPEO_{>8}$	0.10	10	0.10	10	850	0.10	10	850

[1] ERLs for groundwater are set equal to $ERL_{water,\ dissolved}$; consequently, $NC_{groundwater}$, $MPC_{groundwater}$ and $SRCeco_{groundwater}$ are also based on 'dissolved' concentrations.

Table 4. ERLs for octylphenol ethoxylates and nonylphenol ethoxylates for soil and sediment.

	NC [mg.kg^{-1}]	MPC [mg.kg^{-1}]	SRC_{ECO} [mg.kg^{-1}]	NC [mg.kg^{-1}]	MPC [mg.kg^{-1}]	SRC_{ECO} [mg.kg^{-1}]
Compound class	SOIL			SEDIMENT		
$OPE_{1+2}C$	0.0040	0.40	40	0.0040	0.40	40
$OPEO_{1+2}$	0.036	3.6	360	0.036	3.6	360
$OPEO_{3-8}$	0.0045	0.45	150	0.0045	0.45	150
$OPEO_{>8}$	0.0023	0.23	72	0.0023	0.23	72
$NPE_{1+2}C$	0.0015	0.15	38	0.0015	0.15	38
$NPEO_{1+2}$	0.0015	0.15	61	0.0015	0.15	61
$NPEO_{3-8}$	0.045	4.5	270	0.087	8.7	270
$NPEO_{>8}$	0.029	2.9	250	0.029	2.9	250

Abbreviations and variables

AP	alkylphenol
APEO	alkylphenol ethoxylate
A_mPEO_n	C_m-alkylphenol *n*-ethoxylate (*m* C-atoms in the alkyl chain, *n* ethoxy oligomers in the ethoxy chain)
A_mPE_nC	C_m-alkylphenol *n*-ethoxycarboxylic acid (*m* C-atoms in the alkyl chain, *n* ethoxy oligomers in the ethoxy chain which is carboxylated)
CA_mPE_nC	carboxylated alkyl phenol *n*-ethoxycarboxylic acid (*m* C-atoms in the carboxylated alkyl chain, *n* ethoxy oligomers in the carboxylated ethoxy chain)[1]
BCF	bioconcentration factor
CAS	chemical abstract service
CMC	critical micelle concentration
dw	dry weight
EC_{10}, EC_{50}	effect concentration causing 10% or 50% effect, respectively
ED_{50}	dose causing 50% effect
EINECS	European inventory of existing commercial substances
EO	ethoxy/ethoxylate
EPA	Environmental Protection Agency
EqP	equilibrium partitioning
ER-CALUX	estrogen receptor (mediated)-chemical activated luciferase gene expression
ERL	environmental risk limit
EQS	environmental quality standard
ESR	existing substances regulation
EU	European Union
EU-RAR	European Union-risk assessment report
EUSES	European uniform system for the evaluation of substances
EU-TGD	technical guidance document (for risk assessment of new and existing chemicals within the European Union)
HC	hazardous concentration
HPLC	high pressure liquid chromatography
hER	human estrogen receptor
INS	the project setting integrated environmental quality standards
ISO	international organisation for standardisation
IUCLID	international uniform chemical information database
IUPAC	international union of pure and applied chemistry
K_d	linear sorption coefficient soil/water or sediment/water
K_{oc}	organic carbon normalised sorption coefficient
K_{ow}	*n*-octanol/water partition coefficient

[1] The chemical names shown are kept close to the acronym in order to explicate the latter; i.e. they are not official chemical names.

K_p	partition coefficient standard soil/water or standard sediment/water
K_{ppm}	partition coefficient standard suspended matter/water
$K_{p, susp}$	partition coefficient suspended matter/water (nomenclature as used in EU-RAR)
LC_{10}, LC_{50}	lethal concentration (causing 10% or 50% lethality, respectively)
l.o.d.	limit of detection
LOEC	lowest observed effect concentration
LOES	national investigation into the occurrence and effects of estrogenic compounds in the aquatic environment
MPC	maximum permissible concentration
MS	mass spectrometry
NC	negligible concentration
NOEC	no observed effect concentration
NP	nonylphenol
$NPEO_n$	nonylphenol *n*-ethoxylate (*n* ethoxy oligomers in the ethoxy chain)
NPE_nC	nonylphenol *n*-ethoxycarboxylic acid (*n* ethoxy oligomers in the ethoxy chain which is carboxylated at the last C-atom)[1]
o.c.	organic carbon
OECD	organisation for economic co-operation and development
o.m.	organic matter
OP	octylphenol
$OPEO_n$	octylphenol –*n*-ethoxylate (*n* ethoxy oligomers in the ethoxy chain)
OPE_nC	octylphenol –*n*-ethoxycarboxylic acid (*n* ethoxy oligomers in the ethoxy chain which is carboxylated at the last C-atom)[1]
OSPAR	Oslo and Paris commission (for the protection of the marine environment of the North-East Atlantic)
pK_a	dissociation constant
PNEC	predicted no effect concentration
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
QSAR	quantitative structure activity relationship
RAR	risk assessment report of the European Union
RIKZ	National Institute for Coastal and Marine management
RIVM	National Institute of Public health and the Environment
RQ	risk quotient
SRC_{ECO}	ecotoxicological serious risk concentration
STP	sewage treatment plant
S_w	water solubility
VROM	Dutch Ministry of Housing, Spatial Planning and the Environment
VTG	vitellogenin
ww	wet weight

1. Introduction

1.1 Methodology

This report is a result in the project 'Setting Integrated Environmental Quality Standards'. The aim of the project is to derive environmental risk limits (ERLs) for substances in the environment for the compartments air, (ground)water, sediment and soil. Environmental risk limits (ERLs) serve as advisory values to set environmental quality standards (EQS) by the Ministry of Housing, Spatial Planning and the Environment (VROM) for various policy purposes. The term EQS is used to designate all legally and non-legally binding standards that are used in Dutch environmental policy. Table 5 shows the correspondence between ERLs and EQSs.

Table 5. Environmental Risk Limits and the related Environmental Quality Standards are set by the Dutch government in the Netherlands for the protection of ecosystems.

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)
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)
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}).

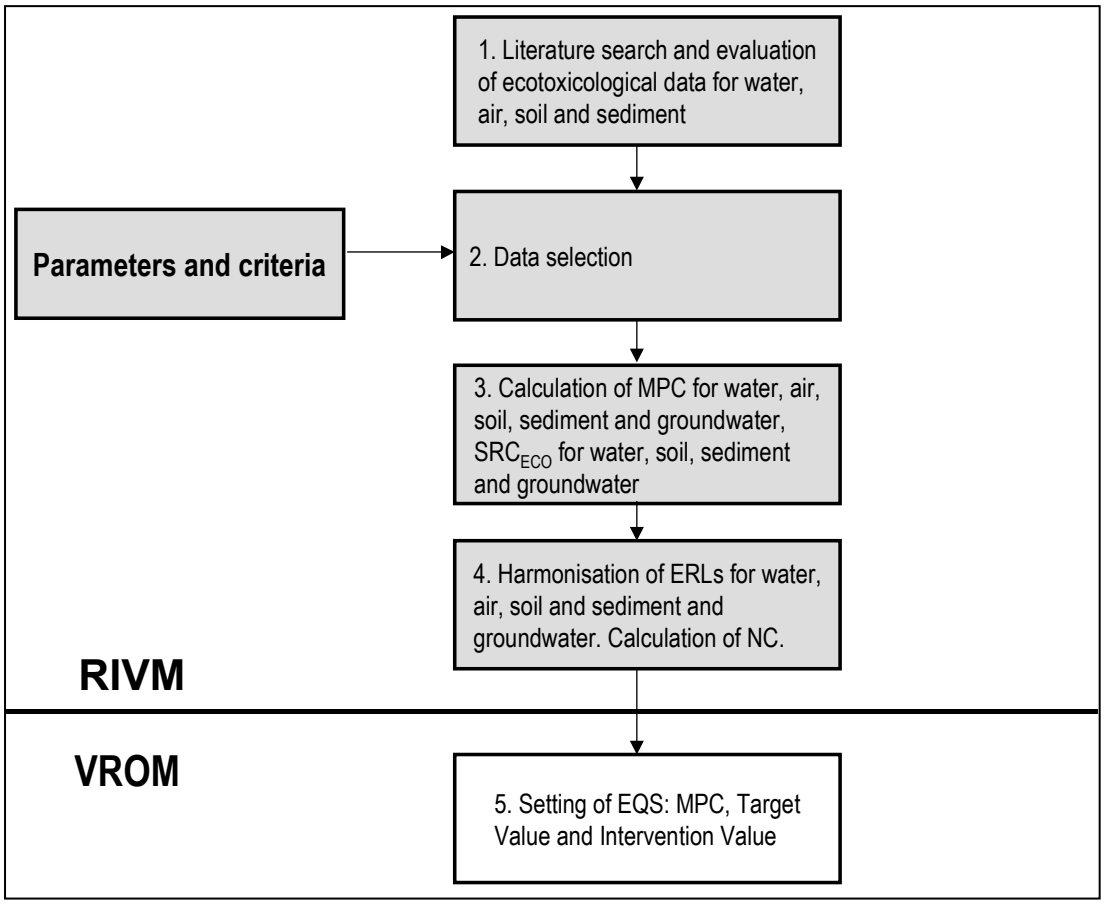


Figure 1. The process of deriving Integrated Environmental Risk Limits. Above the line the method to derive ERLs is indicated, i.e. MPC, NC and SRC_{ECO}. Below the line, the MPC and Target Value is indicated, set by the Ministry of Housing, Spatial Planning and the Environment (VROM).

The process of deriving integrated ERLs is shown schematically in Figure 1. ERLs for soil and sediment are calculated for a standardised soil. ERLs for water are reported for dissolved and total concentrations (including a standard amount of suspended matter) and if found significantly different, differentiated to freshwater and saltwater. Each of the ERLs and its corresponding EQS represents a different level of protection, with increasing numerical values in the order Target Value < MPC[2] < Intervention Value. The EQS demands different actions when one of them is exceeded, explained elsewhere [136].

The report is one of a series of RIVM reports that were published in the framework of the project 'Setting Integrated Environmental Quality Standards', in which ERLs and EQSs were derived for around 250 substances and groups of substances. For an overview of the EQSs set by the Ministry of VROM, see INS [57] and VROM [136].

[2] A complicating factor is that the term MPC is used both as an ERL and as an EQS. For historical reasons, however, the same abbreviation is used.

1.2 Adapted methodology for compounds evaluated in EU

In 1993 the Council of the European Communities adopted Council Regulation (EEC) 793/93 or the Existing Substances Regulation (ESR), thereby introducing a comprehensive framework for the evaluation and control of existing chemical substances. This is a legal instrument that was proposed by the European Commission upon approval of the Fourth Community Action Programme on the Environment (1987-1992) by the Council.

The Commission, in consultation with member states, drew up four priority lists for substances that are to be evaluated for both human and environmental risks. For a given prioritised compound, this process will result in a European Union Risk Assessment Report (RAR) at step 3 of the regulation. In the environmental section of a RAR, environmental risk limits are derived for each environmental compartment, which are called predicted no effect concentrations (PNEC). A PNEC is comparable to the maximum permissible concentration (MPC), which is the environmental risk limit (ERL) used as an advisory value within the Dutch national framework of setting environmental quality standards (EQS). At present the Ministry of Housing, Spatial Planning and the Environment (VROM) has the policy to take over PNEC values from a RAR for an existing substance when these PNECs have already been or are being derived at the time the Ministry seeks advice (that is, requests for an MPC to be derived) for that substance.

1.3 Selected compounds

The aim of this report is to derive ERLs for alkylphenols and alkylphenol ethoxylates. These are two groups of compounds that have less structural relationship to one another than their names suggest. Alkylphenols can have a varying structure of the alkyl chain which can be attached at different positions to an aromatic ring. In addition to that, alkylphenol ethoxylates possess a chain of polymeric ethoxylate units, the length of which can vary considerably. These compounds have various applications: nonylphenol is used in the production of nonylphenol ethoxylates and in polymer industry whereas alkylphenol ethoxylates are surfactants and have very many related applications (in cleaning, lubricating, degreasing, as dispersing agents, etc.). It is noted that nonylphenol has recently been evaluated in the framework of the EU-programme on existing substances. The results of the EU evaluation, including the derived ERLs, have been adopted in this RIVM report (see sections 4.1.1 to 4.1.5).

Within the framework of the European existing substances regulation (793/93/EEC), risk assessments for three alkylphenols is or has been carried out. Within the Dutch framework of setting environmental quality standards, it was decided to take over results from the European environmental risk assessment, if available in final form and not to derive risk limits at the national level when risk assessment at the European level is still ongoing (section 2.3). For this reason, this report is split in two parts. Alkylphenols are treated in the first part, based on available EU-RAR data and the alkylphenol ethoxylates are treated in the second part of the report.

2. Alkylphenols-Methods

2.1 Data Search and selection

Since the PNEC from EU-RARs will be taken over as MPC, no additional data search was performed. The PNECs will be corrected for Dutch environmental circumstances as described in the Guidance document on deriving environmental risk limits [120].

2.2 Selection of compounds

The market share of octylphenol and nonylphenol is over 95% of all alkylphenols [51]. Therefore these two compounds are selected for MPC derivation. In Western-Europe butyl- and dodecylphenols are also produced [51], but at present no information on production amounts is available.

2.3 EU-risk assessment reports

At present, a preliminary draft version of an EU RAR for p-*tert*–butylphenol, a finalised draft version of a targeted (environmental) EU RAR for 4-*tert*-octylphenol [44] and a final EU RAR for 4-nonylphenol (branched) and nonylphenol exist [46]. In compliance with the present viewpoint of the Ministry of VROM (see section 1.1), the PNEC values of nonylphenol will be taken over as MPC values. The RARs for butylphenol and octylphenol are draft versions from which no data may be used for publication until the final report is issued. For that reason we will not present data of those compounds in the present report. To derive an MPC while a PNEC derivation is in progress is not preferable either because new data (e.g. toxicity studies) may be added to the data set that may alter the outcome of the ERL derivation. When a finalised version of the two current draft EU-RARs is issued, RIVM will present the MPCs based on the EU-RAR in a concise report.

The EU RAR for nonylphenol will be used as the sole source for physical and chemical data, toxicity data and MPCs that will be presented in this report.

3. Alkylphenols - Substance properties, use and production

3.1 Alkylphenols

3.1.1 General molecular structure

Alkylphenols are phenol compounds with one or more chained alkyl groups attached to the aromatic ring. Their general structural formula is:

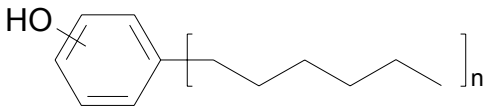


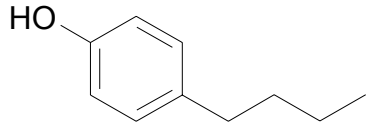
Figure 2. General structural formula of alkylphenols. n *denotes the number of C atoms in the alkyl chain. The alkyl chain is drawn as a linear structure, but it may also be (and usually is) branched.*

The position of the hydroxy group on the aromatic ring, relative to the position of the alkyl chain, may vary. Most commercial products are technical mixtures of compounds in which the structure of the alkyl chain varies. E.g. 4-Nonylphenol is a mixture of phenols that are para substituted with alkyl chains containing nine C atoms, having different degrees of branching. Most individual nonylphenols have their own CAS registry number.

3.1.2 Physico-chemical properties

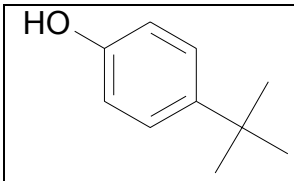
Wherever possible, data are retrieved from open literature and completed with data calculated with modules from EPI Suite [45] and MedChem's ClogP [31]. Data for octylphenol and nonylphenol are taken from the respective EU-RAR that exists for these compounds.

Table 6. General physicochemical properties and identification of 4-butylphenol.



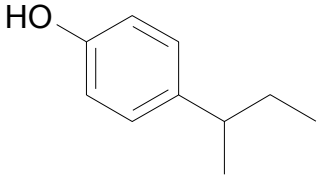
Properties	Value	Reference
IUPAC Name	4-butylphenol	
CAS number	1638-22-8	
EINECS number	n.a.	
Empirical formula	C10 H14 O	
Molar mass (g/mol)	150.22	
n-octanol/water partition coefficient (log K_{ow})	3.65 (exp)	[45]
	3.64 (exp)	[31]
Organic carbon/water sorption coefficient (log K_{oc})	3.455	
Water solubility (mg/l)	219.8 at 25°C	[45]
Melting point (°C)	49.21	[45]
Vapour pressure (Pa)	1.01 at 25°C	[45]
Henry's law constant ($Pa.m^3.mol^{-1}$)	0.15 at 25°C	[45]
pK_a value (dissociation constant)	n.a.	

Table 7. General physicochemical properties and identification of tert-*butylphenol.*

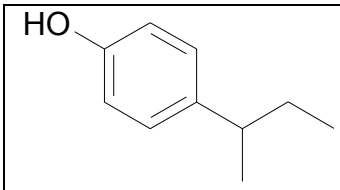


Properties	Value	Reference
IUPAC Name	2-*tert*-, 3-*tert*-; 4-*tert*-butylphenol	
CAS number	88-18-6 (2-*tert*); 585-34-2 (3-*tert*); 98-54-4 (4-*tert*)	
EINECS number	n.a.	
Empirical formula	C10 H14 O	
Molar mass (g/mol)	150.22	
n-octanol/water partition coefficient (log K_{ow})	2-*tert*: 2.7 (exp, HPLC)	[84]
	2-*tert*: 3.31 (exp)	[31]
	3-*tert*: 2.6 (exp, HPLC)	[84]
	3-*tert*: 3.05 (exp)	[31]
	4-*tert*: 3.31 (exp)	[31]
Organic carbon/water sorption coefficient (log K_{oc})	4-*tert*: 3.282	[45]
Water solubility (mg/l)	4-*tert*: 429 at 25°C	[45]
	4-*tert*: 500 at 20°C	[47]
	4-*tert*: 800 at 20°C	[47]
Melting point (°C)	4-*tert*: 6.91	[45]
Vapour pressure (Pa)	4-*tert*: 3.57 at 25°C	[45]
Henry's law constant ($Pa.m^3.mol^{-1}$)	4-*tert*: 0.15 at 25°C	[45]
pK_a value (dissociation constant)	4-*tert*: 10.39 (exp)	[47]
	4-*tert*: 10.39 (calc)	[47]

*Table 8. General physicochemical properties and identification of 4-*sec*-butylphenol.*

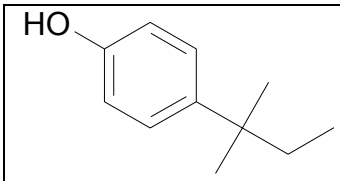


Properties	Value	Reference
IUPAC Name	2-*sec*-, 4-*sec*-butylphenol	
CAS number	89-72-5 (2-*sec*); 99-71-8 (4-*sec*)	
EINECS number	n.a.	
Empirical formula	C10 H14 O	
Molar mass (g/mol)	150.22	
n-octanol/water partition coefficient (log K_{ow})		
	2-*sec*: 3.27 (exp)	[31]
	2-*sec*: 2.8 (exp, HPLC)	[84]
	4-*sec*: 3.08 (exp)	[45]
	4-*sec*: 3.32	[31]
	4-*sec*: 2.1 (exp, HPLC)	[84]
Organic carbon/water sorption coefficient (log K_{oc})	2-*sec*: 3.417	[45]
	4-*sec*: 3.408	[45]
Water solubility (mg/l)	4-*sec*: 674 at 25°C	[45]
	2-*sec*: 464 at 25°C	[45]
Melting point (°C)	38.56	[45]



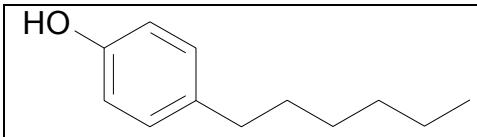
Properties	Value	Reference
Vapour pressure (Pa)	2.31 at 25°C	[45]
Henry's law constant ($Pa.m^3.mol^{-1}$)	0.15 at 25°C	[45]
BCF	4-*sec*-: 37 (k1/k2)	[84]
pK_a value (dissociation constant)	n.a.	

*Table 9. General physicochemical properties and identification of 4-*tert*-pentylphenol.*

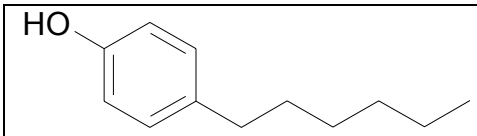


Properties	Value	Reference
IUPAC Name	4-*tert*-pentylphenol (p-*tert*-amylphenol)	
CAS number	80-46-6	
EINECS number		
Empirical formula	C11 H16 O1	
Molar mass (g/mol)	164.25	
n-octanol/water partition coefficient (log K_{ow})	3.91 (est)	[45]
	3.83 (est)	[31]
	2.1 (exp, HPLC)	[84]
Organic carbon/water sorption coefficient (log K_{oc})	3.580	[45]
Water solubility (mg/l)	113.2 at 25°C	[45]
Melting point (°C)	47.70	[45]
Vapour pressure (Pa)	1.04 at 25°C	[45]
Henry's law constant ($Pa.m^3.mol^{-1}$)	0.19 at 25°C	[45]
pK_a value (dissociation constant)	n.a.	

Table 10. General physicochemical properties and identification of 4-hexylphenol.

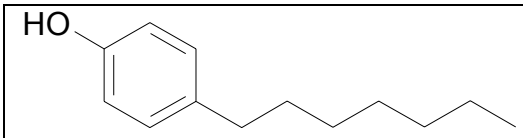


Properties	Value	Reference
IUPAC Name	4-hexylphenol	
CAS number	2446-69-7	
EINECS number	n.a.	
Empirical formula	C12 H18 O1	
Molar mass (g/mol)	178.28	
n-octanol/water partition coefficient (log K_{ow})	4.52 (est)	[45]
	3.6 (exp, HPLC)	[84]
	4.619 (est)	[31]
Organic carbon/water sorption coefficient (log K_{oc})	3.987	[45]
Water solubility (mg/l)	29.71 at 25°C	[45]
Melting point (°C)	70.23	[45]



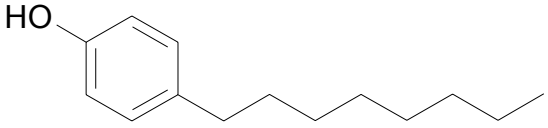
Properties	Value	Reference
Vapour pressure (Pa)	0.096 at 25°C	[45]
Henry's law constant ($Pa.m^3.mol^{-1}$)	0.26 at 25°C	[45]
BCF	350 (k1/k2)	[84]
pK_a value (dissociation constant)	n.a.	

Table 11. General physicochemical properties and identification of 4-heptylphenol.



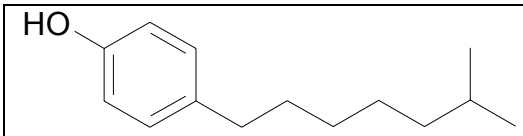
Properties	Value	Reference
IUPAC Name	4—heptylphenol	
CAS number	1987-50-4	
EINECS number	n.a.	
Empirical formula	C13 H20 O1	
Molar mass (g/mol)	192.30	
n-octanol/water partition coefficient (log K_{ow})	5.01 (est)	[45]
	4.0 (exp, HPLC)	[84]
	5.148	[31]
Organic carbon/water sorption coefficient (log K_{oc})	4.253	[45]
Water solubility (mg/l)	9.65 at 25°C	[45]
Melting point (°C)	73.39	[45]
Vapour pressure (Pa)	0.37 at 25°C	[45]
Henry's law constant ($Pa.m^3.mol^{-1}$)	0.34 at 25°C	[45]
pK_a value (dissociation constant)	n.a.	

Table 12. General physicochemical properties and identification of 4-octylphenol.



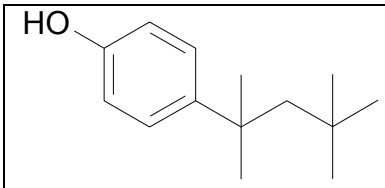
Properties	Value	Reference
IUPAC Name	4-octylphenol	
CAS number	1806-24-4	
EINECS number	n.a.	
Empirical formula	C14 H22 O1	
Molar mass (g/mol)	206.33	
n-octanol/water partition coefficient (log K_{ow})	5.50	[45]
	5.68 (est)	[31]
Organic carbon/water sorption coefficient (log K_{oc})	4.519	[45]
Water solubility (mg/l)	3.11 at 25°C	[45]
Melting point (°C)	82.77	[45]
Vapour pressure (Pa)	0.013 at 25°C	[45]
Henry's law constant ($Pa.m^3.mol^{-1}$)	0.46 at 25°C	[45]
pK_a value (dissociation constant)	n.a.	

Table 13. General physicochemical properties and identification of 4-iso-octylphenol.



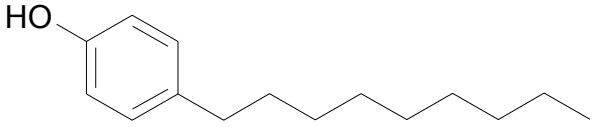
Properties	Value	Reference
IUPAC Name	4-*iso*-octylphenol	
CAS number	11081-15-5	
EINECS number		
Empirical formula	C14 H22 O	
Molar mass (g/mol)	206.33	
n-octanol/water partition coefficient (log K_{ow})	5.42 (est)	[45]
	5.55 (est)	[31]
Organic carbon/water sorption coefficient (log K_{oc})	4.42	[45]
Water solubility (mg/l)	3.6 at 25°C	[45]
Melting point (°C)	80.2	[45]
Vapour pressure (Pa)	0.023 at 25°C	[45]
Henry's law constant ($Pa.m^3.mol^{-1}$)	0.46 at 25°C	[45]
pK_a value (dissociation constant)	n.a.	

*Table 14. General physicochemical properties and identification of 4-*tert*-octylphenol.*



Properties	Value	Reference
IUPAC Name	4-*tert*-octylphenol	
CAS number	140-66-9	
EINECS number	205-426-2	
Empirical formula	C14 H22 O	
Molar mass (g/mol)	206.33	
n-octanol/water partition coefficient (log K_{ow})	5.28 (est)	[45]
	5.157 (est)	[31]
	4.12 (exp)	[2]
	3.6; 3.9 (est)	[2]
	3.7 (exp, HPLC)	[84]
Organic carbon/water sorption coefficient (log K_{oc})	4.189	[45]
Water solubility (mg/l)	4.82 at 25°C	[45]
Melting point (°C)	72.79	[45]
Vapour pressure (Pa)	0.09 at 25°C	[45]
Henry's law constant ($Pa.m^3.mol^{-1}$)	0.46 at 25°C	[45]
BCF	634 (est)	[44]
pK_a value (dissociation constant)	n.a.	

Table 15. General physicochemical properties and identification of 4-nonylphenol.

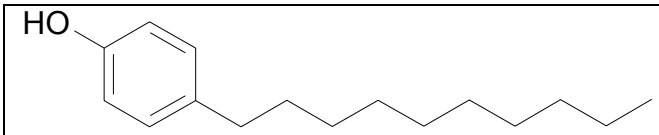


The alkyl chain is drawn as a linear structure but may also be branched.

Properties	Value	Reference
IUPAC Name	4-nonylphenol	
CAS number	84852-15-3; branched 25154-52-3; straight chain 11066-49-2; 4-*iso*-nonylphenol 104-40-5; "4-nonylphenol" 90481-04-2; "branched 4-nonylphenol"	
EINECS number	284-325-5; branched 246-672-0; straight chain	
Empirical formula	C15 H24 O1	
Molar mass (g/mol)	220.56	
n-octanol/water partition coefficient (log K_{ow})	5.76 (exp, straight chain)	[45]
	5.61 (exp. *iso*-nonylphenol)	[45]
	4.48 (exp, branched)	[2]
	4.2 (exp, branched, HPLC)	[84]
	4.1; 4.2 (est)	[2]
	6.21 (est, straight chain)	[31]
	6.1 (est, *iso*-nonylphenol)	[31]
Organic carbon/water sorption coefficient (log K_{oc})	3.58[a]	[90]
	4.79 (straight chain)	[45]
	4.71 (*iso*-nonylphenol)	[45]
Water solubility (mg/l)	1.57 at 25°C	[45]
	7, 6.35 at 25°C (exp.; straight chain)	[45]
	4.9 ± 0.4 at 25°C	[21]
	89.9 (est.; *iso*-nonylphenol)	[45]
Melting point (°C)	42 (exp.; straight chain)	[45]
Vapour pressure (Pa)	0.0126 at 25°C (*iso*-nonylphenol)	[45]
	0.0126 at 25°C (exp.; straight chain)	[45]
Henry's law constant ($Pa.m^3.mol^{-1}$)	3.4 (exp.; straight chain)	[45]
	0.6 at 25°C (*iso*-nonylphenol)	[45]
	at 25°C (straight chain)	[45]
BCF	280 (k1/k2)	[84]
	1280 (est)	[46]
pK_a value (dissociation constant)	n.a.	

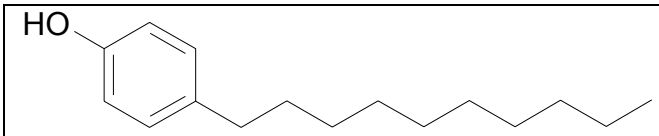
[a]Average of 3 values measured in 3 different soils.

Table 16. General physicochemical properties and identification of 4-dodecylphenol.



The alkyl chain is drawn as a linear structure but may also be branched.

Properties	Value	Reference
IUPAC Name	4-dodecylphenol	
CAS number	104-43-8	
EINECS number	n.a.	



The alkyl chain is drawn as a linear structure but may also be branched.

Properties	Value	Reference
Empirical formula	C18 H30 O1	
Molar mass (g/mol)	262.44	
n-octanol/water partition coefficient (log K_{ow})	7.91 (exp)	[45]
	5.5 (exp, HPLC)	[84]
	7.793[a] (est)	[31]
Organic carbon/water sorption coefficient (log K_{oc})	5.582	[45]
Water solubility (mg/l)	0.013 at 25°C	[45]
Melting point (°C)	117.12	[45]
Vapour pressure (Pa)	0.0003 at 25°C	[45]
Henry's law constant ($Pa.m^3.mol^{-1}$)	1.42 at 25°C	[45]
BCF	6000 (k1/k2)	[84]
pK_a value (dissociation constant)	n.a.	

[a]ClogP comments: very unrealistic logP unrealistic in nature.

3.1.3 Use, production and discharge

Use

Generally, alkylphenols are basically used as intermediate in the production of alkylphenol ethoxylates and phenolic oximes, and as monomer in phenolic resins and plastics production. The distribution of total nonylphenol use within the EU in 1997 was: 60% nonylphenol ethoxylate production, 37% phenolic resins/plastics production and 3% phenolic oxime production[46]. The market share of octylphenol and nonylphenol is over 95%, leaving only a minor proportion for butyl-, pentyl-, hexyl-, heptyl- and dodecylphenol.

IUCLID [47] shows the following uses for 4-*tert*-butylphenol: chemical synthesis; paints, lacquers and varnishes industry; polymers industry, printing ink, adhesive; binding agents; cosmetics; insulating materials; intermediates; odour agents; surface–active agents; vulcanising agents.

IUCLID [47] shows the following uses for tetramethylbutylphenol (an octylphenol): chemical synthesis; paints, lacquers and varnishes industry; printing ink; adhesive, binding agents; insulating materials; intermediates; surface–active agents; vulcanising agents; printing ink binder. Some other uses are summed in [44]: anti-oxidant, in copy paper,

Nonylphenols are used as intermediate in the production of nonylphenol ethoxylates. There are several other industrial applications such as phenolic resins, which in turn are used in the manufacture of surface coating compositions, brake and clutch linings, and in the manufacture of printing inks. Other industrial applications of nonylphenol are plastic stabilisers and anti-oxidants (phenolic oximes) used during rubber manufacture and in the extraction of copper from ore.

Production

Octylphenol and nonylphenol have similar production processes: phenol and alkenes are reacted in the presence of a catalyst. The structure of the resulting alkyl chain in the product is

influenced by choosing the appropriate alkene. Di-isobutene (4-*tert*-octene) is used in the production of 4-*tert*-octylphenol and tripropylene (isononene) is used to produce nonylphenol. The resulting alkylphenol is always a mixture of branched chain isomers [44, 46]. There are no production sites of alkylphenols in the Netherlands [46, 51].

Discharge
Since the biodegradation of alkylphenol ethoxylates in the environment may lead to formation of alkylphenols, the discharge of ethoxylates in industrial and domestic wastewater is an important emission source. It is estimated that 60-70% of overall nonylphenol ethoxylate use will end up in waste waters [51].

After production and use, the main entry into the environment for alkylphenols is via waste water that may or may not pass a sewage treatment plant (STP) before entry into surface water. Emission to soil may take place in agricultural areas that receive alkylphenols from the use of pesticides or indirectly via spreading of manure containing residues of veterinary drugs. In the Netherlands, sewage sludge derived from STPs is not allowed to be spread over land, therefore this route will not contribute to nonylphenol emission to soil. An inventory performed in 1996 [88] reported an estimated use of 44 tonnes.y^{-1} of nonylphenol (unspecified) in agricultural pesticide use in the Netherlands. At present there are no registered pesticides or veterinary drugs in the Netherlands with an alkylphenol as active ingredient [23, 28]. However, formulations of pesticides or veterinary drugs may contain alkylphenols or their ethoxylates as additives. Adjuvants containing alkylphenols as active component are another application in pesticide use. These adjuvants are added to the pesticide formulation as wetting or sticking agent before application. Use and registration of these adjuvants is poorly regulated in the Netherlands, making emission estimates practically impossible.

4. Alkylphenols - Derivation of MPCs and NCs for water

4.1 Nonylphenol

The general name nonylphenol designates a group of isomeric compounds that may vary in the position of the nonyl chain on the phenol ring and the degree of branching of the nonyl group. The isomer that is predominantly produced commercially is 4-nonylphenol, in which the degree of branching varies and is usually undefined. Nonylphenol is defined as straight chain (unbranched) nonylphenol only by Chemical Abstract Service (CAS). However, straight chain nonylphenol is produced only in minor quantities in commercial mixtures. For this reason nonylphenol as used in the EU-RAR covers all isomers that are not 4-nonylphenol. Hence, the EU-RAR addresses the potential risks of all nonylphenols, with 4-nonylphenol named explicitly, and with nonylphenol used as general name for all other isomers.

4.1.1 PNEC derivation: general remark

It is emphasised here, that PNEC values (and consequently MPC values based on PNEC values) derived in the following sections (4.1.2, 4.1.3 and 4.1.4) are *not* derived according to INS guidance, but according to EU-TGD guidance and are in fact cited from the EU-RAR for nonylphenol [46], the reason for which is explicated in section 1.2 (2nd paragraph). Observed deviations from INS guidance are therefore attributable to the choice to use EU-TGD based risk limits, that are based on a different underlying framework for environmental risk assessment.

4.1.2 $PNEC_{water}$

Table 17 shows the lowest values of chronic and acute toxicity data for algae, invertebrates and fish for nonylphenol; these values are used to derive the PNEC. For an overview of all toxicity data we refer to the EU-RAR [46].

Table 17. Toxicity data used for the derivation of the $PNEC_{water}$ for nonylphenol [46].

Trophic level	Species	Endpoint	Parameter	Duration (d)	Concentration (µg/l)
Acute data, freshwater					
Invertebrates	*Ceriodaphnia dubia*	EC_{50}	n.r.	4	69
	Daphnia magna	EC_{50}	n.r.	2	85
	Hyalella azteca	EC_{50}	immobilisation	4	20.7
Fish	*Pimephales promelas*	LC_{50}	lethality	4	128
Acute data, salt water					
Invertebrates	*Mysidopsis bahia*	LC_{50}	lethality	4	43
Fish	*Cyprinodon variegatus*	LC_{50}	lethality	4	310
Chronic data, freshwater					
Algae	*Scenedesmus subspicatus*	EC_{10}	biomass	3	3.3

Trophic level	Species	Endpoint	Parameter	Duration (d)	Concentration (µg/l)
	Scenedesmus subspicatus	EC_{50}	biomass	3	56.3
	Scenedesmus subspicatus	EC_{10}	growth rate	3	25.1
	Scenedesmus subspicatus	EC_{50}	growth rate	3	323
	Selenastrum capricornutum	EC_{50}	cell growth	4	410
Invertebrates	*Ceriodaphnia dubia*	NOEC	reproduction	7	88.7
	Daphnia magna	NOEC	lethality F1	21	24
Fish	*Pimephales promelas*	NOEC	lethality	33	7.4
Chronic data, saltwater					
Algae	*Skeletonema costatum*	EC_{50}	cell growth	4	27
Invertebrates	*Mysidopsis bahia*	NOEC	growth	28	3.9

n.r. = not reported

Remarks

1. The algal toxicity data in Table 17 are placed under the *chronic* toxicity data because the test duration in algal tests lasts for several algal generations and is therefore considered to be chronic with respect to the organism. According to the TGD the EC_{50} from algal tests is used to complete the base-set (in that case, treating the results as acute data), from which the most sensitive trophic level during acute exposure is identified [41]. If necessary, the EC_{10} of an algal test can be used as NOEC for the assessment of long term effects on the trophic level of primary producers.
2. Before combining toxicity data of freshwater and salt water species for PNEC derivation it should be tested whether the sensitivity of these two groups to nonylphenol does not differ significantly. Since this comparison was not reported in the EU-RAR, the data were checked for differences in sensitivity (F-test followed by an unpaired t-test with Welch's correction in case of unequal variances). Acute toxicity of nonylphenol did not differ significantly between freshwater and salt water invertebrates (P=0.60) nor between freshwater and salt water fish (P=0.93). A statistical comparison between algal data could not be made because there was only one test result for a marine algal species available. A statistical comparison between chronic data could not be made because there were no NOEC values for salt water algae, only one NOEC value for salt water invertebrates and no chronic data for salt water fish. Based on the data that could be compared, freshwater and salt water species did not differ in sensitivity to nonylphenol and the combination of datasets is justified.

Acute toxicity data at three trophic levels (see remark 1 in the above text) for both freshwater and salt water are available as well as chronic toxicity data at three trophic levels for freshwater and at two trophic levels for salt water. The most sensitive species in chronic toxicity tests is the green alga *Scenedesmus subspicatus*, which showed an EC_{10} of 3.3 µg/l

for toxicity of nonylphenol to biomass growth. An assessment factor of 10 is applied to this value, leading to a $PNEC_{water}$ of 0.33 µg/l.

4.1.2.1 Recalculation into $PNEC_{water, total}$ and $PNEC_{water, dissolved}$

In the Netherlands, ERLs for water are derived for both the dissolved and total fraction. Dutch standard water contains 30 mg suspended matter (dw/l), with 20% organic matter (11.72% organic carbon). For the calculation method we refer to the Guidance document on deriving environmental risk limits [120]. The partition coefficient between suspended matter and water used in the calculation is derived from the value as reported in the EU-RAR, which is based on an organic carbon content of 10%. EUSES uses:
$K_{p, susp} = Foc_{susp} * K_{oc}$ with a K_{oc} value of 5360 $l.kg^{-1}$. This means that for the Dutch situation $K_{p, susp} = 0.1172 * 5360 = 628$ $l.kg^{-1}$.

The $PNEC_{water}$ of 0.33 $\mu g.l^{-1}$ should be regarded as $PNEC_{water, dissolved}$. $PNEC_{water, total}$ is calculated to be approximately equal to $PNEC_{water, dissolved}$, i.e. 0.33 $\mu g.l^{-1}$.

4.1.3 $PNEC_{soil}$

There is a limited number of toxicity data available for terrestrial organisms. For an overview of the data we refer to the EU-RAR for nonylphenol [46]. Toxicity data are available for micro-organisms (2 processes), plants (4 species) and invertebrates (2 species).Table 18 shows the most sensitive species from three trophic levels.

Table 18. Toxicity data used for the derivation of the $PNEC_{soil}$ for nonylphenol [46].

Trophic level	Species	Endpoint	Parameter	Duration (d)	Concentration (mg/kg)
Micro-organisms	Soil community	NOEC	CO_2 production	40	≥100
	Soil community	NOEC	N-mineralisation	100	≥500
	Soil community	LOEC	nitrification	100	≥500
Plants	*Sorghum bicolor*	NOEC	growth	21	100
	Helianthus rodeo	NOEC	growth	21	100
	Glycine max	NOEC	growth	21	100
Invertebrates	*Apporectodea caliginosa*	EC_{10}	reproduction	21	3.44

Since toxicity data are available for three trophic levels, an assessment factor of 10 may be applied to the lowest NOEC. Reproduction of the earthworm *A. caliginosa* was the most sensitive endpoint, showing an EC_{10} of 3.44 mg/kg. The EC_{10} value is regarded as equivalent to a NOEC. The $PNEC_{soil}$ is calculated to be 0.34 mg/kg_{ww}.
Communication with the drafter of the EU-RAR gave the information that the EC_{10} value for *A. caliginosa* is most likely not normalised for organic carbon content and based on wet soil. This hampers recalculation of the PNECsoil to an MPC since MPCs are expressed as dry weight values, normalised to Dutch standard soil. We will therefore not derive an MPC_{soil} here, but various options are discussed in Appendix 7.

4.1.4 $PNEC_{sediment}$

The EU-RAR on nonylphenol does not report a $PNEC_{sediment}$. Since the method for dervation of a –Dutch– $MPC_{sediment}$ from an EU-RAR based $PNEC_{sediment}$ is still under debate, a final proposal can not be made here. Methods to arrive at an MPC value that may be used in Dutch standard setting are discussed in Appendix 7.

4.1.5 ERLs for nonylphenol

The $PNECs_{water}$ derived in the foregoing sections are set equivalent to the MPC and are reported as such in Table 19.

Table 19. MPCs for nonylphenol.

Compartment	Value	Unit	Method	Partition coefficient	value	Unit
$MPC_{water, total}$	0.33	[µg.l^{-1}]	INS Guidance	$K_{p, susp}$	628	l.kg^{-1}
$MPC_{water, dissolved}$	0.33	[µg.l^{-1}]	EC_{10}/10			

SRC_{ECO} values are not derived within the EU existing substances framework. They are not reported here, but can be derived based on the data in the EU-RAR if necessary. Table 20 shows the ERLs derived for nonylphenol.

Table 20. ERLs for nonylphenol for $water_{total}$, $water_{dissolved}$ and groundwater.

	$WATER_{TOTAL}$		$WATER_{DISSOLVED}$		GROUNDWATER	
Compound	NC [µg.l^{-1}]	MPC [µg.l^{-1}]	NC [µg.l^{-1}]	MPC [µg.l^{-1}]	NC [µg.l^{-1}]	MPC [µg.l^{-1}]
Nonylphenol	0.0033	0.33	0.0033	0.33	0.0033	0.33

5. Alkylphenols – Preliminary risk analysis

5.1 Environmental distribution

In this section we report measured NP concentrations in Dutch surface waters. Since no literature search was performed for alkylphenols we have used the same references from which alkylphenol ethoxylate data for the Netherlands were found: [33, 63, 133]. The NP concentrations found in those references are shown in Table 21 and Table 22.

Table 21. Nonylphenol concentrations in surface water in the Netherlands.

Location	Year	Concentration [µg.l^{-1}]	Reference
Main waterways[a]	1997	<l.o.d-0.14	[33]
Rhine estuary[b]	1999	0.031-0.147	[63]
Scheldt estuary[c]	1999	0.035-0.93	[63]
Canal Gent-Terneuzen	1999	0.32	[63]
Various rivers[d]	1999	0.72, 4.1[e]	[134]
River Rhine	2001	0.22[f] (0.15-0.40)	[64]
River Meuse	2001	0.28[g] (0.17-0.38)	[64]
Estuaries[h]	1999	2.0[i]	[134]
Haringvliet	2001	0.13[j]	[64]
North Sea[k]	1999	<0.19-<0.58	[134]

[a]*n*=3; Canal Gent-Terneuzen, Canal: Noordzeekanaal-location IJmuiden and Seaway: New Waterway-location Beneluxtunnel; [b]reported values are minimum and maximum concentrations along the salinity gradient from 0.2-19 ‰ ; [c]reported values are minimum and maximum concentrations along the salinity gradient from 1.5-32.2 ‰; [d]16 locations measured 1, 2 or 3 times in 1999; [e]2 (of 40) measurements were > l.o.d..; [f]mean of pooled data from three locations, sampled at two dates (*n*=6); [g]mean of data from one location sampled at two dates (*n*=2); [h]9 locations measured 2 or 3 times in 1999; [i]1 (of 19) measurements was > l.o.d.; [j]one location, one sample (*n*=1); [k]4 locations measured 2 or 3 times in 1999, all measurements <l.o.d. (l.o.d. range reported).

Table 22. Nonylphenol concentrations in sediment in the Netherlands.

Location	Year	Concentration [mg.kg$_{d.w.}^{-1}$]	Reference
Main waterways[a]	1997	0.63-1.70	[33]
Rhine estuary[b]	1999	0.0015-0.092	[63]
Scheldt estuary[b]	1999	<l.o.d.-1.1	[63]
Various rivers[c]	1999	0.13-2.8[d]	[134]
Estuarine sediments[e]	1999	0.05-3.8[f]	[134]
Marine sediments[g]	1999	0.04-0.26[h]	[134]
Estuarine and marine sediments[i]	1997	0.0001-0.017	[33]

[a]*n*=3; Canal Gent-Terneuzen, Canal: Noordzeekanaal-location IJmuiden and harbour Amerikahaven; [b]reported values are minimum and maximum concentrations along the salinity gradient; [c]11 locations sampled once in 1999; [d]10 (of 11) values were >l.o.d.; [e] 5 locations sampled once in 1999; [f]3 (of 5) values were >l.o.d.; [g]5 locations sampled once in 1999; [h]5 (of 7) values were >l.o.d.[i]22 estuarine and marine locations in the North Sea and Irish Sea;

5.2 Preliminary risk analysis

5.2.1 Water

This risk analysis is indicative since a specific literature search on occurrence of NP was not performed. Comparing the highest values from the ranges shown in Table 21 with the MPC from Table 20 (viz. 0.33 $\mu g.l^{-1}$) indicates that the MPC was exceeded in two river measurements and in one estuarine measurement. The locations where the MPC was exceeded are: the canal 'Apeldoorns kanaal', canal 'Koudevaart' (Sint Annaparochie) and canal 'Gent-Terneuzen'. The first two locations are known to receive water from sewage treatment and the second and third location receive industrial waste water. The most recent measurements (2001) showed that mean values were below the MPC, but maximum concentrations measured in Rhine and Meuse (0.40 and 0.38 $\mu g.l^{-1}$, respectively) were just above the MPC.

5.2.2 Sediment

Comparing the highest values from the ranges shown in Table 22 with the preliminary MPC from Table A7. 2 (viz. 0.105 $mg.kg^{-1}$) indicates that the MPC was exceeded on several occasions. The majority of river sediments sampled in 1999 [133] exceeded the MPC (10 out of 11) without a clear relation to location. It must be noted that from this small data series, the river Dommel showed the highest sediment concentrations. Furthermore, measurements in estuarine sediments often show the Scheldt to have the highest concentrations. Generally, marine sediments show lower NP sediment concentrations, the values from [133] that exceed the MPC (*please note that this MPC is not specifically derived as seawater ERL*) are 2 out of 7 measurements: one was a 'clean' reference location in the North Sea (which showed a concentration <MPC (viz. 0.07 $mg.kg^{-1}$) when sampled on another occasion) the other was in the Wadden Sea (n=1), which is also thought to be a relatively clean area.

5.2.3 Conclusion

NP concentrations in Dutch surface waters or sediments exceeded the MPC at some locations. Relatively high concentrations can usually be related to industrialised areas or discharge of sewage treatment effluents. In sediments, concentrations around the MPC or higher than the MPC are more common and do not seem to be specifically related to industry or sewage treatment outlets. This is probably caused by the fact that sediment concentrations reflect accumulation more than water concentrations. Accumulation of NP is possible since it is thought to be not easily biodegradable (see section 8.2.).

5.3 Nonylphenol – emission reduction in the EU

The world demand of NP and NPEO is still expected to grow slightly in the coming years [51] with 1-2% per year for NP and 2-3% per year for NPEO. The need to reduce emissions of AP and APEO to the environment is addressed by both industry and regulatory authorities. Some policy measures at European level are outlined below.

In 2001, the OSPAR Commission has published its opinion for a risk reduction strategy with regard to NP/NPEO [96]. The recommended actions are (a.o.): to support EC risk reduction measures on use in agricultural pesticide use and in emulsion polymers and to support an EC limit on concentrations in sewage sludge. Plans for a monitoring strategy will be developed

and the need for action with regard to NP/NPEO use in offshore industry will be considered. A review on further (OSPAR) measures to be taken and the need to supplement EC measures, is scheduled for 2003.
Recently (in March 2003), the EC has issued a presidency Non-paper [40] for a Directive of the European parliament and of the Council. In this paper, several proposals are given for decisions to be taken on risk reduction with regard to NP and NPEO. A short overview of the most important *proposals* for measures to be taken:

- the commission shall submit proposals of control for the cessation or phasing-out of discharges, emissions and losses of such substances,
- an invitation to consider concentration limits of NP and NPEO in sewage sludge that is to be spread on land,
- placing on the market of NP and NPEO should be restricted for uses that result in discharges, emissions or losses to the environment,
- annex I of Directive 76/769/EEC is amended for NP and $NPEO_n$, meaning that both compounds will be restricted in their placing on the market or in their use as constituent of preparations, in concentrations ≥0.1% (w/w) for several purposed (a.o. cleaning applications, textile processing, emulsifier in agricultural teat dips, cosmetics),
- Plant protection products or biocidal products containing NPEO as co-formulant, that have a national registration, will not be affected by the Directive, *until these registrations expire*.

Note that this Directive has not yet been issued.

6. Alkylphenol ethoxylates - Methods

6.1 Data Search and selection

An on-line literature search was performed for the period 1995-2001. The TOXLINE PLUS database was searched from 1995 to January 2001 and CURRENT CONTENTS were searched over 2001 (+ week 1 of 2002). Also, literature was retrieved from relevant papers via retrospective search. An important and recent source of both information and literature is the RIKZ report of Groshart *et al.*: 'Chemical study on alkylphenols' [51]. There were several reviews that were scanned for relevant data and references: Lewis [72], Warhurst [137], Staples [115] and Servos [111]. Relevant references from these reviews were retrieved and reviewed. A considerable number of data however, was not available in public literature, such as confidential study reports or conference proceedings that could not be retrieved. These entries were not included in the evaluation. The only exception to this criterion were data in Staples [115] that were not available in public literature; these data were used since data evaluation of this author were accepted as reliable in earlier reports.

A toxicity study is considered reliable if the design of the experiment is in agreement with internationally accepted guidelines, e.g. OECD guidelines. To judge studies that have not been performed according to these guidelines criteria are developed for this project, as documented in Traas [120]. Effects on growth, reproduction or survival are used in the derivation of ERLs, as they are related to population dynamics. Toxicity data from soil or sediment studies are normalised to 10% organic matter. For each species and each compound, the most sensitive toxicity test is selected. If for a single species several toxicity values are found for the same effect parameter, the geometric mean is calculated.

6.2 EU-risk assessment reports

For alkylphenol ethoxylates, no EU-RARs are available. Currently no alkylphenol ethoxylates are prioritised within the framework of the European existing substances programme.

6.3 Selection of compounds

Data have been collected for octylphenol ethoxylate and nonylphenol ethoxylate.

6.4 Derivation of ERLs

The maximum permissible concentrations and negligible concentrations are derived according to the methods generally applied within the project 'Setting Integrated Environmental Quality Standards' [120].
In short, data on chronic and acute toxicity for aquatic and terrestrial species and terrestrial processes of a compound are searched for. They are evaluated, and selected or rejected. For compounds with a log K_{ow} higher than 3.0, or for compounds for which secondary poisoning is expected, also toxicity data for mammals and birds are searched for. The maximum permissible concentration (MPC) is derived using either the refined assessment method as described by Aldenberg and Jaworska [9], or assessment factors as laid down in the Technical

Guidance Document [41], developed for EU council regulation 793/93. The MPCs are harmonised according to the equilibrium partition theory. In this way it is prevented that a concentration on an MPC-level in one compartment leads to exceeding the MPC in another compartment.

When the method of derivation of a NOEC, LC_{50} or EC_{50} was not clearly stated in the original work, a recalculation was performed. A logistic equation was fitted through effect data versus the logarithms of concentrations (preferably measured values) using non-linear regression [49]. Either the EC_{50} (LC_{50}) or the EC_{10} was calculated. When data of a chronic experiment were fitted, an EC_{10} was calculated, which was interpreted as NOEC. Recalculation of data is mentioned in the footnotes of the tables in Appendix 4 and 5 using the statement 'logistic dose response curve fitted through data from author'.

6.4.1 Preliminary effect assessment

If chronic or acute toxicity data are available for less than four taxonomic groups, assessment factors are used. The assessment factors used are laid down in the Technical Guidance Document [41] which is developed in the framework of EU council regulation 793/93. In case there is no complete base-set (acute toxicity to algae, daphnia and fish), the modified EPA method as described in the guidance document [120] is used.

6.4.2 Refined effect assessment

The aim of environmental quality standards as derived in the project 'Setting Integrated Environmental Quality Standards' is to protect all species in the ecosystem. For statistical considerations the MPC is set equal to the concentration at which 95% of the species is protected, i.e. the HC_5, assuming thereby to protect the whole ecosystem [126, 135]. A detailed description of the statistical background of the refined effect assessment method is given in the literature [9, 10, 67, 129].
It is assumed that the log of sensitivities of species in an ecosystem can be described by a normal probability distribution. The goodness of fit of the normal distribution is tested with the Kolmogorov-Smirnov $D^*\sqrt{(n)}$ test and the Anderson-Darling test [8]. The Kolmogorov-Smirnov test focuses in the middle of the distribution, while the latter highlights the differences between the tails of the fitted distribution and the data. The average, the standard deviation, and the number of the underlying data define this distribution. Extrapolation factors as derived previously [9] are used to estimate the HC_5, and its upper (95%) and lower (5%) estimate, constituting a 90% two-sided confidence interval.

6.4.3 Derivation of negligible concentrations (NCs)

Multiplying the MPCs with a factor 0.01 derives NCs. This factor is supposed to function as protection against mixture toxicity, since species in the environment are always exposed to mixtures of chemicals and complex mixtures of chemicals are generally best described as concentration-additive [34, 127].

6.4.4 Equilibrium partitioning and harmonisation between the compartments

By applying the equilibrium-partitioning concept [37], it is assumed that there is equilibrium between the concentration in organic carbon and (pore) water. In addition, it is assumed that toxicity is related to pore water concentrations, and that the sensitivity of aquatic organisms is comparable to that of organisms living in soil or sediment. The partition coefficient between organic carbon in the soil/sediment and water (K_{oc}) is used to derive an MPC for soil/sediment when no data on terrestrial or sediment-dwelling organisms are available. By applying equilibrium partitioning, the K_{oc} is used to harmonise the MPCs between the different compartments.

7. Alkylphenol ethoxylates - Substance properties, use and production

7.1 General molecular structure

Alkylphenol ethoxylates are phenolic compounds of which (i) the phenol group is ethoxylated (CH_3-CH_2-O-)$_n$ with one or more ethoxy groups, and that (ii) possess an alkyl chain attached to the aromatic ring. Their general structural formula is:

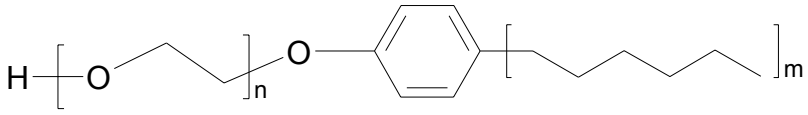


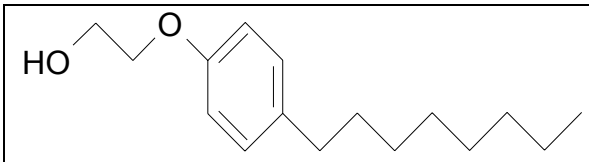
Figure 3. General structural formula of alkylphenol ethoxylates. n *denotes the number of ethoxy oligomers composing the ethoxylate chain,* m *denotes the number of C atoms in the alkyl chain. The alkyl chain is drawn as a linear structure, but it may also be (and usually is) branched.*

Most commercial alkylphenol ethoxylates are in fact technical mixtures of compounds for which the number of C atoms in the alkyl chain is fixed, but the structure of the alkyl chain and the number of ethoxy oligomers varies. A fictitious example: for nonylphenol deca-ethoxylate, all molecules have an alkyl chain containing 9 C-atoms (with varying degree of branching), but the number of ethoxy oligomers may range from e.g. 4 to 15 with an average length of 10. Alkylphenol ethoxylates are amphiphilic compounds, they possess both a hydrophilic part (the 'head', i.e. the ethoxy oligomer chain) and a hydrophobic part ('tail' i.e. the alkyl moiety). These structural characteristics give the compounds their typical properties of surface tension lowering and micelle formation, which classifies them as surfactants. Since the average length of the ethoxylate chain can be varied, a widely applicable class of surfactants is created, explaining their widespread use and their many applications.

7.2 Physico-chemical properties

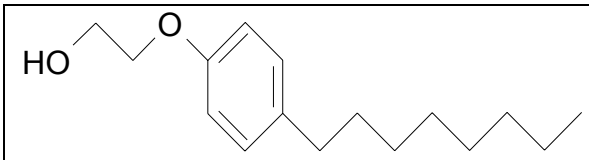
Wherever possible, data are retrieved from open literature and completed with data calculated with modules from EPI Suite [45] and MedChem's ClogP [31].

Table 23. General physicochemical properties and identification of octylphenol mono-ethoxylate ($OPEO_1$).



The alkyl chain is drawn as a linear structure but may also be branched.

Properties	Value	Reference
IUPAC Name	octylphenol mono-ethoxylate	
CAS number		
EINECS number	n.a.	
Empirical formula	C16 H26 O2	
Molar mass (g/mol)	250.38	
n-octanol/water partition coefficient (log K_{ow})	5.09	[45]

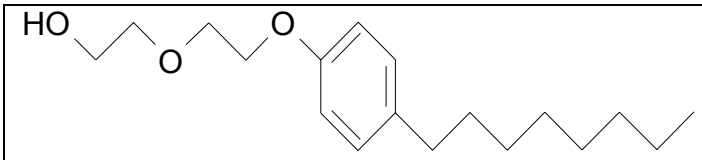


The alkyl chain is drawn as a linear structure but may also be branched.

Properties	Value	Reference
	5.39	[31]
	3.3[b], 4.1[c]	[2]
Soil/sediment water sorption coefficient (log K_{oc})	3.1 (est)	[45]
	6.02±0.15[e] (exp)	[55]
Water solubility (mg/l)	3.46 at 25°C	[45]
	8.0 ± 0.18[d] at 20.5°C	[1]
Melting point (°C)	107.2	[45]
Vapour pressure (Pa)	4.8×10^{-7} at 25°C	[45]
Henry's law constant ($Pa.m^3.mol^{-1}$)	0.013 at 25°C	[45]

n.a. = not available; [b]QSAR based on partitioning of $OPEO_n$ in *iso*-octanol transformed to $NPEO_n$ and octanol, details see [2]; [c]QSAR based on aqueous solubility [2], [d]generator column method on individual isomer obtained via preparative HPLC, n=3, [e]field determined K_{oc} for suspended matter/water, n=12.

Table 24. General physicochemical properties and identification of octylphenol di-ethoxylate ($OPEO_2$).

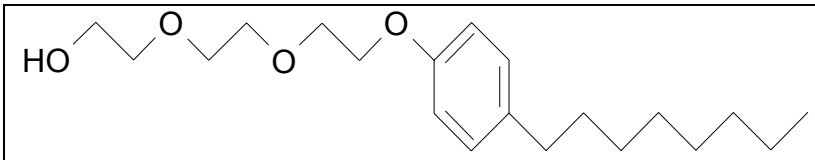


The alkyl chain is drawn as a linear structure but may also be branched.

Properties	Value	Reference
IUPAC Name	octylphenol di-ethoxylate	
CAS number	n.a.	
EINECS number	n.a.	
Empirical formula	C18 H30 O3	
Molar mass (g/mol)	294.44	
n-octanol/water partition coefficient (log K_{ow})	4.81	[45]
	5.454	[31]
	2.9[b], 4.0[c]	[2]
Soil/sediment water sorption coefficient (log K_{oc})	2.71 (est)	[45]
	6.24±0.16[e] (exp)	[55]
Water solubility (mg/l)	3.3 at 25°C	[45]
	13.2 ± 0.21[d] at 20.5°C	[1]
Melting point (°C)	131.9	[45]
Vapour pressure (Pa)	2.5×10^{-8} at 25°C	[45]
Henry's law constant ($Pa.m^3.mol^{-1}$)	0.0002 at 25°C	[45]

n.a. = not available; [b]QSAR based on partitioning of $OPEO_n$ in *iso*-octanol transformed to $NPEO_n$ and octanol, details see [2]; [c]QSAR based on aqueous solubility [2], [d]generator column method on individual isomer obtained via preparative HPLC, n=3, [e]field determined K_{oc} for suspended matter/water, n=12.

Table 25. General physicochemical properties and identification of octylphenol tri-ethoxylate ($OPEO_3$).

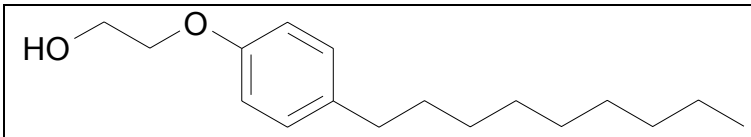


The alkyl chain is drawn as a linear structure but may also be branched.

Properties	Value	Reference
IUPAC Name	octylphenol tri-ethoxylate	
CAS number	n.a.	
EINECS number	n.a.	
Empirical formula	C20 H34 O4	
Molar mass (g/mol)	338.49	
n-octanol/water partition coefficient (log K_{ow})	4.54	[45]
	5.32	[31]
	2.6[b], 3.9[c]	[2]
Soil/sediment water sorption coefficient (log K_{oc})	2.24	[45]
Water solubility (mg/l)	3.1 at 25°C	[45]
	18.4 ± 0.55[d] at 20.5°C	[1]
Melting point (°C)	160.5	[45]
Vapour pressure (Pa)	1.08×10^{-9} at 25°C	[45]
Henry's law constant ($Pa.m^3.mol^{-1}$)	3.0×10^{-6} at 25°C	[45]

n.a. = not available; [b]QSAR based on partitioning of $OPEO_n$ in *iso*-octanol transformed to $NPEO_n$ and octanol, details see [2]; [c]QSAR based on aqueous solubility [2], [d]generator column method on individual isomer obtained via preparative HPLC, *n*=3.

Table 26. General physicochemical properties and identification of nonylphenol (mono-)ethoxylate ($NPEO_1$).

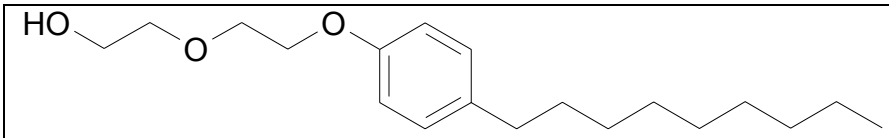


The alkyl chain is drawn as a linear structure but may also be branched.

Properties	Value	Reference
IUPAC Name	nonylphenol (mono-)ethoxylate	
CAS number	9016-45-9	
EINECS number		
Empirical formula	C17 H28 O2	
Molar mass (g/mol)	264.41	
n-octanol/water partition coefficient (log K_{ow})	5.58 (est)	[45]
	5.92 (est)	[31]
	4.17[a] (exp)	[2]
	3.8[b]; 4.4[c] (est)	[2]
Organic carbon/water sorption coefficient (log K_{oc})	3.44 (est)	[45]
	5.60±0.11[e] (exp)	[55]
Water solubility (mg/l)	1.1 at 25°C	[45]
	3.02 ± 0.07[d] at 20.5°C	[1]
Melting point (°C)	116.18	[45]
Vapour pressure (Pa)	2.37×10^{-5} at 25°C.	[45]
Henry's law constant ($Pa.m^3.mol^{-1}$)	0.017 at 25°C	[45]

[a]A commercial mixture of $NPEO_n$ isomers was used in log K_{ow} determination; isomers were separated by normal phase HPLC analysis and quantified individually; [b]QSAR estimate based on partitioning of $OPEO_n$ in *iso*-octane/water transformed to a QSAR for partitioning of $NPEO_n$ in octanol/water, details see [2]; [c]QSAR estimate, based on K_{ow}-aqueous solubility relationship [2] with S_w determined experimentally for individual isomers [1], [d]generator column method on individual isomers obtained via preparative HPLC, *n*=5; [e]field determined K_{oc} for suspended matter/water, *n*=12.

Table 27. General physicochemical properties and identification of nonylphenol di-ethoxylate ($NPEO_2$).

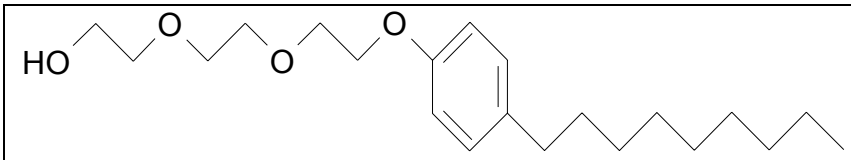


The alkyl chain is drawn as a linear structure but may also be branched.

Properties	Value	Reference
IUPAC Name	nonylphenol di-ethoxylate	
CAS number	27176-93-8	
EINECS number		
Empirical formula	C19 H22 O3	
Molar mass (g/mol)	308.47	
n-octanol/water partition coefficient (log K_{ow})	5.30 (est)	[45]
	5.98 (est)	[31]
	4.21[a] (exp)	[2]
	3.4[b]; 4.4[c] (est)	[2]
Organic carbon/water sorption coefficient (log K_{oc})	2.97 (est)	[45]
	6.38±0.03[e] (field, suspended matter)	[55]
Water solubility (mg/l)	1.05 at 25°C	[45]
	3.38 ± 0.12[d] at 20.5°C	[1]
Melting point (°C)	140.16	[45]
Vapour pressure (Pa)	1.22×10^{-6} at 25°C	[45]
Henry's law constant ($Pa.m^3.mol^{-1}$)	0.0003 at 25°C	[45]

[a]A commercial mixture of $NPEO_n$ isomers was used in log K_{ow} determination; isomers were separated by normal phase HPLC analysis and quantified individually; [b]QSAR estimate based on partitioning of $OPEO_n$ in *iso*-octane/water transformed to a QSAR for partitioning of $NPEO_n$ in octanol/water, details see [2]; [c]QSAR estimate, based on K_{ow}-aqueous solubility relationship [2] with S_w determined experimentally for individual isomers [1], [d]generator column method on individual isomers obtained via preparative HPLC, n=5. [e]field determined K_{oc} for suspended matter/water, n=12.

Table 28. General physicochemical properties and identification of nonylphenol tri-ethoxylate ($NPEO_3$).



The alkyl chain is drawn as a linear structure but may also be branched.

Properties	Value	Reference
IUPAC Name	nonylphenol tri-ethoxylate	
CAS number	27176-95-0	
EINECS number		
Empirical formula	C21 H36 O4	
Molar mass (g/mol)	352.52	
n-octanol/water partition coefficient (log K_{ow})	5.03 (est)	[45]
	6.05 (est)	[31]
	4.20[a] (exp)	[2]
	3.1[b]; 4.3[c] (est)	[2]
Organic carbon/water sorption coefficient (log K_{oc})	2.51	[45]
Water solubility (mg/l)	0.98 at 25°C	[45]
	5.88 ± 0.13[d] at 20.5°C	[1]
Melting point (°C)	168.81	[45]
Vapour pressure (Pa)	5.24×10^{-8} at 25°C	[45]
Henry's law constant ($Pa.m^3.mol^{-1}$)	4.03×10^{-6} at 25°C	[45]

[a]A commercial mixture of $NPEO_n$ isomers was used in log K_{ow} determination; isomers were separated by normal phase HPLC analysis and quantified individually; [b]QSAR estimate based on partitioning of $OPEO_n$ in *iso*-octane/water transformed to a QSAR for partitioning of $NPEO_n$ in octanol/water, details see [2]; [c]QSAR estimate, based on K_{ow}-aqueous solubility relationship [2] with S_w determined experimentally for individual isomers [1], [d]generator column method on individual isomers obtained via preparative HPLC, *n*=3.

The molecular structure of octylphenol ethoxylates and alkylphenol ethoxylates with higher numbers of ethoxy oligomers follows from the drawings in the above tables by simply adding ethoxy units to the polar tail of the molecule; the ethoxy chain retains its linear structure upon addition of ethoxy units. We will therefore not elaborate with more tables on physicochemical properties. More important, alkylphenol ethoxylates are not synthesised on an individual basis but are formed and processed as a mixture containing oligomers with varying numbers of ethoxy units. Therefore physico-chemical parameters for isomers will -in most cases- be estimated values. Some basic identification of a few isomers is given in Table 29 and Table 30.

Table 29. Identification of several octylphenol ethoxylate monomers.

Substance	Abbreviation	CAS number	Empirical formula	Molar mass	S_w [$mg.l^{-1}$]
octylphenol tetra-ethoxylate	$OPEO_4$	n.a.	C22 H38 O5	382.54	24.5±0.89[a]
octylphenol penta-ethoxylate	$OPEO_5$	n.a.	C24 H42 O6	426.59	n.a.
octylphenol hexa-ethoxylate	$OPEO_6$	n.a.	C26 H46 O7	470.64	n.a.
octylphenol hepta-ethoxylate	$OPEO_7$	n.a.	C28 H50 O8	514.69	n.a.
octylphenol octa-ethoxylate	$OPEO_8$	n.a.	C30 H54 O9	558.74	n.a.

n.a. = not available, [a]20.5°C, *n*=3, generator column method on individual isomer obtained via preparative HPLC, [1].

Table 30. Identification of several nonylphenol ethoxylate monomers.

Substance	Abbreviation	CAS number	Empirical formula	Molar mass	S_w [mg.l^{-1}]
nonylphenol tetra-ethoxylate	$NPEO_4$	27176-97-2	C23 H40 O5	396.57	7.65±0.29[a]
nonylphenol penta-ethoxylate	$NPEO_5$	26264-02-8	C25 H44 O6	440.63	9.48±0.49[a]
nonylphenol hexa-ethoxylate	$NPEO_6$	27177-01-1	C27 H48 O7	484.68	n.a.
nonylphenol hepta-ethoxylate	$NPEO_7$	n.a.	C29 H52 O8	528.73	n.a.
nonylphenol octa-ethoxylate	$NPEO_8$	27177-05-5	C31 H56 O9	572.79	n.a.

n.a. = not available, [a]20.5°C, *n*=3, generator column method on individual isomers obtained via preparative HPLC, [1].

7.2.1 Water solubility

The water solubility of APEO is determined by the properties of both the hydrophobic and the hydrophilic part of the molecule. As expected, solubility increases with decreasing size of the hydrophobic alkyl chain. This is demonstrated by the higher water solubilities for OPEO oligomers compared to NPEO oligomers, determined by Ahel and Giger [1]. The solubility mechanism of the hydrophilic part is hydration of the ether bonds by formation of hydrogen bonds [1, 13]. The longer the polyethoxy chain, the more water can be bound. The water solubility of alkylphenol ethoxylates is thus expected to increase with increasing number of ethoxy oligomers. Theory is supported by practical work on determination of aqueous solubilities, although these data are scarce. Results of Ahel and Giger [1] are shown in the tables with physicochemical data. Brix *et al.* [21] have investigated the water solubility of commercially available $NPEO_{12}$ and $NPEO_{100}$, two mixtures of which the NPEO isomer with 12 or 100 ethoxy units respectively, is predominant. $NPEO_{12}$ had an estimated water solubility of approximately 43 mg/l whereas $NPEO_{100}$ is *very* water soluble, with no reported value. As Bailey and Callard [13] have pointed out, ethylene oxide polymers possess the unique property of complete water miscibility, even at extremely high molecular weights (M_w>10^7 g.mol^{-1}).

Alkylphenol ethoxylates are non-ionic surfactants. Being a surfactant means the molecules are amphiphilic, i.e. possessing both a lyophobic and a lyophilic part (in case of water as solvent: a hydrophilic and a hydrophobic part). Their amphiphilic nature brings about unique behaviour of the compounds at interfaces (solid-liquid, liquid-liquid and air-liquid interfaces). In dilute aqueous solution, meaning well below bulk surfactant concentrations, APEO molecules will concentrate at the surface. Since dissolution of the hydrophobic part of the molecule in water requires energy, less energy is needed when the molecule is at the solution surface. The consequence is that a lower amount of work is needed to create area of surface, which can be expressed as a lowering of the surface tension. The hydrophilic part of the molecule is oriented towards the solution and prevents the molecules to be expelled from the interface [102].

Another property of APEO that may become prominent in aqueous solution is micelle formation. In order to lower the energy needed to dissolve the hydrophobic parts, aggregation of the molecules -with their hydrophobic parts directed towards the interior of a micelle- may take place [102]. With the hydrophobic parts directed away from the solvent, the hydrophilic parts are directed towards the water, thus promoting solubility of the micelle. The concentration at which micelles start to form, called the critical micelle concentration (CMC), can be determined by measuring surface tension as a function of surfactant concentration.

Table 31 shows CMC values, measured for a series of octylphenol ethoxylates (individual substances) and a few nonylphenol ethoxylates (individual substances and mixtures).

Table 31. Critical micelle concentrations and water solubility's of some OPEO and NPEO in aqueous solution.

Compound	CMC (M)	CMC (mg.l^{-1})	T (°C)	Reference	S_w (mg.l^{-1}) at T (°C)	Reference
$OPEO_1$	5.0×10^{-5}	13	25	[30]	8 (20.5)	[1]
$OPEO_2$	1.3×10^{-4}	38	25	[102]	13.2 (20.5)	[1]
$OPEO_3$	9.7×10^{-5}	33	25	[102]	18.4 (20.5)	[1]
$OPEO_4$	1.3×10^{-4}	50	25	[102]	24.5 (20.5)	[1]
$OPEO_5$	1.5×10^{-4}	64	25	[102]	n.a.	
$OPEO_6$	2.1×10^{-4}	99	25	[102]	n.a.	
$OPEO_7$	2.5×10^{-4}	129	25	[102]	n.a.	
$OPEO_8$	2.8×10^{-4}	157	25	[102]	n.a.	
$OPEO_{8.5}$ (mixture)	$1.8\text{-}2.3 \times 10^{-4}$	105-134	25	[56]	n.a.	
$OPEO_9$	3.0×10^{-4}	181	25	[102]	n.a.	
$OPEO_{9.5}$ (mixture)	1.7×10^{-4}	107	24-25	[73]	n.a.	
$OPEO_{10}$	3.3×10^{-4}	214	25	[102]	n.a.	
$OPEO_{12}$ (mixture)	2.3×10^{-4}	169			n.a.	
$NPEO_{9.5}$ (mixture)	$7.8\text{-}9.2 \times 10^{-5}$	50-59	25	[56]	n.a.	
$NPEO_{10}$	7.5×10^{-5}	50	25	[102]	n.a.	
$NPEO_{10.5}$ (mixture)	5.4×10^{-5}	37	24-25	[73]	n.a.	
$NPEO_{10.5}$ (mixture)	$7.5\text{-}9 \times 10^{-5}$	51-61	n.r.	[56]	n.a.	
$NPEO_{12}$ (mixture)	5.7×10^{-5}	43	n.r.	[21]	n.a.	
$NPEO_{15}$ (mixture)	$1.1\text{-}1.3 \times 10^{-4}$	97-115	25	[56]	n.a.	
$NPEO_{20}$ (mixture)	$1.35\text{-}1.75 \times 10^{-4}$	150-190	25	[56]	n.a.	
$NPEO_{30}$ (mixture)	$2.5\text{-}3 \times 10^{-4}$	390-460	25	[56]	n.a.	
$NPEO_{31}$	1.8×10^{-4}	285	25	[102]	n.a.	
$NPEO_{100}$ (mixture)	1×10^{-3}	4600	25	[56]	n.a.	

n.a. = not available; n.r. = not reported.

The CMCs derived for $OPEO_{1\text{-}4}$ can be compared to the water solubilities reported by Ahel and Giger [1], since these were also determined for individual compounds. Both parameters are however, determined in different studies, e.g. at different temperatures (25°C for CMCs and 20.5°C for S_w), which prompts for caution in comparison. CMCs for $OPEO_{1\text{-}4}$ decrease slightly with decreasing temperature [30] in the range from 25 to 20.5°C, which would slightly decrease the observed difference between the estimated CMCs and S_w values to roughly a factor 1.5 to 2 at approximately 20°C. Unfortunately, data on NPEO are lacking. Based on OPEO results, we tentatively conclude that micellisation for APEO will start to occur at concentrations in the same range as the aqueous solubility. The selection criterion for (rejecting) toxicity studies carried out with toxicant concentrations above 10 times the water solubility [120] is therefore too wide for APEO. Based on the results discussed above and accounting for uncertainty, the selection criterion is reduced to a factor of 3 in the underlying document.

7.2.2 Octanol-water partitioning

Ahel en Giger [1, 2] are, to the best of our knowledge, two of few authors that have published data on experimentally determined solubility values for individual (octylphenol- and nonylphenol-) ethoxylate isomers. Their work on partitioning between organic phases and water, shows that for $NPEO_{1\text{-}3}$ for which measured values of K_{ow} were available, a calculation

method using a K_{ow}-water solubility (S_w) relationship [27] yields corresponding K_{ow} values. Values estimated using a QSAR derived from partitioning experiments of octylphenol ethoxylates in *iso*-octane which was transformed in order to describe partitioning behaviour of the same compounds in *n*-octanol, are consistently lower than both experimental values and values estimated using the K_{ow}-S_w method described before. The deviation is smallest with a low number of ethoxy units, but the difference with the K_{ow}-S_w method strongly increases with increasing number of ethoxy units. Bearing in mind that alkylphenol ethoxylates are amphiphilic and possess a polar part, the nonpolar organic solvent *iso*-octane probably strongly induces a reduced solubility in the organic phase when compared to *n*-octanol, making the values estimated with this method less accurate. Other estimation methods produce higher values for K_{ow}, as the values generated using MedChem's ClogP [31] and EPI Suite [45] tabulated in Table 26 to Table 28 show. When we take nonylphenol triethoxylate as an example, we find an experimentally determined log K_{ow} value of 4.2 [2], and the following estimated values: 3.1 (*iso*-octane adapted QSAR [2]), 4.3 (log K_{ow}-S_w QSAR [2]), 5.03 (Epi Suite [45]) and 6.03 (ClogP [31]). There is however, reason to be cautious with the experimentally determined values. Since experiments were performed using mixtures of nonylphenol ethoxylate isomers that were allowed to partition between octanol and water, interacting effects between different isomers in solution may have played a role. E.g. an isomer having a higher affinity for water than the others present may prevent dissolution of those other isomers into water to a certain extent. The same applies for dissolution into the organic phase. However, since K_{ow} data on pure isomers are not available we regard the experimental data as the best estimates. Since the values estimated using the K_{ow}-S_w relationship are in correspondence with the three experimental values for nonylphenol ethoxylates and moreover, input in this relationship are measured water solubilities for *individual* isomers, the results from this relationship are regarded to be the most reliable estimates at present. It should be emphasised that this discussion is both triggered as well as hampered by the lack of reliable measurements. This is partly due to the fact that alkylphenol ethoxylates are produced and used as mixtures, taking away the need to determine properties of single isomers.

7.3 Use, production and discharge

Use

The applications of nonylphenol ethoxylates are numerous, the most important being: use in industrial and institutional cleaning (in electrical engineering industry, in laundries, and for floor and surface cleaning), use in textile manufacturing processes like scouring, lubrication and dye levelling, use in the leather industry in wet degreasing of hides, use as wetting agents, dispersant or emulsifiers, use as dispersant in emulsion polymers, in paint resin and as paint mixture stabiliser, in pulp and paper, in metal industry in cleaning processes, steel phosphating and in cutting and drilling oils. Further uses are: lubricating oils, spermicides, developing of photographic film, manufacture of wall construction material and road surface material.

Production

Alkylphenol ethoxylates are non-ionic surfactants, synthesised by the ethoxylation of alkylphenols. The synthesis is carried out in a batch process by reacting alkylphenols with alkene oxides under catalysis (alkali hydroxides, basic ion exchangers or sodium methylate) at 140-180°C and elevated pressure. The ethoxylation process leads to formation of a mixture of compounds with a varying number of ethoxy units (oligomers), which may usually vary between 2 to 80.

Table 32. Production and use of octylphenol and nonylphenol and their ethoxylates within the EU.

Compound	Production volume (tonnes.y^{-1})	Year	Tonnage Use (tonnes.y^{-1})	Year	Source
4-*tert*-octylphenol	22,633	2001	22,858	2001	[44]
octylphenol ethoxylates	n.a.	n.a.	n.a.	n.a.	[44]
nonylphenol	73,500	1997	78,500	1997	[46]
nonylphenol ethoxylates	109808	1994	n.a.	n.a.	[46]
	118000	1997	77600	1997	[46]

Import exceeding export can cause use tonnages to be higher than production volumes.

Discharge

After production and use, the main entry into the environment for alkylphenol ethoxylates is via waste water that may or may not pass a sewage treatment plant (STP) before entry into surface water.

In the Netherlands, sewage sludge derived from STPs is not allowed to be spread over land, therefore this route will not contribute to alkylphenol ethoxylate emission to soil. Emission to soil may take place in agricultural areas that receive alkylphenol ethoxylates from the use of pesticides or indirectly via spreading of manure containing residues of veterinary drugs. Formulations of pesticides or veterinary drugs may contain alkylphenol ethoxylates as additives. An inventory performed in 1996 [88] reported an estimated number of 8.6 tonnes.y^{-1} of octylphenol ethoxylate in agricultural pesticide use in the Netherlands. Adjuvants containing alkylphenol ethoxylates as active component are another application in pesticide use. These adjuvants are added to the pesticide formulation before application as a wetting or sticking agent. Use and registration of these adjuvants is poorly regulated in the Netherlands, making emission estimates practically impossible.

7.4 Mode of action

Effects on the endocrine system, overview

Alkylphenols are known to possess hormonal disrupting properties. In 1991, Soto *et al.* identified *p*-nonylphenol as a compound with weak estrogenic activity (*in vitro*) that was leaching from polystyrene laboratory tubes [112]. *p*-Nonylphenol mimicked estradiol induction of the progesterone receptor and cell proliferation in a breast cancer cell line. This finding, combined with the notion that alkylphenolic compounds and their residues were detected in all parts of the aquatic environment triggered renewed attention. Estrogen-like activity of alkylphenols to rainbow trout (*Oncorhynchus mykiss*) hepatocytes was subsequently reported [60] and effects in avian and mammalian cells were also shown [138].

Evidence of estrogenic action to several other fish species was also reported in *in vivo* studies, a.o.: carp (*Cyprinus carpio*), Japanese medaka (*Oryzias latipes*), fathead minnow (*Pimephales promelas*), summer flounder (*Paralichthys dentatus*), channel catfish (*Ictalurus punctatus*) and zebra fish (*Danio rerio*)[48, 50, 86, 87, 93, 124]. Several types of effect of estrogenic action were identified in these studies, a.o. development of testis-ova (an intersex condition), vitellogenin induction, inhibition of spermatogenesis, effects on Sertoli cells and gonadosomatic index. Work of Kelly and DiGiulio [65] shows developmental toxicity in killifish (*Fundulus heteroclitus*) as a result of exposure to NP and 4-*t*-OP; the hypothesised mechanistic basis for these effects is also binding of the APs to the estrogen receptor. This brief overview is not complete. There is an increasing amount of literature on this subject, yet it is beyond the scope of this section to aim at completeness. See e.g. Servos [111] , Nimrod and Benson [92] for more detail.

Although a different class of compounds, alkylphenol ethoxylates are structurally related to alkylphenols. In the environment, ethoxylates are precursors to alkylphenols since environmental degradation enables formation of alkylphenols (see section 8.2). In many studies in which the estrogenic activity of alkylphenols was investigated, the activity of alkylphenol ethoxylates and/or carboxylated alkylphenol ethoxylates was also addressed. The estrogenicity of alkylphenol ethoxylates decreases with increasing ethoxylate chain length. White *et al.* [138] found that OPEOs with three or more ethoxy oligomers showed little or no estrogenic activity in transfected human breast cancer cells. In the same study $NPEO_2$ and NPE_1C were shown to stimulate vitellogenin gene expression in hepatocytes from rainbow trout, although their potency was relatively low (below approximately 10^{-4} compared to estradiol). In a recombinant yeast estrogen screening test, Routledge and Sumpter [103] identified the estrogenic potency of 4-NP and $NPEO_2$ to be 7×10^{3} and 5×10^{5} times less than that of 17β-estradiol, respectively, indicating a decrease in potency from NP to $NPEO_2$. $NPEO_{12}$ did not show observable estrogenic activity. Jobling and Sumpter showed estrogenic potencies –relative to 17β-estradiol- for $NPEO_2$ and $NPEO_9$ of 6×10^{-6} and 2×10^{-7}, respectively [60] (Table 33).

Table 33. Relative estrogenic potencies of AP and APEO.

Compound	Mean ED50[3] (µM)	Relative potency[1]	parameter	Reference
4-*tert*-BP	2.06	0.00016	VTG-induction	[60]
4-*tert*-OP	2.11	0.000037	VTG-induction	[60]
4-OP		0.00067	yeast; hER induction[2]	[103]
NP	16.15	0.000009	VTG-induction	[60]
4-NP		0.00014	yeast; hER induction[2]	[103]
$NPEO_2$	17.3	0.0000060	VTG-induction	[60]
$NPEO_2$		0.00004	yeast; hER induction[2]	[103]
$NPEO_9$	82.3	0.0000002	VTG-induction	[60]
$NPEO_{12}$		no estrogenic activity	yeast; hER induction[2]	[103]
NPE1C	15.3	0.0000063	VTG-induction	[60]
NPE_1C		0.00004	yeast; hER induction[2]	[103]
NPE_2C		0.000002	yeast; hER induction[2]	[103]

[1]expressed relative to the mean potency of 17β-estradiol; [2]hER binding assay in a recombinant yeast strain; [3]ED50 is the concentration causing 50% effect on VTG production as determined from a sigmoidal dose response relationship.

Mode of action

From the work of White and co-workers [138] we can derive some aspects on the mode of action. APs and APEOs mimic the effects of 17β-estradiol by binding directly to the estrogen receptor. For octylphenol, receptor binding occurred probably in a similar receptor region as did estradiol. OP, NP and NPE_1C showed competition for binding to the trout estradiol receptor with 17ß-estradiol (potencies lower than that of estradiol in the order of a factor 1500, 3000 and 20,000, respectively), indicating their intrinsic capacity to exert estrogenic effects. $NPEO_2$, however, did not show binding competition. All four compounds were able to induce vitellogenin gene expression in trout hepatocytes. Alkylphenol ethoxylates will partition into lipid membranes to a certain extent, depending on their hydrophobicity, which will lead to 'narcotic' toxicity. More specific information on the mechanism of action on possible other sites was not encountered in the literature.

8. Alkylphenol ethoxylates - Environmental fate

8.1 Distribution over air, water and soil

From the estimated values for the Henry's law constant for $NPEO_{1-3}$ (Table 26 - Table 28), air-water partition coefficients (K_{aw}) can be calculated in the order of 10^{-7} for $NPEO_1$ and lower for compounds with increasing number of ethoxy oligomers. This indicates that partitioning into air is a negligible route of distribution for alkylphenol ethoxylates. Based on their production and use and moreover the lack of companies producing alkylphenols and their ethoxylates in the Netherlands, emission to air will also be limited. Since spreading of sewage sludge on land is prohibited in the Netherlands, this largely excludes emission to the soil compartment, meaning that entry and occurrence of the compounds will primarily occur in the water compartment.

A reliable estimation of the sorption behaviour or partitioning between octanol and water of the various APEO is problematic. (i) Experimental determinations of K_{ow} or K_{oc} must be treated with care because of the surface-active properties of APEO. (ii) The shake flask method described by the OECD is unreliable for log K_{ow} values >4, which is probably true for the lower ethoxylated alkylphenols. (iii) Available QSARs are designed for and based on properties of uniformly hydrophobic organic compounds and are less useful for amphiphilic surfactants like APEO. For the three nonylphenol ethoxylates $NPEO_1$, $NPEO_2$ and $NPEO_3$ we observe that the K_{oc} values estimated with EPI Suite [45] tend to decrease with increasing ethoxy number whereas the experimentally determined K_{ow} values [2] remain fairly constant. K_{ow} and K_{oc} values for the three compounds are: 4.2 and 3.4, 4.2 and 3.0, 4.2 and 2.5, respectively. The reason for these series to diverge lies in the fact that the PcKoc module from EPI Suite makes use of a correction factor for polar molecular fragments. Addition of ethoxy units to an alkylphenol ethoxylate molecule thus results in decrease of the calculated K_{oc} value. This is in general accordance with the expected decrease in lipophilicity with increasing EO chain length, however, the decrease seems to occur too rapid. And last but not least, (iv), APEO are always produced and sold as mixtures of monomers which should be separated into monomeric compounds (e.g. using preparative HPLC [1]) to avoid molecular interactions that may influence partitioning behaviour.

Adsorption of APEO onto organic matter is a resultant of two processes [61]. Hydrophobic interactions account for sorption of both the alkyl and ethoxylate part of the molecule onto the organic phase of soil or sediment; sorption of this kind increases with increasing chain length. A second mechanism of sorption are hydrophilic interactions (hydrogen bonding) of the ethoxylate chain with the soil or sediment mineral fraction: this causes sorption to decrease with increasing EO chain length.

Few experimentally determined K_{oc} values are available for APEO. Ahel and Giger [3] have reported distribution coefficients (K_d) between activated sludge and secondary sewage effluent for $NPEO_1$ and $NPEO_2$ and NPE_2C of 1800, 900 and 500 $l.kg^{-1}$, respectively. Characteristics of sludge and effluent in terms or mineral and organic carbon content were not reported, hampering recalculation of K_d to e.g. a K_{oc} value. Urano *et al.* [123] have determined

a K_{oc} value for an $NPEO_{10}$ mixture of 6100 $l.kg^{-1}$ (log K_{oc} = 3.85) using several sediments and water concentrations that were most likely below the CMC. There are some drawbacks in their study that question the reliability of this value: the Freundlich exponent (1/n) was 1.4, analysis was performed only in the water phase with a colorimetric method, sorption data of all tested sediments were plotted in one graph to derive the K_{oc}, rather than determining individual K_{oc} values for each sediment, no measure of fit (e.g. correlation coefficient) is given. It nevertheless indicates relatively strong sorption of this mixture to sediment organic carbon. However, a log K_{oc} calculated from data by John *et al.* [61] for a $NPEO_9$ *mixture* and a river sediment is 3.79. Both K_{oc} values for mixtures are in the same range.
From a study of Liu *et al.* [73], the following K_{oc} values can be calculated for sorption of three commercial APEO onto a grassland soil, performed also with a colorimetric analysis of water phase only. For $OPEO_{12}$ (Igepal CA-720), K_{oc} = 162 $l.kg^{-1}$ (1/n = 1.79), for $OPEO_{9.5}$ (Triton X-100), K_{oc} = 1202 $l.kg^{-1}$ (1/n = 1.34) and for $NPEO_{10.5}$ (Tergitol NP-10), K_{oc} = 393 $l.kg^{-1}$ (1/n=1.67). These K_{oc} values are determined at sub CMC levels as was mentioned by the authors. Again, 1/n values are considerably greater than unity, indicating that the amount of compound sorbed increases with increasing water concentration. The range of log K_{oc} values for the three studies summarised above is thus 2.6 – 3.8 for three $NPEO_{10}$ mixtures and 2.2 – 3.1, determined for $OPEO_{12}$ and $OPEO_{9.5}$ mixtures. John *et al.* [61] have studied sorption of two NPEO mixtures onto natural river sediment (and other adsorbents). They have analysed concentrations of individual NPEO isomers enabling them to derive K_d values for individual NPEO isomers (n=3 to 13). K_{oc} values calculated from their data decrease from 12400 l/kg for $NPEO_3$ to 3800 l/kg for $NPEO_{10}$. From $NPEO_{11}$ K_{oc} values increase as a result of the hydrophilic interactions described above.
Heemken *et al.* [55] reported log K_{oc} values, measured *in situ* between river water and suspended matter of 6.02, 6.24, 5.60 and 6.38 for $OPEO_1$, $OPEO_2$, $NPEO_1$ and $NPEO_2$, respectively. Jonkers *et al.* [63] published field log K_{oc} values (distribution coefficients water/suspended matter) of 5.8 and 5.9 for NPEO (Σ of all measured NPEO oligomers) in water from the Rhine and Scheldt estuary, respectively. These six values are in the same range, however, the last two values were not determined for individual oligomers. These field determined values are rather high compared to K_{oc} values determined by John *et al.*, Liu *et al.*, Urano *et al.*and [61, 73, 123], but the data from the two field studies corroborate each other. The higher sorption coefficients found in the field can be caused by a much higher time for absorption to occur (all laboratory sorption studies lasted 24 h), a higher prominence of lower ethoxylated, more lipophilic oligomers due to biodegradation of higher ethoxylated oligomers in the field (section 8.2) and a higher fraction of organic matter present in suspended matter (all field K_{oc} values were suspended matter K_{oc} values) compared to that in sediment. Summarizing, we have high field K_{oc} (suspended matter) values for lower ethoxylated APEO ($OPEO_{1-2}$ and $NPEO_{1-2}$), contrasting with estimated values (Table 23 to Table 28) that are roughly 3 orders of magnitude lower. For $NPEO_3$-$NPEO_{13}$ the data from John *et al.* are useful. For higher ethoxylated OPEO ($OPEO_3$ and higher) no experimental K_{oc} are available. Some (less reliable) experimental K_{oc} (soil) values for OPEO and NPEO *mixtures* with a median number of 9-12 ethoxy units are available, that are 2 to 4 orders of magnitude lower than the field determined values for *individual* $OPEO_{1-2}$ and $NPEO_{1-2}$. A decrease in lipophilicity with

increasing number of ethoxy groups is qualitatively supported by these data, and data from John *et al.* quantitatively support this.
We therefore conclude –qualitatively- that partitioning into sediment and biota are expected to be relevant for the lower ethoxylated APEO oligomers, based on the K_{oc} values reported and less so for higher ethoxylated compounds. We refer to section 10.2 where the selection of partition coefficients for ERL derivation is outlined.

8.2 Biodegradation

The biodegradation pathway of APEO is complex and several more or less biorefractory intermediates have been identified in various studies. Several biodegradation pathways for biodegradation of APEOs have been proposed. Figure 4 shows the routes that Ahel and co-workers proposed [3] for biodegradation of APEO during wastewater treatment where both aerobic and anaerobic conditions can be identified. The same intermediates were also identified by e.g. Yoshimura [141] who studied biodegradation of A_9PEO_9 by a river sediment inoculum in synthetic medium. In these pathways, APEOs are degraded by progressive shortening of the polyethoxy chain, by (i) hydrolysis of the terminal ether bond of the polyethoxy chain (thereby splitting off an ethyleneglycol) resulting in a new (shorter) terminal alcohol or (ii) first, oxidation of the terminal alcohol leading to a polyethoxy carboxylic acid, followed by reaction (i) (ether bond hydrolysis, splitting off an hydroxyacetic acid molecule). Disappearance of the parent compound A_9PEO_9 was relatively rapid in a reactor with sediment inoculum: over 98% of 20 mg/l A_9PEO_9 had disappeared within 5 days in a stirred reactor and within 10 days in a non stirred situation [141]. Ahel *et al.* [3] determined concentrations of APEO in a survey study of eleven sewage treatment plants in Switzerland. They identified the more biorefractory metabolites: $NPEO_1$, $NPEO_2$, NPE_1C, NE_2PC and NP and also a prominent change in NPEO oligomer composition during sewage treatment, clearly indicating that biodegradation was occurring. Elimination (relative disappearance from primary to secondary effluent) for $NPEO_3$ to $NPEO_{20}$ compounds varied from 78 to 97% but for $NPEO_1$ + $NPEO_2$ this elimination ranged from 80% to –19% (i.e. a 19% increase in concentration). In all STPs a large increase in NPE_1C + NPE_2C was observed, demonstrating both the refractory nature of these compounds as well as their formation due to biodegradation. Similar results were obtained by Ball *et al.* [15] for an OPEO mixture that contained $OPEO_1$ to $OPEO_5$ oligomers. Activated sludge inoculation demonstrated rapid disappearance of the higher ethoxylated OPEO with formation of OPEC, with $OPEC_2$ being the most recalcitrant. Primary sewage inoculation showed accumulation of $OPEO_2$ and, to a lesser extent, $OPEO_1$. Carboxylation of the terminal alcohol was much less favoured, since there was little formation of $OPEC_1$ to $OPEC_3$. Under anaerobic conditions relatively rapid disappearance of OPEO oligomers resulted in accumulation of OP (after 190 days of incubation) and formation of minor amounts of $OPEC_{1-4}$.

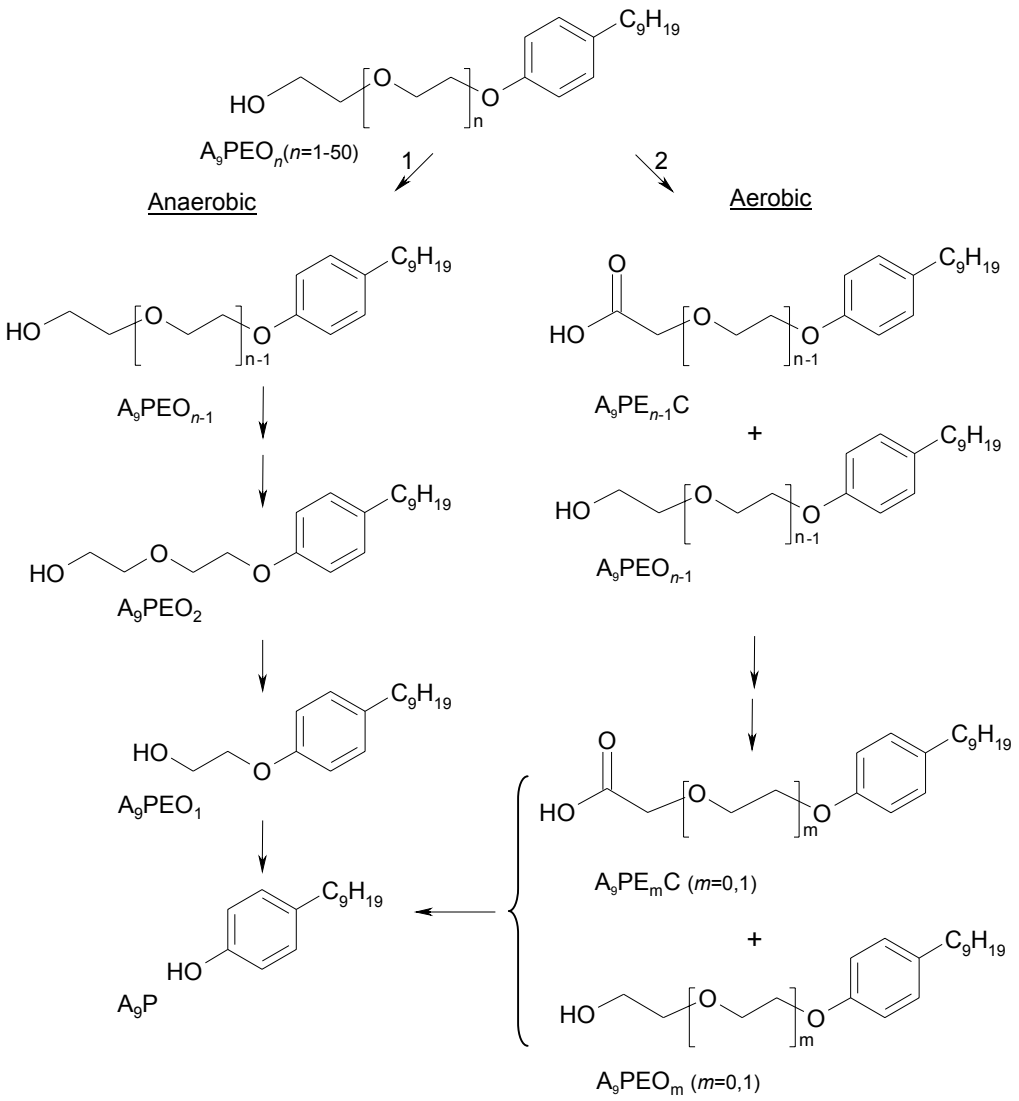


Figure 4. Biodegradation pathways encountered in the literature. Both pathways are proposed by Ahel et al. *([3]) for degradation in wastewater treatment; pathway 1 was proposed by for anaerobic degradation and pathway 2 for aerobic biodegradation.*

Brunner *et al.* [22] confirm the formation of $NPEO_1$ and $NPEO_2$ from $NPEO_n$ and formation of NP from $NPEO_1$ and $NPEO_2$ during sewage treatment, but did not analyse for carboxylated compounds. NP was not significantly degraded under anaerobic conditions and accumulated in the digested sewage sludge. The effect of waste water treatment is finds additional confirmation in surface water measurements in the vicinity of waste water outlets discharging untreated municipal waste water [69]. Kveštak *et al.* reported $NPEO_n$ oligomer distributions from the Krka river estuary (Croatia, Adriatic Sea) that typically show much less degradation: all $NPEO_n$ oligomers with n=1 to 16 were found (bell shaped curve) with a maximum at 8-10 units (approximately 40-70 $\mu g.l^{-1}$). A small secondary maximum was observed for $NPEO_1$ and $NPEO_2$, indicating that degradation is taking place, concomitant with accumulation of short chain oligomers.

The relative persistence of the carboxylated compounds is also reflected in a study in which Ahel *et al.* [4] measured concentrations of the same compounds in water of the river Glatt (Switzerland). This river receives discharged secondary effluent either directly or via

tributaries from several of the investigated STPs from the survey study [3]. NPE_1C + NPE_2C were the most abundant compounds, followed by $NPEO_1$ and $NPEO_2$. NP concentrations were lower and $NPEO_n$ were around (n=3-5) or below (n>5) the detection limit of 1 $\mu g.l^{-1}$. In a river water die away test (aerobic, in the dark, 20°C, untreated river water originating from a chronically AP_nEO polluted river) both a stirred and static test showed efficient degradation of $NPEO_1$ (0.8 $mg.l^{-1}$) and $NPEO_2$ (0.3 $mg.l^{-1}$) and formation of NPE_1C and NPE_2C [5]. Half-lives for disappearance of the parent compounds were 2 days for both compounds in stirred and 3 d for both compounds under static conditions. An inoculum from a pristine forest soil also showed short chain OPEO and NPEO degrading capability, albeit slower than in the former experiment; emphasising that these compounds are biodegradable under aerobic conditions. Higher concentrations of NPE_1C and NPE_2C compared to $NPEO_1$ and $NPEO_2$ were observed in groundwater [6] in an area where the relatively heavy polluted Glatt river (Switzerland) infiltrates into an aquifer. Concentration profiles along the groundwater flow in the aquifer showed $NPEO_1$ and $NPEO_2$ to be strongly reduced within the first few meters away from the river, while NPE_1C and NPE_2C showed much slower elimination. This is thought to be caused by higher resistance to degradation, as well as lower lipophilicity.

Di Corcia *et al.* [35] stated that recalcitrance of APEO to complete degradation was thought to be mainly caused by steric hindrance of the alkyl chain to microbial attack. The hypothesis of formation and analysis (including MS identification) of APEO metabolites possessing a carboxylated alkyl chain [108] was confirmed a.o. by Di Corcia and co-authors. They identified various CA_mPE_nC (carboxylated C_m-alkyl-nonylphenol-n-ethoxy-carboxylate) species in both STP effluent and a biodegradation assay using an STP derived inoculum. In their experiments, CAPEC species were recalcitrant to further degradation. A degradation pathway in which the formation of CAPECs is taken up, was postulated by De Voogt *et al.* [33] and Jonkers *et al.* [62] which is shown in Figure 5. The latter study was a biodegradation study performed with natural river (Rhine) water as the source of bacteria that were allowed to settle on glass beads, and it identified only CAPEC with short (C2 or C4) carboxylated ethoxy chains (see last structure in Figure 5, where m = 0 or 1) but nearly all possible metabolites with (carboxylated) alkyl chain lengths between 5 and 9 were found.

In a recent field sampling study in two Dutch estuaries (Western Scheldt and Rhine estuary), CAPEC metabolites were not detected [63], in contrast with earlier findings in a bioreactor experiment [62] and the results of Di Corcia *et al.* [35]. The field sampling study did show predominance of short chain APEO oligomers in the water phase, with a maximum approximately at $APEO_3$ in both estuaries. Sediment samples did contain higher concentrations of longer chained APEO, indicating a slower biodegradation rate for these compounds in sediment. APEC metabolites were identified in the water phase but hardly in sediment samples. In the Scheldt estuary the APEC/APEO ratio increased from 5 to a maximum of 40 with increasing salinity (i.e. downstream) which is likely to be caused by degradation of APEO into APEC.

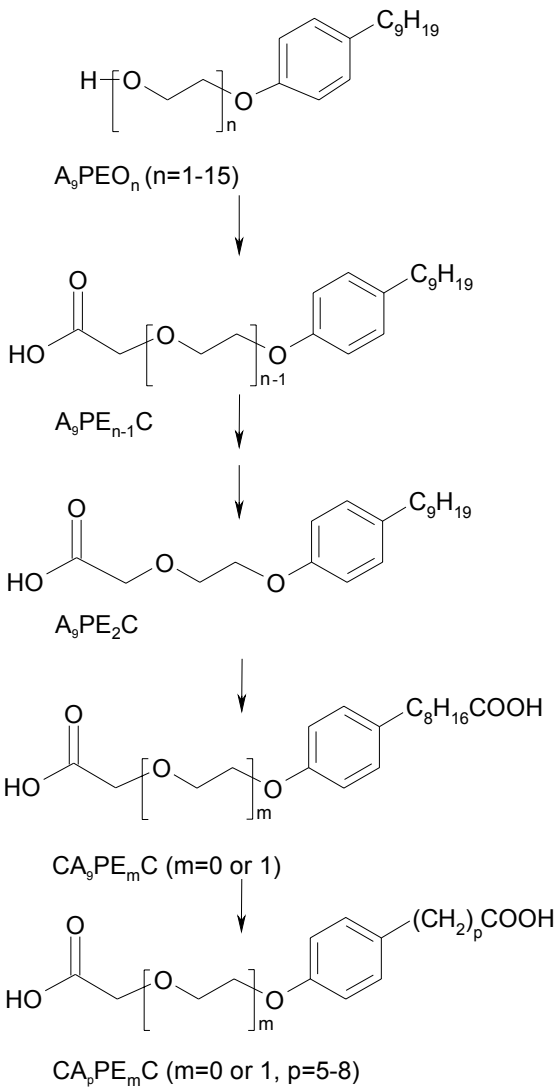


Figure 5. Biodegradation pathway recently proposed in the literature by Jonkers et al. *[62] for aerobic degradation of APEO. The degradation study that generated the intermediates was performed using river Rhine water and its autochthonous microflora in a bioreactor set-up.*

A lake water die-away study confirmed earlier observations: long chain oligomers of $NPEO_9$ to $NPEO_{17}$ disappeared where $NPEO_1$ to $NPEO_5$ oligomers were formed [80]. Formation of APE_1C to APE_3C was based only on appearance of unidentified chromatography peaks that were not further identified since the analysis method was not optimised at those compounds [106]. Interestingly, the degradation proceeded faster in the dark then under (fluorescent tube) illumination, the mechanism of which could not be explained. Maki *et al.* [76] identified only NPE_1C and NPE_2C as degradation products (no $NPEO_1$ and $NPEO_2$) in a study which investigated $NPEO_{9.5}$ degradation in river water with a bacterial inoculum originating from the same river. Manzano *et al.* [81], in a river water die-away test found ethoxylate chain shortening of a $NPEO_{15}$ surfactant to stop at $NPEO_2$, after which $NPEC_2$ and $NPEC_1$ were formed. The formation of NPE_2C as most recalcitrant intermediate from a NPEO surfactant (centre of EO oligomer distribution at 18 EO units) was demonstrated in a die-away study with estuarine water samples [99]. Disappearance of all detectable 'parent' surfactant was complete within 24 days, followed by formation of $NPEO_2$ starting at day 8 and subsequent

formation (starting at day 12) and accumulation of NPE_2C occurred. NPE_1C was also formed but no NP was measured. From mass balance calculations it is inferred that approximately 36-56% of the carbon in this study should be converted to CO_2; this was however, not confirmed analytically. Kveštak and Ahel [68] found half lives for disappearance of total NPEO to be dependent on temperature, substrate concentration and source of inoculum (brackish or saline autochthonous microbial community) in a die-away study. Reported t½-values at 22.5°C and 1 mg NPEO/l were 4 and 35 days for brackish and saline water, respectively and 35 and 69 days at 13°C. Half life values were roughly a factor of 2 lower at 0.1 mg NPEO/l. Slowest degradation rates were observed for $NPEO_2$ and $NPEO_1$, but NP was never detected. Analysis for other metabolites was not performed hampering a further interpretation of the disappearance pattern observed.

Studies in which ultimate biodegradation is reported are less numerous. Biodegradation potential was investigated by Staples *et al.* for NP, OP, $NPEO_{1.5}$, $OPEO_{1.5}$, $NPEO_9$ and $OPEO_9$ in two standardised tests (OECD 301B and ISO headspace CO_2 biodegradation) [114]. Both systems are aerobic, stirred and inoculated with an activated sludge derived bacterial population in a mineral medium and high substrate concentrations (>10 mg/l). A range of 48.2% to 82.5% CO_2 evolution was observed for the various compounds tested in the two tests. Synthesised OPE_1C, OPE_2C, NPE_1C and NPE_2C were also degraded in the OECD 301B test with formation of 59% (NPE_1C) to 80% (OPE_2C) CO_2 [116]. NP was also tested in a different test set up (OECD 301F) and showed ≥ 60% CO_2 formation under aerobic conditions. Ekelund *et al.* [43] demonstrated ~53% $^{14}CO_2$ formation from 11 µg/l ^{14}C-NP (ring labelled) in seawater (at 11°C) after 58 days. In the presence of sediment, initial degradation occurred at a higher rate, but approx. 40% of $^{14}CO_2$ was formed after 58 days, probably due to higher sorption compared to the seawater test. Analysis for metabolites was not performed and the remainder of the radioactivity (47% and 40%, respectively) was not accounted for. Maguire [75] cites a study in which half lives for NP in sediments of 28-104 days are reported.

These results emphasise that there is potential for complete biodegradation when optimal conditions (inoculum, substrate concentration, nutrients, temperature, stirring, etc.) are present. In the field one or more of these factors will usually be suboptimal, explaining e.g. the slower rates in the study of Ekelund *et al.* [43] and the overall lack of reports of complete biodegradation in natural systems or experiments that mimic those conditions.

Photochemical degradation of NPEO has been investigated by Ahel *et al.* [7]. A preliminary study had shown that degradation rates of NPEO oligomers with 3-18 ethoxy units were slower than that of $NPEO_1$ under laboratory conditions. Under those conditions (a.o. distilled water as solvent, a mercury light source and use of a wavelength cut-off filter) first order rate constants for direct photolysis (k_p) were 0.06 (h^{-1}) for $NPEO_1$ and 0.026 (h^{-1}) for $NPEO_6$-$NPEO_{17}$. The degradation rate of $NPEO_1$ was significantly enhanced (k_p=0.52 h^{-1}) in natural lake water containing 4 $mg.l^{-1}$ DOC as a sensitizing agent. Degradation of $NPEO_1$ did not occur when natural conditions were mimicked: a solution of $NPEO_1$ in natural lake water (containing 4 $mg.l^{-1}$ DOC) in quartz vessels that were submerged in a creek (with clear water) was irradiated with natural sunlight (autumn, water temperature 17°C). From these

experiments it is expected that photochemical transformation of NPEO has little influence on their behaviour in the aquatic environment.
The obtained information on environmental degradation is summarised as follows. Degradation of APEO occurs both in STPs as well as in natural waters, although their biotransformation is not rapid. Degradation of APEO involves progressive shortening of the ethoxylate chain. Hydrolytic or biodegradative ether cleavage leads to accumulation of $APEO_2$ and $APEO_1$, the two oligomers that are degraded slowest. Formation of APEC metabolites is also observed in STPs as well as in natural waters, with the short chain APE_1C and APE_2C being most refractory. Formation of AP is observed under anaerobic conditions in STPs but less frequently in studies that used natural waters with autochthonous microflora. There is potential for ultimate biodegradation of APEO, for which the alkyl chain also needs to be transformed, metabolites (CAPEC) of which have been detected in the field. However, evidence of complete degradation under natural conditions is scarce. Photochemical degradation is expected to be negligible under natural circumstances.

8.3 Bioconcentration

Data on bioconcentration factors for C8 and C9 alkylphenol ethoxylates have recently been compiled by Staples *et al.* [115]. No effort was made to collect and review more recent data on this subject. Table 34 shows the retrieved information, all available BCFs for ethoxylates were determined in the field. In order to compare the various data, the BCF were recalculated to - nonlipid based- wet weight.

Table 34. Field, wet weight bioconcentration factors of alkylphenol ethoxylates.

Compound	Taxonomic group	*Species*	$BCF_{fw,\ field}$ [$l.kg^{-1}$]	Notes	Reference
$NPEO_1$	algae	*Cladophora glomerata*	10	1	[115]
	macrophyta	*Fontinalis antipyretica*	2	1	[115]
	macrophyta	*Potamogeton crispus*	2	1	[115]
	mollusca	*Mytilus edulis*	170		[115]
	pisces	*Barbus barbus*	19	2	[115]
	pisces	*Oncorhynchus mykiss*	3	2	[115]
	pisces	*Squalus cephalus*	1	2	[115]
$NPEO_2$	algae	*Cladophora glomerata*	23	1	[115]
	macrophyta	*Fontinalis antipyretica*	3	1	[115]
	macrophyta	*Potamogeton crispus*	10	1	[115]
	mollusca	*Mytilus edulis*	100		[115]
	pisces	*Barbus barbus*	37	2	[115]
	pisces	*Oncorhynchus mykiss*	0.8	2	[115]
	pisces	*Squalus cephalus*	2	2	[115]
$NPEO_3$	mollusca	*Mytilus edulis*	60		[115]

[1]recalculated from dry to wet weight assuming 95% water content, [2]recalculated from dry to wet weight assuming 85% water content.

The data show that $NPEO_1$, $NPEO_2$ and $NPEO_3$ (only one value) have low bioconcentration potential. Based on these data it is unlikely that these compounds will lead to accumulation in the food chain.

9. Alkylphenol ethoxylates - Toxicity data and derivation of MPCs and NCs for water

9.1 Toxicity data

The aquatic toxicity data that are found for the octylphenol ethoxylates are presented in Appendix 4, Table A4. 2-Table A4. 4. A single result was retrieved for octylphenol monoethoxylate carboxylic acid, which can be found in Appendix 4, Table A4. 1. Aquatic toxicity data for nonylphenol ethoxylates are presented in Appendix 4, Table A4. 6-Table A4. 8, with a few data on nonylphenol monoethoxylate carboxylic acid in Table A4. 5. No toxicity data were found for benthic or sediment inhabiting organisms for both groups of compounds. Toxicity data were collected for both freshwater and marine species. For the calculation of the ERLs these data are combined if there are no significant differences between the two sets. In this report, this is tested for all compounds with an unpaired t-test, preceded by an F-test to detect if differences in variance exist; see Verbruggen *et al.* ([132], p. 25) for more detail. Only toxicity studies with endpoints related to survival, growth or reproduction are taken into account.

9.2 Analysis of data

APEOs are mixtures of alkylphenol compounds with a varying number of ethoxy oligomers. This means that it is practically impossible to test the toxicity of a single isomer. In other words: all toxicity tests were performed with *mixtures* of alkylphenol ethoxylate monomers. This means that it is impossible to derive a risk limit for one single monomer based on toxicity data for that specific compound. Usually an alkylphenol ethoxylate is named either after the average or median number of ethoxy oligomers present in the mixture. E.g. $NPEO_9$ contains nonylphenol ethoxylate molecules with ethoxy units ranging from (hypothetical example) 1 till 20, with the molecules with 9 ethoxy units being present in the highest concentration. The lipophilicity of APEOs increases with decreasing number of ethoxy oligomers, which is reflected in an increasing toxicity for the APEO(mixture)s with a lower (average) number of ethoxy oligomers. As a consequence, it cannot be stated with certainty which fraction of a tested mixture is responsible for the observed toxicity.
Figure 7 and Figure 8 show the relationship between the toxicity of a series of APEO for several organisms. In these figures we have plotted data from those authors that investigated the toxicity of a series of APEOs to one test species. We have also plotted water solubilities in these figures. Toxicity values above 3x the water solubility (plotted in Figure 7 and Figure 8) will not be used in risk limit derivation since this raises serious questions on the conditions employed in the test and the reliability of the test result (see [120], adapted in section 7.2.1). Experimentally determined water solubilities for *individual* monomers $OPEO_1$ to $OPEO_4$ and $NPEO_1$ to $NPEO_5$ were available [1] and are also plotted in the appropriate figures. Further data on experimentally determined water solubility of individual APEO isomers are not available in public literature. Schüürmann has developed a model relating lipophilicity (log K_{ow}) of APEO to toxicity [110]. Incorporated is the notion that addition of ethoxy units to

molecules should decrease net lipophilicity whereas most K_{ow} estimation methods do the opposite, which is not in accordance with observations on e.g. APEO water solubility [109, 110]. The model requires a log K_{ow}^0 input (log K_{ow} for alkylphenol monoethoxylate) and an estimated increment factor that reduces the log K_{ow} with increasing number of ethoxy monomers:

$$log\ K_{ow} = log\ K_{ow}^{0} + "EO\text{-}increment\ factor"*(\#EO-1), \qquad \text{Equation 1}$$

in which #EO is the number of ethoxy units in the APEO oligomer. Furthermore, log S_w can be calculated using the relationship of Hansch *et al.* [53]:

$$log\ S_w = -1.214*log\ K_{ow} + 0.85. \qquad \text{Equation 2}$$

Using parameters proposed by Schüürmann [110] (with log K_{ow}^0 = 5.919, calculated using ClogP, and #EO increment factor = -0.1, the latter being derived through fitting the lipophilicity-toxicity model) yields S_w estimations that are too low (see Figure 6, illustrated for nonylphenol ethoxylates) to fit the aqueous solubility data of Ahel and Giger [1]. A better fit is obtained using the following method. The relationship of Chiou *et al.* [27]:

$$log\ K_{ow} = -0.747*log\ S_w + 0.73, \qquad \text{Equation 3}$$

is used to calculate a log K_{ow}^0 (= 4.42 for $NPEO_1$, 4.09 for $OPEO_1$) from an experimentally determined water solubility. With that log K_{ow}^0 value, a linear regression of experimental S_w values versus number of ethoxy units is performed; the Chiou equation is used to fit the data, in which the #EO increment factor is varied (equation 3) in order to obtain a best fit. The #EO increment factor thus obtained is –0.052 for NPEO and –0.082 for OPEO, respectively. The resulting regression equations (r^2 = 0.877 for NPEO, r^2 = 0.951 for OPEO) are plotted in

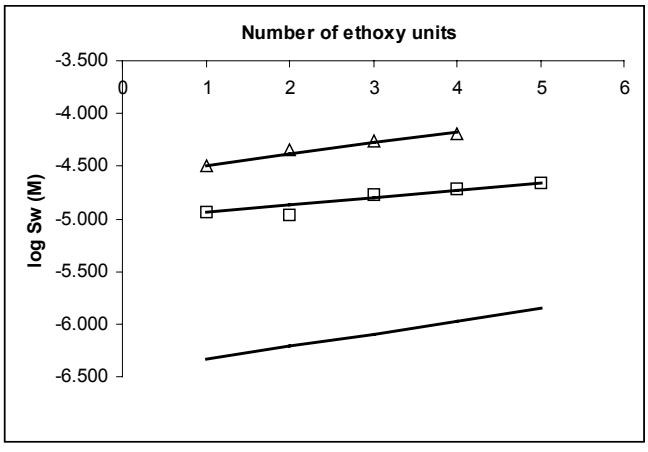


Figure 6. Log water solubility (expressed in mol.l^{-1}) vs number of ethoxy units for octylphenol ethoxylates (triangles) and nonylphenol ethoxylates (squares). Symbols represent experimentally determined values for individual oligomers. Lowest line: equation of Hansch applied to NPEO with #EO increment factor of –0.1, log K_{ow}^0 of 5.919 (ClogP). Middle line (NPEO): equation of Chiou with #EO increment factor of –0.052, log K_{ow}^0 of 4.42 (Chiou). Upper line (OPEO): equation of Chiou with #EO increment factor of –0.082, log K_{ow}^0 of 4.09 (Chiou).

Figure 6, and show good agreement with the experimental S_w values from Ahel and Giger [1]. These equations were used to extrapolate to water solubilities for higher ethoxylated monomers.

Figure 7 and Figure 8 show that some of toxicity data of NPEO for *P. fluorescens* and of OPEO and NPEO for *C. pipiens* are higher than the water solubility of the tested compound. Since APEOs are surfactants ('soap'), they will begin to form micelles above their critical micelle concentration (CMC, see section 7.2.1) which is the reason that testing above the water solubility will –in most cases– not lead to practical problems during testing. However, a high surfactant concentration in aqueous solution will lower the surface tension, which may lead to physical effects in the toxicity tests. The toxicity values (NOECs) for the protozoan *C. maupasi* and the alga *S. quadricauda* were close to or below the water solubility in the range where this could be established. Most LC_{50}'s for *O. latipes* (fish) were lower than the water solubility (see Figure 9).

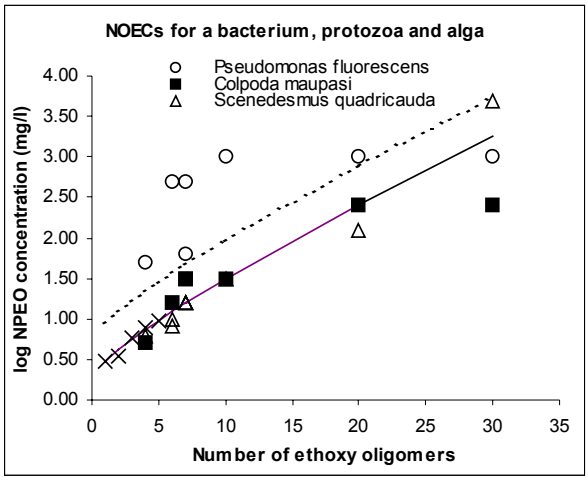


Figure 7. Data from Janicke et al. *[58].* The ^{10}log of the toxicity (NOEC) of several NPEO mixtures for *P. fluorescens*, *C. maupasi* and *S. quadricauda* is presented as a function of ethoxy chain length. Water solubility for $NPEO_1$ to $NPEO_5$ are indicated with x. Solid line is the calculated water solubility, dotted line is 3x the water solubility. Lines are slightly curved because S_w is expressed in mg/l.

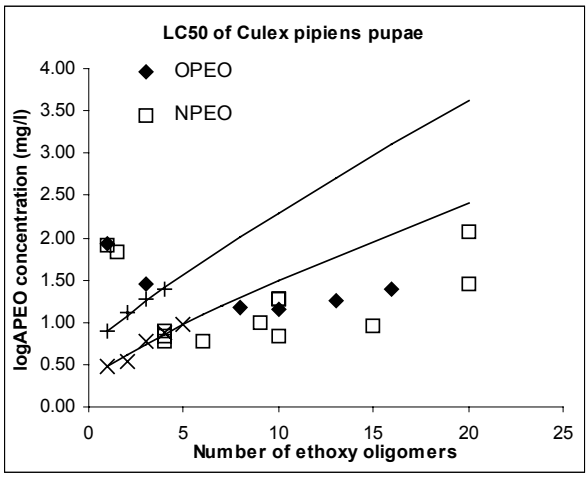


Figure 8. Data from Maxwell and Piper [83]. The ^{10}log of the toxicity (LC_{50}) of several NPEO mixtures to *C. pipiens* is presented as a function of ethoxy chain length. Water solubility for $NPEO_1$ to $NPEO_5$ are indicated with x, water solubility for OPEO1 to OPEO4 are indicated with +. Lower solid line is the calculated NPEO water solubility, upper solid line is the calculated OPEO water solubility. Lines are slightly curved because S_w is expressed in mg/l.

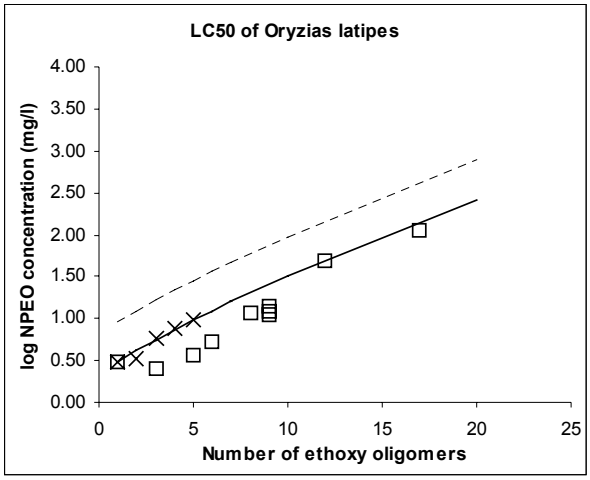


Figure 9. Data from Yoshimura [141]. The ^{10}log of the toxicity (LC_{50}) of several NPEO mixtures to *O. latipes* is presented as a function of ethoxy chain length. Water solubility for $NPEO_1$ to $NPEO_5$ are indicated with x. Solid line is the calculated water solubility, dotted line is 3x the water solubility. Lines are slightly curved because S_w is expressed in mg/l.

The toxicity of $NPEO_n$ for *P. fluorescens* and *C. maupasi* levels off at approximately 1000 and 250 $mg.l^{-1}$, respectively, whereas the toxicity for *S. qaudricauda* and *O. latipes* continues to increase with increasing number of ethoxy units. The toxicity to emerging pupae of *C. pipiens* decreases with increasing number of EO (ethoxy) units but seems to increase slightly from *n*=15 EO units onwards. At present, we do not have an explanation for these various patterns. There are several factors that contribute to a complex picture of the toxicity of these compounds:

1. each toxicity value established in a toxicity test is always determined for a mixture of APEO (containing compounds with varying EO chain length and varying degree of branching in the alkyl chain),
2. the affinity for lipid membranes in target organisms will vary with EO chain length,
3. the possibility to form micelles will enable relatively high water concentrations,
4. surface active properties will favour occurrence of physical effects that intertwine with toxic effects.

Ad 2. Lipophilicity decreases with increasing number of EO units; partitioning into lipid membranes will concomitantly decrease, but this need not be in the same manner for different organisms. Schüürmann [109] found a quantitative relationship for narcotic NPEO toxicity to *Mysidopsis bahia* caused by an additive contribution of EO units, whereas for the protozoan *Tetrahymena elliotti* the relationship was also dependent on other factors than lipophilicity.

Nonetheless, some generalisations can be made: (i) in general, toxicity decreases with increasing number of EO units; (ii) octyl- and nonylphenol ethoxylates are not highly toxic as can be inferred from the figures and the toxicity data tables in Appendix 4.

9.3 Grouping of monomers for ERL derivation

It is impossible to arrive at a risk limit for one single monomeric compound since the available toxicity data have been determined with mixtures of several APEO monomers. Data

analysis in Section 9.2 has shown that grouping of all available toxicity data is not preferable either. Based on results of biodegradation studies as well as monitoring data (see sections 8.2 and 11.2), $APEO_1$ and $APEO_2$ monomers are the compounds that are most prominent in the aquatic environment. Higher ethoxylated compounds are hardly detected, and if so, they will be degraded relatively easy to the more persistent di- and mono-ethoxylate compounds as has been demonstrated in several river water die away studies. We therefore decided to derive one risk limit for $APEO_1$ plus $APEO_2$. Note that in the field mono- and diethoxylate alkylphenols may be both degradation products as well as parent compounds. In this respect we may not overlook the carboxylated mono- and diethoxylate compounds (APE_1C and APE_2C) that are also formed during degradation and have been detected. The number of toxicity data for these compounds is much lower, which implies that there is no knowledge on the relationship between toxicity and number of EO units. Therefore, it seems appropriate to combine APE_1C and APE_2C in one risk limit.
The other toxicity data for the APEO compounds were divided into two large groups: $APEO_{3-8}$ and $APEO_{>8}$. The decision for these two groups was made solely on the number of available toxicity data. By dividing the data as proposed, both groups contain a reasonable amount of data, thus decreasing the uncertainty in risk limit derivation. The toxicity data do not warrant a further division.

9.4 Derivation of ERLs for water

Appendix 2 shows the chronic (NOEC) and acute ($L(E)C_{50}$ toxicity data per taxonomic group, selected for ERL derivation. These data are derived from the tables with individual toxicity data in Appendix 4. The methods of ERL (MPC, NC and SRC_{ECO}) derivation that were followed, are described in Traas [120].

9.4.1 OPE_1C+OPE_2C

Underlying data are presented in Table A2. 1 and Table A4. 1. Only one toxicity result for a fish species is available for OPE_1C. Since the base-set is incomplete, the modified EPA method should be used and an assessment factor of 1000 is applied to the lowest acute toxicity result. The MPC is therefore $L(E)C_{50aqua\ min}/1000 = 5/1000 = 0.005$ mg.l^{-1} or **5 µg.l^{-1}**.

9.4.2 $OPEO_1+OPEO_2$

Underlying data are presented in Table A2. 2 and Table A4. 4. Only one acute toxicity result is available: an LC_{50} of 7.1 mg.l^{-1} for a crustacean. Since the base-set is incomplete, the modified EPA method should be used and an assessment factor of 1000 is applied to the lowest acute toxicity result. MPC = $L(E)C_{50aqua\ min}/1000 = 7.1/1000 = 0.0071$ mg.l^{-1} or **7.1 µg.l^{-1}**.

9.4.3 $OPEO_{3-8}$

Underlying data are presented in Table A2. 3, Table A4. 2 and Table A4. 4. Acute toxicity data for two taxonomic groups at two trophic levels are available (crustaceans and insects) and no chronic data. Since the base-set is incomplete, the modified EPA method should be used and an assessment factor of 1000 is applied to the lowest acute toxicity result. MPC = $L(E)C_{50aqua\ min}/1000 = 1.8/1000 = 0.0018$ mg.l^{-1} or **1.8 µg.l^{-1}**.

9.4.4 $OPEO_{>8}$

Underlying data are presented in Table A2. 4, Table A4. 2, Table A4. 3 and Table A4. 4. Acute toxicity data for 4 taxonomic groups at three trophic levels are present: cyanobacteria and algae, insects and fishes. These do not cover the base-set trophic levels, since data for *Daphnia* are not available. However, since the K_{ow}'s for OPEO>8 are estimated to be >3, base-set completeness is no longer demanded and an assessment factor of 100 should be applied to the lowest NOEC ([120], p. 63 and 64) which is subsequently compared to the outcome of $L(E)C50aqua_{min}/100$. (An assessment factor of 100 is applied to the lowest acute value since ≥3 L(E)C50 values are available [120], p. 65.) Chronic data are available for three taxonomic groups: bacteria, protozoa and algae. $NOEC_{aqua\ min}/100 = 9.1/100 = 0.091$ mg.l^{-1} or 91 µg.l^{-1} compared to $L(E)C50aqua_{min}/100 = 0.21/100 = 2.1$ µg.l^{-1}. The lowest value is selected: MPC=**2.1 µg.l^{-1}**.

9.4.5 NPE_1C+NPE_2C

Underlying data are presented in Table A2. 5 and Table A4. 5. Few acute toxicity data are available for both compounds: 1 value for a crustacean and 2 for fish. The base-set is not complete, therefore the modified EPA method should be used and an assessment factor of 1000 is applied to the lowest acute toxicity result.
Therefore, $MPC=L(E)C_{50aqua\ min}/1000 = 0.99/1000 =$ **0.99 µg.l^{-1}** (reported as **1.0 µg.l^{-1}**).

9.4.6 $NPEO_1+NPEO_2$

Underlying data are presented in Table A2. 6, Table A4. 6 and Table A4. 8. Acute toxicity data at 2 trophic levels for 2 taxonomic groups (crustaceans and fish) are available. The base-set is not complete, therefore the modified EPA method should be used and an assessment factor of 1000 is applied to the lowest acute toxicity result.
$MPC=L(E)C_{50aqua\ min}/1000 = 0.11/1000 =$ **0.11 µg.l^{-1}**.

9.4.7 $NPEO_{3-8}$

Underlying data are presented in Table A2. 7, Table A4. 6 and Table A4. 7. Acute toxicity data for three taxonomic groups are available: insects, fish, amphibians. These do not cover the base-set trophic levels (algae, *Daphnia*, fish). However, since the K_{ow}'s for $NPEO_{3-8}$ are estimated to be >3, base-set completeness is no longer demanded and an assessment factor of 100 should be applied to the lowest NOEC ([120], p. 63 and 64) which is subsequently compared to the outcome of $L(E)C50aqua_{min}/100$. (An assessment factor of 100 is applied to the lowest acute value since ≥3 L(E)C50 values are available [120], p. 65.) There are chronic data at 3 trophic levels: bacteria, protozoans and algae of which the algae were most sensitive. $NOEC_{aqua\ min}/100 = 11/100 = 0.11$ mg.l^{-1} = 110 µg.l^{-1}. This is compared to $L(E)C50aqua_{min}/100$, which is 1.3/100 = 13 µg.l^{-1}. The lowest value of **13 µg.l^{-1}** is selected as MPC.

9.4.8 $NPEO_{>8}$

Underlying data are presented in Table A2. 8, Table A4. 6, Table A4. 7 and Table A4. 8. Acute data for 6 taxonomic groups divided over 3 trophic levels are available: bacteria, algae, molluscs, crustaceans, insects and fish: the base-set is complete. Chronic data for 4 taxonomic groups are available: bacteria, protozoans, algae and insects. This means that refined effect

assessment may be performed: derivation of the HC_5 by the method of Aldenberg and Jaworska [9]. HC_5 calculation was performed using an Excel® based implementation [130] of [9]. The resulting species sensitivity distribution (SSD) is shown in Figure 10. The HC_5 is calculated to be 2.5 $mg.l^{-1}$.

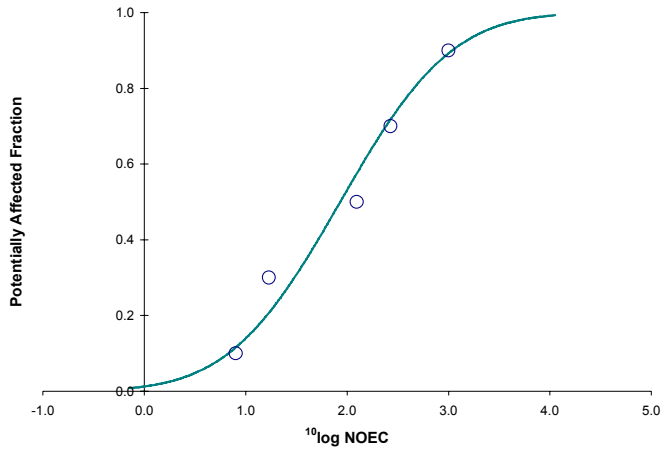


Figure 10. Species sensitivity distribution of $NPEO_{>8}$ for chronic toxicity data to bacteria, protozoans, algae (2 entries) and insects.

However, Table A2. 8 shows that the HC_5 would not be protective for acute toxicity. There are taxonomic groups (crustaceans, fish) not represented in the chronic data set, that show a higher sensitivity compared to the lowest value in the chronic data set. For this reason preliminary risk assessment was followed to derive an MPC for $NPEO_{>8}$.
Since the K_{ow}'s for $NPEO_{>8}$ are estimated to be >3, base-set completeness is no longer demanded and an assessment factor of 100 should be applied to the lowest NOEC. However since there are NOECs for four taxonomic groups a lowering of this factor to 10 seems justified. $NOECaqua_{min}/10 = 8/10 = 0.8$ $mg.l^{-1}$. This is subsequently compared to the outcome of $L(E)C50aqua_{min}/100$ (an assessment factor of 100 is applied to the lowest acute value since ≥3 L(E)C50 values are available [120], p. 65.): $1/100 = 0.01$ $mg.l^{-1}$. The lowest value is selected as the MPC: **10 µg.l^{-1}**

Table 35. Final MPCs, NCs and SRC_{ECO} for OPEO, OPEC, NPEO and NPEC for water.

Compound group	Method for ERL Derivation	Assessment factor applied to derive MPC	NC [µg.l^{-1}]	MPC [µg.l^{-1}]	SRC_{ECO} [µg.l^{-1}]
$OPE_{1+2}C$	mod EPA	$L(E)C_{50aqua\ min}/1000$	0.050	5.0	500
$OPEO_{1+2}$	mod EPA	$L(E)C_{50aqua\ min}/1000$	0.071	7.1	710
$OPEO_{3-8}$	mod EPA	$L(E)C_{50aqua\ min}/1000$	0.018	1.8	620
$OPEO_{>8}$	TGD+mod EPA	$L(E)C_{50aqua\ min}/100$	0.021	2.1	670
$NPE_{1+2}C$	mod EPA	$L(E)C_{50aqua\ min}/1000$	0.010	1.0	260
$NPEO_{1+2}$	mod EPA	$L(E)C_{50aqua\ min}/1000$	0.0011	0.11	45
$NPEO_{3-8}$	TGD+mod EPA	$L(E)C_{50aqua\ min}/100$	0.13	13	410
$NPEO_{>8}$	TGD+mod EPA	$L(E)C_{50aqua\ min}/100$	0.1	10	850

9.5 Calculation of $MPC_{water, total}$ and $MPC_{water, dissolved}$

In the Netherlands, ERLs for water are derived for both the dissolved and total fraction. Dutch standard water contains 30 mg suspended matter (dw/l), with 20% organic matter (11.72% organic carbon). This is twice the amount of organic carbon as in standardised sediment (used to calculate K_p values in EqP). This means that K_{ppm} (partition coefficient suspended matter/water) is two times the K_p sediment/water. The derivation of K_p values for APEO groups is outlined in section 10.2. For the calculation method we refer to the guidance document on deriving environmental risk limits [120]. Table 36 shows the values for K_p, $MPC_{water, dissolved}$ and calculated K_{ppm} and $MPC_{water, total}$ for the various APEO groups.

Table 36. K_{ppm}, $MPC_{water, dissolved}$ and $MPC_{water, total}$ values for APEO groups.

Compound group	K_p [l.kg-1]	K_{ppm} [$l.kg^{-1}$]	$MPC_{water, dissolved}$ [$\mu g.l^{-1}$]	$MPC_{water, total}$ [$\mu g.l^{-1}$]
$OPE_{1+2}C$	80	159	5.0	5.0
$OPEO_{1+2}$	509	1017	7.1	7.3
$OPEO_{3-8}$	249	499	1.8	1.8
$OPEO_{>8}$	108	215	2.1	2.1
$NPE_{1+2}C$	147	294	1.0	1.0
$NPEO_{1+2}$	1364	2728	0.11	0.12
$NPEO_{3-8}$	669	1337	13	14
$NPEO_{>8}$	288	577	10	10

9.6 Endocrine disruptive effects

Table A6. 1 (Appendix 6) shows the hormone related effect data of APEO. Because of the limited number of data we have placed all entries in one table in which the data are grouped per test compound. The distinction between *in vitro* and *in vivo* tests is shown in column 4 (Test type). Van Wezel *et al.* ([131], Chapter 5) have set out a strategy for determination of the relevance of observed endocrine effects, that will also be followed for APEO. In short, this means that *in vitro* tests may predict the possibility for a compound to exert endocrine disruptive effects, but this suspicion should be confirmed in *in vivo* tests. The height of the observed *in vivo* effects is then related to the derived MPCs to establish if the latter are protective for endocrine effects.

In section 7.4 (Table 33) the potency of several APEO is reported, as compared to 17β-estradiol. The overview shows that short (ethoxy) chain APEO have higher potency and that potency decreases with increasing chain length [104, 138]. However, the most potent compounds ($NPEO_2$ and NPE_1C) were a factor of 2.5×10^4 less potent than 17β-estradiol in the recombinant yeast estrogen assay.

In vivo results were obtained for *Daphnia magna* and *Pimephales promelas* with, unfortunately, an NPEO mixture of *unspecified* composition. The lowest concentration at which effects were established (58% inhibition of testosterone elimination in *D. magna*) was 2.5 mg/l. The highest MPC value of 13 $\mu g.l^{-1}$, derived for $NPEO_{3-8}$ (Table 35), would still be protective for these effects. Effects of $NPEO_1$, $NPEO_2$ and NPE_1C on VTG induction, testes

growth inhibition and spermatogenesis in *O. mykiss* (shown in Table A6. 1) are also protected by the respective MPCs.
From these results we can conclude that the current MPCs for $NPE_{1+2}C$, $NPEO_{1+2}$ and $NPEO_{3-8}$ are protective for effects on the endocrine system of aquatic animals based on the data currently available. It is unclear if the MPC for $NPEO_{>8}$ is protective for endocrine effects, this can not be fully underpinned by the data currently available. It is clear that this conclusion is based on a very small number of relevant *in vivo* studies. It is advisable to screen for relevant *in vivo* studies within a few years in order to re-establish the validity of the derived MPCs with respect to endocrine disruptive effects of APEO and APEC.

9.7 Combination toxicity by means of weighed risk quotients

This method makes use of the scaling of environmental concentrations relative to the ERL [121]. This involves dividing the concentration of a compound by the standard, resulting in a risk quotient (RQ) as a relative measure, which is the fraction of the ERL 'filled' by that specific compound. The toxicity of the combination of compounds is tested by summing the RQs (for 1 to *n*) and comparing this result to the 'relative ERL' which equals 1 by the same method of scaling. A combined fraction higher than 1 indicates that the standard is exceeded, a fraction below 1 indicates that the standard is not completely filled by the compounds present in the mixture. This method was extended by Van Straalen [128] by weighing the compounds in the mixture based on the distribution of fractions. In essence, this means that the value of the risk quotient is determined for the largest part by the compounds that are present in the highest concentrations and to a lesser extent by the compounds that are present in lower concentrations in the mixture (for an extended commentary see Mesman and Posthuma [85]).
The method is based on the well accepted concept of Toxic Units (see e.g. Sprague [113]) and is based on concentration addition. It can be applied both 'generic' for a general or average mixture of compounds as well as for a mixture of compounds measured at a local environment.

First, the RQs are calculated for each compound, based on the local concentrations of these *n* compounds (or compound class) in the mixture, and subsequently RQs are summed:

$$\sum_{1}^{n} RQ = \frac{conc_1}{ERL_1} + \frac{conc_2}{ERL_2} + ... \frac{conc_n}{ERL_n}$$

When this value is below 1, no risk is expected under the assumption that the standard is the right measure for the toxicity [121]. When this value exceeds 1, risk is expected.

10. Alkylphenol ethoxylates - Toxicity data and derivation of ERLs for soil and sediment

10.1 Toxicity data

Very few toxicity data (*viz*. 1 publication) for terrestrial organisms were found for the alkylphenol ethoxylates. Results are presented in Appendix 5. Some of the experiments were performed using 1 test concentration. Since it is impossible to determine if the observed effects are dose related, these results are placed in the table with deviating tests. Consequently, data for the inhibition of dehydrogenase activity after several days exposure to $NPEO_3$ and $NPEO_{13}$ mixtures remain. These data will be used to derive the MPC and are considered chronic NOEC values. It is assumed that the APEO toxicity to soil organisms varies with ethoxylate chain length as was observed for aquatic toxicity (section 9.2). An MPC_{soil} for $NPEO_{3-8}$ and $NPEO_{>8}$ will be derived. For $NPEO_{1+2}$ and OPEO no data were available, as explained above.

10.2 Partition coefficients used

Experimental data on sorption coefficients show considerable variability. Section 8.1 describes the experimental values that were retrieved and their deviation from QSAR predicted values. The experimental data of John *et al.* [61] were selected as a source for K_{oc} values of $NPEO_3$ to $NPEO_{13}$. Experimental K_{oc} values for $NPEO_1$ and $NPEO_2$ are available [55], they are however, field data for suspended matter/water partitioning that are 1-2 orders of magnitude higher than values from the monomeric series of John *et al.* We have decided to extrapolate these data to $NPEO_1$ and $NPEO_2$ using a fitted relationship between the number of ethoxy oligomers (#EO) and log K_{oc}. To obtain K_{oc} data for $OPEO_n$, the obtained log K_{oc} - #EO relationship for $NPEO_n$ was corrected for the difference in alkyl chain length (C9 to C8) via the log K_{oc} - log K_{ow} relationship for predominantly hydrophobic chemicals from Sabljić *et al*. [105]. Appendix 3 shows the data of John *et al.* and how these were used to calculate K_{oc} values shown in Table 37.
For the $OPE_{1+2}C$ and $NPE_{1+2}C$ groups no water solubilities, K_{ow}, or K_{oc} values are available. We therefore have to rely entirely on estimated K_{oc} values [45].The K_{oc} values of OPE_1C and NPE_1C will be used for the groups $OPE_{1+2}C$ and $NPE_{1+2}C$, respectively. The highest of two K_{oc} values in a group is chosen, which means a conservative approach with respect to protection of species. All K_{oc} values were recalculated to K_p values in order to calculate MPCs for standard soil and standard sediment [120]. Summarizing, the following log K_{oc} and log K_p values were used for calculations (Table 37):

Table 37. K_{oc} and K_p values for APEO groups that are used in equilibrium partitioning.

Compound group	log K_{oc}	method	K_p [l.kg^{-1}]
$OPE_{1+2}C$	3.13	PcKoc [45]	80
$OPEO_{1+2}$	3.94	Appendix 3	509
$OPEO_{3-8}$	3.63	Appendix 3	249
$OPEO_{>8}$	3.26	Appendix 3	108
$NPE_{1+2}C$	3.40	PcKoc [45]	147
$NPEO_{1+2}$	4.37	Appendix 3	1364
$NPEO_{3-8}$	4.06	Appendix 3	669
$NPEO_{>8}$	3.69	Appendix 3	288

10.3 MPCs for soil

Table A2. 9 and Table A2. 10 in appendix 2 show the terrestial toxicity data per taxonomic group as used for ERL derivation. These data are derived from the tables with individual toxicity data in appendix 5. The methods of ERL (MPC, NC and SRC_{ECO}) derivation that were followed, are described in Traas [120].

10.3.1 $NPEO_{3-8}$

Underlying data are presented in Table A2. 9 and Table A5. 1. Since chronic toxicity results are available for one soil function parameter,
$MPC_{soil} = NOECterr_{min}/100 = 452/100 =$ **4.5 mg.kg$_{d.w}^{-1}$**.

10.3.2 $NPEO_{>8}$

Underlying data are presented in Table A2. 10 and Table A5. 2. Since chronic toxicity results are available for one soil function parameter,
$MPC_{soil} = NOECterr_{min}/100 = 7843/100 =$ **78 mg.kg$_{d.w}^{-1}$**.

10.3.3 ERL_{soil} calculated using EqP

This section shows ERLs for soil as calculated using EqP theory. The following equation was used:

$$MPC\text{soil}_{EqP} = MPC\text{water} \cdot K_p \qquad \text{Equation 4}$$

in which MPC_{water} is taken from Table 35 and K_p from Table 37.

Table 38. MPCs for soil calculated using equilibrium partitioning and using soil toxicity data (MPCdirect).

Compound group	MPCsoil EqP [mg.kg^{-1}]	MPCsoil direct [mg.kg^{-1}]
$OPE_{1+2}C$	0.40	n.a.
$OPEO_{1+2}$	3.6	n.a.
$OPEO_{3-8}$	0.45	n.a.
$OPEO_{>8}$	0.23	n.a.
$NPE_{1+2}C$	0.15	n.a.
$NPEO_{1+2}$	0.15	n.a.
$NPEO_{3-8}$	8.7	4.5
$NPEO_{>8}$	2.9	78

n.a. = not available.

Comparison of MPCsoil derived from toxicity results (MPCsoil direct) with MPCsoil derived using EqP (MPCsoil EqP) is presented in Table 38. The lowest values are selected as ERL: for $NPEO_{3-8}$, MPCsoil = 4.5 $mg.kg^{-1}$ (based on a soil toxicity study) and for $NPEO_{>8}$, MPC soil = 3 $mg.kg^{-1}$ (based on EqP).

Table 39. Final MPCs, NCs and SRC_{ECO} for OPEO, OPEC, NPEO and NPEC for soil.

Compound class	MPC_{soil} [$mg.kg^{-1}$]	Method	NC_{soil} [$mg.kg^{-1}$]	Method	$SRC_{ECO, soil}$ [$mg.kg^{-1}$]	Method
$OPE_{1+2}C$	0.40	EqP	0.0040	MPC/100	40	EqP
$OPEO_{1+2}$	3.6	EqP	0.036	MPC/100	360	EqP
$OPEO_{3-8}$	0.45	EqP	0.0045	MPC/100	150	EqP
$OPEO_{>8}$	0.23	EqP	0.0023	MPC/100	72	EqP
$NPE_{1+2}C$	0.15	EqP	0.0015	MPC/100	38	EqP
$NPEO_{1+2}$	0.15	EqP	0.0015	MPC/100	61	EqP
$NPEO_{3-8}$	4.5	NOEC/100	0.045	MPC/100	270	EqP
$NPEO_{>8}$	2.9	EqP	0.029	MPC/100	250	EqP

10.4 MPCs for sediment

No sediment toxicity data were found in the retrieved literature. The $MPC_{sediment}$ values will therefore be based on equilibrium partitioning.

10.4.1 $MPC_{sediment}$ calculated using EqP

This section shows ERLs for sediment as calculated using EqP theory. The following equation was used:

$$MPC\text{sediment}_{EqP} = MPC \cdot K_p \qquad \text{Equation 5}$$

in which MPC_{water} is taken from Table 35 and K_p from Table 37. The K_{oc} values that were used for soil were also used for sediment EqP.

Table 40. Final MPCs, NCs and SRC_{ECO} for OPEO, OPEC, NPEO and NPEC for sediment calculated using equilibrium partitioning.

Compound class	$MPC_{sediment}$ [$mg.kg^{-1}$]	Method	$NC_{sediment}$ [$mg.kg^{-1}$]	Method	$SRC_{ECO, sediment}$ [$mg.kg^{-1}$]	Method
$OPE_{1+2}C$	0.40	EqP	0.0040	EqP	40	EqP
$OPEO_{1+2}$	3.6	EqP	0.036	EqP	360	EqP
$OPEO_{3-8}$	0.45	EqP	0.0045	EqP	150	EqP
$OPEO_{>8}$	0.23	EqP	0.0023	EqP	72	EqP
$NPE_{1+2}C$	0.15	EqP	0.0015	EqP	38	EqP
$NPEO_{1+2}$	0.15	EqP	0.0015	EqP	61	EqP
$NPEO_{3-8}$	8.7	EqP	0.087	EqP	270	EqP
$NPEO_{>8}$	2.9	EqP	0.029	EqP	250	EqP

11. Alkylphenol ethoxylates - Preliminary risk analysis

11.1 Multiple species/(semi-)field experiments

Except for one study (Lewis [71]), no field toxicity studies with APEO were found in the public literature. Lewis studied the effect of a 10 day exposure of an $OPEO_{11}$ mixture on the phytoplankton community of a freshwater lake. An EC_{10} of 9.1 $mg.l^{-1}$ was derived by fitting a logistic dose response model through the published data. This study was incorporated in the risk assessment as a chronic toxicity value.

11.2 Environmental distribution

Analysis

In the last decades various analytical techniques for measurements of APEOs in several environmental compartments have been employed and optimised. An overview is given by Thiele [119] and Groshart *et al.* [51].

Introduction on occurrence

As a consequence of their widespread use (see section 7.3), alkylphenol ethoxylates have been measured regularly in all parts of the aquatic environment, i.e. in water, sediment and especially near effluents of sewage treatment plants. STPs can be identified as one of the main (point) sources for entry of alkylphenol ethoxylates in rivers. There are various studies that demonstrate the presence of these compounds and their degradation products in STP effluent [3, 25, 32, 33, 35, 36, 106] or in STP sludge [32, 70]. Detection of alkylphenol ethoxylates in wool scouring effluent (Scotland) [117], paper mill sludge (Canada) [54] and household detergents (Taiwan) [26] reflect their various uses. With regard to the latter study (detection in household detergents) it must be noted that in recent years, domestic applications of alkylphenol ethoxylates in Europe have been reduced due to industry led voluntary agreements [51]. This may cause older publications on measurements of alkylphenols and alkylphenol ethoxylates or studies from non-European countries not to be representative of the current situation. A more recent review on occurrence of AP and APEO was published by Bennie [17], and a recent book on analysis and fate of surfactants by Knepper *et al.* [66]. Both deal with occurence of APEO and are more elaborate than this section; they might therefore be consulted when more detail is required.

Table 41 and Table 42 give an overview of measurements of alkylphenol ethoxylates in surface water. Concentrations in this table preceded by a '<' sign are below the detection limit of the analytical method employed, if available.

Table 41. Occurrence of alkylphenol ethoxylates in surface water in the Netherlands.

Location	Year	Compound	Concentration [µg.l^{-1}]	Mean (mn) or median (md) [µg.l^{-1}]	Reference
Main waterways[a]	1997	$OPEO_n$	<0.1		[16]
	1997	$NPEO_n$	<0.1		[16]
Surface waters[b]	1999	$OPEO_n$	<0.17-<1.56		[134]
	1999	$NPEO_n$	<0.18-<2.4[c] 2.1-2.9[d]	2.5[d] (md)	[134]
River Rhine[e]	2001	$NPEO_1$	<0.03-0.116	0.065 (mn); *n*=3[e]	[64]
	2001	$NPEO_2$	0.0091-0.50	0.11 (mn); *n*=6[e]	[64]
	2001	$NPEO_{3-16}$	<0.02-5.21	1.4 (mn); *n*=4[e]	[64]
	2001	NPE_1C	0.06-0.44	0.19 (mn); *n*=6[e]	[64]
	2001	NPE_2C	<0.011-0.23	0.21 (mn); *n*=2[e]	[64]
	2001	$NPE_{3-6}C$	<d.l.-0.45	0.41 (mn); *n*=2[e]	[64]
River Meuse[f]	2001	$NPEO_1$	<0.03-0.102[f]		[64]
	2001	$NPEO_2$		0.074 (mn); *n*=2[f]	[64]
	2001	$NPEO_{3-16}$		0.21 (mn); *n*=2[f]	[64]
	2001	NPE_1C		0.57 (mn); *n*=2[f]	[64]
	2001	NPE_2C		0.49 (mn); *n*=2[f]	[64]
	2001	$NPE_{3-6}C$		0.97 (mn); *n*=2[f]	[64]
Estuaries/sea					
North Sea[g]	1999	$OPEO_n$	<l.o.d.[h] 6.4; 17[i]		[134]
	1999	$NPEO_n$	<l.o.d. 26; 87[g]		[134]
Dutch estuaries[j]	1999	$OPEO_n$	<0.20-<0.42[k]		[134]
	1999	$NPEO_n$	<0.18-<0.70[l] 2.4[m]		[134]
Rhine estuary	1999	$NPE_{1-7}C$	0.6-1.7[n]		[63]
	1999	$NPEO_{1+2}$	0.054-0.47[n]		[63]
	1999	$NPEO_{3-15}$	0.16-0.4[n]		[63]
Scheldt estuary	1999	$NPE_{1-7}C$	0.095-10.9[o]		[63]
	1999	$NPEO_{1+2}$	0.0046-1.0[o]		[63]
	1999	$NPEO_{3-15}$	0.028-1.3[o]		[63]
Canal Gent-Terneuzen	1999	$NPEO_{1+2}$	0.05[p]		[63]
	1999	$NPEO_{3-15}$	0.15[p]		[63]
Haringvliet[q]	2001	$NPEO_1$	<0.03[q]		[64]
	2001	$NPEO_2$	0.0056[q]		[64]
	2001	$NPEO_{3-16}$	0.064[q]		[64]
	2001	NPE_1C	<0.014[q]		[64]
	2001	NPE_2C	<0.011[q]		[64]
	2001	$NPE_{3-6}C$	<l.o.d.[q]		[64]

Blank cells: data were not reported and/or could not be calculated. [a]*n*=3; Canal Gent-Terneuzen, Canal: Noordzeekanaal-location IJmuiden and Seaway: New Waterway-location Beneluxtunnel; [b]19 locations in rivers, channels and seaways, sampled 1, 2 or 3 times in 1999; [c]39 samples<l.o.d.; [d]results and median of pooled individual measurements above detection limit (*n*=9); [e]pooled data from three locations, sampled at two dates; [f]one location sampled at two dates; [g]samples from seawater along the Dutch coastline (3 locations) and open sea (2 locations); [h]8 out of 10 samples were <l.o.d., [i]two -relatively high values- were above l.o.d.; [j]samples taken at 3 locations; [k]all samples<.l.o.d. (*n*=8); [l]most samples<l.o.d. (*n*=7); [m]one sample >l.o.d.; [n]reported values are minimum and maximum concentrations along the salinity gradient from 0.2-19 ‰ for the *sum* of the denoted oligomer range (see column 4); [o]reported values are minimum and maximum concentrations along the salinity gradient from 1.5-32.2 ‰ for the *sum* of the denoted oligomer range (see column 4); [p]one location, reported concentration is sum of denoted oligomers; [q]one location sampled at one date.

Table 42. Occurrence of alkylphenol ethoxylates in surface water of other countries.

Location	Country	Year	Compound	Concentration [µg.l^{-1}]	Mean (mn) or median (md) [µg.l^{-1}]	Reference
River Glatt	CH	1984	$NPEO_1$	<3-69		[4]
	CH	1984	$NPEO_2$	<0.3-30		[4]
	CH	1984	$NPEO_{3-5}$	~1		[4]
	CH	1984	$NPEO_{>6}$	<1		[4]
	CH	1984	NPE_1C	<1-45		[4]
	CH	1984	NPE_2C	2-71		[4]
Various rivers[a]	USA	1990	$NPEO_1$	<0.06.-0.60	0.09 (mn)	[90]
	USA	1990	$NPEO_2$	<0.07-1.2	0.1 (mn)	[90]
	USA	1990	$NPEO_{3-17}$	<1.6-14.9	2.0 (mn)	[90]
Great Lakes	CAN	1994-1995	$NPEO_1$	<0.02-7.8	1.3 (mn)	[18]
	CAN	1994-1995	$NPEO_2$	<0.02-10	1.4 (mn)	[18]
River Lea	UK	1995	$NPEO_1$+$NPEO_2$[b]	<0.6		[20]
River Dee	UK	1995	$NPEO_1$+$NPEO_2$[b]	<0.6		[20]
River Mersey	UK	1995	$NPEO_1$+$NPEO_2$[b]	3.2-4.5		[20]
River Thames	UK	1995	$NPEO_1$+$NPEO_2$[b]	<0.6		[20]
River Exe	UK	1995	$NPEO_1$+$NPEO_2$[b]	<0.6		[20]
River Aire	UK	1995	$NPEO_1$+$NPEO_2$[s]	<0.6-46		[20]
River Elbe[c]	BRD	1998	$OPEO_1$	0.0008-0.0063		[55]
	BRD	1998	$OPEO_2$	0.0006-0.0068		[55]
	BRD	1998	$NPEO_1$	0.01-0.205		[55]
	BRD	1998	$NPEO_2$	0.0036-0.084		[55]
River Saale[d]	BRD	1998	$OPEO_1$	0.0018		[55]
	BRD	1998	$OPEO_2$	0.0015		[55]
	BRD	1998	$NPEO_1$	0.083		[55]
	BRD	1998	$NPEO_2$	0.025		[55]
River Mulde[d]	BRD	1998	$OPEO_1$	0.0017		[55]
	BRD	1998	$OPEO_2$	0.0013		[55]
	BRD	1998	$NPEO_1$	0.041		[55]
	BRD	1998	$NPEO_2$	0.0098		[55]
River Schwarze Elster[d]	BRD	1998	$OPEO_1$	0.0009		[55]
	BRD	1998	$OPEO_2$	0.0008		[55]
	BRD	1998	$NPEO_1$	0.013		[55]
	BRD	1998	$NPEO_2$	0.0043		[55]
River Weisse Elster[d]	BRD	1998	$OPEO_1$	0.003-0.0062	0.0057[e] (md)	[55]
	BRD	1998	$OPEO_2$	0.0015-0.0041	0.0032[e] (md)	[55]
	BRD	1998	$NPEO_1$	0.030-0.115	0.075[e] (md)	[55]
	BRD	1998	$NPEO_2$	0.0088-0.068	28[e] (md)	[55]
St. Lawrence River upstream of effluent	CAN	n.r.	$NPEO_{1-6}$	<0.002[f]		[25]
	CAN	n.r.	$NPEO_7$	0.006		[25]
	CAN	n.r.	$NPEO_8$	<0.001		[25]
	CAN	n.r.	$NPEO_{9-16}$	0.004-1.06[f]		[25]
	CAN	n.r.	OPE_1C	<0.002		[25]
	CAN	n.r.	NPE_1C	0.081		[25]
St. Lawrence River downstream of effluent	CAN	n.r.	$NPEO_{1-7}$	<0.002[f]		[25]
	CAN	n.r.	$NPEO_8$	6.38		[25]
	CAN	n.r.	$NPEO_9$	0.52		[25]
	CAN	n.r.	$NPEO_{10}$	<0.001		[25]
	CAN	n.r.	$NPEO_{11-16}$	0.58-10.3[f]		[25]
	CAN	n.r.	OPE_1C	<0.002		[25]
	CAN	n.r.	NPE_1C	0.51		[25]
Estuaries/sea						
Lune	UK	1995	$NPEO_1$+$NPEO_2$[b]	<0.6		[20]
Exe	UK	1995	$NPEO_1$+$NPEO_2$[b]	<0.6		[20]
Langstone Harbour	UK	1995	$NPEO_1$+$NPEO_2$[b]	<0.6		[20]
Tamar	UK	1995	$NPEO_1$+$NPEO_2$[b]	<0.6		[20]

Location	Country	Year	Compound	Concentration [µg.l^{-1}]	Mean (mn) or median (md) [µg.l^{-1}]	Reference
Dee	UK	1995	$NPEO_1$+$NPEO_2$[b]	<0.6		[20]
Mersey	UK	1995	$NPEO_1$+$NPEO_2$[b]	<0.6		[20]
Tees	UK	1995	$NPEO_1$+$NPEO_2$[b]	<0.6-76		[20]
Tyne	UK	1995	$NPEO_1$+$NPEO_2$[b]	<0.6		[20]
Wear	UK	1995	$NPEO_1$+$NPEO_2$[b]	<0.6		[20]
Poole	UK	1995	$NPEO_1$+$NPEO_2$[b]	<0.6		[20]
Elbe Estuary	BRD	1998	$NPEO_n$	<0.01		[19]
River Elbe tidal part	BRD	1998	$OPEO_1$	0.0005-0.012	0.0041[g] (md)	[55]
	BRD	1998	$OPEO_2$	0.0004-0.021	0.0082[g] (md)	[55]
	BRD	1998	$NPEO_1$	0.024-0.111	0.047[g] (md)	[55]
	BRD	1998	$NPEO_2$	0.0024-0.024	0.010[g] (md)	[55]
North Sea	BRD	1998-1999	$OPEO_1$	0.0001-0.011	0.0012[h] (md)	[55]
	BRD	1998-1999	$OPEO_2$	0.0001-0.019	0.0064[h] (md)	[55]
	BRD	1998-1999	$NPEO_1$	0.0007-0.029	0.0053[h] (md)	[55]
	BRD	1998-1999	$NPEO_2$	0.0001-0.010	0.001[h] (md)	[55]

CH = Switzerland, UK = United Kingdom, US = United States, CAN = Canada. Blank cells: data were not reported and/or could not be calculated. [a]measurements in 30 rivers; 17, 12 and 19 rivers had concentrations of $NPEO_1$, $NPEO_2$ and $NPEO_{3-17}$ below the detection limit, respectively; [b]sum of total extractable $NPEO_1$+$NPEO_2$; [c]measurements at 10 sites along the German trajectory of the river; [d]tributary of the river Elbe, one site sampled; [e]median value (*n*=6); [f]*n*=8; concentrations were measured for each individual congener, these ranges are **not** sum values; [g]3 sites sampled both in 1998 and 1999, for median results of two years were pooled (*n*=6); [h]for median results of two years were pooled (*n*=13).

The measurements reported by Ahel *et al.* [4] in the river Glatt are dominated by the fact that the river Glatt receives effluent from several STPs, eleven of which were screened for the presence of alkylphenols and alkylphenol ethoxylates in their influent and effluent in a separate study [3]. The concentration levels found in the latter study may no longer be representative for the current situation since –as stated by the authors– domestic use of alkylphenol ethoxylates has since been phased out in Switzerland and Germany. The study of Bennie *et al.* [18] reveals the same trend: highest concentrations were most frequently found in areas of effluent discharge from pulp and paper mills, sewage treatment plants and industrial sources. Results for $NPEO_1$ and $NPEO_2$ in American rivers and the Great Lakes (Canada) were roughly in the same range, their mean values were approx. 0.1-2 µg.l^{-1}. Results for two English rivers and the estuary of the river Tees are notably higher, but it must be added that at 20 locations in four other rivers and at 33 locations in 9 other estuaries no $NPEO_{1+2}$ were detected (detection limit 0.6 µg.l^{-1}). The higher concentrations could be associated with sources like wool-scouring plants, domestic and industrial discharge and a APEO manufacturing plant.

In samples from three Dutch waterways, no OPEOs and NPEOs were detected in 1997, i.e. concentrations were not above ~0.1 µg.l^{-1}, the limit of detection, a pattern that is consistent with results from the Elbe in Germany, where concentrations in the ng.l^{-1} range were found. If the compounds are present, they are usually found in the following concentration order: $NPEO_1$> $NPEO_2$> $OPEO_1$> $OPEO_2$. More recent measurements in the Netherlands (1999) also showed values for OPEO (sum of $OPEO_n$) and most NPEO (sum of $NPEO_n$) to be below the limit of detection. Some measurements for $NPEO_n$ were above the limit of detection and had a median value of 2.5 µg.l^{-1}, a level that was also found in other parts of the world. The study that used water samples from the St Lawrence River in Canada shows that sewage effluent causes a concentration increase of NPEO with a high number (*n*>8-16) of ethoxy

oligomers, indicating little transformation (in river or STP), since transformation leads to a predominance of short chain oligomers (*n*=1-3). Measurements in seawater show very low values for the German Bight of the North Sea for individual congeners, and higher values for the Dutch part of the North Sea. The comparison, however, should be made with care since the Dutch values are sum values. Moreover, concentrations in seawater will also be greatly influenced by the sampling location, e.g.: (i) close to the shore versus open sea or (ii) regions receiving estuarine outflow currents versus less influenced regions at open sea. With respect to the measurements in Table 42 it must be noted that the Dutch part of the North Sea receives water from three major rivers: Rhine, Meuse and Scheldt which may partly explain the higher concentrations compared to the German Bight.
Table 43 and Table 44 give an overview of measurements of alkylphenol ethoxylates in sediments. Concentrations in this table preceded by a '<' sign are below the detection limit of the analytical method employed, if available.

Table 43. Occurrence of alkylphenol ethoxylates in sediments in the Netherlands.

Location	Country	Year	Compound	Concentration [$\mu g.kg_{dw}^{-1}$]	Mean (mn) or median (md) [$\mu g.kg_{dw}^{-1}$]	Reference
Main waterways/ harbours[a]	NL	1997	$OPEO_n$	<10		[16]
	NL	1997	$NPEO_n$	2600-5700		[16]
Various canals/ waterways[b]	NL	1999	$OPEO_n$	<5-<28[c]		[134]
	NL	1999	$NPEO_n$	<l.o.d.-2750	170[d] (md)	[134]
Estuaries/sea						
North Sea/Irish Sea[e]	NL, UK, IRL	n.r.	$OPEO_n$	0.2-16		[33]
	NL, UK, IRL	n.r.	$NPEO_n$	12-400		[33]
Estuaries[f]	NL	1999	$OPEO_n$	<l.o.d.[g]		[134]
	NL	1999	$NPEO_n$	20-610[k]	40[k] (md)	[134]
North Sea/Wadden Sea[i]	NL	1999	$OPEO_n$	<4-<34[j]		[134]
	NL	1999	$NPEO_n$	<l.o.d.[k] 80-250[l]	97[l] (md)	[134]
Rhine estuary	NL	1999	$NPE_{1+7}C$	<0.3-185[m]		[63]
	NL	1999	$NPEO_1$	<1.3-34.6[m]		[63]
	NL	1999	$NPEO_2$	2.2-31.5[m]		[63]
	NL	1999	$NPEO_{3-15}$	12.5-247[m]		[63]
Scheldt estuary	NL	1999	$NPE_{1+7}C$	<0.3-239[m]		[63]
	NL	1999	$NPEO_1$	<1.3-17.1[m]		[63]
	NL	1999	$NPEO_2$	<0.3-26.2[m]		[63]
	NL	1999	$NPEO_{3-15}$	<0.6-199[m]		[63]

UK = United Kingdom, IRL = Ireland. Blank cells: data were not reported and/or could not be calculated..
[a]*n*=3; canal Gent-Terneuzen, canal: Noordzeekanaal-location IJmuiden and Amsterdam harbour: Amerikahaven; [b]freshwater sediments at 14 locations; [c]all samples<l.o.d. (*n*=14); [d]*n*=11; [e]22 estuarine and marine locations in North Sea and Irish Sea; [f]estuarine sediments at 3 locations; [g]all samples<l.o.d. (*n*=3); [h]*n*=3; [i]samples from sediments along the Dutch coastline (3 locations) and open sea (2 locations); all samples<l.o.d.; [j]all samples<l.o.d. (*n*=8); [k]4 out of 8 samples<l.o.d.; [l]*n*=4, [m]reported values are minimum and maximum concentrations along the salinity gradient for the *sum* of the denoted oligomer range (see column 4).

Table 44. Occurrence of alkylphenol ethoxylates in sediments of other countries.

Location	Country	Year	Compound	Concentration [µg.kg$_{dw}^{-1}$]	Mean (mn) or median (md) [µg.kg$_{dw}^{-1}$]	Reference
River Glatt	CH	1984	$NPEO_1$	100-8850	660[a] (md)	[4]
	CH	1984	$NPEO_2$	80-2720	410[b] (md)	[4]
River Rhine	BRD	1987	$NPEO_n$	1500		TemaNord, in [51]
Various rivers[c]	USA	1990	$NPEO_1$	<2.3-175	18.1 (mn)	[90]
River Lea	UK	1995	$NPEO_1$+$NEPO_2$[d]	<500		[20]
River Dee	UK	1995	$NPEO_1$+$NEPO_2$[d]	<500		[20]
River Mersey	UK	1995	$NPEO_1$+$NEPO_2$[d]	7200-9200		[20]
River Thames	UK	1995	$NPEO_1$+$NEPO_2$[d]	<500		[20]
River Exe	UK	1995	$NPEO_1$+$NEPO_2$[d]	<500		[20]
River Aire	UK	1995	$NPEO_1$+$NEPO_2$[d]	<500-6100		[20]
River Elbe[e]	BRD	1998	$OPEO_1$	30-113		[55]
	BRD	1998	$OPEO_2$	45-140		[55]
	BRD	1998	$NPEO_1$	323-967		[55]
	BRD	1998	$NPEO_2$	546-1611		[55]
River Elbe, Schnackenburg	BRD	1998-1999	$OPEO_1$	35-93	81[f] (md)	[55]
	BRD	1998-1999	$OPEO_2$	57-125	98[f] (md)	[55]
	BRD	1998-1999	$NPEO_1$	568-1027	795[f] (md)	[55]
	BRD	1998-1999	$NPEO_2$	838-1797	1381[f] (md)	[55]
River Saale[g]	BRD	1998	$OPEO_1$	91		[55]
	BRD	1998	$OPEO_2$	113		[55]
	BRD	1998	$NPEO_1$	809		[55]
	BRD	1998	$NPEO_2$	1593		[55]
River Mulde[g]	BRD	1998	$OPEO_1$	51		[55]
	BRD	1998	$OPEO_2$	79		[55]
	BRD	1998	$NPEO_1$	553		[55]
	BRD	1998	$NPEO_2$	1009		[55]
River Schwarze Elster[f]	BRD	1998	$OPEO_1$	93		[55]
	BRD	1998	$OPEO_2$	110		[55]
	BRD	1998	$NPEO_1$	624		[55]
	BRD	1998	$NPEO_2$	1121		[55]
Estuaries/sea						
Lune	UK	1995	$NPEO_1$+$NEPO_2$[d]	<500		[33]
Exe	UK	1995	$NPEO_1$+$NEPO_2$[d]	<500		[33]
Langstone Harbour	UK	1995	$NPEO_1$+$NEPO_2$[d]	<500		[33]
Tamar	UK	1995	$NPEO_1$+$NEPO_2$[d]	<500		[33]
Dee	UK	1995	$NPEO_1$+$NEPO_2$[d]	<500		[33]
Mersey	UK	1995	$NPEO_1$+$NEPO_2$[d]	<500		[33]
Tees	UK	1995	$NPEO_1$+$NEPO_2$[d]	<500-3600		[20]
Tyne	UK	1995	$NPEO_1$+$NEPO_2$[d]	<500		[20]
Wear	UK	1995	$NPEO_1$+$NEPO_2$[d]	<500		[20]
Poole	UK	1995	$NPEO_1$+$NEPO_2$[d]	<500		[20]

CH = Switzerland, UK = United Kingdom, US = United States, CAN = Canada. Blank cells: data were not reported and/or could not be calculated. [a]median value, *n*=7; [b]median value, *n*=6; [c]concentration reported in **µg.l^{-1}**, measurements in 30 rivers of which 7 were below the detection limit; [d]total extractable $NPEO_1$+$NPEO_2$; [e]measurements at 8 sites along the German trajectory of the river; [f]median of eleven samples with monthly intervals; [g]tributary of the river Elbe, one site sampled.

The lipophilic nature of short chain alkylphenol ethoxylates is reflected by their accumulation in sediments. Most concentrations in Table 43 and Table 44 can be expressed in the mg.kg^{-1} (ppm) range whereas most water concentrations are in the low µg.l^{-1} (ppb) or even ng.l^{-1} (ppt)

range. Measurements done in sediments from the river Elbe show the same concentration order for short chain OPEO and NPEO oligomers as encountered in surface waters: $NPEO_1$> $NPEO_2$> $OPEO_2$> $OPEO_1$. The high affinity of these four compounds to sediment organic matter is reflected in the log K_{oc} values that were determined *in situ* by Heemken *et al.* [55] who used River Elbe water and suspended matter measurements to determine partition coefficients. Four experiments (each with triplicate measurements) were pooled to find log K_{oc} values of 6.02, 6.24, 5.6 and 6.38 for $OPEO_1$, $OPEO_2$, $NPEO_1$ and $NPEO_2$, respectively. These were the only experimentally determined K_{oc} values that were retrieved for APEOs, all other values (see section 7.2) are estimated using the PcKoc module from EpiSuite [45], therefore a detailed comparison is hampered. The observed differences however are two to three orders of magnitude, which gives rise to serious doubts about the estimated values.

Monitoring in the Netherlands

The Dutch monitoring programme LOES (Landelijk onderzoek oestrogene stoffen) was a broad national screening study on occurrence, potency and biological effects of estrogens and xeno-estrogens in the aquatic environment [133]. The cited report shows all available results in detail, while a short summary is presented here. Results of aquatic and sediment concentrations of APEO (measured as Σ oligomers) have been taken up in Table 41 and Table 43. Rainwater has also been analysed at three locations at 2 different dates. The concentrations of APEO (Σ oligomers) were always below the detection limit, i.e. 0.36-0.90 $\mu g.l^{-1}$ for NPEO and 0.21-0.48 $\mu g.l^{-1}$ for OPEO. Biota sampled in the LOES study for APEO (Σ oligomers) were bream (*Abramis brama*), flounder (*Platichthys flesus*), zebra mussel (*Dreissena polymorpha*) and blue mussel (*Mytilus edulis*). The majority of biota samples contained no APEO levels above the detection limit, which ranged from 0.01-0.06 $\mu g.g_{ww}^{-1}$ for OPEO and 0.01-0.11 $\mu g.g_{ww}^{-1}$ for NPEO. For fishes, the height of the incidental levels that were above the detection limit was 0.15-0.5 $\mu g.g_{ww}^{-1}$ NPEO in bream at 3 locations and 0.1 $\mu g.g_{ww}^{-1}$ NPEO in flounder at one location, while 37 locations were sampled in total. For mussels, no APEO were detected in blue mussel, while zebra mussels from one location contained 0.23 $\mu g.g_{ww}^{-1}$ NPEO.

Untreated municipal waste water (at 12 locations), was also analysed for OPEO and NPEO. OPEO was found at one location in 24 $\mu g.l^{-1}$ and NPEO at 9 locations with a median concentration of 37 $\mu g.l^{-1}$. Removal of these compounds was rather efficient since the concentrations encountered in municipal effluent were lower than in untreated waste water: <detection limit for OPEO (0.7 $\mu g.l^{-1}$) at all locations and <detection limit for NPEO (1.9 $\mu g.l^{-1}$) at all but one locations; the one location containing 2.2 $\mu g.l^{-1}$.

One of the outcomes of the LOES project was that plasma VTG concentrations in bream correlated well with body concentrations of NP and NPEO. There was some correlation between levels in fish and occurrence in surface water and suspended matter. There were not enough data to correlate occurrence in sediment to fish body levels. ER-CALUX activity (an *in vitro* assay using human breast cancer cells with endogenous ER receptor and luciferase construct) in bream bile was mainly defined by occurrence of NPEO and dibutylphthalate, another compound with estrogenic potency. The LOES report concludes that although there

are not enough data to definitively identify NP and NPEO as 'causative agents' the findings from plasma VTG and ER-CALUX in bile taken together strongly suggest that NP and/or NPEO are causing these –estrogen mimicking– effects.
In a recent monitoring survey by Greenpeace [98], concentrations of OP, NP, ΣOPEO and ΣNPEO in precipitation (wet + dry deposition) in the Netherlands were measured at 50 locations (of which 3 were in Belgium and Germany). Table 45 shows the results of this study.

Table 45. AP and APEO in precipiation in the Netherlands, data from Peters [98].

Compound/group	minimum concentration	maximum concentration	median	l.o.d.	% samples >l.o.d.
OP	8.4[a]	8.4[a]	8.4[a]	5	2
NP	42	256	82	40	34
ΣOPEO	30	113	69	30	78
ΣNPEO	31	924	91	30	94

All values reported in $ng.l^{-1}$; [a]detected in one sample.

For the APEO detected, the number of ethoxy oligomers generally ranged from 1 to 12, indicating that extensive degradation of the compounds had not yet occured. This suggests that the sources of detected APEO may be related to emission rather than to exchange between environmental compartments. Two possible areas of emission (possibly nearby production or handling facilities or industry using APEO) were identified based on results of individual locations.

11.3 Preliminary risk analysis

In this section the derived ERLs will be held against concentrations that have been measured in the environment. We will focus on concentrations measured in the Netherlands since the ERLs are derived for Dutch environmental policy.

11.3.1 Water

11.3.1.1 APEC

No measurements of OPE_nC have been found, but concentrations of NPEC have recently been reported by Jonkers *et al.* [63] in the Rhine and Scheldt estuary and Jonkers *et al.* [64].
Rhine and Scheldt estuary, sampled in 1999.
Values are reported for Σ APE_nC, however, the analysis enabled quantification of individual NPE_1C and NPE_2C oligomers. Concentration ranges for these individual oligomers had to be read from a graph, making the estimates qualitative in nature. Rhine estuary NPE_1C: 0.3-0.6 $\mu g.l^{-1}$, NPE_2C: 0.15-0.6 $\mu g.l^{-1}$. The MPC for $NPE_{1+2}C$ is 1 $\mu g.l^{-1}$. We calculate the risk quotient (RQ) using the maximum of the ranges (note that the MPC is a group standard for NPE_1C+NPE_2C) as: 0.6/1 + 0.6/1 = 1.2. Since this value exceeds 1, this indicates a potential risk. Two remarks have to be made on this specific case: (1) the sum of NPE_1C and NPE_2C concentrations is >1 $\mu g.l^{-1}$ at only two locations as far as can be seen from the graph, not in the whole estuary and (2) the MPC bears a large uncertainty since it is based on few toxicity

results (compensated by an assessment factor of 1000 in the derivation of the MPC). In the Scheldt estuary, maximum concentrations are higher: NPE_1C: 0.03- ~5 $\mu g.l^{-1}$, NPE_2C: 0.01- ~5 $\mu g.l^{-1}$. In this situation: RQ= 5/1+5/1 = 10. PNEC concentrations for both estuaries show a gross decrease with increasing salinity (i.e. towards sea). For $NPE_{1+2}C$ the sum of their concentrations seems to pass below the MPC only at the end of the estuary -close to the sea-. Note that $NPE_{1+2}C$ concentrations in the Scheldt estuary are roughly 10 times higher than in the Rhine estuary.

River samples, 2001

Concentrations for A_9PE_1C, A_9PE_2C and $\Sigma A_9PE_{3-6}C$ are reported (Table 41). Since a group MPC is available only for A_9PE_1C + A_9PE_2C we will use concentrations these compounds to calculate an RQ. Using the maximum measured values for both compounds as a worst case, we calculate an RQ of 0.67 for the Rhine. For the Meuse, mean values are presented, leading to an RQ of 1.06.

11.3.1.2 $APEO_{1+2}$

For both octyl- and nonylphenol ethoxylates, measurements for Dutch surface waters are available from 1997, 1999 and 2001. Most measurements from 1997 and 1999 however, are reported as Σ OPEO or Σ NPEO. This precludes comparison with ERLs, since these have been derived for selected groups of compounds. The 1997 samples were from 3 locations in industrialised areas, namely canal Gent-Terneuzen, canal Noordzeekanaal (IJmuiden) and the New Waterway (Beneluxtunnel) and all analysis results were below the detection limit of 0.1 $\mu g.l^{-1}$. The MPC for $NPEO_{1+2}$ is equal to this detection limit (viz. 0.11 $\mu g.l^{-1}$), which means that the sensitivity of the analysis method should be increased in order to measure concentrations that are relevant to setting of environmental quality standards for these two compounds. Recent papers [55, 63] show that $ng.l^{-1}$ levels are achieved nowadays.

For the samples that were measured in the LOES project (see section 11.2, 'Monitoring in the Netherlands'), Σ of APEO oligomers were also reported. In this monitoring campaign, incidentally, levels above the detection limit were reported for mixtures of oligomers of unknown composition.[3]

Rhine and Scheldt estuary, sampled in 1999.

In the estuary study [63], $NPEO_{1+2}$ concentrations were reported. $NPEO_{1+2}$ concentrations exceeded the MPC for this group (viz. 0.11 $\mu g.l^{-1}$) at 6 out of 8 sampling points (RQ 2.2 – 4.7) in the Rhine estuary and at 4 out of 11 (RQ 1.6-10) in the Scheldt estuary.

River samples, 2001

Data from [64] (summarised in Table 41), lead to an RQ value for river Rhine data of 5.6, when based on maximum measured values. The RQ for $NPEO_{1+2}$ is still 1.5 when based on mean measured values.

[3] The samples in the LOES project were analysed for Σ APEO since this suffices as a screening to identify presence or absence of the compounds. However, the analytical technique was and is available to quantify for individual oligmers (and samples have been preserved).

11.3.1.3 $APEO_{3-8}$ and $APEO_{>8}$

Reported concentrations for higher ethoxylated oligomers in [63] are presented as one group: $NPEO_{3-15}$. This hampers comparison with the derived group MPCs in the underlying report. However, since the shorter chain APEO are expected to dominate strongly in the environment, an indicative comparison will be made here, with the assumption that the concentrations of $NPEO_{>8}$ do not contribute to a significant extent in the Σ $NPEO_{3-15}$ concentration. The highest Σ $NPEO_{3-15}$ concentration reported is 1.3 $\mu g.l^{-1}$ (Scheldt estuary). The MPC for $NPEO_{3-8}$ is 13 $\mu g.l^{-1}$, therefore, RQ = 0.1, indicating that the risk of the higher ethoxylated NPEO oligomers is small. In water samples from the river Rhine, sampled in 2001, the highest concentration reported for Σ $NPEO_{3-16}$ (5.2 µg/l) leads to an RQ of 0.4.

11.3.2 Sediment

As reported for aqueous concentrations of APEO in the Netherlands, sampling studies in 1997 and 1999 reported only Σ of APEO concentrations in sediment, hampering calculation of risk quotients. Σ OPEO was always below the detection limit, but Σ NPEO was maximally 2.6-5.7 $mg.kg^{-1}$, which is much higher than the MPC of 0.15 $mg.kg^{-1}$ for $NPEO_{1+2}$, the two compounds that are presumably predominant. RQs can be calculated for sediments in the Rhine and Scheldt estuary using data from [63]. This is done in the following sections.

11.3.2.1 $NPE_{1+2}C$

Σ of NPEC concentrations in sediment were reported, these were below l.o.d. in 8 out of 18 sampling sites. RQs can not be calculated because individual oligomer concentrations are not known. Under the assumption that NPE_1C and NPE_2C make up the largest part of the Σ NPEC, we find an RQ>1 (2.2 and 2.8, respectively) at two (n=18) locations, one in the Rhine estuary and one in the Scheldt estuary.

11.3.2.2 $NPEO_{1+2}$

RQs can be calculated based on measurements of individual oligomer concentrations. The sum of the concentrations of the individual oligomers never exceeds the standard (viz. 150 $\mu g.kg^{-1}$). RQ ranges from 0.0026 to 0.42. At three locations an RQ could not be calculated since concentrations of both compounds were below the detection limit (the highest l.o.d. is more than 100 times lower than the MPC).

11.3.2.3 $NPEO_{3-8}$ and $NPEO_{>8}$

Reported concentrations for higher ethoxylated oligomers in sediment are presented as one group: $NPEO_{3-15}$. This hampers comparison with the group-MPCs derived in the underlying report. This is particularly true for Rhine estuary sediment since the average ethoxylate chain length in those sediments was observed to be 2-9 units. In the Scheldt estuary, the centre of the ethoxylate unit distribution lays around 3 in all sediments. For the Scheldt estuary therefore, RQs are calculated for $NPEO_{3-8}$ using Σ $NPEO_{3-15}$ concentrations, assuming that the higher ethoxylated oligomers do not contribute significantly to the sum concentration. RQs range from 0.0006 to 0.16 showing that direct risks are not expected. A remark on these results is, that EqP theory has been applied to calculate sediment MPCs. MPCs for sediment

are therefore based entirely on aquatic toxicity data, because no toxicity data on sediment inhabiting organisms were found.

12. Discussion

Comparison of measured NP and NPEO concentrations in surface water and sediments in the Netherlands often shows levels below the MPC, but in several cases concentrations are higher than the MPC. This means that emission reduction measures for these compounds may be necessary to bring concentration levels below MPC level in the future. Section 5.3 summarises some recent actions taken at the European level with respect to measures proposed by regulatory authorities.

There are indications of effects at lower concentrations. The study of Ashfield *et al.* [12] shows effect concentrations for $NPEO_2$ and NPE_1C in the $\mu g.l^{-1}$ range whereas most other studies show $mg.l^{-1}$ values. An all female population of *O. mykiss* (rainbow trout) was tested starting from the hatchling stage, in a flow through set-up with natural lake water. An exposure period of 22 days led to a significant decrease in body weight of all $NPEO_2$ treatments (1, 10 and 50 $\mu g.l^{-1}$) compared to the control fishes. For NPE_1C the two higher treatments were significantly lower than the control. However, the observed effects were not dose dependent, i.e. the reduction in body weight was more or less equal in those treatments with a significant reduction. The same was observed in a second experiment in which the fish were exposed for 35 days and maintained for another 130 days in clean water. For $NPEO_2$ a significant reduction in weight and length is evident at 60 and 85 days after the start of the experiment for the two lowest treatments (1 and 10 $\mu g.l^{-1}$) but not for the highest (30 $\mu g.l^{-1}$) treatment. Effects for NPE_1C in this study are less pronounced but for this compound, the 10 $\mu g.l^{-1}$ treatment differs from the control whereas the 1 and 30 $\mu g.l^{-1}$ treatment do not. The authors do not have a clear explanation for these observations. We have not incorporated this study in ERL derivation because the mechanism behind the observations is unclear and lack of a dose related response hampers establishment of an effect concentration. The study results are highlighted here because of their potential relevance: some observed effect concentrations are close to the MPC.

$MPCs_{water}$ for APEO are based on toxicity studies, the $MPCs_{sediment}$ however, are derived using EqP without any toxicity study to compare these values with. This is regrettable since the MPCsediment was exceeded at some locations. The soil compartment may receive APEO as wetting agents in formulations of pesticides or veterinary drugs, although the latter route is supposed to be of minor importance. Exposure of the soil compartment via this route is not quantified, and too few toxicity data on terrestrial organisms were available. However, this route of exposure also deserves attention.

13. Conclusions

In this report maximum permissible concentrations (MPCs) and negligible concentrations (NCs) for water, soil and sediment are derived for alkylphenols and MPCs, NCs and SRC_{ECO}s for water, soil and sediment are derived for alkylphenol ethoxylates.
For p-*tert*-butylphenol and 4-*tert*-octylphenol no MPCs were derived as European Risk Assessment Reports (EU-RARs) are under preparation. ERLs for these compounds will be reported when these RARs are finalised. For nonylphenol the MPC for the aquatic, the terrestrial and sediment compartment were based on the PNEC values reported in the EU-RAR [46] and were 0.33 $\mu g.l^{-1}$ (MPC_{water}), 104 $\mu g.kg^{-1}$ (MPC_{soil}) and 105 $\mu g.kg^{-1}$ ($MPC_{sediment}$), respectively.
Alkylphenol ethoxylates are produced and used as mixtures, and toxicity experiments are carried out using such mixtures. This hinders interpretation of the data and MPC derivation for individual compounds is not possible. Alkylphenol ethoxylates occur in the environment as 'mixtures' as well. However, these differ from the original mixtures since the distribution of compounds is altered due to degradation of the higher ethoxylated compounds. The shorter chained alkylphenol ethoxylates (*viz.* mono- and diethoxylates) are relatively persistent and are thus more abundant in environmental samples than in the technical mixtures. Surface water is the main exposure route for alkylphenol ethoxylates. Exposure through air is expected to be of minor importance. The use of alkylphenol ethoxylates as formulant in agricultural pesticides (and to a lesser extent in veterinary drugs) is a potential emission route to soil in the Netherlands. Neither a quantification of exposure for this route nor toxicity data are available, precluding conclusions on the risk to the soil compartment.
The short chained alkylphenol ethoxylates deserve most attention as they occur most and show a toxicity higher than that of the longer chained alkylphenol ethoxylates. The short chained alkylphenol ethoxylates also show the highest potential for endocrine disruption. Based on the chemical structure of the compounds it can be deduced that the water solubility of the alkylphenol ethoxylates increases and lipophilicity decreases with increasing number of ethoxy-groups. This is confirmed by the aquatic toxicity data: toxicity decreases with increasing number of ethoxy groups. The number of toxicity data for soil and sediment were limited. For MPCs calculated using equilibrium partitioning (soil and sediment) experimental K_{oc} values for nonylphenol ethoxylates were used. For octylphenol ethoxylates, no experimental K_{oc} values were available and these were derived from the nonylphenol ethoxylate K_{oc} values. All ERLs are summarised in the table on the following page.
The MPC values were derived for short chain (1-2 ethoxy units), medium chain (3-8 ethoxy units) and long chain (> 8 ethoxy units) alkylphenol ethoxylate for pragmatic reasons: use and occurrence of the compounds as mixtures, the amount of available toxicity data and unworkable high number of ERLs when these would be derived for individual monomers. Priority should be given to (i) the short chain (1-2 ethoxy) alkylphenol ethoxylates as they are expected to be most toxic and most abundant and (ii) to studies on endocrine effects. Future re-evaluation may result in another division of the three groups that have been distinguished here.

Table 46. ERLs for nonylphenol for $water_{total}$, $water_{dissolved}$ and groundwater.

	$WATER_{TOTAL}$		$WATER_{DISSOLVED}$		GROUNDWATER	
Compound	NC [µg.l^{-1}]	MPC [µg.l^{-1}]	NC [µg.l^{-1}]	MPC [µg.l^{-1}]	NC [µg.l^{-1}]	MPC [µg.l^{-1}]
Nonylphenol	0.0033	0.33	0.0033	0.33	0.0033	0.33

Table 47. ERLs for nonylphenol for soil and sediment.

	SOIL		SEDIMENT	
Compound	NC [µg.kg_{dw}^{-1}]	MPC [µg.kg_{dw}^{-1}]	NC [µg.kg_{dw}^{-1}]	MPC [µg.kg_{dw}^{-1}]
Nonylphenol	1.0	104	1.1	105

Table 48. ERLs for octylphenol ethoxylates and nonylphenol ethoxylates for $water_{total}$, $water_{dissolved}$ and groundwater.

	NC [µg.l^{-1}]	MPC [µg.l^{-1}]	NC [µg.l^{-1}]	MPC [µg.l^{-1}]	SRC_{ECO} [µg.l^{-1}]	NC [µg.l^{-1}]	MPC [$^{µg.l-1}$]	SRC_{ECO} [µg.l^{-1}]
Compound class	WATER TOTAL		WATER DISSOLVED			GROUNDWATER [1]		
$OPE_{1+2}C$	0.050	5.0	0.050	5.0	500	0.050	5.0	500
$OPEO_{1+2}$	0.073	7.3	0.071	7.1	710	0.071	7.1	710
$OPEO_{3-8}$	0.018	1.8	0.018	1.8	620	0.018	1.8	620
$OPEO_{>8}$	0.021	2.1	0.021	2.1	670	0.021	2.1	670
$NPE_{1+2}C$	0.010	1.0	0.010	1.0	260	0.010	1.0	260
$NPEO_{1+2}$	0.0012	0.12	0.0011	0.11	45	0.0011	0.11	45
$NPEO_{3-8}$	0.14	14	0.13	13	410	0.13	13	410
$NPEO_{>8}$	0.10	10	0.10	10	850	0.10	10	850

[1] ERLs for groundwater are set equal to $ERL_{water, dissolved}$; consequently, $NC_{groundwater}$, $MPC_{groundwater}$ and $SRCeco_{groundwater}$ are also based on 'dissolved' concentrations.

Table 49. ERLs for octylphenol ethoxylates and nonylphenol ethoxylates for soil and sediment.

	NC [mg.kg^{-1}]	MPC [mg.kg^{-1}]	SRC_{ECO} [mg.kg^{-1}]	NC [mg.kg^{-1}]	MPC [mg.kg^{-1}]	SRC_{ECO} [mg.kg^{-1}]
Compound class	SOIL			SEDIMENT		
$OPE_{1+2}C$	0.0040	0.40	40	0.0040	0.40	40
$OPEO_{1+2}$	0.036	3.6	360	0.036	3.6	360
$OPEO_{3-8}$	0.0045	0.45	150	0.0045	0.45	150
$OPEO_{>8}$	0.0023	0.23	72	0.0023	0.23	72
$NPE_{1+2}C$	0.0015	0.15	38	0.0015	0.15	38
$NPEO_{1+2}$	0.0015	0.15	61	0.0015	0.15	61
$NPEO_{3-8}$	0.045	4.5	270	0.087	8.7	270
$NPEO_{>8}$	0.029	2.9	250	0.029	2.9	250

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90. Bibliotheek RIVM
91-94. Bureau Rapportenbeheer
95-105. Reserve-exemplaren

Appendix 2. Data for APEC and APEO used for extrapolation

Contents

Table A2. 1 $OPE_{1+2}C$ selected data for water (data from Table A4. 1).

taxonomic group	NOEC [$mg.l^{-1}$]	taxonomic group	L(E)C50 [$mg.l^{-1}$]
		pisc	5

Table A2. 2 $OPEO_{1+2}$ selected data for water (data from Table A4. 2).

taxonomic group	NOEC [$mg.l^{-1}$]	taxonomic group	L(E)C50 [$mg.l^{-1}$]
		crus	7.1

Table A2. 3. $OPEO_{3-8}$ selected data for water (data from Table A4. 2).

taxonomic group	NOEC [$mg.l^{-1}$]	taxonomic group	L(E)C50 [$mg.l^{-1}$]
		crus	1.8
		ins	21[a]

a: geometric mean of 29 and 15 mg/l, parameter emergence for *Culex pipiens*.

Table A2. 4 $OPEO_{>8}$ selected data for water (data from Table A4. 2, Table A4. 3, Table A4. 4).

taxonomic group	NOEC [$mg.l^{-1}$]	taxonomic group	L(E)C50 [$mg.l^{-1}$]
bact (gluc-min)	125	cyan	7.4
prot	63	alg	0.21
alg	63	alg	8.8
alg	9.1	ins	18[a]
		pisc	39[b]
		pisc	8.9

a: geometric mean of 14, 18 and 25 mg/l, parameter emergence for *Culex pipiens*.

b: geometric mean of 12, 9.6 and 531 mg/l, parameter mortality for *Lepomis macrochirus*.

Table A2. 5 $NPE_{1+2}C$ selected data for water (data from Table A4. 5).

taxonomic group	NOEC [mg.l^{-1}]	taxonomic group	L(E)C50 [mg.l^{-1}]
		crus	0.99
		pisc	9.2[a]
		pisc	2

a: geometric mean of 9.6 and 8.9 mg/l, parameter mortality for *Oryzias latipes*.

Table A2. 6 $NPEO_{1+2}$ selected data for water (data from Table A4. 6, Table A4. 8).

taxonomic group	NOEC [mg.l^{-1}]	taxonomic group	L(E)C50 [mg.l^{-1}]
		crus	0.87[a]
		crus	0.15
		crus	0.11
		pisc	3

a: geometric mean of 1.04, 0.63 and 1.02 mg/l, parameters mortality and immobility for *Ceriodaphnia dubia*.

Table A2. 7 $NPEO_{3-8}$ selected data for water (data from Table A4. 6, Table A4. 7).

taxonomic group	NOEC [mg.l^{-1}]	taxonomic group	L(E)C50 [mg.l^{-1}]
bact	63	ins	6.7[c]
prot	17[a]	pisc	4.9[d]
alg	11[b]	pisc	1.3
		pisc	4.3
		amph[4]	4.4[e]
		amph[4]	3.8[f]
		amph[4]	8.8[g]
		amph[4]	2.8[h]

a: geometric mean of 5, 16, 31 and 31 mg/l, parameter growth for *Colpoda maupasi*.
b: geometric mean of 6, 10, 16 and 16 mg/l, parameter growth for *Scenedesmus quadricauda*.
c: geometric mean of 7, 6, 8 and 6 mg/l, parameter emergence for *Culex pipiens*.
d: geometric mean of 2.5, 3.6, 5.4 and 11.6 mg/l, parameter mortality for *Oryzias latipes*.
e: geometric mean of 5.1, 4 and 4.1 mg/l, parameter full narcosis for *Bufo marinus*.
f: lowest parameter (full narcosis) for *Crinia insignifera*.
g: lowest parameter (malformation) for *Litoria adelaidensis*.
h: lowest parameter (full narcosis) for *Litoria adelaidensis*.

[4] Note that data for mild narcosis to amphibian species were not incorporated in ERL derivation (Table A4. 6).

Table A2. 8 $NPEO_{>8}$ selected data for water (data from Table A4. 6, Table A4. 7, Table A4. 8).

taxonomic group	NOEC [$mg.l^{-1}$]	taxonomic group	L(E)C50 [$mg.l^{-1}$]
bact	1000[a]	bact	61
prot	130[b]	alg	12
alg	270[c]	alg	1.0
alg	8	moll	5.0
ins	17[d]	moll	18
		moll	12
		crust	14
		crust	1.5
		crust	10
		crust	22[e]
		crust	1.8[f]
		ins	500
		ins	19[g]
		pisc	3.9[h]
		pisc	7.3[i]
		pisc	7.2[j]
		pisc	25[k]
		pisc	4.4[l]
		pisc	3.0
		pisc	8.6
		pisc	1

a: geometric mean of 1000 and 1000 mg/l, parameter glucose mineralisation for *Pseudomonas fluorescens*.
b: geometric mean of 31, 250 and 250 mg/l, parameter growth for *Colpoda maupasi*.
c: geometric mean of 31, 125 and 5000 mg/l, parameter growth for *Scenedesmus quadricauda*.
d: most sensitive parameter (mortality) for *Aëdes aegypti*, geometric mean of 12 and 24 mg/l.
e: geometric mean of 10 and 50 mg/l, parameter mortality for *Leander adspersus*.
f: geometric mean of 2.28, 1.41, 1.23 and 2.57 mg/l, parameter mortality for *Mysidopsis bahia*.
g: geometric mean of 10, 19, 7, 19, 9, 120 and 28 mg/l, parameter emergence for *Culex pipiens*.
h: geometric mean of 6.0 and 2.5 mg/l, parameter mortality for *Gadus morrhua*.
i: geometric mean of 4.9, 7 and 11.2 mg/l, parameter mortality for *Idus idus*.
j: geometric mean of 7.6, 7.9 and 6.3 mg/l, parameter mortality for *Lepomis macrochirus*.
k: geometric mean of 11.2, 12, 14, 48 and 110 mg/l, parameter mortality for *Oryzias latipes*.
l: geometric mean of 6.6, 4.6 and 2.9 mg/l, parameter mortality for *Pimephales promelas*.

Table A2. 9 $NPEO_{3-8}$ selected data for terrestrial processes (data from Table A5. 1).

taxonomic group/ process	NOEC [$mg.kg^{-1}$]	taxonomic group	L(E)C50 [$mg.kg^{-1}$]
dehy	450		

Table A2. 10 $NPEO_{>8}$ selected data for terrestrial processes (data from Table A5. 1).

taxonomic group/ process	NOEC [$mg.kg^{-1}$]	taxonomic group	L(E)C50 [$mg.kg^{-1}$]
dehy	7800		

Appendix 3. K_{oc}; experimental data and extrapolation method

NPEO adsorption onto sediment

John *et al.* [61] have determined K_d values for adsorption of individual NPEO monomers onto a natural river sediment. The adsorption experiment was performed with two NPEO technical mixtures of which the monomers were analysed and quantified. The organic matter content of the sediment was reported to be 20.0%, determined as weight loss after combustion at 550°C. The organic carbon content is not given, it is therefore calculated to be 0.588*% o.m. = 11.76%. Sorption experiments were performed at 25°C, lasted 24 h (equilibration was reached after 2 h) and six concentrations were tested. Using the molar distribution of the NPEO mixtures tested and the reported aqueous concentrations employed, we established that all concentrations were well below the water solubility for NPEO monomers. Table A3. 1 shows reported K_d values [61], calculated K_{oc} values and predicted K_{oc} values. The latter values were obtained after fitting a 2nd order polynome through a plot of log K_{oc} versus #EO (the number of ethoxy units in a $NPEO_n$ monomer) data. This resulted in the following equation:

$$\log K_{oc} = 4.552 - 0.1974 \times (\#EO) + 0.01065 \times (\#EO)^2 \qquad \text{Equation 6}$$

Figure 11 shows this relationship, which has an r^2 of 0.911. A linear fit resulted in much poorer prediction of the experimental data: r^2=0.410. The reason for the non-linearity of the relationship is that adsorption of APEO is thought to be influenced by two processes, that have opposite effects on K_{oc}.

Table A3. 1. Experimental and estimated adsorption constants for NPEO monomers onto river sediment.

Compound	K_d [l.kg^{-1}]	s.e.[a]	log K_{oc}	estimated log K_{oc}[b]
$NPEO_1$	n.d.	n.d.	n.d.	4.37
$NPEO_2$	n.d.	n.d.	n.d.	4.20
$NPEO_3$	1460	140	4.09	4.06
$NPEO_4$	930	60	3.90	3.93
$NPEO_5$	750	110	3.80	3.83
$NPEO_6$	700	70	3.77	3.75
$NPEO_7$	590	60	3.70	3.69
$NPEO_8$	550	60	3.67	3.65
$NPEO_9$	540	60	3.66	3.64
$NPEO_{10}$	450	80	3.58	3.64
$NPEO_{11}$	550	110	3.67	3.67
$NPEO_{12}$	750	110	3.80	3.72
$NPEO_{13}$	640	180	3.74	3.79

n.d.=not determined; [a]s.e.=standard error of the linear regression of K_d; [b]calculated using Equation 6.

Table A3. 1 and Figure 11 also show the extrapolated K_{oc} values for $NPEO_1$ and $NPEO_2$. Also plotted in Figure 11 are the four field determined K_{oc} values for suspended matter/water

partitioning from Heemken *et al.* [55]. The field K_{oc} (suspended matter) are considerably higher than the K_{oc} (sediment) values based on extrapolation.

Estimation of K_{oc} for $OPEO_n$

Conversion of experimental K_{oc} data for $NPEO_n$ to $OPEO_n$ was performed in the following manner. A single data point on the regression line was selected: the estimated K_{oc} value for $NPEO_3$ (any other point would yield identical results). The structural difference between $NPEO_3$ and $OPEO_3$ is one CH_2 group. The difference in K_{oc} due to that contribution was calculated using the slope of the regression equation for the log K_{oc} vs log K_{ow} relationship for predominantly hydrophobic chemicals from Sabljić *et al*. [105], which is 0.81. In equation:

$$\log K_{oc\ C8} = \log K_{oc\ C9} - 0.81 \times (\log K_{ow\ C9} - \log K_{ow\ C8}) \qquad \text{Equation 7}$$

K_{ow} estimates for both compounds were calculated using the ClogP routine [31]. Next, equation 6 was translated along the y-axis over the distance $K_{oc\ NPEO3} - K_{oc\ OPEO3}$, resulting in:

$$\log K_{oc} = 4.124 - 0.1974 \times (\#EO) + 0.001065 \times (\#EO)^2 \qquad \text{Equation 8}$$

which was used for K_{oc} estimation of $OPEO_n$. Table A3. 2 shows the estimated log K_{oc} for $OPEO_n$.

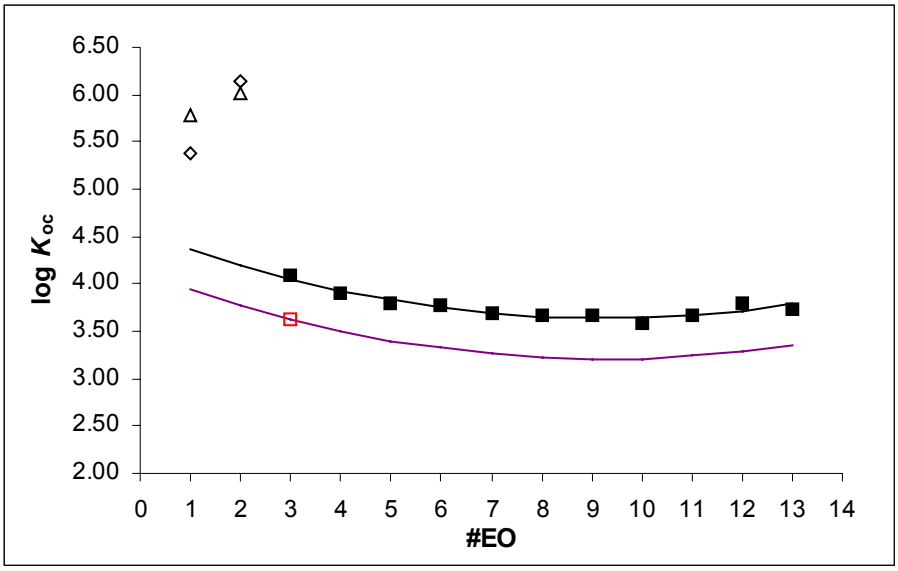

Figure 11. Experimental log K_{oc} [61] vs number of ethoxy units in $NPEO_n$ monomers (black squares). Also shown are the fitted regression equation through the experimental K_{oc} values (upper line); calculated K_{oc} for $OPEO_3$ (open square) and the extrapolated regression equation for $OPEO_n$ monomers (lower line). Field $K_{oc,\ susp}$ values (suspended matter/water) are also shown: diamond symbols for $NPEO_1$ and $NPEO_2$ and triangles for $OPEO_1$ and $OPEO_2$.

Table A3. 2 Experimental and estimated adsorption constants for OPEO monomers.

Compound	estimated log K_{oc}[1]
$OPEO_1$	3.94
$OPEO_2$	3.77
$OPEO_3$	3.63
$OPEO_4$	3.50
$OPEO_5$	3.40
$OPEO_6$	3.32
$OPEO_7$	3.26
$OPEO_8$	3.23
$OPEO_9$	3.21
$OPEO_{10}$	3.21
$OPEO_{11}$	3.24
$OPEO_{12}$	3.29
$OPEO_{13}$	3.36

[1]calculated using equation 8.

Selection of representative K_{oc} for APEO groups discerned in ERL derivation

For ERL derivation, three APEO groups are discerned (section 9.3). A representative K_{oc} value for each group should be selected to enable EqP calculations for ERL derivation. The experimental K_d's show that the difference between K_{oc} decreases with increasing number of EO groups. Table A3. 1 also shows the reported standard errors of the K_d values which allows for indicative investigation if two values are expected to be different. One assumption has to be made: K_d values are reported (i.e. linear sorption coefficients) and the confidence intervals of K_d are symmetrical, we assume the authors have plotted their adsorption data on linear axes (i.e. *not* log-log transformed). However, this detail was not reported. Comparing K_d for $NPEO_3$ and $NPEO_8$ (plus or minus two times the standard error of the linear regression) shows that these values are likely to be different. For $NPEO_9$ and $NPEO_{13}$, this is not the case. Figure 11 illustrates that K_{oc} levels off at a higher number of ethoxy units. It therefore seems appropriate to choose the K_{oc} of $NPEO_3$ as representative for the group $NPEO_{3\text{-}8}$, and the geometric mean of K_{oc} values for $NPEO_9$-$NPEO_{13}$ (*n=5*). For the group $NPEO_1$ + $NPEO_2$, no experimental data are available. We have chosen the K_{oc} for $NPEO_1$ for this group, since this is the higher value, which means a conservative approach with respect to protection of species. For the $OPEO_{1+2}$, $OPEO_{3\text{-}8}$ and $OPEO_{>8}$ groups, the same approach was followed. Table A3. 3 shows the resulting K_{oc} values and respective K_p values for use in equilibrium partitioning. K_p values are calculated according to INS guidance [120].

Table A3. 3. K_{oc} and K_p values selected for ERL derivation.

APEO group	log K_{oc}	K_p
$OPEO_{1+2}$	3.94	509
$OPEO_{3\text{-}8}$	3.63	249
$OPEO_{>8}$	3.26	108
$NPEO_{1+2}$	4.37	1364
$NPEO_{3\text{-}8}$	4.06	669
$NPEO_{>8}$	3.69	288

Appendix 4. Aquatic toxicity data

Legend

Species	organism used in the test, if available followed by age, size, weight or life stage
Analysed	Y = test substance analysed in test solution N = test substance not analysed in test solution or no data
Test type	S = static, R = static with renewal, F = flow through
Substance purity	percentage active ingredient
Test water	am = artificial medium, asw = artificial seawater, dist.w = distilled water, nfs = natural filtered seawater, nw = natural water, rtw = reconsituted tap water (+additional salts), river w = river water, sw = sea water, tw = tap water
Exposure time	h = hours, d = days, w = weeks, m = months, min. = minutes
Criterion	L(E)C50 = lowest short term test result showing 50% effect or mortality; NOEC = no observed effect concentration, ECx = effect concentration causing x% effect
Test endpoint	min. = mineralisation, cell no. = cell number
Value	test result; > and ≥ symbols = no effect observed at highest test concentration

In this appendix aquatic toxicity data for octylphenol ethoxylates, nonylphenol ethoxylates and their carboxylated derivatives are presented.

Contents

Table A4. 1 Acute toxicity of carboxylated octylphenol ethoxylates to freshwater aquatic organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Exposure time	Criterion	Test endpoint	Value [mg/l]	Notes	Reference
OPE_1C													
Pisces													
Pimephales promelas		Y	F					96 h	LC50	mortality	5	1	[115]

Notes

1. data from review.

Table A4. 2 Acute toxicity of octylphenol ethoxylates to freshwater aquatic organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Exposure time	Criterion	Test endpoint	Value [mg/l]	Notes	Reference
$OPEO_3$													
Insecta													
Culex pipiens	pupae, 24 hr	N	S	n.r.	dist. w	7.5-8.0	n.r.		LC50	emergence	29	1	[83]
Notes													
1. animals exposed until emergence; non-emergence was taken as mortality score; average number of ethoxy units was 3 (on a molar basis); 5 g/l alcohol as carrier was shown to be non-toxic.													
$OPEO_{4-5}$													
Pisces													
Lepomis macrochirus	1 g	Y	S		nw	7.1	35	96 h	LC50	mortality	>2.8 <3.2	1	[74]
Notes													
1. test substance is Triton X-45.													
$OPEO_8$													
Insecta													
Culex pipiens	pupae, 24 hr	N	S	n.r.	dist. w	7.5-8.0	n.r.		LC50	emergence	15	1	[83]
Notes													
1. animals exposed until emergence; non-emergence was taken as mortality score; average number of ethoxy units was 7.5 (on a molar basis); 5 g/l alcohol as carrier was shown to be non-toxic.													
$OPEO_{10}$													
Insecta													
Culex pipiens	pupae, 24 hr	N	S	n.r.	dist. w	7.5-8.0	n.r.		LC50	emergence	14	1	[83]
Pisces													
Lepomis macrochirus	1 g	Y	S		nw	7.1	35	96 h	LC50	mortality	12	3	[74]
Lepomis macrochirus	1 g	Y	F		nw	7.1	38	168 h	LC50	mortality	9.6	2, 3	[74]
Pimephales promelas		Y	F					96 h	LC50	mortality	8.9	4	[115]
Notes													
1. incipient LC50.													
2. animals exposed until emergence; non-emergence was taken as mortality score; average number of ethoxy units was 3 (on a molar basis); 5 g/l alcohol as carrier was shown to be non-toxic.													

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Exposure time	Criterion	Test endpoint	Value [mg/l]	Notes	Reference

3. test substance is Triton X-100.
4. data from review.

$OPEO_{11}$

Cyanobacteria													
Microcystis sp.								96 h	EC50	growth	7.4	1	[71]
Algae													
Selenastrum sp.								96 h	EC50	growth	0.21	1	[71]

Notes

1. test substance = octylphenolphenoxy polyethoxyethanol; test performed acc. to ASTM guideline (1984, draft 7), no further details reported.

$OPEO_{13}$

Insecta													
Culex pipiens	pupae, 24 hr	N	S	n.r.	dist. w	7.5-8.0	n.r.		LC50	emergence	18	1	[83]
Notes													

1. animals exposed until emergence; non-emergence was taken as mortality score; average number of ethoxy units was 12.5 (on a molar basis); 5 g/l alcohol as carrier was shown to be non-toxic.

$OPEO_{16}$

Insecta													
Culex pipiens	pupae, 24 hr	N	S	n.r.	dist. w	7.5-8.0	n.r.		LC50	emergence	25	1	[83]

Notes

1. animals exposed until emergence; non-emergence was taken as mortality score; average number of ethoxy units was 16 (on a molar basis) ; 5 g/l alcohol as carrier was shown to be non-toxic.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Exposure time	Criterion	Test endpoint	Value [mg/l]	Notes	Reference
$OPEO_{30}$													
Insecta													
Culex pipiens	pupae, 24 hr	N	S	n.r.	dist. w	7.5-8.0	n.r.		LC50	emergence	>250	1	[83]
Pisces													
Lepomis macrochirus	1 g	Y	S		nw	7.1	35	96 h	LC50	mortality	531	2	[74]

Notes

1. animals exposed until emergence; non-emergence was taken as mortality score; average number of ethoxy units was 30 (on a molar basis); 5 g/l alcohol as carrier was shown to be non-toxic.
2. test substance is Triton X-305.

Table A4. 3 Chronic toxicity of octylphenol ethoxylates to freshwater aquatic organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Exposure time	Criterion	Test endpoint	Value [mg/l]	Notes	Reference
$OPEO_9$													
Bacteria													
Pseudomonas fluorescens		N	S	n.r.	river water	7.5-7.8	204	16-24 h	NOEC	glucose mineralisation	125	1	[58]
Protozoa													
Colpoda maupasi		N	S	n.r.	river water	7.5-7.8	204	20 h	NOEC	growth	63	1	[58]
Algae													
Scenedesmus quadricauda		N	S	n.r.	river water	7.5-7.8	204	96 h	NOEC	growth	63	1	[58]

Notes

1. average number of ethoxy groups is 9, with 95% between 5-15.

$OPEO_{10}$													
Algae													
Chlorella fusca		N	S		am			6 d	NOEC	growth rate	≥ 523	1, 4	[140]

Notes

1. no effects observed up till the highest concentration.

$OPEO_{11}$													
Algae													
Field population	Lake water plankton	Y	Enclosure		Lake water			10 d	EC10	species no.	9.1	1	[71]

Notes

1. EC10 determined by fitting a logistic dose response model through data from author.

Table A4. 4 Acute toxicity of octylphenol ethoxylates to marine aquatic organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Salinity [‰]	Exposure time	Criterion	Test endpoint	Value [mg/l]	Notes	Reference
$OPEO_{1.5}$														
Crustacea														
Mysidopsis bahia	3-8 d old	Y	R	99%	natural	7.4-8.1	90-130	24-29	48 h	LC50	mortality	7.07	1	[52]

Notes

1. highly branched octylphenol ethoxylate; molar ratio of 1.5 ethoxylate units.

$OPEO_5$

Crustacea														
Mysidopsis bahia	3-8 d old	Y	R	99%	natural	7.4-8.1	90-130	24-29	48 h	LC50	mortality	1.83	1	[52]

Notes

1. highly branched octylphenol ethoxylate; molar ratio of 5 ethoxylate units.

$OPEO_{10}$

Algae														
Nitzschia holsatica		N	S		medium	7			5 d	EC50	growth	8.8	1	[94]
Nitzschia holsatica		N	S		medium	7			5 d	EC50	growth	14.4	2	[94]

Notes

1. tested at 15°C; a.i. = Triton X-100; only graphical determination of EC50 possible; this study is selected because 15°C is a more realistic sea water temperature for the Gulf of Finland from which the species was isolated.
2. tested at 25°C; a.i. = Triton X-100; only graphical determination of EC50 possible.

Table A4. 5 Acute toxicity of carboxylated nonylphenol ethoxylates to freshwater aquatic organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Exposure time	Criterion	Test endpoint	Value [mg/l]	Notes	Reference
NPE_1C													
Pisces													
Oryzias latipes	2 cm, 0.2 g	N	S		tw	7.2	50	48 h	LC50	mortality	8.9	1	[141]
Pimephales promelas		Y	F					96 h	LC50	mortality	2	2	[115]

Notes

1. tested as the sodium salt.
2. data from review.

NPE_2C													
Crustacea													
Daphnia magna	24 h old	N	S	n.r.	ISO-hard water			48 h	LC50	mortality	0.99	1	[77]
Pisces													
Oryzias latipes	2 cm, 0.2 g	N	S		tw	7.2	50	48 h	LC50	mortality	9.6	2	[141]

Notes

1. test was performed in "ISO hard water"; no further details reported.
2. tested as the sodium salt.

Table A4. 6 Acute toxicity of nonylphenol ethoxylates to freshwater aquatic organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Exposure time	Criterion	Test endpoint	Value [$mg.l^{-1}$]	Notes	Reference
$NPEO_1$													
Pisces													
Oryzias latipes	2 cm, 0.2 g	N	S		tw	7.2	50	48 h	LC50	mortality	3	1	[141]
Notes													
1. test result has the obscure footnote: "As dispersant, Tween 80 was used 2 times as much as water"; average number of ethoxy units was 1.													
$NPEO_{1,2}$													
Crustacea													
Ceriodaphnia dubia		N	S	n.r.	dist w	~8	n.r.	48 h	EC50	immobility	1.04	1	[11]
Notes													
1. NPEO1 + NPEO2; no carrier solvent; test water was 9 Millipore:1 mineral water													
$NPEO_2$													
Crustacea													
Ceriodaphnia dubia		Y	R					96 h	EC50	immobility	0.626	1	[115]
Ceriodaphnia dubia		Y	R					96 h	LC50	mortality	1.016	1	[115]
Ceriodaphnia dubia		Y						7 d	NOEC	reproduction	0.285	1	[115]
Ceriodaphnia dubia		Y						7 d	NOEC	mortality	0.285	1	[115]
Daphnia magna	24 h old	N	S	n.r.	ISO-hard water			48 h	LC50	mortality	0.148	2	[77]
Notes													
1. data from review.													
2. test was performed in "ISO hard water"; no further details reported.													
$NPEO_3$													
Pisces													
Oryzias latipes	2 cm, 0.2 g	N	S		tw	7.2	50	48 h	LC50	mortality	2.5	1	[141]
Notes													
1. test result has the obscure footnote: "As dispersant, Tween 80 was used 2 times as much as water"; average number of ethoxy units was 3.3.													

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Exposure time	Criterion	Test endpoint	Value [$mg.l^{-1}$]	Notes	Reference
$NPEO_4$													
Insecta													
Culex pipiens	pupae, 24 hr		S	n.r.	dist w	7.5-8.0	n.r.		LC50	emergence	7	1	[83]
Culex pipiens	pupae, 24 hr		S	n.r.	dist w	7.5-8.0	n.r.		LC50	emergence	6	1	[83]
Culex pipiens	pupae, 24 hr		S	n.r.	dist w	7.5-8.0	n.r.		LC50	emergence	8	1	[83]
Pisces													
Lepomis macrochirus	1 g	Y	S		nw	7.1	35	96 h	LC50	mortality	1.3		[74]

Notes

1. animals (pupae) exposed until emergence (partial life cycle exposure, therefore: acute test); non-emergence was taken as mortality score; average number of ethoxy units was 4 (on a molar basis); 5 g/l alcohol as carrier was shown to be non-toxic.

$NPEO_5$													
Pisces													
Lepomis macrochirus	1 g	Y	S		nw	7.1	35	96 h	LC50	mortality	> 2.4 < 2.8		[74]
Oryzias latipes	2 cm, 0.2 g	N	S		tw	7.2	50	48 h	LC50	mortality	3.6	1	[141]

Notes

1. average number of ethoxy units was 5.

$NPEO_6$													
Insecta													
Culex pipiens	pupae, 24 hr		S	n.r.	dist w	7.5-8.0	n.r.		LC50	emergence	6	1	[83]
Pisces													
Oryzias latipes	2 cm, 0.2 g	N	S		tw	7.2	50	48 h	LC50	mortality	5.4	2	[141]

Notes

1. animals (pupae) exposed until emergence (partial life cycle exposure, therefore: acute test); non-emergence was taken as mortality score; average number of ethoxy units was 6 (on a molar basis); 5 g/l alcohol as carrier was shown to be non-toxic
2. average number of ethoxy units was 6.4.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Exposure time	Criterion	Test endpoint	Value [$mg.l^{-1}$]	Notes	Reference
$NPEO_8$													
Amphibia													
Bufo marinus		N	R	100%	dtw	7.0-7.6		96 h	EC50	mild narcosis	2.8	5	[79]
Bufo marinus		N	R	100%	dtw	7.0-7.6		96 h	EC50	full narcosis	5.1	5	[79]
Bufo marinus	feeding stage	N	R	100%	dtw	7.0-7.6		96 h	EC50	mild narcosis	3.5	5	[79]
Bufo marinus	feeding stage	N	R	100%	dtw	7.0-7.6		96 h	EC50	full narcosis	4	5	[79]
Bufo marinus	hind-limb stage	N	R	100%	dtw	7.0-7.6		48 h	EC50	mild narcosis	4.1	5	[79]
Bufo marinus	hind-limb stage	N	R	100%	dtw	7.0-7.6		48 h	EC50	full narcosis	4.1	5	[79]
Crinia insignifera	14-29 mm snout-vent	N	R	100%	dtw	7.0-7.6		5.6 d	LC50	mortality	6.4		[78]
Crinia insignifera	14-29 mm snout-vent	N	R	100%	dtw	7.0-7.6		5.6 d	EC50	malformation	4.5	2	[78]
Crinia insignifera	14-29 mm snout-vent	N	R	100%	dtw	7.0-7.6		5.6 d	NOEC	growth inhibition	4		[78]
Crinia insignifera	14-29 mm snout-vent	N	R	100%	dtw	7.0-7.6		48 h	EC50	mild narcosis	2.7	5	[79]
Crinia insignifera	14-29 mm snout-vent	N	R	100%	dtw	7.0-7.6		48 h	EC50	full narcosis	3.8	5	[79]
Litoria adelaidensis	34-47 mm sv	N	R	100%	dtw	7.0-7.6		5.8 d	LC50	mortality	9.2		[78]
Litoria adelaidensis	34-47 mm sv	N	R	100%	dtw	7.0-7.6		5.8 d	EC50	malformation	8.8	1	[78]
Litoria adelaidensis	34-47 mm sv	N	R	100%	dtw	7.0-7.6		5.8 d	LOEC	growth inhibition	2-6		[78]
Xenopus laevis		N	R	100%	dtw	7.0-7.6		96 h	LC50	mortality	3.9-5.4		[78]
Xenopus laevis		N	R	100%	dtw	7.0-7.6		96 h	EC50	malformation	2.8-4.6	1	[78]
Xenopus laevis		N	R	100%	dtw	7.0-7.6		96 h	LOEC	growth inhibition	1-3		[78]
Xenopus laevis		N	R	100%	dtw	7.0-7.6		48 h	EC50	mild narcosis	1.1	5	[79]
Xenopus laevis		N	R	100%	dtw	7.0-7.6		48 h	EC50	full narcosis	2.8	5	[79]
Pisces													
Oncorhynchus mykiss	12-16 cm	N	F	100%	tw	7.3-7.4	290-310	96 h	LC50	mortality	4.7	4	[24]
Oncorhynchus mykiss	12-16 cm	N	F	100%	tw	7.3-7.4	290-310	14 d	LC50	mortality	4.25	4	[24]
Oryzias latipes	2 cm, 0.2 g	N	S		tw	7.2	50	48 h	LC50	mortality	11.6	3	[141]

Notes

1. malformations included cardiac edema, microphthalmia an improper gut coiling.
2. malformations included generalised edema, failure of the tail to straighten and severe stunting.
3. average number of ethoxy units was 8.4.
4. 96 h acute value is from the same test; the 14 day result is selected for risk limit derivation.
5. full narcosis is selected for ERL derivation when both mild and full narcosis results were available.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Exposure time	Criterion	Test endpoint	Value [$mg.l^{-1}$]	Notes	Reference
$NPEO_9$													
Bacteria													
Vibrio fisheri	saltwater	N	S					5 min	EC50	luminescence	60.6		[38]
Algae													
Pseudokirchneriella subcapitata		Y	S					96 h	EC50	growth	12	7	[38]
Crustacea													
Daphnia magna	< 24 h	Y	R					48 h	EC50	immobility	14		[38]
Daphnia magna	< 24 h	Y	R					7 d	NOEC	mortality	10		[38]
Daphnia magna	< 24 h	Y	R					7 d	NOEC	growth	10		[38]
Insecta													
Culex pipiens	pupae, 24 hr		S	n.r.	dist w	7.5-8.0	n.r.		LC50	emergence	10	1	[83]
Pisces													
Lepomis macrochirus	1 g	Y	S		nw	7.1	35	96 h	LC50	mortality	7.6	4	[74]
Lepomis macrochirus	1 g	Y	S		nw	7.1	35	96 h	LC50	mortality	7.9	5	[74]
Lepomis macrochirus	1 g	Y	F		nw	7.1	38	8 d	LC50	mortality	6.3	2	[74]
Oryzias latipes	2 cm, 0.2 g	N	S		tw	7.2	50	48 h	LC50	mortality	11.2	3	[141]
Oryzias latipes	2 cm, 0.2 g	N	S		river w	7.0	3400	48 h	LC50	mortality	12	3	[141]
Oryzias latipes	2 cm, 0.2 g	N	S		model river w	7.0	25	48 h	LC50	mortality	14	3	[141]
Pimephales promelas		Y	F					96 h	LC50	mortality	6.6	6	[115]
Pimephales promelas	7-27 d	Y	S					96 h	LC50	mortality	4.6		[38]
Pimephales promelas	7-27 d	Y	S					7 d	LC50	mortality	2.9		[38]
Pimephales promelas	7-27 d	Y	S					7 d	NOEC	mortality	1.8		[38]
Pimephales promelas	7-27 d	Y	S					7 d	NOEC	growth	1		[38]

Notes

1. animals (pupae) exposed until emergence (partial life cycle exposure, therefore: acute test); non-emergence was taken as mortality score; average number of ethoxy units was 9 (on a molar Basis); 5 g/l alcohol as carrier was shown to be non-toxic.
2. incipient LC50; test substance Igepal CO-630.
3. average number of ethoxy units was 8.9.
4. test substance Surfonic N-95.
5. test substance Igepal CO-630.
6. data from review.
7. formerly known as Selenastrum capricornutum.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Exposure time	Criterion	Test endpoint	Value [$mg.l^{-1}$]	Notes	Reference
$NPEO_{9,10}$													
Pisces													
Idus idus	5.0-7.0 cm	N	R/F	99.9%			150	48 h	LC50	mortality	4.9	2	[100]
Idus idus	5.0-7.0 cm	N	S	99.9%			268	96 h	LC50	mortality	7		[100]
Idus idus	5.0-7.0 cm	N	S	99.9%			268	96 h	LC50	mortality	11.2		[100]
Rasbora heteromorpha	1.3-3.0 cm	N	R/F	99.9%			20	96 h	LC50	mortality	8.6	1	[100]
Salmo trutta	2.8/5.8 cm	N	R/F	99.9%			26-30	96 h	LC50	mortality	1	1	[100]

Notes

1. test was either a continuous flow or renewal, but not reported as such.
2. no 96 h value available; test was either a continuous flow or renewal, but not reported as such.

$NPEO_{10}$

Insecta													
Culex pipiens	pupae, 24 hr		S	n.r.	dist w	7.5-8.0	n.r.		LC50	emergence	19	1	[83]
Culex pipiens	pupae, 24 hr		S	n.r.	dist w	7.5-8.0	n.r.		LC50	emergence	7	1	[83]
Culex pipiens	pupae, 24 hr		S	n.r.	dist w	7.5-8.0	n.r.		LC50	emergence	19	2	[83]

Notes

1. animals (pupae) exposed until emergence (partial life cycle exposure, therefore: acute test); non-emergence was taken as mortality score; average number of ethoxy units was 9.5 (on a molar basis); 5 g/l alcohol as carrier was shown to be non-toxic.
2. animals (pupae) exposed until emergence (partial life cycle exposure, therefore: acute test); non-emergence was taken as mortality score; average number of ethoxy units was 10 (on a molar basis); 5 g/l alcohol as carrier was shown to be non-toxic

$NPEO_{11}$

Insecta													
Aëdes aegypti	2^{nd} & 3^{rd} stage larvae	N		100%				24 h	LC50	mortality	500	1	[125]

Notes

1. little information on test set-up; branched alkyl chain.

$NPEO_{12}$

Pisces													
Oryzias latipes	2 cm, 0.2 g	N	S		tw	7.2	50	48 h	LC50	mortality	48	1	[141]

Notes

1. average number of ethoxy units was 13.1.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Exposure time	Criterion	Test endpoint	Value [$mg.l^{-1}$]	Notes	Reference
$NPEO_{15}$													
Insecta													
Culex pipiens	pupae, 24 hr		S	n.r.	dist w	7.5-8.0	n.r.		LC50	emergence	9	1	[83]

Notes

1. animals (pupae) exposed until emergence (partial life cycle exposure, therefore: acute test); non-emergence was taken as mortality score; average number of ethoxy units was 15 (on a molar basis); 5 g/l alcohol as carrier was shown to be non-toxic.

$NPEO_{17}$

Pisces													
Oryzias latipes	2 cm, 0.2 g	N	S		tw	7.2	50	48 h	LC50	mortality	110	1	[141]

Notes

1. average number of ethoxy units was 16.6.

$NPEO_{20}$

Insecta													
Culex pipiens	pupae, 24 hr		S	n.r.	dist w	7.5-8.0	n.r.		LC50	emergence	>200	1	[83]
Culex pipiens	pupae, 24 hr		S	n.r.	dist w	7.5-8.0	n.r.		LC50	emergence	120	1	[83]
Culex pipiens	pupae, 24 hr		S	n.r.	dist w	7.5-8.0	n.r.		LC50	emergence	28	1	[83]

Notes

1. animals (pupae) exposed until emergence (partial life cycle exposure, therefore: acute test); non-emergence was taken as mortality score; average number of ethoxy units was 20 (on a molar basis); 5 g/l alcohol as carrier was shown to be non-toxic.

$NPEO_{30}$

Insecta													
Culex pipiens	pupae, 24 hr		S	n.r.	dist w	7.5-8.0	n.r.		LC50	emergence	>400	1	[83]
Pisces													
Lepomis macrochirus	1 g	Y	S		nw	7.1	35	96 h	LC50	mortality	>1000		[74]

Notes

1. animals (pupae) exposed until emergence (partial life cycle exposure, therefore: acute test); non-emergence was taken as mortality score; average number of ethoxy units was 30 (on a molar basis); 5 g/l alcohol as carrier was shown to be non-toxic

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Exposure time	Criterion	Test endpoint	Value [$mg.l^{-1}$]	Notes	Reference
$NPEO_{50}$													
Insecta													
Culex pipiens	pupae, 24 hr		S	n.r.	dist w	7.5-8.0	n.r.		LC50	emergence	>400	1	[83]

Notes

1. animals (pupae) exposed until emergence (partial life cycle exposure, therefore: acute test); non-emergence was taken as mortality score; average number of ethoxy units was 50 (on a molar basis); 5 g/l alcohol as carrier was shown to be non-toxic.

Table A4. 7 Chronic toxicity of nonylphenol ethoxylates to freshwater aquatic organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Exposure time	Criterion	Test endpoint	Value [$mg.l^{-1}$]	Notes	Reference
$NPEO_4$													
Protozoa													
Colpoda maupasi		N	S	n.r.	river w	7.5-7.8	204	20 h	NOEC	growth	5		[58]
Algae													
Scenedesmus quadricauda		N	S	n.r.	river w	7.5-7.8	204	96 h	NOEC	growth	6		[58]
$NPEO_6$													
Protozoa													
Colpoda maupasi		N	S	n.r.	river w	7.5-7.8	204	20 h	NOEC	growth	16		[58]
Algae													
Scenedesmus quadricauda		N	S	n.r.	river w	7.5-7.8	204	96 h	NOEC	growth	10		[58]
$NPEO_7$													
Bacteria													
Pseudomonas fluorescens		N	S	n.r.	river w	7.5-7.8	204	16-24 h	NOEC	glucose min.	63		[58]
Protozoa													
Colpoda maupasi		N	S	n.r.	river w	7.5-7.8	204	20 h	NOEC	growth	31		[58]
Colpoda maupasi		N	S	n.r.	river w	7.5-7.8	204	20 h	NOEC	growth	31		[58]
Algae													
Scenedesmus quadricauda		N	S	n.r.	river w	7.5-7.8	204	96 h	NOEC	growth	16		[58]
Scenedesmus quadricauda		N	S	n.r.	river w	7.5-7.8	204	96 h	NOEC	growth	16		[58]

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Exposure time	Criterion	Test endpoint	Value [$mg.l^{-1}$]	Notes	Reference
$NPEO_9$													
Algae													
Pseudokirchneriella subcapitata		Y	S					96 h	NOEC	growth	8		[38]
Notes													
1. formerly known as Selenastrum capricornutum.													
$NPEO_{10}$													
Protozoa													
Colpoda maupasi		N	S	n.r.	river w	7.5-7.8	204	20 h	NOEC	growth	31		[58]
Algae													
Scenedesmus quadricauda		N	S	n.r.	river w	7.5-7.8	204	96 h	NOEC	growth	31		[58]
$NPEO_{11}$													
Insecta													
Aëdes aegypti	eggs	N		100%				10 d	EC10	hatching	117	1,2	[125]
Aëdes aegypti	2^{nd} & 3^{rd} stage larvae	N		100%				10 d	LC10	mortality	24	3	[125]
Aëdes aegypti	4^{th} stage larvae	N		100%				11 d	LC10	mortality	12	4	[125]
Notes													
1. little information on test set-up; branched alkyl chain.													
2. EC10 determined using nonlinear regression with logistic dose-response model using data from author; little information on test set-up; branched alkyl chain.													
3. LC10 calculated by dividing the LC50 reported by the author by the EC50/EC10 ratio of logistic dose response curve as fitted through egg hatching data (see footnote 2).													
4. LC10 calculated by dividing the LC50 reported by the author by the EC50/EC10 ratio of logistic dose response curve as fitted through egg hatching data (see footnote 2); LC50 corresponds to the number of dead pupae, test started with 4^{th} instar larvae; little information on test set-up; branched alkyl chain.													
$NPEO_{20}$													
Bacteria													
Pseudomonas fluorescens		N	S	n.r.	river w	7.5-7.8	204	16-24 h	NOEC	glucose min.	1000		[58]
Protozoa													
Colpoda maupasi		N	S	n.r.	river w	7.5-7.8	204	20 h	NOEC	growth	250		[58]
Algae													

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Exposure time	Criterion	Test endpoint	Value [$mg.l^{-1}$]	Notes	Reference
Scenedesmus quadricauda		N	S	n.r.	river w	7.5-7.8	204	96 h	NOEC	growth	125		[58]

$NPEO_{30}$

Bacteria													
Pseudomonas fluorescens		N	S	n.r.	river w	7.5-7.8	204	16-24 h	NOEC	glucose min.	1000		[58]
Protozoa													
Colpoda maupasi		N	S	n.r.	river w	7.5-7.8	204	20 h	NOEC	growth	250		[58]
Algae													
Scenedesmus quadricauda		N	S	n.r.	river w	7.5-7.8	204	96 h	NOEC	growth	5000		[58]

Table A4. 8 Acute toxicity of nonylphenol ethoxylates to marine aquatic organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Salinity [‰]	Exposure time	Criterion	Test endpoint	Value [mg/l]	Notes	Reference
$NPEO_{1.5}$														
Crustacea														
Mysidopsis bahia	3-8 d old	Y	R	99%	nw	7.4-8.1	90-130	24-29	48 h	LC50	mortality	0.11	1	[52]

Notes

1. tripropylene (highly branched) nonylphenol ethoxylate; molar ratio of 1.5 ethoxylate units.

$NPEO_9$

Crustacea														
Mysidopsis bahia	3-8 d old	Y	R	99%	nw	7.4-8.1	90-130	24-29	48 h	LC50	mortality	0.9-2	1	[52]
Mysidopsis bahia	9-12 d old	Y	R	99%	nw	7.4-8.1	90-130	24-29	48 h	LC50	mortality	2.28	1	[52]
Mysidopsis bahia	3-8 d old	Y	R	99%	nw	7.4-8.1	90-130	24-29	48 h	LC50	mortality	1.41	1	[52]
Mysidopsis bahia			R						48 h	LC50	mortality	1.23	2	[97]

Notes

1. tripropylene (highly branched) nonylphenol ethoxylate; molar ratio of 9 ethoxylate units.
2. no details on test reported.

$NPEO_{10}$

Algae														
Chaetoceros gracilis		N	S		am				72 h	EC50	growth inhibition	1		[89]
Crustacea														
Balanus balanoides	stage II nauplius larvae		R		sw			32-34	96 h; 6-8°C	LC50	mortality	1.5	1	[118]
Balanus balanoides	adult		R		sw			32-34	96 h; 6-8°C	LC50	mortality	<25	1	[118]
Balanus balanoides			R		sw			32-34	96 h; 15-17°C	LC50	mortality	<25	1	[118]
Carcinus maenas			R		sw			32-34	96 h; 6-8°C	LC50	mortality	>100	1	[118]
Eupagurus bernhardus			R		sw			32-34	96 h; 6-8°C	LC50	mortality	>100	1	[118]
Hyas araneus	stage I zoea larvae		R		sw			32-34	96 h; 6-8°C	LC50	mortality	10	1	[118]
Hyas araneus	adult		R		sw			32-34	96 h; 6-8°C	LC50	mortality	>100	1	[118]
Leander adspersus	intermoult phase		R		sw			32-34	96 h; 15-17°C	LC50	mortality	50	1	[118]
Leander adspersus	postmoult phase		R		sw			32-34	96 h; 15-17°C	LC50	mortality	10	1	[118]
Leander adspersus			R		sw			32-34	96 h; 6-8°C	LC50	mortality	>100	1	[118]
Leander squilla			R		sw			32-34	96 h; 6-8°C	LC50	mortality	>100	1	[118]

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Salinity [‰]	Exposure time	Criterion	Test endpoint	Value [mg/l]	Notes	Reference
Mollusca														
Cardium edule			F		sw			32-34	96 h; 6-8°C	LC50	mortality	5	1	[118]
Cardium edule	juvenile		F		sw			32-34	96 h; 15-17°C	LC50	mortality	<<10	1	[118]
Mya arenaria			F		sw			32-34	96 h; 6-8°C	LC50	mortality	18	1	[118]
Mya arenaria			F		sw			32-34	96 h; 15-17°C	LC50	mortality	<10	1	[118]
Mytilus edulis			F		sw			32-34	96 h; 6-8°C	LC50	mortality	12	1	[118]
Mytilus edulis			F		sw			32-34	96 h; 15-17°C	LC50	mortality	<10	1	[118]
Pecten maximus			F		sw			32-34	96 h; 15-17°C	LC50	mortality	<<5	1	[118]
Pecten opercularis			F		sw			32-34	96 h; 15-17°C	LC50	mortality	<<10	1	[118]
Pisces														
Gadus morrhua			F		sw			32-34	96 h; 6-8°C	LC50	mortality	6.0	1	[118]
Gadus morrhua			F		sw			32-34	96 h; 15-17°C	LC50	mortality	2.5	1	[118]
Pleuronectes flesus			F		sw			32-34	96 h; 15-17°C	LC50	mortality	3.0	1	[118]

Notes

1. branched nonyl chain.

$NPEO_{15}$

Crustacea														
Mysidopsis bahia	3-8 d old	Y	R	99%	nw	7.4-8.1	90-130	24-29	48 h	LC50	mortality	2.57	1	[52]
Notes														

1. tripropylene (highly branched) nonylphenol ethoxylate; molar ratio of 15 ethoxylate units.

$NPEO_{40}$

Crustacea														
Mysidopsis bahia	3-8 d old	Y	R	99%	nw	7.4-8.1	90-130	24-29	48 h	LC50	mortality	>40	1	[52]
Mysidopsis bahia	3-8 d old	Y	R	99%	nw	7.4-8.1	90-130	24-29	48 h	LC50	mortality	>100	1	[52]
Mysidopsis bahia	9-12 d old	Y	R	99%	nw	7.4-8.1	90-130	24-29	48 h	LC50	mortality	>1000	1	[52]

Notes

1. tripropylene (highly branched) nonylphenol ethoxylate; molar ratio of 40 ethoxylate units.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$]	Salinity [‰]	Exposure time	Criterion	Test endpoint	Value [mg/l]	Notes	Reference
$NPEO_{50}$														
Crustacea														
Mysidopsis bahia	3-8 d old	Y	R	99%	nw	7.4-8.1	90-130	24-29	48 h	LC50	mortality	>4110	1	[52]

Notes

1. tripropylene (highly branched) nonylphenol ethoxylate; molar ratio of 50 ethoxylate units.

Table A4. 9 Acute toxicity of alkylphenol ethoxylates to aquatic organisms, deviating tests.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$] or Salinity [‰]	Exposure time	Criterion	Test endpoint	Value [$mg.l^{-1}$]	Notes	Reference
APEO unspecified													
crustacea													
Hyalella azteca	0-2 d	N	S		nw	7.4-8.1	40	96 h	LC50	mortality	0.55	1	[29]
Hyalella azteca	2-4 d	N	S		nw	7.4-8.1	40	96 h	LC50	mortality	0.4	1	[29]
Hyalella azteca	4-6 d	N	S		nw	7.4-8.1	40	96 h	LC50	mortality	0.9	1	[29]
Hyalella azteca	6-8 d	N	S		nw	7.4-8.1	40	96 h	LC50	mortality	0.75	1	[29]
Hyalella azteca	10-12 d	N	S		nw	7.4-8.1	40	96 h	LC50	mortality	0.95	1	[29]
Hyalella azteca	16-18 d	N	S		nw	7.4-8.1	40	96 h	LC50	mortality	0.9	1	[29]
Hyalella azteca	20-22 d	N	S		nw	7.4-8.1	40	96 h	LC50	mortality	1.3	1	[29]
Hyalella azteca	24-26 d	N	S		nw	7.4-8.1	40	96 h	LC50	mortality	1.55	1	[29]

Notes

1. the number of ethoxylate units of the active ingredient is not given; all LC50 values determined graphically.

$OPEO_1$

Insecta													
Culex pipiens	pupae, 24 hr	N	S	n.r.	dist. w	7.5-8.0	n.r.		LC_{50}	emergence	85	1	[83]

Notes

1. test results >3x water solubility; animals exposed until emergence; non-emergence was taken as mortality score; average number of ethoxy units was 1 (on a molar basis); 5 g/l alcohol as carrier was shown to be non-toxic.

$OPEO_{10}$

Algae													
Poterioochromonas malhamensis		N	S					72 h	LC100	Cell no.	124.3	1	[101]
Selenastrum capricornutum			S	technical				21 d	LOEC	Cell no.	>100	2	[95]
Crustacea													
Daphnia magna	< 24 h	N	S	n.r.	river w	7.5-7.8	204	48 h	NOEC	mortality	31	3	[58]

Notes

1. test substance = Triton X-100, little information on test set up, only LC100 available.
2. a steady increase of growth observed with increasing concentration, however results were reported not to be significant; a.i. = Triton X-100; cells cultured for 21 d at 25°C, cell counts performed only at day 21.
3. average number of ethoxy groups is 9, with 95% between 5-15.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$] or Salinity [‰]	Exposure time	Criterion	Test endpoint	Value [$mg.l^{-1}$]	Notes	Reference
$OPEO_{40}$													
Algae													
Poterioochromonas malhamensis		N	S					72 h	LC100	Cell no.	17784	1	[101]

Notes

1. test substance = Triton X-405, little information on test set up, only LC100 available.

$NPEO$ unspecified

Crustacea													
Daphnia magna	< 24-h-old	N	S		am	8		48 h	LC50	mortality	8.6		[14]
Daphnia magna	< 24-h-old	N	S		am			3 w	EC35	reproduction	5.0		[14]
Daphnia magna	< 24-h-old, 2^{nd} gen		S		am			2 w	NOEC	reproduction	>2.5		[14]
Pisces													
Pimephales promelas		Y	F				90	42 d	NOEC	mortality	> 7.9	1	[91]
Pimephales promelas		Y	F				90	42 d	NOEC	fecundity	> 7.9	1	[91]

Notes

1. no dose-response relationship; "technical mixture" of alkylphenol ethoxylates, no further specification.

$NPEO_1$

Insecta													
Culex pipiens	pupae, 24 hr		S	n.r.	dist. w	7.5-8.0	n.r.		LC_{50}	emergence	80	1	[83]

Notes

1. test result >3x water solubility; animals (pupae) exposed until emergence (partial life cycle exposure, therefore: acute test); non-emergence was taken as mortality score; average number of ethoxy units was 1 (on a molar basis); 5 g/l alcohol as carrier was shown to be non-toxic.

$NPEO_{1,2}$

Insecta													
Culex pipiens	pupae, 24 hr		S	n.r.	dist. w	7.5-8.0	n.r.		LC_{50}	emergence	67	1	[83]

Notes

1. test result >3x water solubility; animals (pupae) exposed until emergence (partial life cycle exposure, therefore: acute test); non-emergence was taken as mortality score; average number of ethoxy units was 1.5 (on a molar basis); 5 g/l alcohol as carrier was shown to be non-toxic

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$] or Salinity [‰]	Exposure time	Criterion	Test endpoint	Value [$mg.l^{-1}$]	Notes	Reference
$NPEO_2$													
Pisces													
Oncorhynchus mykiss	all female; hatchlings	N	F		lake water	6.5	12.5	22 d	LOEC	growth	0.001	1	[12]

Notes

1. growth measured as weight; all test concentrations significantly reduced with no dose related response. Explanation for observed effects lacks. see text.

Ad 1. These test results (see also NPE_1C) are shown because they occur at concentrations that are three orders of magnitude below other effects. They are significantly different from control treatments and not caused by a solvent effect. The effects are however, not dose related and their mechanism unclear.

$NPEO_4$

Bacteria													
Pseudomonas fluorescens		N	S	n.r.	river w	7.5-7.8	204	16-24 h	NOEC	glucose min.	50	1	[58]
Crustacea													
Daphnia magna	< 24 h	N	S	n.r.	river w	7.5-7.8	204	48 h	NOEC	mortality	5		[58]

Notes

1. test result >3x water solubility.

$NPEO_6$

Bacteria													
Pseudomonas fluorescens		N	S	n.r.	river w	7.5-7.8	204	16-24 h	NOEC	glucose min.	500	1	[58]
Algae													
Selenastrum capricornutum			S	technical				21 d	LOEC	Cell no.	>500	2	[95]
Crustacea													
Daphnia magna	< 24 h	N	S	n.r.	river w	7.5-7.8	204	48 h	NOEC	mortality	5		[58]

Notes

1. rest result >3x water solubility.
2. cells cultured for 21 d at 25°C, cell counts performed only at day 21.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$] or Salinity [‰]	Exposure time	Criterion	Test endpoint	Value [$mg.l^{-1}$]	Notes	Reference
$NPEO_7$													
Bacteria													
Pseudomonas fluorescens		N	S	n.r.	river w	7.5-7.8	204	16-24 h	NOEC	glucose min.	500	1	[58]
Crustacea													
Daphnia magna	< 24 h	N	S	n.r.	river w	7.5-7.8	204	48 h	NOEC	mortality	5		[58]
Daphnia magna	< 24 h	N	S	n.r.	river w	7.5-7.8	204	48 h	NOEC	mortality	10		[58]

Notes

1. rest result >3x water solubility.

$NPEO_9$													
Algae													
Chlorella sp.		N	S		sw+nutrients	8	22-27‰	12-14 d	LOEC	Cell no.	<1	1	[122]
Protococcus sp.		N	S		sw+nutrients	8	22-27‰	12-14 d	EC50	Cell no.	1000	2	[122]
Selenastrum capricornutum			S	technical				21 d	LOEC	Cell no.	>500	3	[95]

Notes

1. two species tested together in one test; growth only measured at end of test; EC50 estimated graphically.

Ad 1. In this study, several other species were tested together at family (taxonomic) level, making use of these data at *species* level impossible. In many cases only one effect concentration can be read from the graphs, which is too few to determine a dose-effect relationship. Moreover since tests lasted 12-14 d at 20°C and only one growth (optical density) measurement was performed at the end of the tests, the results will not be used in the risk assessment.

2. growth only measured at end of test; EC50 estimated graphically.
3. cells cultured for 21 d at 25°C, cell counts performed only at day 21.

$NPEO_{10}$													
Bacteria													
Pseudomonas fluorescens		N	S	n.r.	river w	7.5-7.8	204	16-24 h	NOEC	glucose min.	1000	1	[58]
Algae													
Chlorella sp.		N	S		sw+nutrients	8	22-27‰	12-14 d	EC50	Cell no.	100	2	[122]
Protococcus sp.		N	S		sw+nutrients	8	22-27‰	12-14 d	NOEC	Cell no.	≥1000	3	[122]
Crustacea													
Daphnia magna	< 24 h	N	S	n.r.	river w	7.5-7.8	204	48 h	NOEC	mortality	10		[58]

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$] or Salinity [‰]	Exposure time	Criterion	Test endpoint	Value [$mg.l^{-1}$]	Notes	Reference
Pisces													
Oncorhynchus mykiss	various life stages	N	S		tw	7.3-7.4	240-260	3 h	LC50	mortality	2.5-62	4	[82]
Oncorhynchus mykiss	various life stages	N	S		tw	7.3-7.4	240-260	6 h	LC50	mortality	2.1-42	4	[82]

Notes

1. rest result >3x water solubility.
2. average of 9.5 ethoxy units per molecule; two species tested together in one test; growth only measured at end of test; EC50 estimated graphically.
3. average of 9.5 ethoxy units per molecule; growth only measured at end of test; NOEC estimated graphically: slight effect observed at highest test concentration, no statistical information.
4. test duration too short. Eight life stages test from 1 till 200 d after hatching.

$NPEO_{11}$

Algae													
Chlorella sp.		N	S		sw+nutrients	8	22-27‰	12-14 d	EC40	Cell no.	100	1	[122]
Protococcus sp.		N	S		sw+nutrients	8	22-27‰	12-14 d	NOEC	Cell no.	≥1000	2	[122]

Notes

1. average of 10.5 ethoxy units per molecule; two species tested together in one test; growth only measured at end of test; EC40 estimated graphically.
2. average of 10.5 ethoxy units per molecule; growth only measured at end of test; no effect observed at highest test concentration, no statistical information.

$NPEO_{15}$

Algae													
Chlorella sp.		N	S		sw+nutrients	8	22-27‰	12-14 d	EC50	Cell no.	100	1	[122]
Protococcus sp.		N	S		sw+nutrients	8	22-27‰	12-14 d	NOEC	Cell no.	≥1000	2	[122]

Notes

1. average of 15 ethoxy units per molecule; two species tested together in one test; growth only measured at end of test; EC50 estimated graphically.
2. average of 15 ethoxy units per molecule; growth only measured at end of test; no effect observed at highest test concentration, no statistical information.

Species	Species properties	Analysed	Test type	Substance purity	Test water	pH	Hardness [mg $CaCO_3.l^{-1}$] or Salinity [‰]	Exposure time	Criterion	Test endpoint	Value [$mg.l^{-1}$]	Notes	Reference
$NPEO_{20}$													
Algae													
Chlorella sp.		N	S		sw+nutrients	8	22-27‰	12-14 d	EC70	Cell no.	10-1000	1	[122]
Protococcus sp.		N	S		sw+nutrients	8	22-27‰	12-14 d	NOEC	Cell no.	≥1000	2	[122]
Crustacea													
Daphnia magna	< 24 h	N	S	n.r.	river w	7.5-7.8	204	48 h	NOEC	mortality	1000		[58]

Notes

1. average of 20 ethoxy units per molecule; two species tested together in one test; growth only measured at end of test; approx. 70% inhibition at 10, 100 and 1000 mg/l.
2. average of 20 ethoxy units per molecule; growth only measured at end of test; no effect observed at highest test concentration, no statistical information.

$NPEO_{30}$													
Algae													
Chlorella sp.		N	S		sw+nutrients	8	22-27‰	12-14 d	EC70	Cell no.	100-1000	1	[122]
Protococcus sp.		N	S		sw+nutrients	8	22-27‰	12-14 d	NOEC	Cell no.	≥1000	2	[122]
Selenastrum capricornutum			S	technical				21 d	LOEC	Cell no.	>500	3	[95]
Crustacea													
Daphnia magna	< 24 h	N	S	n.r.	river w	7.5-7.8	204	48 h	NOEC	mortality	>10000		[58]

Notes

1. average of 30 ethoxy units per molecule; two species tested together in one test; growth only measured at end of test; approx. 50% inhibition at 100 and 1000 mg/l.
2. average of 30 ethoxy units per molecule; growth only measured at end of test; slight effect observed at highest test concentration, no statistical information.
3. cells cultured for 21 d at 25°C, cell counts performed only at day 21.

NPE_1C													
Pisces													
Oncorhynchus mykiss	all female; hatchlings	N	F		lake water	6.5	12.5	22 d	NOEC	growth	0.001	1	[12]
Oncorhynchus mykiss	all female; hatchlings	N	F		lake water	6.5	12.5	22 d	LOEC	growth	0.01	2	[12]

Notes

1. growth measured as weight; all test concentrations significantly reduced with no dose related response. Explanation for observed effects lacks, see text.
2. same test as result under footnote 1.

Appendix 5. Soil and sediment toxicity data

Legend

Species/Process/Activity	organism used or process/activity followed in the test, if applicable and available followed by age, size, weight or life stage
Analysed	Y = test substance analysed in test solution N = test substance not analysed in test solution or no data
O.m.	percentage organic matter of test soil
Clay	percentage clay of test soil
Temp	test temperature
Exp. time	h = hours, d = days, w = weeks, m = months, min. = minutes
Criterion	NOEC = observed effect concentration; ECx = effect concentration causing x % effect
Results test soil	> and ≥ values = highest concentration used in the test
NOEC stand. soil	test result converted to (if possible) NOEC, in Dutch standard soil, expressed in d.w.

In this appendix soil or sediment toxicity data for octylphenol ethoxylates, nonylphenol ethoxylates and their carboxylated derivatives are presented.

Contents

Table A5. 1 Toxicity of nonylphenol ethoxylates to soil organisms, soil microbial processes and enzyme activity.

Species/Process/Activity	Species properties	Soil type	pH	o.m. [%]	Clay [%]	Temp [°C]	Exp. time	Criterion	Test endpoint	Result test soil [mg/kg$_{dw}$]	NOEC stand. soil [mg/kg$_{dw}$]	Notes	Reference
$NPEO_3$													
Enzyme activity													
dehydrogenase		sandy cambisol	5.44-6.35	1.24-2.67			1-2 d	EC10	activity inhibition	132	1148	1	[139]
dehydrogenase		sandy cambisol	5.44-6.35	1.24-2.67			5-7 d	EC10	activity inhibition	52	452	1	[139]

Notes

1. EC10 determined by fitting a logistic curve through data from author.

$NPEO_{13}$													
Enzyme activity													
dehydrogenase		sandy cambisol	5.44-6.35	1.24-2.67			1-2 d	EC10	activity inhibition	>1000	>8696	1	[139]
dehydrogenase		sandy cambisol	5.44-6.35	1.24-2.67			5-7 d	EC10	activity inhibition	902	7843	1	[139]

Notes

1. EC10 determined by fitting a logistic curve through data from author.

Table A5. 2 Toxicity of nonylphenol ethoxylates to soil organisms, soil microbial processes and enzyme activity: deviating tests.

Species/Process/Activity	Species properties	Soil type	pH	o.m. [%]	Clay [%]	Temp [°C]	Exp. time	Criterion	Test endpoint	Result test soil [mg/kg$_{d.w.}$]	NOEC stand. soil [mg/kg$_{d.w.}$]	Notes	Reference
$NPEO_3$													
Enzyme activity													
dehydrogenase		sandy cambisol	5.44-6.35	1.24-2.67			2.5 h	EC20	activity inhibition	159	690	1, 2	[139]
dehydrogenase		sandy cambisol	5.44-6.35	1.24-2.67			4 w	EC70	activity inhibition	159	138	1, 3	[139]
dehydrogenase		sandy cambisol	5.44-6.35	1.24-2.67			8 w	EC75	activity inhibition	159	138	1, 3	[139]

Notes

1. data from one experiment, one concentration tested, dehydrogenase activity measured weekly; inhibitory effect increased with time and stabilised after 4 wk of exposure; no statistical information.
2. NOEC=LOEC/2.
3. NOEC=LOEC/10.

$NPEO_6$

Enzyme activity													
dehydrogenase		sandy cambisol	5.44-6.35	1.24-2.67			2.5 h	EC20	activity inhibition	218	948	1, 2	[139]
dehydrogenase		sandy cambisol	5.44-6.35	1.24-2.67			2.5 h	EC56	activity inhibition	218	190	1, 3	[139]
dehydrogenase		sandy cambisol	5.44-6.35	1.24-2.67			2.5 h	EC66	activity inhibition	218	190	1, 3	[139]

Notes

1. data from one experiment, one concentration tested, dehydrogenase activity measured weekly; inhibitory effect increased with time and stabilised after 4 wk of exposure; no statistical information.
2. NOEC=LOEC/2.
3. NOEC=LOEC/10.

$NPEO_9$

Enzyme activity													
dehydrogenase		sandy cambisol	5.44-6.35	1.24-2.67			2.5 h	EC20	activity inhibition	278	1207	1, 2	[139]
dehydrogenase		sandy cambisol	5.44-6.35	1.24-2.67			2.5 h	EC54	activity inhibition	278	241	1, 3	[139]
dehydrogenase		sandy cambisol	5.44-6.35	1.24-2.67			2.5 h	EC63	activity inhibition	278	241	1, 3	[139]

Notes

1. data from one experiment, one concentration tested, dehydrogenase activity measured weekly; inhibitory effect increased with time and stabilised after 4 wk of exposure; no statistical information.
2. NOEC=LOEC/2.
3. NOEC=LOEC/10.

Species/Process/Activity	Species properties	Soil type	pH	o.m. [%]	Clay [%]	Temp [°C]	Exp. time	Criterion	Test endpoint	Result test soil [mg/kg$_{d.w.}$]	NOEC stand. soil [mg/kg$_{d.w.}$]	Notes	Reference
$NPEO_{13}$													
Enzyme activity													
dehydrogenase		sandy cambisol	5.44-6.35	1.24-2.67			2.5 h	EC20	activity inhibition	357	1552	1, 2	[139]
dehydrogenase		sandy cambisol	5.44-6.35	1.24-2.67			2.5 h	EC46	activity inhibition	357	310	1, 3	[139]
dehydrogenase		sandy cambisol	5.44-6.35	1.24-2.67			2.5 h	EC47	activity inhibition	357	310	1, 3	[139]

Notes

1. data from one experiment, one concentration tested, dehydrogenase activity measured weekly; inhibitory effect increased with time and stabilised after 4 wk of exposure; no statistical information.
2. NOEC=LOEC/2.
3. NOEC=LOEC/10.

Appendix 6. Endocrine effect data

Legend

Species	organism used in the test, if available followed by age, size, weight or life stage
Analysed	Y = test substance analysed in test solution N = test substance not analysed in test solution or no data
Test type	S = static, R = static with renewal, F = flow through
Substance purity	percentage active ingredient
Test water	am = artificial medium, asw = artificial seawater, dist.w = distilled water, nfs = natural filtered seawater, nw = natural water, rtw = reconsituted tap water (+additional salts), river w = river water, sw = sea water, tw = tap water
Exposure time	h = hours, d = days, w = weeks, m = months, min. = minutes
Criterion	EC50 = lowest short term test result showing 50% effect; LOEC = lowest observed effect concentration; NOEC = no observed effect concentration; ECx = effect concentration causing x% effect
Test endpoint	hER = human estrogen receptor
Value	test result; > and ≥ symbols = no effect observed at highest test concentration

In this appendix endocrine effect/toxicity data for octylphenol ethoxylates, nonylphenol ethoxylates and their carboxylated derivatives are presented.

Contents

Table A6. 1 Effects on endocrine system or hormone related effects of alkylphenol ethoxylates to aquatic organisms.

Species	Species properties	Analysed	Test type	Substance purity	Test water	Exposure time	Criterion	Test endpoint	Value [mg/l]	Notes	Reference
$OPEO_2$											
Yeast											
Saccharomyces cerevisiae	recombinant yeast assay		*in vitro*			3 d	EC50	hER binding + activation	9.53	1	[107]

Notes

1. EC50 expressed relative to the half maximal gene activation response produced by the natural estrogen E2 (from Routledge & Sumpter [104]).

$OPEO_3$											
Yeast											
Saccharomyces cerevisiae	recombinant yeast assay		*in vitro*			3 d	EC50	hER binding + activation	41.6	1	[107]

Notes

1. EC50 expressed relative to the half maximal gene activation response produced by the natural estrogen E2 (from Routledge & Sumpter [104]).

NPEO unspecified											
Pisces											
Pimephales promelas	mature	Y	F, *in vivo*			42 d	NOEC	secondary sex characteristics	>0.0055	1, 8	[86]
Pimephales promelas	mature	Y	F, *in vivo*			42 d	NOEC	testes and ovary histology	>0.0055	8	[86]
Crustacea											
Daphnia magna	10-d-old females	N	S, *in vivo*		am	48 h+16 h	NOEC	metabolic testosterone elimination	>5	2, 9	[14]
Daphnia magna	10-d-old females	N	S, *in vivo*		am	3 w+16 h	EC100	metabolic testosterone elimination	5	3, 9	[14]
Daphnia magna	10-d-old females	N	S, *in vivo*		am	3 w+16 h	EC87	metabolic testosterone elimination	5	4, 9	[14]
Daphnia magna	10-d-old females	N	S, *in vivo*		am	3 w+16 h	EC110	metabolic testosterone elimination	2.5	5, 9	[14]
Daphnia magna	10-d-old females	N	S, *in vivo*		am	3 w+16 h	EC58	metabolic testosterone elimination	2.5	6, 9	[14]
Daphnia magna	10-d-old females	N	S, *in vivo*		am	3 w+16 h		total metabolic androgenisation	5	7, 9	[14]

Notes

1. tubercles and fatpad
size.
2. daphnids were exposed 48 h to NPPG alone and afterwards 16 h to NPPG and 14C-testosterone.

Species	Species properties	Analysed	Test type	Substance purity	Test water	Exposure time	Criterion	Test endpoint	Value [mg/l]	Notes	Reference

3. elimination of testosterone as glucose conjugate; at 2.5 mg/l elimination was 48% higher than in controls.
4. elimination of testosterone as sulphate conjugate; at 2.5 mg/l elimination was about 10% higher than in controls
5. elimination of testosterone as oxido-reduced metabolites , 110 and 220% higher at 2.5 and 5 mg/l, respectively.
6. elimination of testosterone as hydroxylated derivatives 50 and 17% lower than in controls at 2.5 and 5 mg/l, respectively.
7. overall metabolic androgenisation increased at 2.5, significantly at 5 mg/l.
8. "technical mixture" of alkylphenol ethoxylates, no further specification.
9. test substance called "nonylphenol polyethylene glycol" (NPPG) but also referred to as nonylphenol polyethoxylate, no further specification.

$NPEO_2$

Yeast											
Saccharomyces cerevisiae	recombinant yeast estrogen screen		*in vitro*			3 d	EC50	hER binding + activation	77	1	[103]
Saccharomyces cerevisiae	recombinant yeast assay		*in vitro*			3 d	EC50	hER binding + activation	8.8	2	[104]
Pisces											
Oncorhynchus mykiss	cultured hepatocytes		*in vitro*			2 d	EC50	vitellogenin production	5.3		[60]
Oncorhynchus mykiss	cultured hepatocytes		*in vitro*				LOEC	vitellogenin production	0.31	3	[138]
Oncorhynchus mykiss	juvenile males	Y	F, *in vivo*		borhole	3 w	EC	vitellogenin induction	38.3	4	[59]
Oncorhynchus mykiss	juvenile males	Y	F, *in vivo*		borhole	3 w	EC	testes growth inhibition	38.3	5	[59]
Oncorhynchus mykiss	juvenile males	Y	F, *in vivo*		borhole	3 w	EC	spermatogenesis	38.3	6	[59]

Notes

1. logistic dose response model fitted through data derived from graph.
2. logistic dose response model fitted through data derived from graph. Same data are used by Schmieder et al. (2000), but these authors calculated the EC50 relative to the half maximal gene activation response produced by the natural estrogen E2.
3. at 10 E-5 M the response was 4.3 times less than that of cells exposed to 10 E-8 M beta-estradiol.
4. one concentration tested; significant elevation of VTG concentration observed, the effect was not quantified.
5. one concentration tested; significant decrease in testicular growth observed, the effect was not quantified.
6. one concentration tested; significant increase of spermatogonia A.

$NPEO_9$

Pisces											
Oncorhynchus mykiss	cultured hepatocytes		*in vitro*			2 d	EC50	vitellogenin production	50.8		[60]

Species	Species properties	Analysed	Test type	Substance purity	Test water	Exposure time	Criterion	Test endpoint	Value [mg/l]	Notes	Reference
$NPEO_{12}$											
Yeast											
Saccharomyces cerevisiae	recombinant yeast estrogen screen		*in vitro*			3 d	NOEC	hER binding + activation	>100	1	[103]

Notes

1. determined graphically, indicative use only.

$NPEC_1$

Yeast											
Saccharomyces cerevisiae	recombinant yeast estrogen screen		*in vitro*			3 d	LOEC	hER binding + activation	~0.4	1	[103]
Pisces											
Oncorhynchus mykiss	cultured hepatocytes		*in vitro*			2 d	EC50	vitellogenin production	4.25		[60]
Oncorhynchus mykiss	juvenile males	Y	F, *in vivo*		borhole	3 w	EC	vitellogenin induction	31.8	2	[59]
Oncorhynchus mykiss	juvenile males	Y	F, *in vivo*		borhole	3 w	EC	testes growth inhibition	31.8	3	[59]
Oncorhynchus mykiss	juvenile males	Y	F, *in vivo*		borhole	3 w	EC	spermatogenesis	31.8	4	[59]

Notes

1. determined graphically, indicative use only; 4-OP: 1500 x; 4-NP: 7000 x: NP1EC and NP2EC: 25000 x; NP2EO: 500000- fold less potency than 17b-estradiol
2. one concentration tested; significant elevation of VTG concentration observed, the effect was not quantified.
3. one concentration tested; significant decrease in testicular growth observed, the effect was not quantified.
4. one concentration tested; significant increase of spermatogonia A, significantly reduced levels of spermatogonia B, and spermatocyte A and B.

$NPEC_2$

Yeast											
Saccharomyces cerevisiae	recombinant yeast estrogen screen		*in vitro*			3 d	LOEC	hER binding + activation	~0.4	1	[103]

Notes

1. determined graphically, indicative use only.

Appendix 7. Recalculation of nonylphenol PNECs to MPCs; options for Dutch ERL derivation

Introduction

This appendix is written to support the discussion on the use of EU-RAR derived PNECs in the Dutch national framework. We outline various possibilities to arrive at –proposals for– Dutch MPCs using PNECs from an EU-RAR as a starting point. Focus is on the options that are applicable to the nonylphenol case. We thereto discuss the derivation of the MPC_{soil} from $PNEC_{soil}$ for nonylphenol. The EU-RAR for nonylphenol [46] is taken as a basis for PNEC values used in the following sections.

A $PNEC_{soil}$ can be reported in several ways in a given EU-RAR:

A. A $PNEC_{soil}$ is not reported.
B. The $PNEC_{soil}$ is reported but it is unclear whether it is based on wet weight or dry weight and/or normalised to o.c. content.
C. The $PNEC_{soil}$ is reported and it is known to be based on either wet weight (with a known or unknown moisture content) or dry weight, but not normalised to o.c. content.
D. The $PNEC_{soil}$ is reported and it is based on either wet or dry weight and normalised to a known o.c. content.

In the EU-RAR for nonylphenol a $PNEC_{soil}$ is reported. However, it is known that this value is based on wet weight and not normalised to organic carbon (o.c.) content [39]. The moisture content and o.c. content of the test soil are unkown. This directs us to possibility C. We can now discern several options on how to use or convert these $PNECs_{soil}$ to an MPC_{soil}.

Ad C.

An MPC_{soil} is not derived since $PNEC_{soil}$ is wet weight based and not normalised to o.c. content.

When it is desirable to derive an MPC_{soil}, six options are discerned:

1. The $PNEC_{soil}$ is taken as MPC_{soil} without further calculations (either wet weight or dry weight).
2. When the $PNEC_{soil}$ is based on wet weight, recalculate the $PNEC_{soil}$ to dry weight soil. Since nothing is mentioned on normalisation to o.c. content, *assume* that the reported PNEC is recalculated to the o.c. content of the standard EUsoil (viz. 2% o.c.), as recommended in the TGD. Do not normalise to Dutch standard soil.
3. When the $PNEC_{soil}$ is based on wet weight, recalculate the $PNEC_{soil}$ to dry weight soil. Since nothing is mentioned on normalisation to o.c. content, *assume* that the reported PNEC is recalculated to the o.c. content of the standard EUsoil (viz. 2% o.c.), as recommended in the TGD. Subsequently recalculate the MPC_{soil} to Dutch standard soil (5.88% o.c.).

4. The INS method (applied when an MPC_{soil} is absent) is followed: a $PNEC_{soil}$ is calculated from the $PNEC_{water}$ using EqP. This $PNEC_{soil}$ is converted to a PNEC for dry soil and normalised to EUstandard soil (2% o.c.) and subsequently taken as MPC_{soil}.
5. The INS method (applied when an MPC_{soil} is absent) is followed: a $PNEC_{soil}$ is calculated from the $PNEC_{water}$ using EqP. This $PNEC_{soil}$ is converted to a PNEC for dry soil and normalised to Dutch standard soil (5.88% o.c.) and subsequently taken as MPC_{soil}.
6. Harmonisation. If options 2 and 3 are considered valid (making assumptions on o.c. content of a test soil) and option 4 and 5 (EqP) have been carried out, two $PNEC_{soil}$ values are available (one direct and one derived via EqP). Both values are compared and the lowest value is subsequently selected as MPC.

MPC_{soil} nonylphenol

We now have several options, of which not deriving an MPC_{soil} is the first one. Below, the other options are worked out.

Option C1 leads to an $\mathbf{MPC_{soil,\,1}}$ of **340 µg.kg$_{ww}^{-1}$**. This value is based on wet weight soil and *not* normalised to o.c. content.

Option C2 is worked out in the following sections.
Assumption 1. We propose to use the wet weight:dry weight conversion factor from EUSES [39] to recalculate the PNEC to a dry weight value. According to the EUSES manual, wet soil is composed of 20% v/v air (density 0.0013 kg/l), 20% v/v water (density 1 kg/l) and 60% solid particles (density 2.5 kg/l), leading to a 'wet' density of (0.2*0.0013) + (0.2*1) + (0.6*2.5) = 1.7 kg/l. The dry weight of the solid particles is 0.6*2.5 = 1.5 kg (per litre of wet soil) and the ratio wet:dry is therefore 1.7/1.5 = 1.13.
Assumption 2. We assume the test soil has the organic carbon content of the EU standard soil, i.e. 2%. The $\mathbf{MPC_{soil,\,2}}$ is therefore 340 × 1.13 = **384 µg.kg$_{dw}^{-1}$** ('normalised' to EU standard soil, **2% o.c**.).

Option C3 gives an $\mathbf{MPC_{soil,\,3}}$ of 340 × 1.13 × 5.88/2 = **1130 µg.kg$_{dw}^{-1}$** ('normalised' to Dutch standard soil, **5.88% o.c**.).

Option C4: a $PNEC_{soil}$ is calculated using EqP theory and converted to EU standard soil. Since the $PNEC_{soil}$ is derived using preliminary risk assessment, the $PNEC_{soil}$ is also calculated using equilibrium partitioning [120]. Within the EU framework the following equation is used:

$$PNEC_{\text{soil ww, EqP}} = \frac{K_{\text{soil-water}} \cdot PNEC_{\text{water}} \cdot 1000}{RHO_{\text{soil}}} \qquad \text{Equation 9}$$

in which:

$PNEC_{\text{soil ww, EqP}}$ predicted no effect concentration for the soil compartment (µg.kg$_{ww}^{-1}$)

$K_{soil\text{-}water}$	soil to water partition coefficient ($m^3.m^{-3}$)
$PNEC_{water}$	predicted no effect concentration for the water compartment ($\mu g.l^{-1}$)
1000	conversion factor from litres to m^3 ($l.m^{-3}$)
RHO_{soil}	bulk density of wet soil ($kg.m^{-3}$)

The $PNEC_{soil\ ww,\ EqP}$ is calculated using $PNEC_{water}$ = 0.33 $\mu g.l^{-1}$, $K_{soil\text{-}water}$ = 161 $m^3.m^{-3}$ [39], and RHO_{soil} = 1700 $kg.m^{-3}$ [39]. The $PNEC_{soil\ ww,\ EqP}$ is calculated to be 31.3 $\mu g.kg_{ww}^{-1}$.

The $PNEC_{soil\ ww,\ EqP}$ (31.3 $\mu g.kg_{ww}^{-1}$) is recalculated as follows. According to the TGD, the ratio wet soil:dry soil is 1.13 (see previous page for calculation). The $PNEC_{soil\ dw,\ EqP}$ is therefore 35.5 $\mu g.kg_{dw}^{-1}$. Since the organic carbon content of soil particles in EUSES is 2%, $\mathbf{MPC_{soil,\ 4} = 35.5\ \mu g.kg_{dw}^{-1}}$.

Option C5: a $PNEC_{soil}$ is calculated using EqP theory and converted to Dutch standard soil. The procedure is identical to option C4 described above. Conversion to Dutch standard soil is as follows:

The organic carbon content of soil particles in EUSES is 2%. For Dutch ERLs the PNEC is recalculated to standard soil containing 5.88% o.c.. The $PNEC_{soil\ dw,\ EqP}$ in Dutch standard soil is therefore 35.5*5.88/2 = $\mathbf{104\ \mu g.kg_{dw}^{-1}}$, designated here as $\mathbf{MPC_{soil,\ 5}}$.

Option C6. Harmonisation.
Compare the outcomes of options 2 and 4 *or* the outcomes of options 3 and 5. In each case, the lowest value is selected as MPC. This gives $\mathbf{MPC_{soil,\ 6,\ EU} = 35.5\ \mu g.kg_{dw}^{-1}}$ (normalised to EU standard soil) or $\mathbf{MPC_{soil,\ 6,\ NL} = 104\ \mu g.kg_{dw}^{-1}}$. (normalised to Dutch standard soil).

Table A7. 1 Overview of various MPCsoil values.

Option	Value (mg/kg)	dry or wet soil	% o.c.	Remarks
$\mathbf{MPC_{soil,\ 1}}$	340	wet	unknown	MPC incomparable to other Dutch MPCs
$\mathbf{MPC_{soil,\ 2}}$	384	dry	2	assumption moisture and o.c. content; MPC incomparable to Dutch MPCs
$\mathbf{MPC_{soil,\ 3}}$	1130	dry	5.88	assumption on moisture and o.c. content
$\mathbf{MPC_{soil,\ 4}}$	35.5	dry	2	EqP; MPC incomparable to Dutch MPCs
$\mathbf{MPC_{soil,\ 5}}$	104	dry	5.88	EqP; MPC comparable to Dutch MPCs
$\mathbf{MPC_{soil,\ 6,\ EU}}$	35.5	dry	2	EqP; MPC incomparable to Dutch MPCs
$\mathbf{MPC_{soil,\ 6,\ NL}}$	104	dry	5.88	EqP; MPC comparable to Dutch MPCs

All presented MPCs have their disadvantages. E.g. because MPCs based on wet weight can no longer be compared to MPCs that have been derived in the past (all Dutch $MPCs_{soil}$ are dry weight based). The same holds for MPCs that are not normalised to Dutch standard soil (all Dutch $MPCs_{soil}$ for organic substances are normalised to o.c. content). To our opinion, option 6 (giving $MPC_{soil,\ 6,\ NL}$ = 104 mg/kg) would be the best choice in the case of nonylphenol: this

MPC is based on dry weight, normalised to o.c. content, harmonised with the aquatic compartment and therefore comparable to other Dutch MPCs.

$MPC_{sediment}$

For derivation of the $MPC_{sediment}$ a scheme comparable to that for MPC_{soil} can be drawn up. For this reason, we will not elaborate on $MPC_{sediment}$ derivation. The EU-RAR for nonylphenol does not present a $PNEC_{sediment}$. There are now three options:

1. Since no $PNEC_{sediment}$ is not available, an $MPC_{sediment}$ will not be derived,
2. The INS method is followed: a $PNEC_{sediment}$ is calculated from the $PNEC_{water}$ using EqP, but recalculated to EU standard sediment (10% o.c.).
3. The INS method is followed: a $PNEC_{sediment}$ is calculated from the $PNEC_{water}$ using EqP but recalculated to Dutch standard sediment (5.88% o.c.).

Option 2 is worked out in the following sections (only for Dutch standard sediment):
The method followed within INS, is to calculate an $MPC_{sediment}$ from an MPC_{water}[5] using EqP when sediment toxicity data are absent. In analogy with this method, a $PNEC_{sediment}$ can be calculated from the $PNEC_{water}$. Since a $PNEC_{water}$ for nonylphenol is available, this method can be performed.
Within the EU framework the following equation is used:

$$PNEC_{\text{sediment ww, EqP}} = \frac{K_{\text{susp-water}} \cdot PNEC_{\text{water}} \cdot 1000}{RHO_{\text{susp}}} \qquad \text{Equation 10}$$

in which:

$PNEC_{\text{sediment ww, EqP}}$	predicted no effect concentration for the sediment compartment ($\mu g.l^{-1}$)
$K_{\text{susp-water}}$	suspended matter to water partition coefficient ($m^3.m^{-3}$)
$PNEC_{water}$	predicted no effect concentration for the water compartment ($\mu g.l^{-1}$)
1000	conversion factor from litres to m^3 ($l.m^{-3}$)
RHO_{susp}	bulk density of suspended matter ($kg.m^{-3}$)

Note: $K_{\text{susp-water}}$ is used to calculate partitioning into sediment in the updated version of the TGD [42]. The $PNEC_{\text{sediment ww, EqP}}$ is calculated using equilibrium partitioning theory (see Equation 2) using $PNEC_{water} = 0.33\ \mu g.l^{-1}$, $K_{\text{susp-water}} = 135\ m^3.m^{-3}$ [39], and $RHO_{susp} = 1150\ kg.m^{-3}$ [39]. The $PNEC_{\text{sediment ww, EqP}}$ is calculated to be 38.7 $\mu g.kg_{ww}^{-1}$.

13.1.1.1 Recalculation to dry weight and standard sediment

According to the TGD, wet sediment is composed of 90% v/v water (density 1 kg/l) and 10% v/v solid particles (density 2.5 kg/l), leading to a 'wet' density of

[5] Note that the EqP method is also applied to an MPC_{soil} or $MPC_{sediment}$ when this MPC_{soil} or $MPC_{sediment}$ *is* based on toxicity data for soil or sediment inhabiting organisms. This step is called harmonisation and is performed to prevent the possibility of concentrations in one compartment exceeding the MPC in another compartment.

(0.9*1) + (0.1*2.5) = 1.15 kg/l. The dry weight of the solid particles is 0.25 kg (per litre of wet sediment) and the ratio wet:dry is therefore 1.15/0.25 = 4.6. The $PNEC_{sediment\ dw,\ EqP}$ is therefore 178 $\mu g.kg_{dw}^{-1}$.

The organic carbon content of suspended matter in EUSES is 10%, which is equal to 17% organic matter. For Dutch ERLs the PNEC is recalculated to standard Dutch sediment containing 10% organic matter. The $PNEC_{sediment\ dw,\ EqP}$ in standard Dutch sediment is therefore 178*10/17 = **105 $\mu g.kg_{dw}^{-1}$**.

Table A7. 2 shows the MPC values for nonylphenol as proposed by the authors. The derivation of these MPCs is in line with the current INS guidance [120]. The final MPCs may differ from the values presented here, depending on the outcome of the discussion on how to use PNECs from EU-RARs as ERLs at the national level.

Table A7. 2. Proposed ERLs for nonylphenol for soil and sediment.

	SOIL		SEDIMENT	
Compound	NC [$\mu g.kg_{dw}^{-1}$]	MPC [$\mu g.kg_{dw}^{-1}$]	NC [$\mu g.kg_{dw}^{-1}$]	MPC [$\mu g.kg_{dw}^{-1}$]
Nonylphenol	1.0	104	1.1	105