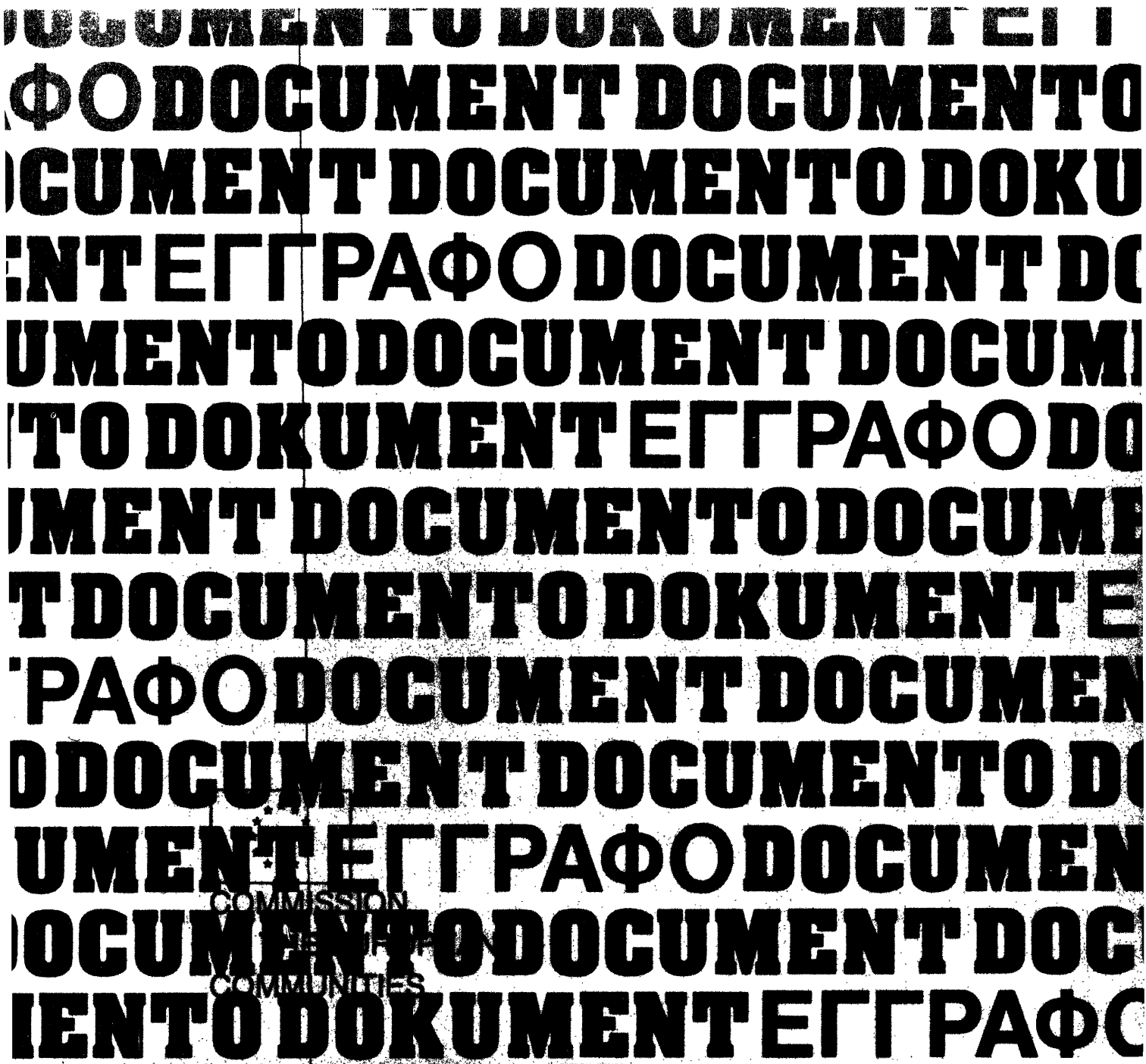
UPDATING OF DATA CONCERNING THE IMPACT ON THE AQUATIC ENVIRONMENT OF CERTAIN DANGEROUS SUBSTANCES, SECOND PART

Part III — Chloronitrobenzenes and 4-chloro-2-nitroaniline



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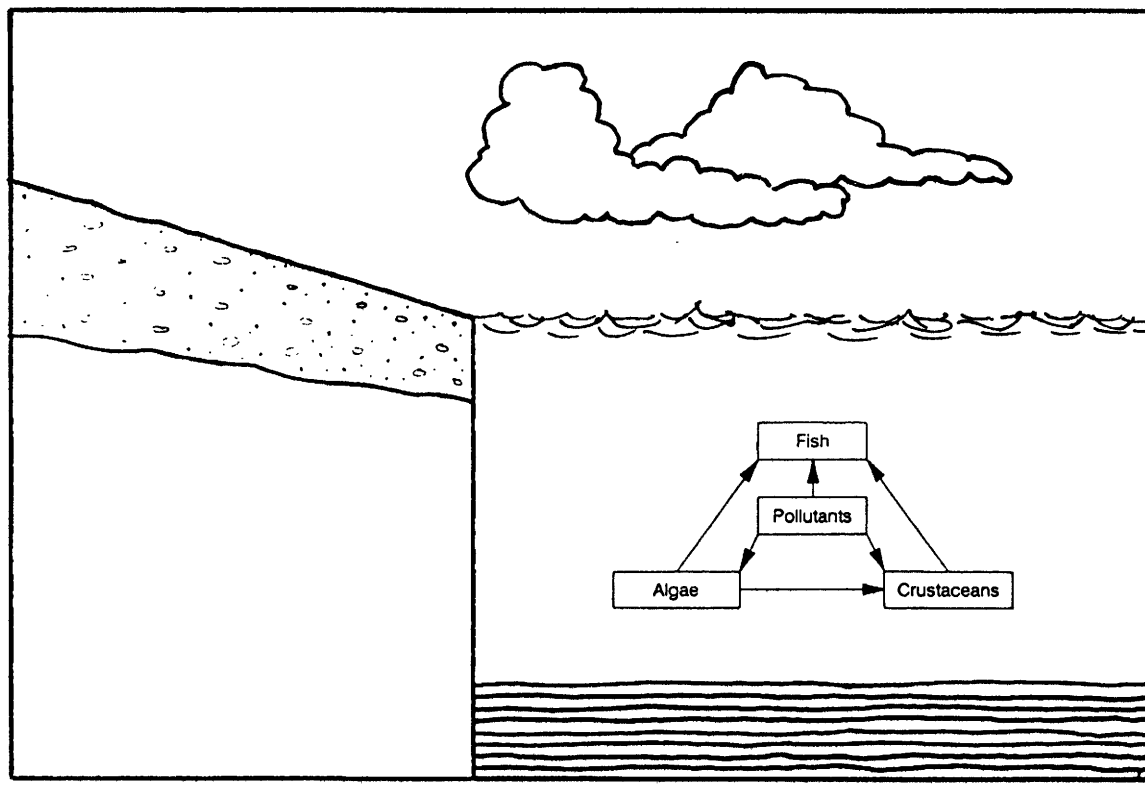
XI/A/3

Updating of data concerning the impact on the aquatic environment of certain dangerous substances, 2nd part

Part III Chloronitrobenzenes and 4-chloro-2-nitroaniline



May, 1992

bkh consulting engineers

PREFACE

The Commission of the European Communities, Directorate-General for Environment, Nuclear Safety and Civil Protection has commisioned BKH Consulting Engineers to carry out Study Contract B6612-90-006688:

Updating of data concerning the impact on the aquatic environment of certain dangerous substances, 2nd part: benzenes.

The study deals with the following dangerous substances which belong or should belong to List I of Directive 76/464/EEC:

benzene (7)
ethylbenzene (79)
isopropylbenzene (87)
chlorobenzene (20, 53, 54, 55, 109, 117, 118)
chloronitrobenzene (27, 28, 29, 30, 63)
chloroanilines (17, 18, 19, 52)

The study updates information on the description of the substances, the level of contamination of the aquatic environment, the persistence of the substances in the aquatic environment and other media, the toxicity (mainly in the aquatic environment) and bioaccumulation. On the basis of the available data, water quality standards are proposed.

The study is presented in four parts:

Part I	Benzene, ethylbenzene and isopropylbenzene
Part II	Chlorinated benzenes
Part III	Chloronitrobenzenes and 4-chloro-2-nitroaniline
Part IV	Chloroanilines

The study has been carried out by F. Balk, P.C. Okkerman, M. Hof, A. van de Bovekamp and J.W. Dogger. Critical remarks of J. Blok were greatly appreciated.

SUMMARY

The impact of monochloronitrobenzenes, dichloronitrobenzenes and 4-chloro-2-nitroaniline on the aquatic environment is evaluated in order to provide a toxicological basis to derive a proposal for water quality criteria. Data concerning physical and chemical properties, degradability, toxicity, chemical detection and environmental concentrations have been reviewed. The availability of data on the different subjects is summarized in Table i.

The three isomers of monochloronitrobenzene and the six isomers of dichloronitrobenzene except the 2,6-isomer are used widely for a variety of products in the chemical industry.
4-chloro-2 nitroaniline is a base chemical for dye stuff manufacturing.
Total production levels in the EC of 2-, 3-, 4-chloronitrobenzene and 4-chloro-2-nitroaniline were >25000 (1985), >4000 (1987), >45000 (1985) and 500-1000 ton/year (1987), respectively.

Chlorinated nitroaromates can be chemically analyzed by GC and ECD up to a detection limit of 50 ng/l, however the experience seems to be rather limited. Measured concentrations in water of rivers in industrial areas vary between 0.01 and 2 µg/l.

Elimination from the aquatic environment is by biodegradation, but the rate may be low because a high biomass concentration with adapted organisms seems to be necessary. Data on biodegradability are incomplete for all isomers and for different environmental conditions. Photodegradation and volatilization do not seem to contribute significantly to the elimination.
As the substances solve well in water and log K_{ow} is low, the accumulation on sediment and in fat tissue of organisms is low. Based on fat tissue calculations a bioconcentration factor of about 1000 is normal for all isomers, whereas no biomagnification through the food chain was shown.

The toxicity to aquatic organisms is not completely documented for all isomers. Chloronitrobenzenes do not show an increase of toxic effects at prolonged exposure. The range of toxicity data for the different isomers as well as for different test species is small. The data vary between 1.5 and 11 mg/l.
The maximum tolerable concentration in the ecosystem is calculated by the modified EPA method: the lowest LC_{50} was divided by 100 to give 10 µg/l. The toxic effects of the chloronitrobenzenes are expected to be additive. Therefore a water quality criterion of 10 µg/l is proposed for the sum of all chloronitrobenzenes. (N.B. This level does not take into account that other industrial pollutants may be present at the same time.) This level is a factor 5 to 1000 above the concentrations measured in river water.

The proposal for a water quality standard of 10 µg/l for the sum of all chloronitrobenzenes is comparable with the proposed standard of the Rhine Action Program (1991) of 1 µg/l for both 2-chloronitrobenzene and 4-chloronitrobenzene.

Data on mammalian toxicity are incomplete. The lowest dose causing chronic effects is reported for 2-chloronitrobenzene: 40 mg/kg body weight/day (oral administration to a rat during 78 weeks).
Based on the proposed water quality standard of 10 µg/l the maximum daily intake by man is estimated at 3.1 µg/kg body weight/day, which is far below the lowest reported effect level.

Table i Information available for chloronitrobenzenes and 4-chloro-2-nitroaniline on the different subjects.

Subject:	2-NCB	3-NCB	4-NCB	2,3-DCNB	2,4-DCNB	2,5-DCNB	2,6-DCNB	3,4-DCNB	3,5-DCNB	4-C-2-NA
1. PHYSICO-CHEMICAL CHARACTERISTICS	+	+	+	+	+	+	+	+	+	+
Production levels	+	+	+	-	-	-	-	-	-	+
2. ANALYTICAL DETECTION TECHNIQUES										
Detection methods	+	+	+	+	+	+	+	+	+	+
Detection levels	+	+	+	+	+	+	+	+	+	+
4. ENVIRONMENTAL LEVELS										
Residues in the atmosphere	-	-	-	-	-	-	-	-	-	-
Residues in soil and groundwater	-	-	-	-	-	-	-	-	-	-
Residues in surface water and sediment	±;-	±;±	±;-	-	-	-	-	-	-	-
Residues in aquatic organisms	±	±	±	±	±	±	±	±	±	±
Residues in terrestrial organisms	-	-	-	-	-	-	-	-	-	-
5. PERSISTENCE AND DEGRADATION PATHWAYS										
Abiotic degradation	-	-	+	-	-	-	-	-	-	-
Biological degradation and metabolism	±	±	±	±	±	±	-	±	-	-
6. DISTRIBUTION BETWEEN ENVIRONMENTAL COMPARTMENTS										
Volatization	+	+	+	+	+	+	+	+	+	+
Sorption	+	+	+	+	+	+	+	+	+	+
Bioaccumulation:										
Aquatic organisms	+	+	+	+	+	+	-	±	±	-
Terrestrial organisms	-	-	-	-	-	-	-	-	-	-
Biomagnification	±	±	±	-	-	-	-	-	-	-
7. TOXICITY										
Aquatic toxicity:										
Acute toxicity (freshwater; marine)	+;±	+;±	+;±	+;±	±;±	±;±	-;-	-;±	±;±	±;-
Chronic toxicity (freshwater; marine)	+;-	±;-	+;-	±;-	±;-	±;-	-;-	-;-	±;-	-;-
Quantitative structure activity relations (QSARs)	±	±	±	±	±	±	±	±	±	-
Toxicity to terrestrial organisms	±	±	-	±	-	-	-	-	-	-
(semi)field studies	-	-	-	-	-	-	-	-	-	-
Toxicity to mammals (acute; chronic)	+;+	+;-	+;+	-	-	-	-	-	-	+;-
Carcinogenic, mutagenic and teratogenic effects	-;±;-	-;-;-	-;-;±	-;-;-	-;-;-	-;-;-	-;-;-	-;-;-	-;-;-	-;-;-

+ data available
± insufficient data available
- no data available

ZUSAMMENFASSUNG

Die Wirkung von Monochloronitrobenzolen, Dichloronitrobenzolen und 4-Chloro-2-Nitroanilin auf die aquatische Umwelt wurde ermittelt mit der Absicht eine toxikologische Grundlage zu beschaffen auf welcher ein Vorschlag für Wasserqualitätskriterien abgeleitet werden könnte.
Werte bezüglich physischen und chemischen Eigenschaften, Abbaubarkeit, Toxizität, chemischer Determinierung und Umweltkonzentrationen wurden untersucht. In Tafel i sind die Ergebnisse dargestellt über die verfügbare Daten der verschiedene Gegenstände.

Die drei Isomeren von Monochloronitrobenzol und die sechs Isomeren von Dichloronitrobenzol mit Ausnahme der 2,6 Isomeren finden eine breite Anwendung für eine Vielfalt von Produkten der chemischen Industrie.
Das 4-Chloro-2-Nitroanilin ist ein chemischer Rohstoff für die Farbstoffherstellung.

Die totale Produktion (tonne/Jahr) von 2-, 3-, ind 4-Chloronitrobenzol und 4-Chloro-2-nitroanilin in der EG wird aufeinfolgend eingeschätzt auf >25000 (1985), >4000 (1987), >45000 (1984) und 500-1000 (1987).

Chlorinierte Nitroaromate können chemisch analisiert werden durch GL und ECD bis an der Determinierungsgrenze von 50 ng/l, aber die Erfahrungen hiermit scheinen beschränkt zu sein.

Die gemessenen Konzentrationen im Flusswasser von Industriegebieten variieren zwischen 0,01 und 2 µg/l.

Eliminierung aus der aquatischen Umwelt erfolgt durch biologischen Abbau, aber der Vorgang könnte langsam vor sich gehen, weil eine hohe Biomassekonzentration mit modifizierten Organismen notwendig scheint. Verfügbare Werte bezüglich biologischen Abbau sind unvollständig für alle Isomeren und unter die verschiedenen Umweltbedingungen.
Photogenischer Abbau und Verflüchtigung scheint nicht wesentlich an der Eliminierung beizutragen.
Da die Substanzen gut im Wasser löslich sind und die log K_{ow} niedrig ist, ist die Akkumulation an Sedimenten und in Fettgeweben von Organismen niedrig.

Ausgehend von Fettgewebe-Berechnungen ist ein Biokonzentrationsfaktor von etwa 1000 normal für alle Isomere, wobei keine Biomagnifizierung durch die Nahrungskette nachgewiesen wurde.

Die Toxizität gegenüber aquatischen Organismen ist nicht vollständig dokumentiert für alle Isomeren.
Chloronitrobenzene zeigen keine Zunahme von toxischen Effekten während längerer Aussetzung. Die Streuung von Toxizitätswerte für unterschiedliche Isomere somit für verschiedene Testarten ist beschränkt und variiert zwischen 1,5 und 11 mg/l. Die maximal zulässige Konzentration im Oekosystem wurde berechnet an Hand der modifizierten EPA-Methode: die niedrigste LC_{50} wurde durch 100 geteilt um 10 µg/l zu erreichen. Die toxischen Effekte von Chloronitrobenzolen sind erwartungsgemäss additiv. Deswegen wird ein Wasserqualitätskriterium von 10 µg/l vorgeschlagen für die Summierung von alle Chloronitrobenzolen.

(N.B. Dieses Niveau trägt keine Rechnung mit der Tatsache, daß weitere Verunreinigungen industrieller Herkunft gleichzeitig anwesend sein könnten.)
Dieses Niveau liegt ein Faktor 5 bis 1000 über die im Flusswasser gemessenen Konzentrationen.

Das vorgeschlagene Wasserqualitätskriterium (10 µg/l) für die Summe alle Chloronitrobenzolen ist vergleichbar mit dem Kriterium der Rhein Aktion Programm (1 µg/l für 2- und 4-Chloronitrobenzol).

Toxizitätswerten von Säugetieren sind unvollständig. Die niedrigste Menge, welche chronische Effekte verursacht, wurde gemeldet für 2-Chloronitrobenzol: 40 mg/kg Körpergewicht/Tag (orale Verabreichung an einer Ratte während 78 Wochen).

Ausgehend vom vorgeschlagenen Wasserqualitätskriterium von 10 µg/l wurde die maximale täglich durch Menschen aufzunehmende Menge geschätzt auf 3,1 µg/kg Körpergewicht/Tag, welcher Wert weit niedriger ist als das niedrigst aufgezeignete Effektniveau.

RÉSUMÉ

L'effet des monochloronitrobenzènes, des dichloronitrobenzènes et des 4-chloro-2-nitroanilines sur l'environnement aquatique a été évalué afin de fournir une base toxicologique pour en dériver une proposition concernant les critères de qualité de l'eau. Les données concernant les propriétés physiques et chimiques, la dégradabilité, la toxicité, la détection chimique et les concentrations environnementales ont été considérées. Le tableau i comprend un résumé de la disponibilité de données concernant les divers sujets.

On utilise sur un plan large dans l'industrie chimique les trois isomères du monochloronitrobenzène et les six isomères du dichloronitrobenzène, à l'exception du 2,6-isomère. Le 4-chloro-2-nitroaniline est une base chimique pour la production des colorants.
La production dans la CEE du 2-, 3-, 4-chloronitrobenzène et du 4-chloro-2-nitroaniline fut > 25.000 (1985), > 4.000 (1987), > 45.000 (1985) et 500-1000 tonnes/an respectivement.

Les nitroaromates chlorés peuvent être analysés chimiquement par CG et par DCE (détecteur à capture d'électron) jusqu'à une limite de 50 ng/l, quoique l'expérience semble être assez restreinte. Des concentrations mesurées dans les eaux fluviales des régions industrielles varient entre 0,01 et 2 µg/l.

L'élimination de l'environnement aquatique se fait par biodégradation, mais l'effet peut être bas parce qu'une concentration élevé de biomasse d'organismes adaptés semble être nécessaire. Des données sur la biodégradabilité sont incomplètes pour tous les isomères et dans des conditions environnementales différentes. Il semble que la photodégradation et la volatilisation ne contribuent pas considérablement à l'élimination.
Comme les substances se solvent bien dans l'eau et log K_{ow} est bas, l'accumulation dans les sédiments et dans la matière grasse animale est basse. Prenant comme base les calculations pour la matière grasse, une facteur de bioconcentration de 1000 environ est normale pour tous les isomères, tandis qu'il n'y était pas preuve de bioaugmentation dans la chaîne alimentaire.

La toxicité pour organismes aquatiques n'a pas été documentée exhaustivement pour tous les isomères. Les chloronitrobenzènes ne montrent pas une augmentation d'effets toxiques après exposition prolongée. La dispersion de données de la toxicité pour les différents isomères ainsi que pour les différentes espèces de test est petite. Les données varient entre 1,5 et 11 mg/l.
La concentration acceptable au maximum dans l'écosystème a été calculée par la méthode d'EPA modifiée: la CL_{50} la plus basse fut divisée par 100 pour avoir comme résultat 10 µg/l. On s'attend à ce que les effets des chloronitrobenzènes soient additifs. C'est pourquoi on propose une norme de qualité aquatique de 10 µg/l pour l'ensemble de tous les chloronitrobenzènes. (N.B.: Ce niveau ne tient pas compte du fait que d'autres polluants industriels peuvent être présents en même temps.) Ce niveau est une facteur 5 à 1000 au-dessus des concentrations mesurées dans les eaux fluviales.

La proposition d'une norme de qualité aquatique de 10 µg/l pour l'ensemble de tous les chloronitrobenzènes est comparable à celle du Programme Rhin Action (1991) de 1 µg/l pour les isomères le 2-chloronitrobenzène et le 4-chloronitro.

Les données sur la toxicité pour les mammifères sont incomplètes. La dose la plus basse qui cause d'effets chroniques a été mentionnée pour le 2-chloronitrobenzène: 40 mg/kg poids/jour (administration orale à un rat pendant 78 semaines).

Si l'on se base sur la norme de qualité aquatique proposée de 10 µg/l, la prise maximale par jour pour l'homme sera estimée à 3,1 µg/kg poids/jour, ce qui est beaucoup plus bas que la dose la plus basse pour laquelle a èté mentionnée des effets.

SAMENVATTING

Het effect van monochloornitrobenzenen, dichloornitrobenzenen en 4-chloor-2-nitroaniline op het aquatisch milieu is geëvalueerd om een toxicologische basis te verschaffen aan een voorstel voor waterkwaliteitsnormen. Informatie is verzameld aangaande hun fysisch en chemische eigenschappen, afbreekbaarheid, toxiciteit, chemische detectie en concentraties in het milieu. Tabel i geeft een overzicht van de beschikbaarheid van gegevens over deze onderwerpen.

De drie monochloornitrobenzeen isomeren en alle zes dichloornitrobenzeen isomeren behalve het 2,6-isomeer vinden uitgebreide toepassing in de chemische industrie in een groot scala aan produkten. 4-Chloor-2-nitroaniline is een grondstof voor de kleurstoffenindustrie.
De gezamenlijke produktie in de EG van de stoffen 2-, 3-, 4-, en 4-chloor-2-nitroaniline was respectievelijk > 25000 (1985), > 4000 (1987), > 45000 (1985) en 500 - 1000 ton per jaar (1987).

Gechloreerde nitroaromaten kunnen chemisch worden geanalyseerd met gaschromatografie en ECD, waarbij een detectiegrens van 50 ng/l kan worden bereikt. Hiermee lijkt echter nog niet veel ervaring te bestaan. Concentraties gemeten in rivierwater in industriegebieden variëren tussen 0,01 en 2 µg/l.

De stoffen kunnen uit het aquatische systeem verdwijnen door biodegradatie, maar omdat hiervoor waarschijnlijk een hoge concentratie biomassa met geadapteerde organismen nodig is, zal de afbraaksnelheid wel laag zijn. De kennis over de biologische afbraak onder verschillende milieuomstandigheden en voor alle isomeren is onvolledig. Fotodegradatie en vervluchtiging lijken geen belangrijke bijdrage te leveren aan het verdwijnen van de stoffen uit het water.
Aangezien de stoffen goed wateroplosbaar zijn en een lage log K_{ow} hebben, is de accumulatie in sediment en dierlijk vetweefsel gering. Uit berekeningen volgt een bioconcentratiefactor in vetweefsel van 1000 voor alle isomeren, maar biomagnificatie in de voedselketen is niet aangetoond.

De aquatische toxiciteit is niet voor alle isomeren volledig beschreven. Chloornitrobenzenen vertonen bij verlengde blootstellingsduur geen toename van de toxische effecten. De spreiding van de toxiciteitsgegevens is klein, zowel voor de verschillende isomeren als voor de verschillende testsoorten. De waarden liggen tussen 1,5 en 11 mg/l.
De $NOEC_{ecosysteem}$ is geschat met behulp van de gewijzigde EPA methode: de laagste LC_{50} is gedeeld door 100, hetgeen resulteert in een concentratie van 10 µg/l. De toxische werking van de chloornitrobenzenen is naar verwachting additief. Daarom wordt een waterkwaliteitsnorm van 10 µg/l voorgesteld voor de som van alle chloornitrobenzenen. (N.B. Dit niveau houdt er dus geen rekening mee dat er tegelijkertijd ook andere verontreinigingen van industriële herkomst aanwezig kunnen zijn.) Deze voorgestelde norm ligt een factor 5 tot 1000 boven de concentraties die in rivierwater zijn gemeten.

Het voorstel voor een waterkwaliteitsnorm van 10 µg/l voor de som van alle chloornitrobenzenen is goed vergelijkbaar met de voorstellen van het Rijn Actie Programma (1991) van 1 µg/l voor twee isomeren, namelijk 2-chloornitrobenzeen en 4-chloornitrobenzeen.

De gegevens over de toxiciteit voor zoogdieren zijn onvolledig. De laagste dosis waarbij chronische effecten optreden is beschreven voor 2-chloornitrobenzeen: 40 mg/kg lichaamsgewicht/dag (orale toediening aan een rat gedurende 78 weken). Uitgaande van de voorgestelde norm van 10 µg/l wordt de dagelijkse inname voor de mens ruwweg geschat op 3,1 µg/kg lichaamsgewicht/dag en dit ligt ver onder de laagste dosis waarvoor effecten zijn beschreven.

CONTENTS

CONTENTS (cont'd)

1 DESCRIPTION

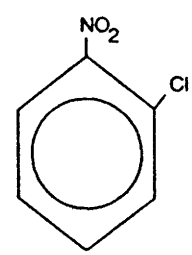
The group of chloronitrobenzenes consists of 3 isomers: 2-chloro-, 3-chloro- and 4-chloronitrobenzene. Chloronitrobenzenes are widely used in the chemical industry in the manufacture of nitrophenols, nitroanilines and chloroanilines or as intermediates in the dye stuff, pigments and rubber industries, in the pharmaceutical and plant-protection sectors and as corrosion-inhibitors.
In the environment they may be produced by oxidation of chloroanilines and they are detected in tap water as a result of the chlorination of water containing nitrobenzene traces.

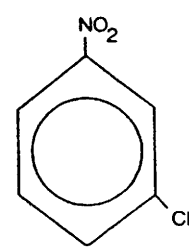
Dichloronitrobenzenes consists of 6 isomers: 2,3-dichloro-, 2,4-dichloro-, 2,5-dichloro-, 2,6-dichloro-, 3,4-dichloro-, and 3,5-dichloronitrobenzene. Most of these isomers are widely used in the chemical industry for the manufacture of dichloroanilines, dichlorodinitrobenzenes, chloronitrophenols, chloronitroanisoles and chloronitroanilines which can be used for the production of pesticides like Flamprop or dye stuffs. Only 2,6-dichloronitrobenzene is technically unimportant.

4-Chloro-2-nitroaniline can be formed from ammonolysis of 2,5-dichloronitrobenzene or chlorination of 2-nitroaniline. It is used in dye industries for the development of dyestuffs on fibres. Several dye stuffs are manufactured with the diazonium-salt of 4-chloro-2-nitroaniline from which it can be released under reducing conditions. Examples of dye stuffs from which it can be released are Pigment Yellow 3, C.I. 11710; Pigment Red 6, C.I. 12090; Pigment Red 15, C.I. 12465.

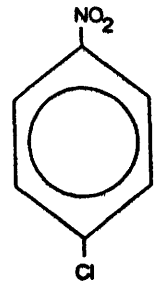
Data were derived from Cabridenc (1984) and De Bruin (1985)

1.1 Identification

2-chloronitrobenzene	
List I dir. 76/464/EEC	28
EINECS-no	2018549
CAS no.	88-73-3
Synonyms:	1-chloro-2-nitrobenzene O-nitrochlorobenzene O-chloronitrobenzene
Molecular formula:	$C_6H_4ClNO_2$
Structural formula:	
WLN formula:	WNR BG

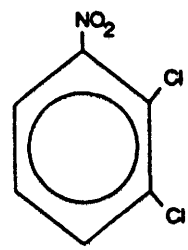
3-chloronitrobenzene	
List I dir. 76/464/EEC	29
EINECS-no	2044961
CAS no.	121-73-3
Synonyms:	1-chloro-3-nitrobenzene m-nitrochlorobenzene m-chloronitrobenzene
Molecular formula:	$C_6H_4ClNO_2$
Structural formula:	
WLN formula:	WNR CG

4-chloronitrobenzene
List I dir. 76/464/EEC 30
EINECS-no 2028096
CAS no. 100-00-5
Synonyms: 1-chloro-4-nitrobenzene
p-chloronitrobenzene
p-nitrochlorobenzene
Molecular formula: $C_6H_4ClNO_2$
Structural formula:



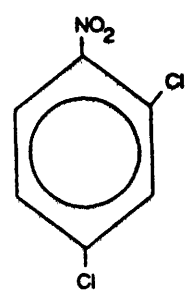
WLN formula: WNR DG

2,3-dichloronitrobenzene
List I dir. 76/464/EEC 63.001
EINECS-no.
CAS no. 3209-22-1
Synonyms: 1,2-dichloro-3-nitrobenzene
Molecular formula: $C_6H_3Cl_2NO_2$
Structural formula:



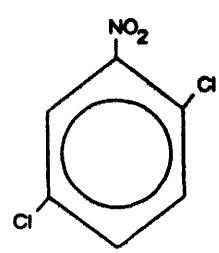
WLN-formula: WNR BG CG

2,4-dichloronitrobenzene
List I dir. 76/464/EEC 63
EINECS-no.
CAS no. 611-06-3
Synonyms: 2,4-dichloro-1-nitrobenzene
Molecular formula: $C_6H_3Cl_2NO_2$
Structural formula:



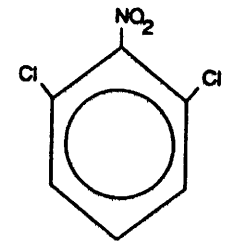
WLN formula: WNR BG DG

2,5-dichloronitrobenzene
List I dir. 76/464/EEC 63
EINECS-no.
CAS no. 89-61-2
Synonyms: 1,4-dichloro-2-nitrobenzene
Molecular formula: $C_6H_3Cl_2NO_2$
Structural formula:



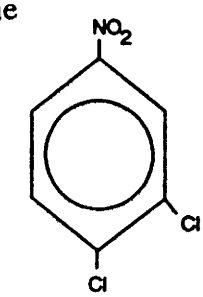
WLN formula: WNR BG EG

2,6-dichloronitrobenzene
List I dir. 76/464/EEC 63
EINECS-no.
CAS no. 89-61-2
Synonyms: 1,3-dichloro-2-nitrobenzene
Molecular formula: $C_6H_3Cl_2NO_2$
Structural formula:



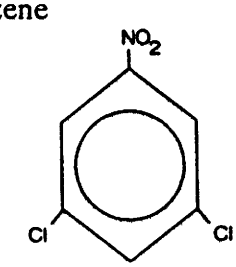
WLN formula: WNR BG FG

3,4-dichloronitrobenzene
List I dir. 76/464/EEC 63.002
EINECS-no.
CAS no. 99-54-7
Synonyms: 1,2-dichloro-4-nitrobenzene
Molecular formula: $C_6H_3Cl_2NO_2$
Structural formula:



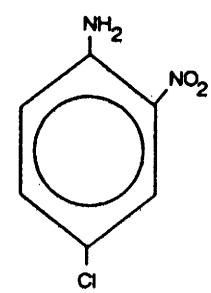
WLN formula: WNR CG DG

3,5-dichloronitrobenzene
List I dir. 76/464/EEC 63
EINECS-no.
CAS no. 618-62-2
Synonyms: 1,3-dichloro-5-nitrobenzene
Molecular formula: $C_6H_3ClNO_2$
Structural formula:



WLN formula: WNR CG EG

4-chloro-2-nitroaniline
List I dir. 76/464/EEC 27
CAS no. 89-63-4
Synonyms: p-chloro-o-nitroaniline
Red base 3 GL
azoic coupling component 9, C.I. 37040
Molecular formula: $C_6H_5ClN_2O_2$
Structural formula:



WLN formula: ZR DG BNW

The data were derived from Cabridenc (1984), Sax (1989), Verschueren (1983)

1.2 Physicochemical characteristics

	2-CNB	3-CNB	4-CNB	2,3-DCNB	2,4-DCNB
mol. weight	157.6	157.6	157.6	192	192
COD (mg O_2/mg substance)	1.22	1.22	1.22	0.96	0.96
mg substance/mg organic Cl	4.44	4.44	4.44	2.71	2.71
melting point (°C)	34	46	84	62	34
boiling point (°C)	246	236	242	258	258
density (20° / 4°C)					
vapour pressure (mm Hg) at 20°C	0.0015	0.0031	0.002	0.0065	0.0034
water solubility (mg/l)	2700	1200	450	200	450
log K_{ow}	2.24	2.44	2.4	3.07	3.06
Henry's constant (atm.m3/mol)	1.2*10-7	5.4*10-7	10-6	3.7*10-7	3.7*10-7
standard half-life (h) (volatilization)	9400	2000	1000	1400	3200
pKa					
Koc	150	210	200	720	700
BCF	30	42	39	130	130

	2,5-DCNB	2,6-DCNB	3,4-DCNB	3,5-DCNB	4-C-2-NA
mol. weight	192	192	192	192	172.6
COD (mg O2/mg substance)	0.96	0.96	0.96	0.96	1.16
mg substance/mg organic Cl	2.71	2.71	2.71	2.71	4.87
melting point (°C)	56	73	43	25	117
boiling point (°C)	267	258	256	253	273
density (20° / 4°C)					
vapour pressure (mm Hg) at 20°C	0.00065	0.00067	0.00078	0.00093	0.00017
water solubility (mg/l)	240	160	300	490	290
log K_{ow}	3.07	3.04	3.12	3.13	2.23
Henry's constant (atm.m3/mol at 20°C)	11*10-7	8.5*10-7	6.6*10-7	4.9*10-7	1.3*10-7
standard half-life (h) (volatilization)	3200	1100	1800	2400	8500
pKa		1.9			
Koc	720	680	790	800	140
BCF	120	120	140	140	29

Data were derived from Keuning and Janssen (1987), Sax (1989), Verschueren, (1983), Cabridenc (1984) and De Bruin (1985).

1.3 Production levels

Data on production of chloronitrobenzeen in EC are presented in Table 1.1., derived for EURECO (1990).
No data were available for dichlorobenzenes.

Table 1.1 Production levels of chloronitrobenzenes and 4-chloro-2-nitroaniline in EC countries

Country	Capacity in t/y * actual production								Producer
	2-CNB		3-CNB		4-CNB		4-C-2-NA		
Belgium									
Denmark									
France	+	[1]	+	[4]	+	[1,4]	700 (y88)	[1,5]	ICMD (Mulhouse)
FRG (Germany)	+	[1]	+	[4,1]	1-3000 y87	[1,4]	350 y90	[2]	Bayer AG (Leverkusen)
	+	[2]	+	[2]	+	[2]	350* y90	[2]	Hoecht AG (Frankfurt)
	25000 y85	[3]	1-3000 y85	[4]	25-45000 y85	[4]			Total FRG
Greece									
Ireland									
Italy	+	[1]	+	[4]	+	[1,4]	+	[1]	ACNA Chimica Organica (Cengio)
Luxemburg									
Netherlands									
Portugal									
Spain									
United Kingdom	340* y90	[2]	850* y90	[2]	120* y90	[2]	-		Hicskon & Welch Ltd. (Castleford)
	-		-		1340* y90	[2]	-		ICI (Huddersfield/-Severnside)
Total Production EC			>4000 (y87)	[1]			500-1000 (y87)	[1]	

1 Water Research Centre (1987)
2 Information obtained from industry (EURECO, 1990)
3 Gesellschaft Deutscher Chemiker (1985)
4 Gesellschaft Deutscher Chemiker (1988)
5 Water Research Centre (1984)

2 ANALYTICAL DETECTION TECHNIQUES

2.1 Detection methods

In the previous report to the EC, Cabridenc (1984) did not report on detection methods for chlorinated nitroaromates.

Feltes et al. (1990) compared several methods for the determination of nitroaromatic compounds. They concluded that a good detection is possible by extraction with dichloromethane or by adsorption on Amberlite resins, followed by gas chromatography, using a Electron Capture Detector (ECD) or Thermo-Energy Analysis (TEA). ECD-detection is more sensitive but less selective having a detection limit of 50 ng/l and a relative standard deviation (RSD) of less than 9%. TEA is less sensitive but more selective having a detection limit of 500 ng/l and a RSD less than 10%. Definite compound assignment can usually be achieved with GC-MS.

Scholz and Palauschek (1988) studied the detection of substituted aromatic amines in water and in sediment.
After extraction with toluene and/or dichloromethane water and sediment samples were pretreated by gel permeation chromatography (GPC) or by hydrochloric acid (HCl). As detection method was used gas chromatography (GC) with alkali flame ionization detector (NFID) or GC with mass spectrometry (MS).
The detection limit for 4-chloro-2-nitroaniline was (with internal standard) 10 µg/kg in sediment and 0.5 µg/l in water samples.

Rivera et al. (1987) studied the concentration of many organic pollutants in the river Lobregat in Spain. They also analysed 1-chloro-3-nitrobenzene. As detection methods they used GC-FID, GC-MS and HPLC.

2.2 Conclusions

Limited literature is found on detection methods for chlorinated nitroaromates. However, from the available literature it can be concluded that after extraction and separation with GC and HPLC various detection techniques can be used, such as ECD, TEA, NFID and MS. Detection limits can be as low as 50 ng/l with ECD. The detection limit will also be dependant on the complexity of the samples.

3 ENVIRONMENTAL LEVELS

Chlorinated nitroaromates are widely used in the chemical industry and may be released into the environment directly as a result of their application in the manufacturing process or indirectly after decomposition of materials in which they were used as raw material, e.g. pesticides.
In the environment chlorinated nitroaromates may be produced by oxidation of chloroanilines and they may be detected in tapwater as a result of the chlorination of water containing nitrobenzene traces.

3.1 Residues in the atmosphere

No data have been found on atmospheric levels of chlorinated nitroaromates.

3.2 Residues in soil and sediment

For 3-chloronitrobenzene Alberti (1982) reported a concentration of 0.05 µg/kg in dry sediment in the river Rhine in Germany.
For the other selected nitroaromates no data have been found.

3.3 Residues in water

In 1976 sum concentrations of chloronitrobenzenes are measured in the river Waal and Meuse of 0.80 and 0.03-0.10 µg/l, respectively (ECETOC, 1988).

Petersen (1986) studied the concentration of chloronitrobenzenes at many locations in three rivers in Germany: the Rhine, Main and Elbe. For 4-chloronitrobenzene the following concentration ranges were reported: Rhine 0.01 - 0.50 µg/l; Main 0 - 1 µg/l; Elbe 0.1 - 1.19 µg/l. For each of the chloronitrobenzenes concentrations were found to be between 0.03 and 1.7 µg/l.

Rivera et al. (1987) analysed the water of the Llobregat river in Spain and identified among many other substances 3-chloronitrobenzene. Nothing was reported on the concentration of this substance.

Scholz and Palauschek (1988) reported that concentrations of 4-chloro-2-nitroanaline together with 2-chloro-5-nitroaniline in surface water and waste water samples range between 0.9 and 39 µg/l. The authors did not give information on the location where the samples were taken.

Feltes (1990) reported concentration levels in the River Rhine at Mainz: 0.08-0.12 µg/l for 2-chloronitrobenzene and 0.17-0.19 µg/l for 2,3-dichloronitrobenzene.

3.4 Residues in aquatic organisms

Environmental monitoring studies showed chloronitrobenzenes to be present in fish from the River Rhine although no concentrations have been reported (Steinwandter, 1987). Residues of three monochloronitrobenzenes and two dichloronitrobenzenes found in several species of fish from the Mississippi River, were generally in the range of 0.05 to 0.2 mg/kg (Yurawecz and Puma, 1983).

3.5 Residues in terrestrial organism

No data have been found on concentration levels in terrestrial organisms.

3.6 Conclusions

Chlorinated nitroaromates have been identified in the environment, especially in water and in fish. The concentration levels varied between 0.01 and 2 µg/l. No data are available on concentration levels in the atmosphere and in terrestrial organisms. Therefore, it is not possible to determine the actual partitioning of these compounds between the environmental compartments.

4 PERSISTENCE AND DEGRADATION PATHWAYS

4.1 Abiotic degradation in the aquatic environment

4.1.1 Abiotic degradation

In the previous evaluation for the EC, Cabridenc (1984) did not report chemical degradation for the nitroaromates.

It is expected that the reactivity of the chlorinated nitroaromates is low due to the stability of the aromatic ring. This might be a reason for the fact that not much is published on this subject.

Guittonneau et al. (1989) found a half-life of >60 and 9 minutes for the photo-degradation of 4-chloronitrobenzene with UV-light and UV-light with hydroxyl radicals, respectively. However, the question remains whether the results of this type of laboratory experiments can be interpreted in relation to the occurrence of chemical degradation processes in the aquatic environment.

4-Chloronitrobenzene was determined as a product of the photo-oxidation of 4-chloroaniline with UV-light. In this experiment 4-chloronitrobenzene was found to be rather stable to photochemical degradation (Miller and Crosby, 1983).

No data have been found on the other selected chlorinated nitroaromates.

4.1.2 Conclusions

Information on the abiotic degradation of nitroaromates in the aquatic environment is absent. This might be caused by the low reactivity of these substances under environmental conditions.

4.2 Biological degradation and metabolism

The following literature study is based on a review report on biodegradability of priority chemicals by Keuning and Janssen (1987). In an additional search relevant international literature from 1986 until the beginning of 1991 was screened for publications on biodegradation of chloronitrobenzenes.

4.2.1 Biodegradation under experimental conditions

Standardised tests are available to determine biodegradation under aerobic conditions (Annex V in Dir. 79/831/EEC). However, most of the studies reported in literature do not comply with these standardised methods. Therefore an attempt is made to classify the substances in line with definitions used by OECD and EC on the basis of the available data on test conditions and results. The following definitions are used:
Primary degradation is the alteration of the chemical structure resulting in the loss of a specific property; or the loss of the parent compound. Ultimate biodegradation or mineralization is achieved when the test compound is totally utilized by micro-organisms, producing carbondioxide, water, mineral salts and new biomass.
A substance is classified as readily biodegradable if it shows a positive result in some defined stringent test methods which provide limited opportunities for biodegradation and acclimatization. Readily biodegradable substances are assumed to undergo rapid and ultimate biodegradation in the environment. Substances that biodegrade under more favourable test conditions (prolonged exposure, high biomass concentration, low substance concentration) may be classified as inherently

biodegradable. This does not necessarily mean that mineralization is complete, nor that rapid and reliable biodegradation in the environment will occur.

A negative result in a ready biodegradability test does not necessarily mean that the chemical will not be biodegraded under relevant environmental conditions. If for example in the test, the test substance is at a level which inhibits microbial activity, the method is not appropriate.

According to Canton et al. (1985) the revised OECD test (1971), the Pitter test (Pitter, 1976) and/or the Repetitive Die Away Test (Blok, 1979) indicated that 2-chloronitrobenzene, 3-chloronitrobenzene, 4-chloronitrobenzene and 2,3-dichloronitrobenzene cannot be biodegraded in these tests where conditions are comparable to ready biodegradability tests, with both non-adapted and adapted inoculum.
The isomers 2-chloronitrobenzene and 4-chloronitrobenzene were also not biodegradable in MITI's test for ready biodegradability (MITI, 1985).

However, Canton et al. (1985) nor MITI (1985) indicate inclusion of a toxicity control in their experiments. Information on the toxicity of chloronitrobenzenes for bacteria is limited to Microtox data (*Photobacterium phosphoreum*), which range between 1.5 and 30 mg/l, see Chapter 7. This implies that the negative results in tests for ready biodegradability could possibly be connected to inhibition of the microbial activity. Another possibility is the lack of adapted micro-organisms in the standard tests. Indeed, inherent biodegradability of chloronitrobenzenes was shown in studies with adapted micro-organisms which had been exposed for longer periods.

4.2.2 Biodegradation in simulation tests

According to Grote et al. (1983) micro-organisms from an industrial treatment plant can adapt (in an activated sludge aeration tank) to degrade 3,4-dichloronitrobenzene which was added to industrial wastewater at a concentration of 0.5 - 8 mg/l. The first step of the metabolism consists of the reduction of 3,4-dichloronitrobenzene to 3,4-dichloroaniline, which is degraded almost immediately to levels below the detection limit. Shock loadings of 3,4-dichloronitrobenzene and/or 3,4-dichloroaniline can interfere with the metabolic pathway of 3,4-dichloronitrobenzene. In this case the effluent may contain both 3,4-dichloronitrobenzene and 3,4-dichloroaniline. These results indicate that 3,4-dichloronitrobenzene may be considered as inherently biodegradable.

Jakobczyk et al. (1984) also observed adaptation of micro-organisms from treatment plants to chloronitrobenzenes. After an adaptation period of approximately 6 months in an activated sludge aeration tank, a mixture of chloro-nitrocompounds in industrial wastewater (e.g. 1-chloro-2,4-dinitrobenzene, 2- and 4-chloronitrobenzene and 1,4-dichloro-2-nitrobenzene; total concentration in influent approximately 60 mg/l) a degradation of 70 to 90 % was reached with a mean residence time of 0.9 days at 34oC. The primary degradation of a mixture with a total concentration up to 100 mg/l reached 99% in a biological film settled on a disc at 22°C. Therefore the tested compounds may be considered as inherently biodegradable.

Voelskow (1984) isolated from soil and activated sludge pure and mixed cultures that could degrade chloronitrobenzenes. Addition of an easily biodegradable substrate like nitrobenzene or ethanol enhanced the capacity to degrade

chloronitrobenzene. A *Pseudomonas* was isolated that grew on a mixture of 3-chloronitrobenzene and ethanol.

Corbett and Corbett (1981) studied the aerobic metabolism of 4-chloronitrobenzene by species of the yeast *Rhodosporium*. Degradation took place via a reductive route and 4-chloronitrobenzene was partially and co-metabolically degraded. The main metabolites were 4-chloro-acetanilide and 4-chloro-2-hydroxyacetanilide. The aromate ring was left intact.

Tahara et al. (1981) described the metabolism of 2,4-dichloronitrobenzene by the fungus *Mucor javanicus*. Metabolites were 2,4-dichloroaniline, 4-chloro-2-methylthio-1-nitrobenzene and 4-chloro-2-methylthiobenzenamine. Further degradation of these metabolites was not described.

Almost no data are available on the anaerobic degradation of chloronitrobenzenes. Gvodzdyak et al. (1982, abstract) described the complete degradation of 4-chloronitrobenzene in a concentration of 0.05 mg/l in wastewater by immobilised micro-organisms under anaerobic conditions. During the anaerobic degradation the amount of sulfate-reducing and denitrifying bacteria increased.

A summary of the data supplied by the present study is given in Table 4.2.1.

Almost no data are available on biodegradation of chloronitrobenzenes in the natural environment. In view of the results of laboratory experiments it seems possible that chloronitrobenzenes are biodegraded under aerobic conditions in natural environments as a result of adaptation of native populations of micro-organisms.

4.2.3 Conclusions

In the previous report to the EC, (Cabridenc, 1984) it was concluded that 2-, 3- and 4-chloronitrobenzene could be partly metabolized by pre-adapted organisms but that their total ("ultimate") biodegradation had not been proven.

In the present study no studies were found on the biodegradation of 2,6-dichloro- and 3,5-dichloronitrobenzene and on 4-chloro-2-nitroaniline.

The present study indicates that both 2-chloro- and 4-chloronitrobenzene may be considered as inherently biodegradable. Also 2,4-dichloro-, 2,5-dichloro- and 3,4-dichloronitrobenzene were shown to be inherently biodegradable. Both 3-chloronitrobenzene and 2,3-dichloronitrobenzene were not tested in systems that could indicate inherent biodegradability, but in view of the above results with isomers, inherent biodegradation cannot be precluded.
Activated sludge can adapt to the degradation of these substances, so removal of chloronitrobenzenes from wastewater seems possible.

Biodegradation under anaerobic conditions seems possible, but data are very limited.

Table 4.2.1 Biodegradation of chloronitrobenzenes

Compound	Conditions	Results	Ref.
2-chloronitrobenzene	OECD*, RDA*, Pitter, adapted inoculum	not readily biodegradable	1
	MITI*	not readily biodegradable	2
	activated sludge or biofilm, adapted, mixture with related substances, ≤100 mg/l	biodeg. >99%, inherently biodegradable	4
3-chloronitrobenzene	OECD*, RDA*, Pitter*, adapted inoculum	not readily biodegradable	1
4-chloronitrobenzene	OECD*, RDA*, Pitter*, adapted inoculum	not readily biodegradable	1
	MITI*	not readily biodegradable	2
	activated sludge or biofilm, adapted, mixture with related substances, ≤100 mg/l	biodeg. >99%, inherently biodegradable	4
	Rhodosporidium culture (yeast)	cometabolic primary degradation reductive route	5
	anaerobic conditions, immobilized micro-organisms, 0.05 mg/l in waste water	complete degradation, growth of sulphate reducing and denitrifying bacteria	7
2,3-dichloronitrobenzene	OECD*, Pitter*, adapted inoculum	not readily biodegradable	1
2,4-dichloronitrobenzene	activated sludge or biofilm, adapted, mixture with related substances, ≤100 mg/l	biodeg. >99%, inherently biodegradable	4
	Mucor javanicus culture (fungus)	primary degradation	6
2,5-dichloronitrobenzene	activated sludge or biofilm, adapted, mixture with related substances, ≤100 mg/l	biodeg. >99%, inherently biodegradable	4
2,6-dichloronitrobenzene			
3,4-dichloronitrobenzene	activated sludge, adapted, fed with 0.5 - 8 mg/l added to industrial waste water	biodegrad. 90-98%, inherently biodegradable	3
3,5-dichloronitrobenzene			
4-chloro-2-aniline			

*) Conditions comparable to screening tests for ready biodegradability according to OECD

References:

1. Canton et al., 1985;
2. MITI, 1985;
3. Grote et al., 1983;
4. Jacóbczyk, 1984;
5. Corbett and Corbett, 1981;
6. Tahara et al., 1981;
7. Gvodzdyak et al., 1982.

5 DISTRIBUTION BETWEEN ENVIRONMENTAL COMPARTMENTS

The behaviour of a chemical is not only dependant on degradation but also on a number of physical and chemical characteristics such as volatilization, sorption and bioaccumulation.

5.1 Volatilization

No volatilization data have been found on chlorinated nitroaromates.

In recent years several models have been developed to estimate the volatilization behaviour of substances in the natural environment. In this evaluation study the estimation method developed by De Bruin (1985) is used to estimate the volatilization half-life ("standard half-life"). The calculation is based on physical parameters like water solubility, vapour pressure, water flow rate (1 m/s), air flow (3 m/s) and water depth (1 m). The calculation method is presented in Appendix 1. Table 5.1.1 shows the calculated half-lives for the selected chlorinated nitroaromates.

Table 5.1.1 The calculated volatilization rate (standard half-life) of the chlorinated nitroaromates according to De Bruin (1985).

Substance	Half-life (h)
2-chloronitrobenzene	9400
3-chloronitrobenzene	2000
4-chloronitrobenzene	1000
2,3-dichloronitrobenzene	1400
2,4-dichloronitrobenzene	3200
2,5-dichloronitrobenzene	3200
2,6-dichloronitrobenzene	1100
3,4-dichloronitrobenzene	1800
3,5-dichloronitrobenzene	2400
4-chloro-2-nitroaniline	8500

For a proper comparison of the volatility of the substances, Table 5.1.1 can be used, since those calculations are based on identical physical and chemical properties and assumptions. The calculated half-lives are relatively long, implying that volatilization of these substances is not an important factor for elimination from the aquatic environment. For example, for 2,4-dichloronitrobenzene it can be calculated that it will have been volatilized from the aquatic environment for 95 % only after ± 580 days.

5.2 Sorption

For the fate of a substance in the environment, sorption can play an important role. Substances may adsorb on sediment where they can remain for a long time. After adsorption a substance may return to the aquatic environment by desorption. It is possible to measure a distribution coefficient of a substance between sediment and water. This parameter is the sediment/water partition coefficient. The value of this coefficient is dependant on physical and chemical properties of the substances e.g. the solubility and on the organic carbon content of the sediment. Usually the partition coefficient is calculated for the carbon content of the sediment. This parameter is called the "organic carbon partition coefficient" (Koc).

For many substances the K_{oc} has been measured. For other substances the K_{oc} can be estimated from the octanol/water partition coefficient (K_{ow}) or from the water solubility of that substance. In Table 5.2.1 the estimated K_{oc}-data are presented for the selected chlorinated nitroaromates. These data have been taken from chapter 1.

Table 5.2.1 Estimated K_{oc}-values for chlorinated nitroaromates

Substance	K_{oc}-value
2-chloronitrobenzene	150
3-chloronitrobenzene	210
4-chloronitrobenzene	200
2,3-dichloronitrobenzene	720
2,4-dichloronitrobenzene	700
2,5-dichloronitrobenzene	720
2,6-dichloronitrobenzene	680
3,4-dichloronitrobenzene	790
3,5-dichloronitrobenzene	800
4-chloro-2-nitroaniline	140

From Table 5.2.1 it can be concluded that the K_{oc}-values for chlorinated nitroaromates are moderately low.

5.3 Bioaccumulation

5.3.1 Aquatic organisms

If experimental data are absent, the tendency of an organic substance to bioaccumulate may be estimated from its water-octanol partition coefficient, expressed as log K_{ow}, see chapter 1.2. If log K_{ow} is above 3, the substance is potentially accumulating in biomass. Whether accumulation actually occurs, depends among other things on the capacity of the organisms to metabolise or eliminate the substance. For both mono- and dichloronitrobenzenes, data on bioaccumulation were found for two fish species, as presented in Table 6.1.1. No accumulation data were found for 3,6-dichloronitrobenzene and 4-chloro-2-nitroaniline.

Experiments with *Poecilia reticulata* and *Salmo gairdneri* (Deneer et al., 1987 and Nimmi et al., 1989) showed that for chloronitrobenzenes and dichloronitrobenzenes steady state is reached after 6 h or at least within 5 days of exposure. Nimmi et al. (1989) found no significant correlation of BCF-values for rainbow trout *Salmo gairdneri* and the K_{ow}. However the BCF_{fat} for *Poecilia reticulata* is very well predicted by the relation log K_{ow} = BCF_{fat}. This would imply that the bioaccumulation process in *Poecilia reticulata* is a passive process governed by diffusion, and active elimination does not take place. Uptake directly from water, therefore is an important pathway for accumulation, and could account for elevated residue levels in environmental samples.

Table 5.3.1 Bioaccumulation factors for waterborne chloronitrobenzenes in different species

Compound/ test organisms	Expo/ depur. time	Expo. conc (µg/l)	BCF[1] fat	BCF[1] wet weight	Ref.
2-chloronitrobenzene					
Poecilia reticulata	72 h	6000	195	16	1
Salmo gairdneri	36 d	0.72	1488	125	2
3-chloronitrobenzene					
Poecilia reticulata	72 h	3000	263	21	1
Salmo gairdneri	36 d	0.8	928	78	2
4-chloronitrobenzene					
Poecilia reticulata	72 h	1200	288	23	1
Salmo gairdneri	36 d	0.78	1202	101	2
2,3-dichloronitrobenzene					
Poecilia reticulata	72 h	840	1023	81	1
Salmo gairdneri	36 d	0.77	1726	145	2
2,4-dichloronitrobenzene					
Poecilia reticulata	72 h	1340	1047	84	1
Salmo gairdneri	36 d	0.75	1404	118	2
2,5-dichloronitrobenzene					
Poecilia reticulata	72 h	980	831	66	1
Salmo gairdneri	36 d	0.77	1345	113	2
2,6-dichloronitrobenzene					
3,4-dichloronitrobenzene					
Salmo gairdneri	36 d	0.73	1393	117	2
3,5-dichloronitrobenzene					
Poecilia reticulata	72 h	1140	1023	81	1
Salmo gairdneri	36 d	0.76	2000	168	2
4-chloro-2-nitroaniline					

[1] BCF: Steady state conc. in organism / conc. in water.

References:
1 Deneer et al., 1987
2 Nimmi et al., 1989

5.3.2. Terrestrial organisms

No references were found on bioaccumulation of chloronitrobenzenes in terrestrial species.

5.3.3 Biomagnification

No detectable levels were found in fish after dietary exposure to chloronitrobenzene suggesting that these chemicals do not accumulate in organisms. Biomagnification is presumably minimal because of short half-life and low dietary absorption efficiency (Nimmi, 1989).

5.3.4 Conclusions on bioaccumulation

Chloronitrobenzenes bioaccumulate in fish. For guppy the level is reliably predicted by the log K_{ow}-value. However, biomagnification of these substances are presumably minimal.

5.4 Environmental distribution

Although only limited information is available, some generalizations on environmental distribution of chloronitrobenzenes can be made. Chloronitrobenzenes which are released into the aquatic environment will solve in water. Volatilization is not considered to be important. The substances are expected to partition to organic matter in the sediment and a partition equilibrium will be maintained by adsorption/desorption processes. Chloronitrobenzenes will also accumulate in fish (see chapter 6). The chemical reactivity of these substances under environmental conditions is considered to be very low. However, as most of the mono- and dichloronitrobenzenes were shown to be inherently biodegradable, they may be degraded in the sediment but only under favourable conditions. Biodegradation seems to be the only pathway to eliminate chlorinated nitrobenzenes. Therefore it is expected that under conditions with low microbial activity these substances may persist in the aquatic environment for a rather long time.

6 TOXICITY

6.1 Aquatic organisms

6.1.1 Chloronitrobenzenes

All information available on chloronitrobenzenes is summarized in Table 6.1.1 to 6.1.3. The tables presented in the previous EC report (Cabridenc, 1984) with E(L)C50-data of 2-chloronitrobenzene, 3-chloronitrobenzene and 4-chloronitrobenzene are included in the Tables.

Freshwater organisms

Toxicity data are available for algae, crustaceans and fish. The acute E(L)C50-values for the three isomers range from 1.2 to 34 mg/l. No specific sensitive species could be distinguished.

Limited information on chronic toxicity was available; only for 2-chloronitrobenzene and 4-chloronitrobenzene a prolonged test for *Daphnia magna* was available with a NOEC of 4.0 and 0.32 mg/l, respectively. These data show that prolonged exposure to these substances does not significantly lower the effect levels in *Daphnia magna*.

Marine organisms

From acute toxicity data in Microtox experiments with *Photobacterium phosphoreum* it may be concluded that 2-chloronitrobenzene is slightly more toxic than the other two isomers. Toxicity data available on freshwater test species like algae, Daphnia and guppy, however, do not support this finding. One acute LC50 of 0.55 mg/l is mentioned in the previous EC report (Cabridenc, 1984) for 2-chloronitrobenzene for a marine fish, which is relatively low in comparison to the freshwater toxicity data.

No data for the chronic toxicity of chloronitrobenzenes were found for marine organisms.

6.1.2 Dichloronitrobenzenes

All information available on dichloronitrobenzenes is summarized in Tables 6.1.4 to 6.1.9. If data were available for both freshwater and marine organisms they have been reported in separate tables (a and b). No toxicity data were found on 2,6-dichloronitrobenzene.

Freshwater organisms

For 2,3-dichloronitrobenzene, 2,4-dichloronitrobenzene and 2,5-dichloro-nitrobenzene acute toxicity data were found for bacteria, algae, crustaceans and fish. For most of the species and most of the isomers the E(L)C50 values ranged from 1.5 to 11 mg/l. No specific sensitive species could be distinguished. The lowest EC50-value was 0.39 mg/l for 2,3-dichloronitrobenzene in a test with *Poecilia reticulata*.

It has to be noted that only a small difference exists between chronic E(L)C50-values (3.5-6.7 mg/l) and acute E(L)C50-values. No chronic NOEC-values were available.

Marine organisms

No information is available on the toxicity of dichloronitrobenzenes to marine organisms.

Table 6.1.1a Single species toxicity data for 2-chloronitrobenzene - freshwater organisms

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Hardness/ mg $CaCO_3$/l	Expo time	Parameter	Results (mg/l) (95% C.V.)	Reference	Quality
Algae												
Chlorella pyrenoidosa	-	N	-	-	-	-	-	4 d	EC_{50} growth	6.9 (5.7-8.4)	Deneer et al., 1987	#2
Scenedesmus pannonicus	-	A	-	>99.9%	-	-	-	4 d	EC_{50} growth	24	Canton et al., 1985	#2 OECD, 1979
Crustaceans												
Daphnia magna	-	A	-	>99.9%	-	-	-	2 d	EC_{50} immobility	3.2	Canton et al., 1985	#2 OECD, 1979
Daphnia magna	24 h	N	R (3-4 d)	-	Enr. deionized water + tapwater	8.0	250	21 d	NOEC repr. + mort.	4.0	Kühn et al., 1989	#2
Daphnia magna	24 h	N	S	-	Enr. deionized water + tapwater	8.0	250	1 d	EC_{50} immobility	5.0	Kühn et al., 1989	#2
Daphnia magna	-	N	R	-	Art. medium	8.4	200	21 d	EC_{50} immobility	10.7 (10.3-11.0)	Deneer et al., 1987	#2NEN6502 (1980)
									LOEC pop.growth rate	10		
									LOEC immobility	10		
Daphnia magna	-	N	S	-	Art. medium	8.4	200	2 d	EC_{50} immobility	24 (18-32)	Deneer et al., 1987	#2 NEN 6501 (1980)
Fish												
Brachydanio rerio	-	N	-	>98% (DMSO)	Standard water	8.2	250	7 d	LC_{50}	14 (3.2-32)	Maas-Diepeveen, 1986	#2
									EC_{50} development	14 (3.2-32)		
Poecilia reticulata	-	A	-	>99.9%	-	-	-	4 d	EC_{50} behav.	1.8	Canton et al., 1985	#2 OECD, 1979
									LC_{50}	30		
Poecilia reticulata	2-3 month	A	R	>99%	Standard water	6.8-7.2	25	14 d	LC_{50}	30	Deneer et al., 1987	#1

Table 6.1.1b Single species toxicity data for 2-chloronitrobenzene - marine organisms

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Salinity ‰	Expo time	Parameter	Results (mg/l) (95% C.V.)	Reference	Quality
Bacteria												
Photobacterium phosphoreum	-	-	Microtox	-	-	-	-	30 min	EC_{50} photoluminescense	4.3	Devillers et al., 1986	#2
Photobacterium phosphoreum	-	N	Microtox	-	-	-	-	15 min	EC_{50} photoluminescense	4.6 (4.4-4.8)	Deneer et al., 1987	#2

Table 6.1.2a Single species toxicity data for 3-chloronitrobenzene - freshwater organisms

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Hardness/ mg $CaCO_3$/l	Expo time	Parameter	Results (mg/l) (95% C.V.)	Reference	Quality
Algae												
Chlorella pyrenoidosa	-	N	-	-	-	-	-	4 d	EC_{50} growth	1.9 (1.5-2.6)	Deneer et al., 1987	#2
Scenedesmus pannonicus	-	A	-	99.7%	-	-	-	4 d	EC_{50} growth	3.6	Canton et al., 1985	#2 OECD, 1979
Crustaceans												
Daphnia magna	-	A	-	99.7%	-	-	-	2 d	EC_{50} immobility	4.5	Canton et al., 1985	#2 OECD, 1979
Daphnia magna 6501	-	N	S	-	Art. medium	8.4	200	2 d	EC_{50} immobility	20 (10-32)	Deneer et al., 1987	#2 NEN (1980)
Fish												
Brachydanio rerio	-	N	-	>98% (DMSO)	Standard water	8.2	250	7 d	EC_{50} development	39 (10-100)	Maas-Diepeveen, 1986	#2
								7 d	LC_{50}	56 (32-100)		
Pimephales promelas	31-35 d 148 mg		F 67 ml/ min	98%	Lakewater	6.9-7.7	44.9 (42-47)	4 d	LC_{50}	18.0 (17.7-18.3)	Holcombe et al.,1984	#1
Poecilia reticulata	-	A	-	99.7%	-	-	-	21 d	LOEC survival	1.0	Canton et al., 1985	#2 OECD, 1979
									LOEC pop. growth rate	1.8		
									EC_{50} mort. + behav.	2.0		
								4 d	LC_{50}	20		1979 #2
Poecilia reticulata	2-3 month	A	R	>98%	Standard water	6.8-7.2	15	14 d	LC_{50}	15	Deneer et al., 1987	#1

Table 6.1.2b Single species toxicity data for 3-chloronitrobenzene - marine organisms

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Salinity ‰	Expo time	Parameter	Results (mg/l) (95% C.V.)	Reference	Quality
Bacteria												
Photobacterium phosphoreum	-	N	Microtox	-	-	-	-	15 min	EC_{50} photoluminescense	13 (12.8-13.5)	Deneer et al., 1987	#2
Photobacterium phosphoreum	-	-	Microtox	-	-	-	-	30 min	EC_{50} photoluminescense	20	Devillers et al., 1986	#2

Table 6.1.3a Single species toxicity data for 4-chloronitrobenzene - freshwater organisms

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Hardness/ mg $CaCO_3$/l	Expo time	Parameter	Results (mg/l) (95% C.V.)	Reference	Quality
Algae												
Chlorella pyrenoidosa	-	N	-	-	-	-	-	4 d	EC_{50} growth	4.9	Deneer et al., 1987	#2
Scenedesmus pannonicus	-	A	-	>99.5%	-	-	-	4 d	EC_{50} growth	5.5	Canton et al., 1985	#2 OECD, 1979
Crustaceans												
Daphnia magna	24 h	N	R (3-4 d)	-	Enr. deionized water + tapwater	8.0	250	21 d	NOEC reproduction	0.32	Kühn et al., 1989	#2
Daphnia magna	-	N	R	-	Art. medium	8.4	200	21 d	LOEC pop. growth rate LOEC survival EC_{50} immobility	1.8 3.2 4.5 (4.3-5.0)	Deneer et al., 1987	#2 NEN 6502 (1980)
Daphnia magna	-	A	-	>99.5%	-	-	-	2 d	EC_{50} immobility	2.7	Canton et al., 1985	#2 OECD, 1979
Daphnia magna	24 h	N	S	-	Enr. deionized water + tapwater	8.0	250	21 h	EC_{50} immobility	3.3	Kühn et al., 1989	#2
Daphnia magna	-	N	S	-	Art. medium	8.4	200	2 d	EC_{50} immobility	6.7	Deneer et al., 1987	#2 NEN 6501 (1980)
Fish												
Brachydanio rerio	-	N	-	>98% (DMSO)	Standard water	8.2	250	7 d	LC_{50} EC_{50} development	45 (34-59) 14 (10-19)	Maas-Diepeveen, 1986	#2
Poecilia reticulata	-	A	-	>99.5%	-	-	-	-	LC_{50} EC_{50} mort. + behav.	13 1.8	Canton et al., 1985	#2 OECD, 1979
Poecilia reticulata	2-3 month	A	R	>98%	Standard water	6.8-7.2	6.0	14 d	LC_{50}	6.0	Deneer et al., 1987	#1

Table 6.1.3b Single species toxicity data for 4-chloronitrobenzene - marine organisms

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Salinity ‰	Expo time	Parameter	Results (mg/l)	Reference	Quality
Bacteria												
Photobacterium phosphoreum	-	-	Microtox	-	-	-	-	30 min	EC_{50} photoluminescense	24	Devillers et al., 1986	#2
Photobacterium phosphoreum	-	N	Microtox	-	-	-	-	15 min	EC_{50} photoluminescense	34	Deneer et al., 1987	#2

Table 6.1.4a Single species toxicity data for 2,3-dichloronitrobenzene - freshwater organisms

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Hardness mg $CaCO_3$/l	Expo time	Parameter	Results (mg/l)	Reference	Quality
Algae												
Chlorella pyrenoidosa	-	N	-	-	-	-	-	4 d	EC_{50} growth	2.9	Deneer et al., 1987	#2
Scenedesmus pannonicus	-	A	-	99%	-	-	-	4 d	EC_{50} growth	10	Canton et al., 1985	#2 OECD, 1979
Crustaceans												
Daphnia magna	-	A	-	99%	-	-	-	2 d	EC_{50} immobility	1.6	Canton et al., 1985	#2 OECD, 1979
Daphnia magna 6502	-	N	R	-	Art. medium	8.4	200	21 d	EC_{50} immobility	3.5	Deneer et al., 1987	#2 NEN (1980)
Daphnia magna 6501	-	N	S	-	Art. medium	8.4	200	2 d	EC_{50} immobility	4.2	Deneer et al., 1987	#2 NEN (1980)
Fish												
Poecilia reticulata	-	A	-	99%	-	-	-	4 d	EC_{50} behav. LC_{50}	0.39 3.9	Canton et al., 1985	#2 OECD, 1979
Poecilia reticulata	2-3 month	A	R	>98%	Standard water	6.8-7.2	4.2	14 d	LC_{50}	4.2	Deneer et al., 1987	#1

Table 6.1.4b Single species toxicity data for 2,3-dichloronitrobenzene - marine organisms

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Salinity ‰	Expo time	Parameter	Results (mg/l)	Reference	Quality
Bacteria												
Photobacterium phosphoreum	-	-	Microtox	-	-	-	-	30 min	EC_{50} photoluminescense	1.5	Devillers et al., 1986	#2
Photobacterium phosphoreum	-	N	Microtox	-	-	-	-	15 min	EC_{50} photoluminescense	1.5	Deneer et al., 1987	#2

Table 6.1.5a Single species toxicity data for 2,4-dichloronitrobenzene - freshwater organisms

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Hardness/ mg $CaCO_3$/l	Expo time	Parameter	Results (mg/l)	Reference	Quality
Algae												
Chlorella pyrenoidosa	-	N	-	-	-	-	-	4 d	EC_{50} growth	2.4	Deneer et al., 1987	#2
Crustaceans												
Daphnia magna	-	N	R	-	Art. medium	8.4	200	2 d	EC_{50} immobility	4.2	Deneer et al., 1987	#2 NEN 6501 (1980)
Fish												
Poecilia reticulata	2-3 month	A	R	>98%	Standard water	6.8-7.2	6.7	14 d	LC_{50}	6.7	Deneer et al., 1987	#1

Table 6.1.5b Single species toxicity data for 2,4-dichloronitrobenzene - marine organisms

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Salinity ‰	Expo time	Parameter	Results (mg/l)	Reference	Quality
Bacteria												
Photobacterium phosphoreum	-	-	Microtox	-	-	-	-	30 min	EC_{50} photoluminescense	3.2	Devillers et al., 1986	#2
Photobacterium phosphoreum	-	N	Microtox	-	-	-	-	15 min	EC_{50} photoluminescense	1.7	Deneer et al., 1987	#2

Table 6.1.6a Single species toxicity data for 2,5-dichloronitrobenzene - freshwater organisms

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Hardness/ mg $CaCO_3$/l	Expo time	Parameter	Results (mg/l) (95% C.V.)	Reference	Quality
Algae												
Chlorella pyrenoidosa	-	N	-	-	-	-	-	4 d	EC_{50} growth	2.1	Deneer et al., 1987	#2
Crustaceans												
Daphnia magna	-	N	S	-	Art. medium	8.4	200	2 d	EC_{50} immobility	11	Deneer et al., 1987	#2 NEN 6502 (1980)
Daphnia magna	-	N	R	-	Art. medium	8.4	200	21 d	LOEC pop. growth rate LOEC immobility EC_{50} immobility	1.8 3.2 3.8	Deneer et al., 1987	#2 NEN 6502 (1980)
Fish												
Poecilia reticulata	2-3 month	A	R	>98%	Standard water	6.8-7.2	4.9	14 d	LC_{50}	4.9	Deneer et al., 1987	#1

Table 6.1.6b Single species toxicity data for 2,5-dichloronitrobenzene - marine organisms

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Salinity ‰	Expo time	Parameter	Results (mg/l)	Reference	Quality
Bacteria												
Photobacterium phosphoreum	-	-	Microtox	-	-	-	-	30 min	EC_{50} photoluminescense	8.8	Devillers et al., 1986	#2
Photobacterium phosphoreum	-	N	Microtox	-	-	-	-	15 min	EC_{50} photoluminescense	8.4	Deneer et al., 1987	#2

Table 6.1.7b Single species toxicity data for 3,4-dichloronitrobenzene - marine organisms

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Salinity ‰	Expo time	Parameter	Results (mg/l)	Reference	Quality
Photobacterium phosphoreum	-	-	Microtox	-	-	-	-	30 min	EC_{50} photoluminescense	10	Devillers et al., 1986	#2

Table 6.1.8a Single species toxicity data for 3,5-dichloronitrobenzene - freshwater organisms

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Hardness/ mg $CaCO_3$/l	Expo time	Parameter	Results (mg/l) (95% C.V.)	Reference	Quality
Algae												
Chlorella pyrenoidosa	-	N	-	-	-	-	-	4 d	EC_{50} growth	0.59 (0.5-0.7)	Deneer et al., 1987	#2
Crustaceans												
Daphnia magna	-	N	S	-	Art. medium	8.4	200	2 d	EC_{50} immobility	7.5 (5.6-10)	Deneer et al., 1987	#2 NEN 6501 (1980)
Daphnia magna	-	N	R	-	Art. medium	8.4	200	21 d	EC_{50} immobility	2.7 (2.3-3.2)	Deneer et al., 1987	#2 NEN 6502 (1980)
									LOEC pop. growth rate	0.56		
									LOEC immobility	1.0		
Fish												
Poecilia reticulata	2-3 month	A	R	>98%	Standard water	6.8-7.2	5.7	14 d	LC_{50}	5.7	Deneer et al., 1987	#1

Table 6.1.8b Single species toxicity data for 3,5-dichloronitrobenzene - marine organisms

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Salinity ‰	Expo time	Parameter	Results (mg/l) (95% C.V.)	Reference	Quality
Bacteria												
Photobacterium phosphoreum	-	-	Microtox	-	-	-	-	30 min	EC_{50} photoluminescense	17	Devillers et al., 1986	#2
Photobacterium phosphoreum	-	N	Microtox	-	-	-	-	15 min	EC_{50} photoluminescense	18 (16-20)	Deneer et al., 1987	#2

Table 6.1.9 Single species toxicity data for 4-chloro-2-nitroaniline

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Hardness/ Salinity mg $CaCO_3$/l or %	Expo time	Parameter	Results (mg/l)	Reference	Quality
Chinook Salmon	-	-	-	-	-	-	-	24 h	non toxic	1	Mac Phee and Ruelle, 1969	#3 Rem. 2
								0-1 h	sickness	5		
								16-20 h	death	5		
								0-1 h	sickness	10		
								4-7 h	death	10		
Coho Salmon	-	-	-	-	-	-	-	24 h	non toxic	1	Mac Phee and Ruelle, 1969	#3 Rem. 2
								0-1 h	sickness	5		
								4-6 h	death	5		
								0-1 h	sickness	10		
								1-2 h	death	10		
Lepomis macrochirus	-	-	-	-	-	-	-	0.5 h	sickness	5	Applegate et al., 1957	#3 Rem. 2
Lepomis macrochirus	-	-	-	-	-	-	-	3 h	death	5	Wood, 1954	#3 Rem. 2
Northern squawfish	-	-	-	-	-	-	-	24 h	non toxic	1	Mac Phee and Ruelle, 1969	#3 Rem. 2
								0-1 h	sickness	5		
								20-22 h	death	5		
								0-1 h	sickness	10		
								1-2 h	death	10		
Poecilia reticulata	-	-	-	-	-	-	-	3 h	death	5	Wood, 1954	#3 Rem. 2
Salmo gairdneri	-	-	-	-	-	-	-	0.5 h	sickness	5	Applegate et al., 1957	#3 Rem. 2
Salmo gairdneri	-	-	-	-	-	-	-	23 h	death	5	Wood, 1954	#3 Rem. 2

Rem. 2: Data from Newsome et al., 1987

Abbreviations:

A	Analysed concentrations during the experiment	Art.	Artificial
N	Nominal concentrations	Enr.	Enriched
S	Static system		95% C.V.95% confidence values
R	Renewal system (at least once)		
F	Flow through system	Parameters:	
Purity	Purity of the test chemical		
Solvent	Solvent used to solve the test chemical	repr.	Reproduction
		mort.	Mortality
		behav.	Behaviour

# 1	Well performed experiment with reliable test results; sufficiently documented
# 2	Experiment with reliable test results; insufficiently documented
# 3	Experiment with unreliable test results

6.1.3 4-Chloro-2-nitroaniline

The information on 4-chloro-2-nitroaniline is restricted to acute experiments performed with fish, which are reviewed by Newsome et al. (1987). A concentration of 5 mg/l is lethal within 24 hours. Comparison to the toxicity of chloronitrobenzenes indicates that 4-chloro-2-nitroaniline may be slightly more toxic to fish.

6.1.4 Quantitative structure activity relations (QSARs)

Although chloronitrobenzenes are slightly more toxic than anaesthetic chemicals, a QSAR is available for *Poecilia reticulata* (14 days LC_{50}), based on the K_{ow} and the halfwave reduction potential (E½). The halfwave reduction potential represents the tendency of these compounds to be transformed through reduction of the nitro-group. The QSAR-equation is:

$$\log LC_{50} \text{ (mmol/l)} = -0.96 \log K_{ow} - 8.8\ E½ - 3.7 \qquad (n=20;\ r=0.924;\ s=0.18)$$

6.2 Terrestrial organisms

Toxicity data on terrestrial organisms are available for 2-chloronitro-benzene, 3-chloronitrobenzene and 2,3-dichloronitrobenzene tested on the plant *Lactuca sativa*. 14 day- EC50 values for growth were 5.4 and 12 mg/kg respectively. In the same experiments NOEC-values for growth were 1.0 and 3.2 mg/kg, respectively (Adema and Henzen, 1990).
For 2,3-dichloronitrobenzene tested on *Lactuca sativa* a 21-d EC50-growth of 0.32-1 mg/l was estimated in a nutrient medium.

6.3 Toxicity to mammals

Chloronitrobenzenes have methemoglobinic effects (either directly or through their metabolites), causing in the long term cyanosis and haemolytic anaemia. They also have narcotic effects and are depressants.
Toxicity data on chloronitrobenzenes are presented in Table 6.3.1. The lowest chronic dose causing effects was 40 mg 2-chloronitrobenzene/kg body weight/day, orally administered to rats. Contradicting data for mouse were a relatively high TDLo of 256 mg 2-chloronitrobenzene/kg body weight/day compared to an acute LD_{50}-value of 135 mg/kg body weight.

No toxicity data are available on dichloronitrobenzenes.
For 2-chloro-4-nitroaniline oral rat and mouse LD50-values were 6430 and 1250 mg/kg respectively. For mouse LDLo-values for intraperitonal and intervenal dosed 2-chloro-4-nitroaniline were 500 and 50 mg/kg, respectively (Sax, 1989).

Due to the lack of reliable chronic data a 'tentative acceptable daily intake' for man at lifetime exposure could not be estimated.

Table 6.3.1 Toxicity of chloronitrobenzenes and 2-chloro-4-nitroaniline to mammals (Sax, 1989)

Compound test organism	route of administration	Expo. time	Criteria	Result (mg/ kg b.w.)
2-chloronitrobenzene				
rat	oral	78 w	TDLo	40 *
rat	oral		LD_{50}	288
mouse	oral		LD_{50}	135
mouse	oral	78 w	TDLo	256 *
rabbit	oral		LD_{50}	280
3-chloronitrobenzene				
rat	oral		LD_{50}	470
mouse	oral		LD_{50}	380
4-chloronitrobenzene				
rat	oral		LD_{50}	420
mouse	oral		LD_{50}	650
mouse	oral	78 w	TDLo	355 *
rat	skin		LD_{50}	16000
2-chloro-4-nitroaniline				
rat	oral		LD_{50}	6430
mouse	oral		LD_{50}	1250

TDLo: lowest dose that has induced toxicological reactions to test animals

* : mg/kg body weight/day

6.4 Carcinogenic, mutagenic and teratogenic effects

In the previous report to the EC, Cabridenc (1984) reported for 2-chloronitrobenzene and 4-nitrochlorobenzene changes in DNA molecules in *Salmonella typhimurium*. These mutagenic effects were observed with doses of 200 µg per plate. Furthermore in mice intraperitoneal injections of 60 to 1000 mg 4-chloronitrobenzene/kg body weight damaged brain, liver and kidneys within 4 hours. This was attributed to the genotoxic effects of the nitro radicals.

Although chloronitrobenzenes are not evaluated by the IARC (1987a; 1987b) it is considered that these substances are not highly genotoxic substances. However, for definite conclusions additional research is necessary.

7 ENVIRONMENTAL IMPACT ASSESSMENT

7.1 Comparison of exposure and effects

When chloronitrobenzenes are released into the aquatic environment, they will distribute between the water and sediment compartments. Moreover, the substances may bioaccumulate in fish. Chemical reactivity under environmental conditions is not expected to occur. The only elimination pathway for these substances is probably by biodegradation, however, the inherent biodegradability of these substances does not necessarily mean that biodegradation in the environment will be a fast process.

Most reported environmental concentrations for chloronitrobenzenes were between 0.1 and 2 µg/l, but only few data were available. The relatively low log K_{ow}-values (between 2.2 and 3.1) indicate that chloronitrobenzenes do not have strong bioaccumulative properties. Experimental data show that BCF-values in fish could be predicted by the log K_{ow}-value. Yet concentrations in several fish species were reported in the range of 0.005 to 0.2 mg/kg (Mississippi River). Sum Concentrations of chloronitrobenzenes in the rivers Waal and Meuse (1976) were 0.8 and 0.03-0.10 µg/l, respectively.
The toxicity of these substances is well below their water solubility (less than 2.7 g/l). Although for several isomers only limited number of data is available, it seems that most isomers are about equally toxic. The toxicity of 2,3-dichloronitrobenzene seems to be consistently lower, but always within a factor 10. The lowest No observed effect concentration in a chronic test is 0.3 mg/l for *Daphnia magna*.

Comparison of the toxicity data with the above mentioned environmental levels leads to the conclusion that concentrations found are considerably lower than the lowest NOEC of 0.32 mg/l. The summed concentration of all chloronitro-benzenes present in the river Waal and Meuse (0.8 µg/l, in 1976) was also considerably lower than the lowest NOEC.

7.2 Water quality standard

For the estimation of a 'safe' level for the environment, an extrapolation factor can be applied to the available toxicity data which accounts for the different sensitivity of other, non-tested species in the ecosystem. Various approaches have been proposed to extrapolate from single species toxicity data to a concentration where the aquatic ecosystem is not affected (OECD, 1991). This $NOEC_{ecosystem}$ may also be called maximal tolerable concentration or MTC. As there are only a limited number of chronic data available, effects assessment is restricted to the 'modified US-EPA method', which can be applied even if only one LC_{50}-value is available. The method applies an assessment factor of 10 to account for each additional level of uncertainty: (1) from one or several chronic values to the $NOEC_{ecosystem}$, (2) from acute LC_{50}-values for at least algae, Daphnia and fish to a chronic NOEC-value, and (3) from only one acute LC_{50}-value to a chronic value. Thus, the assessment factors are 10, 100 and 1000, respectively.

As the different chloronitrobenzene isomers have similar working mechanisms and are about equally toxic, the data for all isomers are grouped and the modified EPA method is applied to derive a MTC for the sum of all chloronitrobenzenes. The results are listed in Table 7.2.1.

Table 7.2.1. Maximum Tolerable Concentrations for chloronitrobenzenes

Extrapolation method	MTC (µg/l)	Remarks
Modified EPA:		
Acute LC_{50}	10	lowest of several LC_{50} / 100
Chronic NOEC	30	lowest NOEC / 10

Another safety factor should account for the additional effects of the many other xenobiotic chemicals present in the environment that have a comparable working mechanism. Chloronitrobenzenes and many other 'industrial' chemicals are neutral substances that show a narcosis-type toxicity. The effects of these substances are supposed to be additive (Hermens et al., 1984). The order of magnitude for this safety factor is unknown at the present state of the art. One could suggest a safety factor of 10 when not many other environmental contaminants are expected, but when the environmental load is high, a safety factor of 1000 could be more appropriate.

The magnitude of the safety factor is not only a matter of science but political considerations are involved as well. Therefore no safety factor is applied to the MTC to derive a water quality standard for the sum of all chloronitrobenzenes of 10 µg/l. It should be realized that the proposed water quality standard does not take into account that other industrial pollutants may be present at the same time.

This level is detectable by the analytical techniques described in chapter 2.

In the previous report to EC (Cabridenc, 1984) no maximal permissible concentration for the environment could be proposed.

When the proposed water quality standard is compared to the environmental levels found in the river (total concentrations, max. 0.8 µg/l in 1976), the proposed water quality standard is not exceeded.

For both 2-chloronitrobenzene and 4-chloronitrobenzene standards were proposed by the Rhine Action Program (1991) of 1.0 µg/l. These standards are based on the EC-guideline 75/440/EWG on drinking water production and the EC-guideline 80/778/EWG on human use of water. Considering the fact that our proposal for a water quality standard is based on the sum of all chloronitrobenzenes, it is concluded that both standards are comparable.

7.3 Human exposure

Exposition of man to substances in the aquatic environment may occur through oral intake from (drinking) water and from fish, shellfish or crayfish. Other possible exposition routes are dermal contact and inhalation. The route of dermal contact is relevant if a substance is lipophilic, whereas inhalation is important for highly volatile substances. Both routes are considered to be neglectable in relation to the oral uptake for chloroanilines. The human exposure analysis is therefore exclusively based on oral intake.

For the calculations the total concentration of chloronitrobenzenes in the water is assumed to be at the level of the proposed water quality standard: 10 µg/l. Assuming a daily water consumption of 2 liter, the oral intake of chloroanilines from the water will be 20 µg/day.
The concentration in fish is estimated from the highest bioconcentration factor in Table 5.3.1 (C_{fish}/C_{water} = 170) to be 1700 µg/kg fish. If furthermore a (relatively high) figure for the daily consumption of fish is assumed to be 100 g, the oral intake will be 170 µg/day.
The total oral intake of chloronitrobenzenes is estimated at 190 µg/day or for a 60 kg person 3 µg/kg body weight/day. Comparison with the lowest 78 weeks LDLo of 40 mg/kg body weight/day found for rats shows that the margin of safety is rather high. Therefore the risk of human exposure to chloronitrobenzenes present in aquatic systems in a concentration of 10 µg/l is expected to be negligible.

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APPENDIX 1.

The calculation method for the volatilization standard half-life according to De Bruin (1985).

In the calculation method some assumptions have been made:

- water flow rate = 1 m/s
- air velocity = 3 m/s
- water depth = 1 m
- temperature = 10 °C

The calculation consists of 6 different steps that will be described below:

1 Henry Constant (H):

$H = p/s$

p = vapour pressure (atm.)
s = water solubility (mol/m^3)
H = Henry Constant ($atm \cdot m^3/mol$)

2 dimensionless Henry constant (H'):

$H' = H/RT$

$RT = 0.024$

3 Liquid-Phase Exchange Constant (k(l)):

if $M < 65$:

$k(l) = 20\sqrt{(44/M)}$

if $M > 65$:

$k(l) = 41.93\sqrt{(32/M)}$

M = molecular weight

4 Gas-Phase Exchange Constant (k(g)):

$k(g) = 4550\sqrt{(18/M)}$

5 Overall liquid-phase mass transfer coefficient (K(L)):

$K(L) = \{H' \cdot k(g) \cdot k(l)\} / \{H' \cdot k(g) + k(l)\}$

6 Half-life (t(½)):

$t(½) = 69.3/K(L)$

t(½) = half-life (hours)

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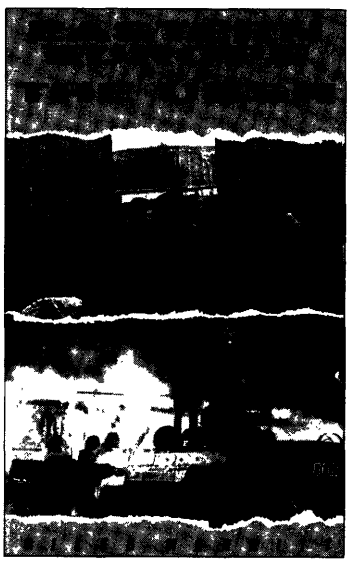

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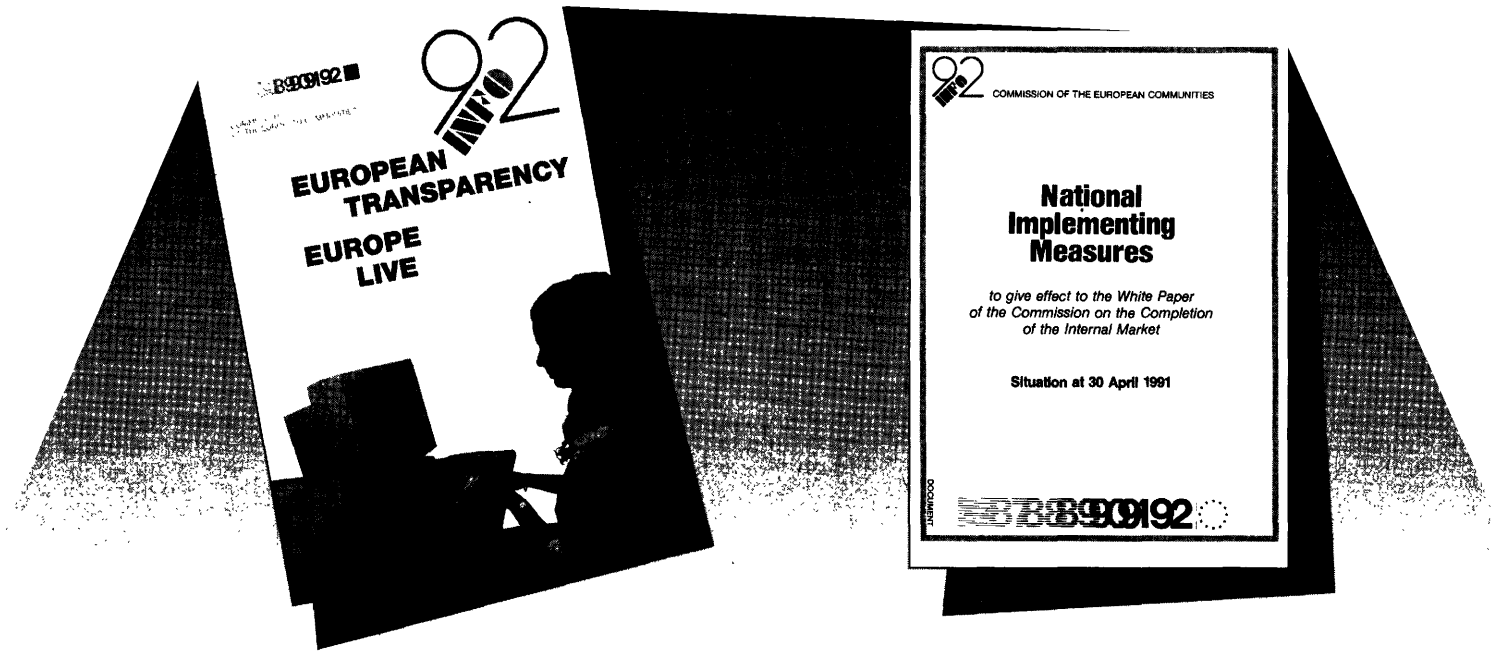

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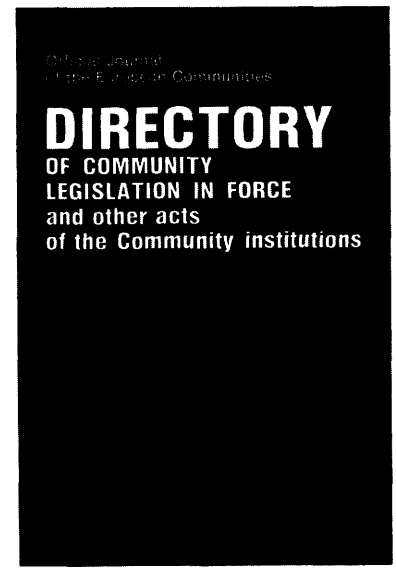

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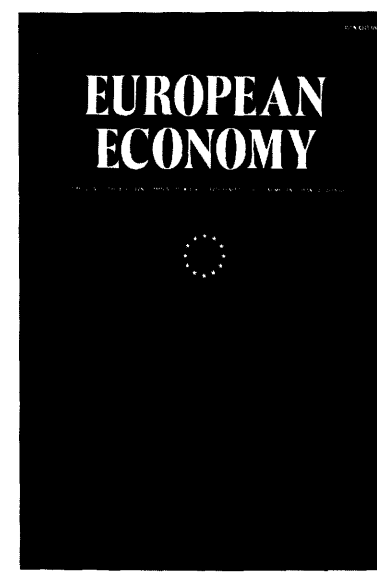

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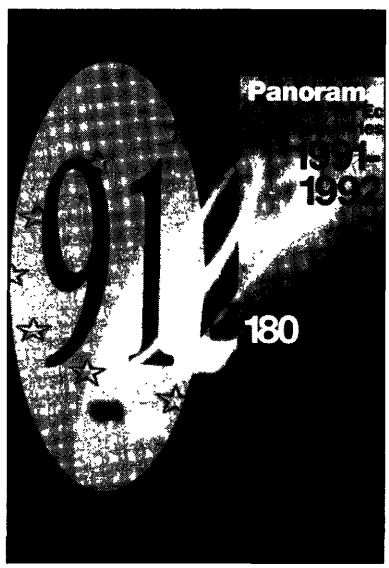

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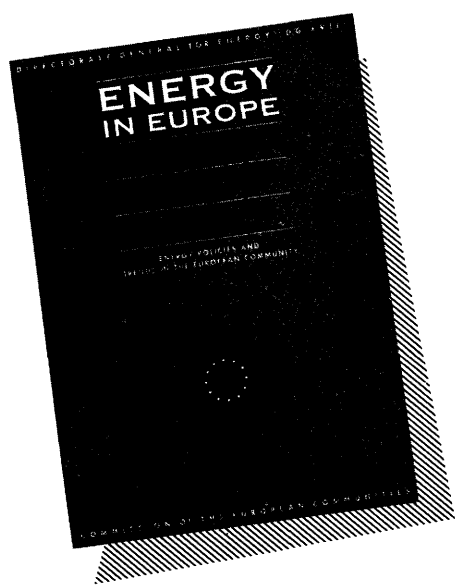

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