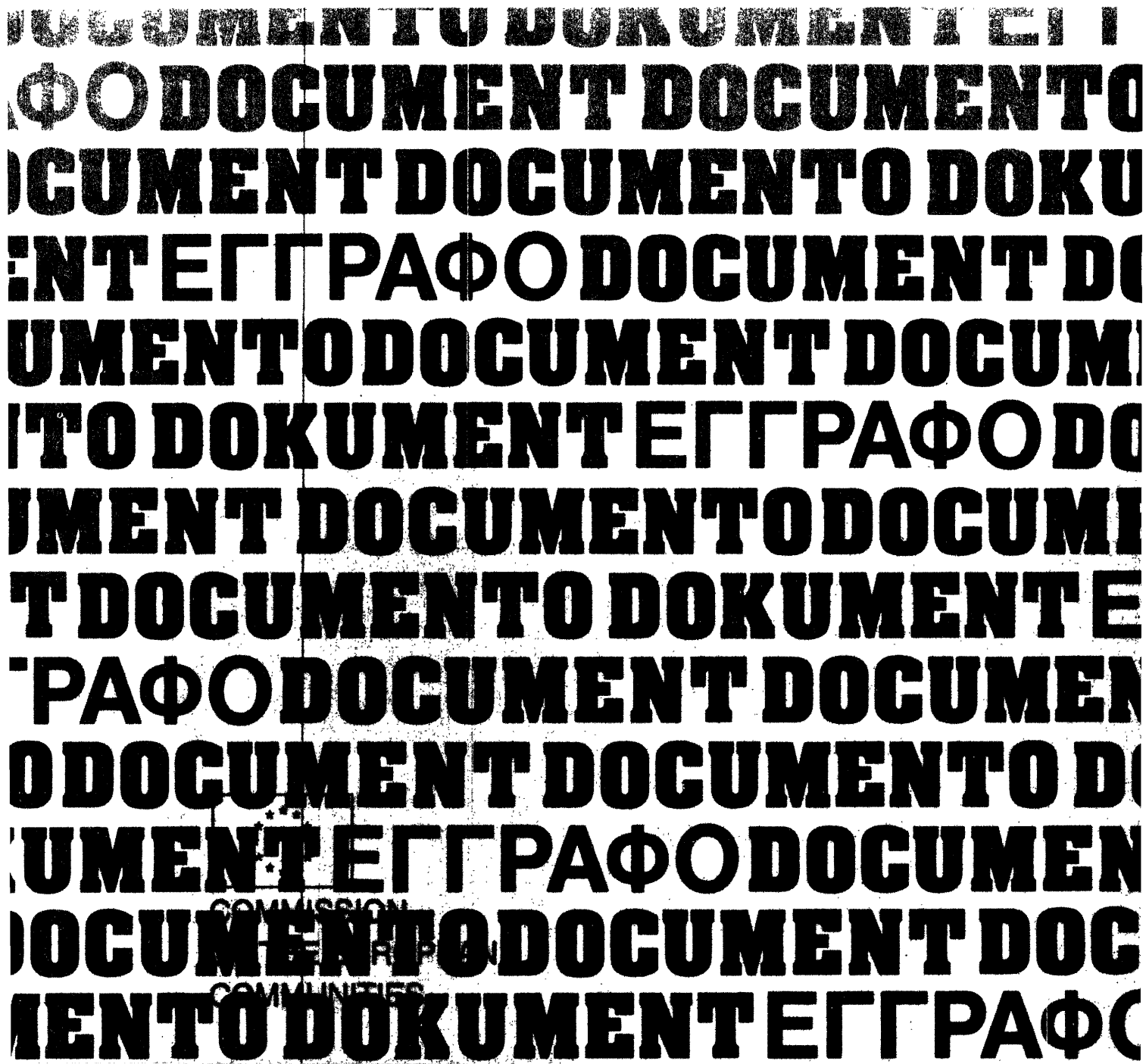
UPDATING OF DATA CONCERNING THE IMPACT ON THE AQUATIC ENVIRONMENT OF CERTAIN DANGEROUS SUBSTANCES, SECOND PART

Part IV — Chloroanilines



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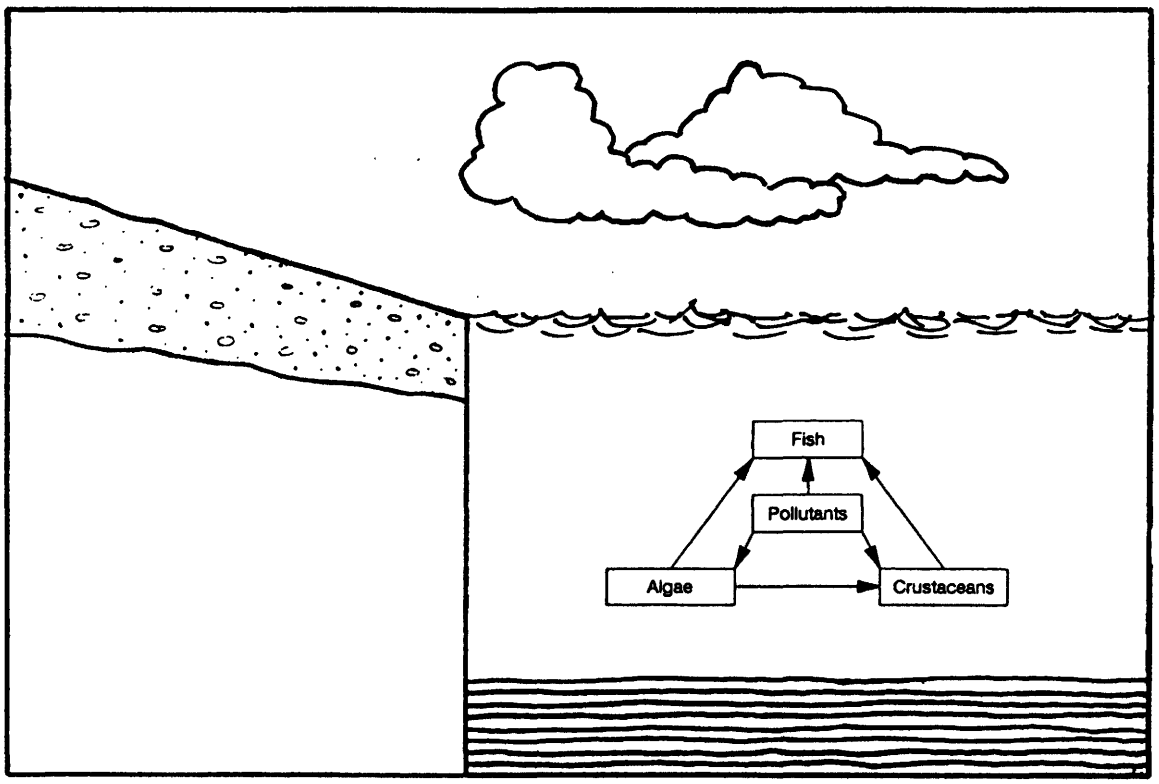
Updating of data concerning the impact on the aquatic environment of certain dangerous substances, 2nd part

Part IV Chloroanilines



May, 1992

bkh consulting engineers

PREFACE

The Commission of the European Communities, Directorate-General for Environment, Nuclear Safety and Civil Protection has commissioned 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 chloroanilines 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 for chloroanilines. The availability of data on the different subjects is summarized in Table i.
The three isomers of monochloroaniline are generally used in chemical industry. Of the six isomers of dichloroaniline only the 3,4- and 3,5-substituted isomers are regularly produced as raw materials or intermediates of pesticides or are released from pesticides by hydrolysis.
Generally, data for the other isomers fail or are only scarce.
Total production levels in the EC of 2- and 3-chloroaniline were 1-2000 and 1-4000 t/year (1985).

Chemical analysis of chloroanilines in environmental samples is possible by several usual methods such as GC, HPLC, and MS giving a detection limit around 0.01 µg/l.
Concentrations in polluted rivers are above this limit and can be monitored.
In the rivers Rhine, Meuse and Scheldt the water concentrations appear to have decreased during the last ten years. In 1979 the regularly used isomers were present at 0.1 - 4 µg/l, whereas the concentrations over 1990 are all below 0.05 µg/l.
Mono- as well as dichloroanilines are sensitive to photodegradation. Depending on the circumstances in light exposed water the half-life is between several hours and several days.
The three monochloro isomers as well as 3,4-dichloroaniline are inherently biodegradable and ultimately completely mineralized if conditions are favourable. Such conditions exist in adapted activated sludge, anaerobic fermentors in the methanogenic stage and adapted soil columns. More strict standard tests, however, failed to demonstrate that chloroanilines are readily biodegradable.
Volatilization from surface water to the atmosphere is another process that contributes to the disappearance of chloroanilines. Depending on the conditions and type of isomer the half-lives vary between two days and one month.
Chloroanilines are relatively good water soluble up to several hundreds or thousands mg/l and have a moderate lipophylicity. For this reason accumulation on sediment and in fat tissue of animals is only moderate with concentration factors between 50 and 1000.
Data for toxicity of chloroanilines are far from complete for all isomers. Nevertheless it may be concluded that the differences in toxicity between the isomers are rather small in comparison with the differences in sensitivity of different test species. Generally the chronic test with *Daphnia magna* is the most sensitive, the lowest NOEC value being 10 µg/l. Toxicity for aquatic species can also be calculated on the basis of lipophylicity by Quantitative Structure Activity Relationships (QSAR).
A concentration of 5 µg/l is expected to be safe for 95% of the aquatic species ($NOEC_{ecosystem}$).
As the toxicity and the working mechanism of the isomers is almost identical, the environmental concentrations of all chloroanilines should be added for a proper risk assessment. For the river Rhine in 1990 this results in a mean value of 0.15 µg/l and maximum value of 0.4 µg/l. Thus the environmental values in the river Rhine are well below the $NOEC_{ecosystem}$. The likelihood of additive effects of many other chemicals with a comparable working mechanism (narcosis) is not taken into account.

The proposed water quality standard for the sum of all chloroanilines (5µg/l) is an order of magnitude above the levels proposed for individual chloroanilines (0.01 to 0.1 µg/l) as proposed by the Rhine Action Program.
The toxicity data of chloroanilines to mammals and birds show a remarkably great difference between short term and long term exposure. LD_{50} values for oral exposure vary between 200 and 1000 mg/kg body weight and chronic NOEC values for daily oral uptake vary between 0.005 and 0.2 mg/kg body weight/day.

A worst case exposure of man based on drinking unpurified river water containing chloroanilines at the level of the above quality standard and a daily fish consumption from that river is estimated at 0.4 µg/(kg body weight.day). This is approximately 10 times higher than a tentative "acceptable daily intake" of 0.05 µg/kg body weight/day. The risk may be considerable. Therefore it is advisable that a more refined human risk assessment is made.
The same worst case assessment method applied to the actual situation in the Rhine shows that the daily intake of chloroanilines by man would be 2/3 of the tentative "daily intake", indicating that the water does not cause direct danger, but also that the water is not completely safe to drink unpurified.

Table i Information available for chloroanilines on the different subjects.

Subject:	2-CA	3-CA	4-CA	2,3-DCA	2,4-DCA	2,5-DCA	2,6-DCA	3,4-DCA	3,5-DCA
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 Chloroanilinen auf die aquatische Umwelt wurde ermittelt mit de Absicht eine toxikologische Grundlage zu beschaffen auf welcher ein Vorschlag für Wasserqualitätskriterien abgeleitetet werden könnte. Werte bezüglich physischen und chemischen Eigenschaften, Abbaubarkeit, Toxizität, chemischer Determinierung und Umweltkonzentrationen wurden revidiert. In Tafel i sind die Ergebnissen dargestellt über die verfügbare Daten der verschiedenen Gegenstände.
Die drei möglichen Isomeren von Monochloroanilin finden im allgemeinen Anwendung in der chemischen Industrie.
Von den sechs verfügbaren Isomeren von Dichloroanilin werden in der Regel nur die 3,4- und 3,5- substituierten Isomeren als Rohstoffe produziert oder als Zwischenverbindungsstoffe für Pflanzenschutzmittel gering produziert oder entweichen aus den Pflanzenschutzmittel mittels Hydrolyse. Im allgemeinen fehlen die Werte von den übrigen Isomeren oder sind nur beschränkt vorhanden.
Die totale Produktion von 2- und 3-Chloro-anilinen in der EG wird eingeschätzt auf 1-200 und 1-4000 Tonne/Jahr in 1985.
Chemische Analyse von Chloro-Anilinen in Umwelt-Probemuster ist auf mehreren gebräuchlichen Methoden möglich wie GC, HPLC und MS welche einen Determinierungsgrenzwert ermöglichen von ungefähr 0,01 µg/l.

Die Konzentrationen in verunreinigten Flüssen liegen über diesen Wert und können laufend festgestellt werden.
In den Flüssen Rhein, Maas und Schelde haben in den letzten zehn Jahren die Chloroanilin-Konzentrationen nachgelassen. In 1979 wurden die gebräuchliche Isomeren festgestellt in Konzentrationen zwischen 0,1-4 µg/l, während die gemessenen Konzentrationen in 1990 sich alle unter den Wert von 0,05 µg/l befanden.
Mono-wie Dichloranilinen sind empfindlich für Photogemischer Abbau.
In mit Licht durchleuchtetes Wasser liegt der Halbierungszeit, abhängig von den Umständen, zwischen mehreren Stunden und mehreren Tagen.
Die drei Monochloro Isomeren sowie das 3,4-Dichloroanilin sind inherent biologisch abbaubar und werden Schlussendlich unter günstigen Verhältnissen vollständig mineralisiert.
Solche Verhältnissen herrschen vor in angepassten aktivierten Schlämme, anaeroben Gärstoffe während der methanogenische Prozesstufe und in angepassten Böden. Bei genauer durchgeführten Standardprüfungen konnte aber nicht festgestellt werden dass Chloroanilinen direkt biologisch abbaubar sind.
Verflüchtigung aus offenen Gewässer in der Atmosphäre ist ein weiteres Verfahren welches beiträgt an der Verschwindung von Chloroanilinen. Abhängig von den Umständen und Isomerenart variiert der Halbierungszeit zwischen zwei Tagen und ein Monat.
Chloroanilinen sind bis zu mehreren Hunderten oder Tausenden mg/l relativ gut löslich in Wasser und haben eine mässige Lipophylizität. Aus diesem Grund ist die Akkumulation in Sedimenten und in Fettgeweben von Tieren nur mässig mit Konzentrationsfaktoren zwischen 50 und 1000.
Die Toxizitätswerten von Chloroanilinen sind bei weitem nicht Vollständig für alle Isomeren. Dennoch kann festgestellt werden, dass die Unterschieden in Toxizität zwischen den Isomeren ziemlich gering ist im Vergleich mit den Unterschieden welche durch die Empfindlichkeitsvariationen von verschiedenen Versuchsarten verursacht werden. Im allgemeinen gilt der chronischen Versuch mit Daphnia magna als der meist empfindliche und ergibt einen NOEC Wert von 10 µg/l. Einen

Wert von 5 µg/l wird als ungefährlich für 95% der aquatischen Arten betrachtet ($NOEC_{ecosystem}$).
Toxizität für aquatischen Arten kann ausserdem berechnet werden auf Grund der Lipophylizität durch "Quantitative Structure Activity Relationship (QSAR)". Da die Toxizität und das Wirkungsmechanismus der Isomeren fast Identisch sind, sollten bei einer guten Risikoprüfung die Umweltkonzentrationen addiert werden.

Für den Rhein ergab dieses im Jahr 1990 einen Mittelwert von 0,15 µg/l und ein Maximalwert von 0,4 µg/l. Das bedeutet, dass die Umweltwerten im Rhein deutlich unter dem $NOEC_{ecosystem}$ liegen. Die mögliche Addierungseffekten welche auftreten könnten durch eine Vielzahl anderer Chemikalien mit vergleichbaren Wirkungsmechanismen (Narkosis) sind nicht in weiteren Betracht gezogen.
Mit einem Sicherheitsfaktor von 100 für dieses Additiv sollte der vorgeschlagene Wasserqualitätsnormwert 0,05 µg/l betragen. Gemäss dieser Norm entspricht den Rhein in 1990 den Anforderungen noch nicht.
Das vorgeschlagene Wasserqualitätskriterium für die Summierung aller Chloroanilinen (5µg/l) liegt ein Faktor zehn über den Niveau für individuellen Chloroanilinen (0,01 - 0,1 µg/l) wie vorgeschlagen durch das Rhein Aktionsprogramm.

Die Toxizitätswerten von Chloroanilinen bezogen auf Säugetiere und Vögel zeigen ein bemerkenswerter grossen Unterschied zwischen kurzdauernder und langdauernder Aussetzung. LD_{50} Werte bei oraler Einnahme variieren zwischen 200 und 1000 mg/kg Körpergewicht und NOEC Werte bei chronischer tägliche orale Aufnahme variieren zwischen 0,005 und 0,2 mg/kg Körpergewicht pro Tag.

Die möglichst schlimmste Aussetzung eines Menschen auf Grund von trinken von ungeklärtes Flusswasser mit obengenanntem Qualitätsnormwert und ein täglicher Fischkonsum aus diesem Fluss wird eingeschätzt auf 0,004 µg/kg Körpergewicht pro Tag. In diesem Fall beträgt der Sicherheitsfaktor etwa 1000.
Für den Rhein in 1990 beträgt der Sicherheitsfaktor etwa 100.

RÉSUMÉ

L'effet des chloroanilines 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 pour les chloroanilines. Le tableau i comprend un résumé de la disponibilité de données concernant les divers sujets. On utilise généralement les trois isomères du monochloroaniline dans l'industrie chimique. Des six isomères du dichloroaniline uniquement le 3,4- et le 3,5-isomères substitués sont fabriqueés régulièrement comme matière brute ou comme intermédiaires de pesticides ou bien ils sont distillés de pesticides par moyen d'hydrolyse. En général les données sur les autres isomères font défaut ou on n'en a que très peu.

La production dans la CEE du 2- et du 3-chloroaniline fut 1-2000 et 1-4000 tonnes/an (1988).

L'analyse chimique des chloroanilines dans les échantillons environnementales est possible par plusieurs méthodes habituelles comme CG, HCPL et SM donnant une limite de détection d'environ 0,01 µg/l.
Des concentrations dans des fleuves pollués sont au-dessus de cette limite et peuvent être surveillées. Il paraît que dans le Rhin, la Meuse et l'Escaut les concentrations ont diminué pendant les derniers 10 ans. En 1979 les isomères utilités régulièrement étaient présents à un niveau de 0,1-4 µg/l, tandis que les concentrations en 1990 étaient toutes au-dessous de 0,05 µg/l.
Le mono- aussi bien que le dichloroaniline sont susceptibles à la photodégradation. Dépendant des circonstances et de la lumière dans l'eau le temps de réduction de moitié est entre quelques heures et quelques jours.

Les trois monochloro- aussi bien que le 3,4-dichloroaniline sont intrinsèquement biodégradables et finalement ils seront minéralisés complètement si les conditions sont favorables. De telles conditions existent dans la boue activée, qui a été activée, les installations de fermentation anaérobie en stade de méthanogénèse et dans les colonnes de terre adaptés. Des tests standards plus strictes pourtant n'ont pas pu démontrer que les chloroanilines sont facilement biodégradables.

Un autre procédé qui contribue à la disparition des chloroanilines est la volatilisation des eaux de surface dans l'atmosphère. Dépendant de circonstances et du type d'isomère le temps de réduction de moitié varie entre deux jours et un mois.

Les chloroanilines sont relativement bien solubles dans l'eau jusqu'à quelques cents ou milles mg/l et ils ont une lipophylicité modérée. C'est pourquoi l'accumulation dans les sédiments et dans la matière grasse des animaux est modérée avec des facteurs de concentration entre 50 et 1000.

Les données sur la toxicité des chloroanilines sont loin d'être complètes pour tous les isomères. Pourtant on peut conclure que les différences en toxicité entre les isomères sont assez petites comparées aux différences en sensibilité des espèces de test diverses.

En général le test à durée avec le Daphnia magna est le plus sensible, étant donné que la valeur NOEC la plus basse est 10 µg/l. La toxicité pour les espèces aquatiques peut aussi être calculée à base de lipophylicité par la Relation Quantitative de la Structure et l'Activité.

On suppose qu'une concentration de 5 µg/l soit sûre pour 95% des espèces aquatiques ($NOEC_{écosystème}$). Comme la toxicité et le fonctionnement des isomères sont presqu'identiques, les concentrations environnementales de tous les chloroanilines devraient être totalisées pour en déduire une estimation propre de risques. Pour le Rhin ceci résulte en 1990 en une valeur moyenne de 0,15 µg/l et une valeur maximale de 0,4 µg/l. Ainsi les valeurs environnementales dans le Rhin sont bien au-dessous de $NOEC_{écosystème}$. La probabilité d'effets additifs de beaucoup de'autres produits chimiques contenant un fonctionnement comparable (la narcose) n'a pas été envisagé. La norme de qualité de l'eau proposée pour la totalité de tous les chloroanilines (5 µg/l) est beaucoup plus haute que les niveaux proposés pour les chloroanilines isolés (0,01 à 0,1 µg/l) comme l'a proposée le Programme Rhin Action.

Les données sur la toxicité des chloroanilines pour les mammifères et les oiseaux montrent une différence remarquablement grande entre l'exposition de courte ou de longue durée. Les valeurs DL_{50} pour l'exposition orale varient entre 200 et 1000 mg/kg poids et les valeurs chroniques NOEC pour la prise orale par jour varient entre 0,005 et 0,2 mg/kg poids/jour pour l'homme. Au pire l'exposition de l'homme a été estimée 0,4 µg/kg poids/jour, c'est-à-dire s'il buvait de l'eau fluviale impure contenant des chloroanilines presqu'à un niveau de la norme de qualité mentionnée ci-dessus, et s'il mangeait de la poisson de ce fleuve tous les jours. Ceci est à peu près dix fois plus haut que la prise acceptable par jour provisoire de 0,05 µg/kg poids/jour. Le risque peut être considérable. C'est pourquoi il faudrait établir une estimation de risques humaines plus raffinée.

La même méthode d'estimer l'exposition au pire appliquée sur la situation actuelle dans le Rhin montre que la prise par jour de chloroaniline par l'homme serait 2/3 de la prise acceptable par jour provisoire, ce qui indique que l'eau ne cause pas de danger directe, mais aussi qu'il n'y a pas de sécurité totale si l'on boit l'eau impure.

SAMENVATTING

Het effect van chlooranilines 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 isomeren van monochlooraniline worden algemeen gebruikt in de chemische industrie. Van de zes isomeren van dichlooraniline worden alleen 3,4- en 3,5-isomeren regelmatig geproduceerd als grondstof of intermediair in de produktie van bestrijdingsmiddelen; daarnaast komen ze ook vrij bij de hydrolyse van bestrijdingsmiddelen. Gegevens over de andere isomeren ontbreken of zijn schaars. De gezamenlijk produktiecijfers binnen de EG voor 2- en 3-chlooraniline waren respectievelijk 1000 tot 2000, en 1000 tot 4000 ton per jaar (1985).

Voor de chemische analyse van chlooranilines in het milieu kunnen diverse bekende technieken toegepast worden zoals GC, HPLC en MS met een detectiegrens van ongeveer 0,01 µg/l. De concentraties in verontreinigde rivieren liggen hierboven. Gedurende de laatste tien jaar blijken de concentraties in de Rijn, de Maas en de Schelde te zijn afgenomen. In 1979 lagen de concentraties van meest gebruikte isomeren tussen 0,1 en 4 µg/l, terwijl die in 1990 alle lager waren dan 0,05 µg/l.
Zowel mono- als dichlooranilines zijn gevoelig voor fotodegradatie. De halfwaardetijd in water varieert, afhankelijk van de belichting en andere omstandigheden, tussen enkele uren en enkele dagen.
De drie monochloor isomeren en 3,4-dichlooraniline zijn "inherently degradable" en volledig te mineraliseren onder gunstige omstandigheden. Dergelijke omstandigheden komen voor in geadapteerd actief slib, in anaërobe fermentoren in de methanogene fase en in geadapteerde grondkolommen. In de strengere standaardtesten kon echter niet worden aangetoond dat de chlooranilines gemakkelijk (readily) afbreekbaar zijn.
Vervluchtiging is een ander proces dat bijdraagt aan het verdwijnen van chlooranilines uit het oppervlaktewater. De halfwaardetijden variëren, afhankelijk van de omstandigheden en van het isomeer, tussen twee dagen en een maand.
Chlooranilines lossen redelijk goed op in water, tot enkele honderden of duizenden mg/l en zijn matig lipofiel. Hun accumulatie in sediment en in dierlijk vetweefsel is daardoor beperkt; concentratiefactoren variëren tussen 50 en 1000.
De toxiciteitsgegevens voor alle chlooraniline isomeren is verre van volledig. Toch kan geconcludeerd worden dat de verschillen in toxiciteit tussen de isomeren nogal klein is in vergelijking met de verschillen in gevoeligheid tussen de verschillende testsoorten. In het algemeen is de chronische test met *Daphnia magna* het gevoeligst met een laagste NOEC van 10 µg/l. De toxiciteit voor aquatische soorten kan ook worden berekend uit de lipofiliteit met behulp van kwantitatieve structuur-activiteitsrelaties (QSARs).
Naar verwachting is een concentratie van 5 µg/l veilig voor 95% van alle aquatische soorten ($NOEC_{ecosysteem}$).
Aangezien de toxiciteit en het werkingsmechanisme voor de isomeren ongeveer identiek zijn, zouden voor een goede risicoschatting de concentraties van alle chloroanilines bij elkaar moeten worden opgeteld. In 1990 was de gemiddelde waarde in de Rijn van de som chloroanilines 0,15 µg/l en het maximum was 0,4 µg/l. Deze concentraties in het Rijnwater liggen dus ruim onder de $NOEC_{ecosysteem}$.
Er is hierbij geen rekening gehouden met de vele andere chemische stoffen met eenzelfde werkingsmechanisme die tegelijkertijd aanwezig kunnen zijn. De

voorgestelde waterkwaliteitsnorm voor de som van alle chlooranilines ligt een ordegrootte boven de concentraties die in het Rijn Actie Programma zijn voorgesteld voor de individuele chlooranilines (0,01 tot 0,1 µg/l).

Bij de toxiciteit voor zoogdieren en vogels is er een groot verschil tussen kortdurende en langerdurende blootstelling. LD_{50} waarden bij orale blootstelling liggen tussen 200 en 1000 mg/kg lichaamsgewicht, terwijl chronische NOEC waarden voor orale opname tussen 0,005 en 0,2 mg/kg lichaamsgewicht/ dag liggen.

Een conservatieve (worst case) schatting van de blootstelling van mensen die ongezuiverd rivierwater drinken waarin de totale concentratie chlooranilines 5 µg/l is en ook dagelijks vis uit die rivier eten, is 0,4 µg/kg lichaamsgewicht /dag. Dit is ongeveer tienmaal hoger dan een voorlopige "acceptable daily intake" van 0,05 µg/kg lichaamsgewicht/dag en het risico zou dus aanzienlijk kunnen zijn. Daarom is het raadzaam dat er een nauwkeuriger schatting wordt gemaakt van het risico voor de mens.
Als dezelfde grove benadering wordt toegepast op de huidige situatie in de Rijn, blijkt dat de dagelijkse inname van chloroanilines door de mens 2/3 bedraagt van de bovengenoemde voorlopige "acceptable daily intake". Dit betekent dat het water niet direct gevaarlijk is, maar ook dat het niet volkomen veilig is om het ongezuiverd te drinken.

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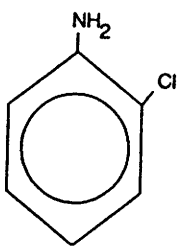
1 DESCRIPTION

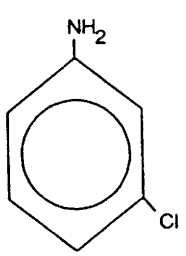
The group of chloroanilines consists of three isomers: 2-, 3- and 4-chloroaniline. Chloroanilines are intermediates in the manufacture of dye stuffs, and in the petroleum, pigments, pharmaceutical and plant-protection products industries.
Dichloroanilines consist of six isomers: 2,3-, 2,4-, 2,5- 2,6-, 3,4- and 3,5-dichloroaniline of which 3,4-dichloroaniline is the most important. 3,4-Dichloroaniline is mainly used as raw-material for several pesticides such as diuron, linuron, neburon and propanil. 3,4-Dichloroaniline can be released from these pesticides by means of hydrolysis. 3,5-Dichloroaniline is also used as an intermediate for the production of some pesticides, such as the fungicides ipordion, procymidon and vinchlozolin, and can be released when these pesticides are hydrolysed. The other dichloroanilines (2,3-, 2,4-, 2,5- and 2,6-dichloroaniline) have limited applications.

1.1 Identification

2-chloroaniline

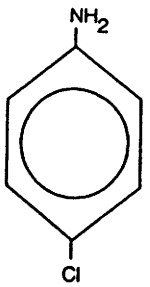
List I Dir. 76/464/EEC	17	
EINECS-no.	202-426-4	
CAS no.	95-51-2	
Synonyms:	Benzenamine, 2-chloro	Fast yellow GC base
	o(rtho)-chloroaniline	
	2-chlorobenzenamino	
	1-amino-2-chlorobenzene	
Molecular formula:	C_6H_6ClN	
Structural formula:		
WLN formula:	ZR BG	

3-chloroaniline

List I Dir. 76/464/EEC	18	
EINECS-no.	203-581-0	
CAS no.	108-42-9	
Synonyms:	m-aminochlorobenzene	3-chlorobenzeneamine
	1-amino-3-chlorobenzene	m-chlorophenylamine
	3-chlooraniline	3-chlorophenylamine
	m-chloraniline	Fast orange GC base
	m-chloroaniline	orange GC base
Molecular formula:	C_6H_6ClN	
Structural formula:		
WLN formula:	ZR CG	

4-chloroaniline
List I dir. 76/464/EEC 19
EINECS-no. 203-401-0
CAS no. 106-47-8
Synonyms: 1-amino-4-chlorobenzene; 4-chlorobenzenamino; 4-chloranilin (CZECH); 4-chlorobenzeneamino; p-chloraniline; 4-chlorophenylamine; p-chloroaniline; NCI-C02039; RCRA Wastenumber PQ

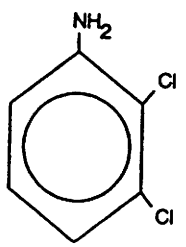
Molecular formula: C_6H_6ClN
Structural formula:



WLN formula: ZR DG

2,3-dichloroaniline
List I dir. 76/464/EEC 52
EINECS-no. 2101579
CAS no. 608-27-5
Synonyms: 2,3-dichlooraniline; 2,3-dichloraniline; 2,3-dichloranilin; 2,3-dichlorobenzenamine; 2,3-DCA; 1-amino-2,3-dichlorobenzene

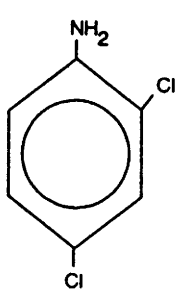
Molecular formula: $C_6H_5Cl_2N$
Structural formula:



WLN formula: ZR BG CG

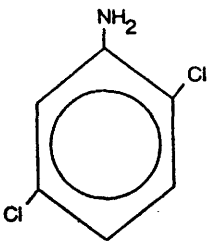
2,4-dichloroaniline
List I dir. 76/464/EEC 52
EINECS-no. 2090578
CAS no: 554-00-7
Synonyms: 2,4-dichlooraniline; 2,4-DCA; 1-amino-2,4-dichlorobenzene; 2,4-dichlorobenzenamine; 2,4-dichloranilin; 2,4-dichloraniline

Molecular formula: $C_6H_5Cl_2N$
Structural formula:

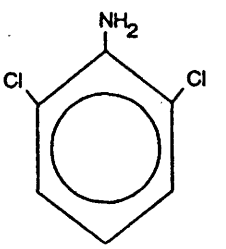


WLN formula: ZR BG DG

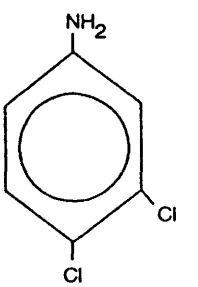
2,5-dichloroaniline

List I dir. 76/464/EEC	52	
EINECS-no.	20224552	
CAS no.	95-82-9	
Synonyms:	azobase DCA	Lake scarlet GG base
	azofix scarlet GG salt	Scartlet base CIBA 1
	Hiltonil fast scarlet 2G	Spectrolene scarlet 2G
	2,5-dichloroanilin	Symulin scarlet 2G salt
	2,5-dichloro benzeneamine	Fast red SGG base
	C.I. azoic diazo component 3	
	amarthol fast scarlett GG base	
Molecular formula:	$C_6H_5Cl_2N$	
Structural formula:		
WLN formula:	ZR BG EG	

2,6-dichloroaniline

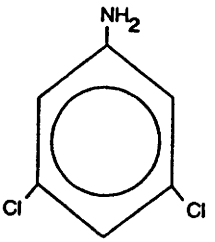
List I dir. 76/464/EEC	52
EINECS-no.	
CAS no.	608-31-1
Synonyms:	2,6-dichlooraniline
Molecular formula:	$C_6H_5Cl_2N$
Structural formula:	
WLN formula:	ZR BG FG

3,4-dichloroaniline

List I dir. 76/464/EEC	52	
EINECS-no.	2024484	
CAS no.	95-76-1	
Synonyms:	1-amino-3,4-dichlorobenzene	3,4-dichloraniline
	3,4-DCA	4,5-dichloroaniline
	3,4-dichloranilin	3,4-dichlorobenzenamine
Molecular formula:	$C_6H_5Cl_2N$	
Structural formula:		
WLN formula:	ZR CG DG	

3,5-dichloroaniline
List I dir. 76/464/EEC 52
EINECS-no.
CAS no. 626-43-7
Synonyms: 3,5-dichlooraniline

Molecular formula: $C_6H_5Cl_2N$
Structural formula:



WLN formula: ZR CG EG

Data were obtained from: Cabridenc (1984), Sax (1989), Verschueren (1983).

1.2 Physico-chemical characteristics

	2-CA	3-CA	4-CA
property	liquid	liquid	crystal
mol.weight	127.6	127.6	127.6
melting point (°C)	-14*	-10	73
boiling point (°C)	209	229	231
density at 20/4 °C	1.213	1.215	1.169
vapour pressure (mm Hg) at 20°C	0.18	0.05	0.08
water solubility (mg/l)	6,100	6,600	2,000
log K_{ow}	1.9+	1.9+	1.9+
Henry's constant ($atm.m^3/mol$)	$5*10^{-6}$	$1.5*10^{-6}$	$7.1*10^{-6}$
pKa	2.7	3.5	4.2
BCF	17	16	14
log K_{oc}	1.9	1.9	
standard half-life (h) (volatilization)	200	640	47

	2,3-DCA	2,4-DCA	2,5-DCA	2,6-DCA	3,4-DCA	3,5-DCA
property	-	-	-	-	cryst.	cryst.
mol.weight	162.0	162.0	162.0	162.0	162.0	162.0
melting point (°C)	24	63.6	50	-	71.5	52
boiling point (°C)	245-272	245-272	245-272	-	272	261
density at 20/4 °C (g/cm^3)	-	-	-	-	-	-
vapour pressure (mm Hg) at 20°C	-	-	19	-	224	-
water solubility (mg/l)	-	-	660-730	-	230	345
log K_{ow}	2.86⁺	2.91⁺	2.92⁺	2.82⁺	2.70	2.71
Henry's constant ($atm.m^3/mol$)	-	-	-	-	-	-
pKa	-	-	-	-	-	-
BCF[1]	88	96	98	82	66	68
log K_{oc}	2.47	2.48	2.45	2.38	2.49	2.46
standard half-life (h) (volatilization)	95	91	170	270	330	270

⁺ Data from De Bruin (1985) : Slow stirring method
* Sax (1989) found a melting point at -1.94°C for 2-chloroaniline
[1] BCF is calculated from log(BCF)=0.76 log(K_{ow}) - 0.23 (Veith et al., 1980)

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

1.3 Production levels

Data on the production of chloroanilines in EC are presented in Table 1.1, derived from EURECO (1990). No data are available on 4-chloroaniline and dichloroanilines.

Table 1.1 Production levels of chloroanilines in EC Countries

Country	Capacity in t/y * actual production 2-chloroaniline	3-chloroaniline	Producer
Belgium			
Denmark			
France	+ [1]	+ [1]	SPMC de Mulhouse (Mulhouse)
FRG (Germany)	+ [1,2]	+ [1]	Bayer AG (leverkusen)
	+ [3]	+ [3]	Hoecht AG (Frankrijk)
Greece			
Ireland			
Italy			
Luxembourg			
Netherlands			
Portugal			
Spain			
United Kingdom	430* y90 [2]	640* y90 [2]	Hickson & Welch Ltd. (Castleford)
Total production EC	2-4000 (y87) [1]	1-2000 (y87) [1]	

1 Water Research Centre (1987)
2 IKSRV
3 Information obtained from industry (1990); EURECO, 1990.

2 ANALYTICAL DETECTION TECHNIQUES

2.1 Detection methods

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

Corcia and Samperi (1990) developed a method for the detection of mono- and dichloroanilines in environmental waters. The method consists of a two-trap system including a cartridge filled with graphitized carbon Black (Carbopack B) and an exchanger column containing a strong acid (Amberlite CG-120-II). For the determination the chloroanilines are moved from the Carbopack to the ion exchanger by means of acidified acetonitrile. In a next step the chloroanilines are extracted from the resin and the extract is injected into the HPLC apparatus. The UV-detector was set at 240 nm.
Dependant on the resolution, the detection limit is 10 to 50 ng/l. The standard deviation for this method is less than 4%.

Wegman and De Korte (1981) described a method for the detection of all mono- and dichloroanilines in surface water. The substances are extracted by isooctane or petroleum ether (boiling range 40-60°C). Before detection with GC-ECD the anilines are brominated with hydrobromic acid. In Table 2.1.1. the detection limits are presented for this method.

Table 2.1.1 Detection limits for chloroanilines in surface water (Wegman and De Korte, 1981)

Substance	Detection limit (µg/l)
2-chloroaniline	0.005
3-chloroaniline	0.005
4-chloroaniline	0.005
2,3- and 2,5-dichloroaniline	0.005
2,4-dichloroaniline	0.010
2,6-dichloroaniline	0.05
3,4-dichloroaniline	0.005
3,5-dichloroaniline	0.010

Geerdink (1988) described a method for the determination of aniline derivatives in the aquatic environment by HPLC with fluorescence detection. He used two methods (A and B). The difference was the shorter time for method A compared to method B. For these two methods the detection limits as absolute quantities are presented in Table 2.1.2.

Table 2.1.2 Detection limits for chloroanilines in the aquatic environment (Geerdink, 1988)

Substance	Detection limit (ng)	
	method A	method B
2-chloroaniline	2.0	0.2
3-chloroaniline	0.2	0.05
4-chloroaniline	0.05	0.02
2,3-dichloroaniline	35	1
2,4-dichloroaniline	7.5	0.3
2,5-dichloroaniline	35	1
2,6-dichloroaniline	-	-
3,3-dichloroaniline	0.5	0.1
3,5-dichloroaniline	0.5	0.1

Scholz and Palauschek (1988) studied the determination 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 methods use was made of gas chromatography (GC) with an alkali flame ionisation detector (NFID) or GC with mass spectrometry (MS). The detection limits for chloroanilines were (with internal standard) 1 µg/kg in sediment and 0.1 µg/l in water samples.

Böer et al. (1990) presented an analytical method for the determination of 13 substituted anilines in drinking and surface water. The method involves extraction by C18-reversed phase material, elution with ethyl acetate and capillary gas chromatography using cold on-column injection and a nitrogen-specific detector. The detection limit was approximately 0.025 µg/l.

Kaczvinsky et al. (1983) developed a method of precleaning the water samples with a cation-exchange resin. Detection takes place with GC-MS. This method can be used for chloroanilines and many amine substituted substances. No detection limits were mentioned.

2.2 Conclusions

From the available literature it can be concluded that many detection techniques can be used for the analysis of chloroanilines such as ECD, FID, HPLC and MS. Detection limits can be in the nanogram range. The detection limits will also be dependant on the complexity of the samples. Generally used pretreatment methods are cation-exchange columns and extraction with an organic solute.

3 ENVIRONMENTAL LEVELS

Chloroanilines may be released into the environment directly as a result of their manufacture or utilizations or may occur in the environment indirectly as a result of the decomposition of certain pesticides, in particular those of the phenylcarbamate, acylanalide, phenylurea groups, (e.g. Monuron, Fenuron, Linron, Neburon, Linuron) or insecticides (e.g. Diflubenzuron) (Cabridenc, 1984).

Dichloroanilines may enter surface waters as a contaminant in applications of agricultural herbicides, as a metabolite of several herbicides, or in industrial effluents from dye manufacturing plants.

3.1 Residues in the atmosphere

No data on the occurrence of chloroanilines in the atmosphere are available.

3.2 Residues in soil and groundwater

Data on the residues of chloroanilines in soil and groundwater are not available. One value is indicative for the level in soil after the use of a pesticide which degrades via 3,4-dichloroaniline. Linuron was applied to sandy clay soil at a dose of 250 kg/km^2. Assuming a topsoil of 10 cm with a density of 2.5 g/cm^3, the applied dose corresponds with a original concentration of 1 mg/kg. After 90 days, 3,4-dichloroaniline was found at a level of approximately 0.07 mg/kg.

3.3 Residues in surface water and sediment

Data on the occurrence of chloroaniline in surface water and sediment were found only for the rivers Rhine, Meuse and Scheldt. These data are presented in Table 3.3.1. Note that the presented data might be not very accurate as most of them are near the detection limit.
The monochloroaniline concentrations in surface water decreased considerably since 1979, especially in the river Rhine, where 2-chloroaniline decreased from 0.54 µg/l in 1979 to 0.02 µg/l in 1990; 3-chloroaniline from 0.14 µg/l to 0.02 µg/l and 4-chloroaniline from 0.22 µg/l to 0.01 µg/l. Dichloroaniline concentrations generally remained at the same level, except for the 3,4-dichloroaniline concentration in the river Rhine, which decreased considerably (from 0.39 µg/l to 0.01 µg/l) and in the river Meuse (from 0.29 µg/l to below detection limit) (Linders et al., 1981).
Table 3.3.2 presents mean concentrations of chloroanilines in sediment and suspended sediment particles, in The Netherlands in 1982.
More recent data than those presented in Table 3.3.2 are not available. If the decrease in environmental levels in the surface water as shown in Table 3.3.1. is taken into consideration, it may be expected that the concentrations in the sediment probably will also have decreased in the last years.

3.4 Residues in aquatic organisms

Data on the residues of chloroanilines in aquatic organisms are not available.

3.5 Residues in terrestrial organisms

Data on the residues of chloroanilines in terrestrial organisms are not available.

Table 3.3.1 Concentrations of chloroanilines in the rivers Rhine, Meuse and Scheldt (Korte and Wegman, 1981[1]; Slooff et al., 1991[2])

Compound/location	Concentration (1979)[1]		(1990)[2]	
	Mean (µg/l)	Max. (µg/l)	Mean (µg/l)	Max. (µg/l)
2-chloroaniline				
Rhine (Lobith)	0.54	3.9	0.02	0.05
Meuse (Eijsden)	0.15	0.86	0.01	0.02
Scheldt	-	-	0.05	0.1
3-chloroaniline				
Rhine (Lobith)	0.14	1.8	0.02	0.06
Meuse (Eijsden)	0.01	0.06	0.01	0.04
Scheldt	-	-	0.01	0.03
4-chloroaniline				
Rhine (Lobith)	0.22	0.74	0.01	0.04
Meuse (Eijsden)	0.02	0.08	0.01	0.03
Scheldt	-	-	0.01	0.03
2,3-dichloroaniline				
Rhine (Lobith)	0.04	0.39	0.02	0.05
Meuse (Eijsden)	0[3]	0[3]	0[3]	0[3]
Scheldt	-	-	0[3]	0[3]
2,4-dichloroaniline				
Rhine (Lobith)	0.02	0.76	0.01	0.03
Meuse (Eijsden)	0[3]	0[3]	0[3]	0[3]
Scheldt	-	-	0.04	0.09
2,5-dichloroaniline				
Rhine (Lobith)	0.04	0.39	0.02	0.05
Meuse (Eijsden)	0[3]	0[3]	0[3]	0[3]
Scheldt	-	-	0[3]	0[3]
2,6-dichloroaniline				
Rhine (Lobith)	0[3]	0[3]	0.01	0.03
Meuse (Eijsden)	-	-	0.01	0.03
Scheldt	-	-	0.01	0.04
3,4-dichloroaniline				
Rhine (Lobith)	0.39	1.2	0.01	0.02
Meuse (Eijsden)	0.29	2.1	0[3]	0[3]
Scheldt	-	-	0[3]	0[3]
3,5-dichloroaniline				
Rhine (Lobith)	0.02	0.19	0.03	0.07
Meuse (Eijsden)	-	-	0[3]	0[3]
Scheldt	-	-	0[3]	0[3]

-: no data available
*: sampling possibly took place near emission-source
[3]: concentration below detection limit (< 0.005 µg/l or < 0.01 µg/l)

Table 3.3.2 Mean concentrations of chloroanilines in sediment and suspended sediment particles from surface water in The Netherlands (Koten-Vermeulen et al., 1989)

Compound	Year	Concentration (mg/kg dry weight)	
		Sediment	Suspended particles
2-chloroaniline	1982	0.46	1.59
3-chloroaniline	1982	0.23	0.45
4-chloroaniline	1982	0.21	0.59

4 PERSISTENCE AND DEGRADATION PATHWAYS

4.1 Abiotic degradation in the aquatic environment

4.1.1 Abiotic degradation

In the previous study for the EC, Cabridenc (1984) did not report any information on the abiotic degradation of chloroanilines in the aquatic environment.

Chlorinated anilines can be photo-degraded in the aquatic environment. Often the rate of photolysis is increased by radicals and substances that can initiate radical formation under the influence of light (UV and/or visible). Radicals that are found in the aquatic environment are, for example, hydroxyl ($OH^{\cdot}$), carbonate ($CO_3^{\cdot}$), and singlet oxygen ($O^{\cdot}$).

According to Wolff and Crossland (1985) hydrolysis is not expected to occur, since the covalent bond of a substituent, attached to an aromatic ring, is resistant to photolysis because of the high negative charge-density of the aromatic nucleus.

Larson et al. (1989) found that riboflavin (Vitamin B2) acts as a photosensitizer for the decomposition of substituted anilines. For the photosensitized degradation of 4-chloroaniline they found a half-life of 2.3 minutes. For direct photolysis a half-life of 4.6 minutes was found.

Ishikawa et al. (1989) studied the photo-decomposition of 2-chloroaniline by irradiation with a low pressure mercury lamp. They found a rate constant of 0.107 h^{-1}. The reaction products were 1,2-dichlorophenol acetate, phenol acetate, chlorobenzene and 1,2-dichloronitrobenzene. No data were available on the amounts of the different reaction products.

Miller and Crosby (1983) studied the photolysis of 4-chloroaniline by UV light (310 nm). After 6 hours the concentration of 4-chloroaniline had decreased below detection level. 4-chloronitrobenzene and 4-chloronitrobenzene were found as the reaction products. Of these products 4-chloronitrobenzene was found to be stable to photolysis; 4-chloronitrobenzene degraded further.

In acidic aqueous systems Laha and Luthy (1990) found oxidation of aniline and primary substituted anilines by manganese dioxide. They expect that this reaction can also take place in moderately acidic subsurface environments, since manganese dioxide is also present in the aquatic environment (e.g. sediment).

Wolff and Crossland (1985) studied the fate of 3,4-dichloroaniline in the laboratory and in outdoor ponds and found photo-transformation as the dominant loss process. The average temperature of the ponds used for the experiment was 20°C at a depth of 0.2 meter (19°C at 0.8 meter). The pH varied from 9 to 7.5 during the time of the experiments. They used a theoretical model to calculate the reaction rate and an empirical rate to correct for the average cloud cover. From this a rate constant for the direct photo-transformation of 3,4-dichloraniline was calculated of 0.12 to 0.20 d^{-1}. The half-life of 3,4-dichloroaniline in the outdoor ponds varied from 4.1 to 6.3 days.

According to Miller et al. (1979) the main photo-degradation product of 3,4-dichloroaniline is 2-chloro-5-aminophenol (± 78 %). A minor amount of 3-chloro-aniline was also found. 2-chloro-5-aminophenol degrades about three times more rapidly than 3,4-dichloroaniline under the same circumstances.

Larson and Zepp (1988) found that oxidation of aniline derivatives can also take place by means of the carbonate radical. This radical is formed by hydroxyl radicals that are formed by sun UV light irradiation (313 nm). For 3,4-dichloroaniline it was found that the first order rate constant of the reaction with carbonate radicals is 0.029 min^{-1}. Direct photolysis with UV-light gave a first-order rate constant of 0.015 min^{-1}.

Hwang et al. (1987) studied the photolysis of 4-chloroaniline and 2,4-dichloraniline in distilled water in the laboratory and in estuarine water. In Table 4.1.1 the rate constants for the photolysis of 1,4-dichloroaniline and 2,4-dichloroaniline are given:

Table 4.1.1 Photolysis of 4-chloraniline and 2,4-dichloroaniline (Hwang et al., 1987)

Substance and water	Season (temp. °C)	Rate constant (h^{-1})	Half-life (h)
4-chloroaniline			
- distilled	summer (25)	0.8 ± 0.1	0.9
	winter (15)	0.26 ± 0.02	2.7
- estuary	summer (25)	0.49 ± 0.05	1.4
	winter (15)	0.26 ± 0.02	2.7
2,4-dichloroaniline			
- distilled	summer (25)	0.071 ± 0.009	10
	winter (15)	0.033 ± 0.005	21
- estuary	summer (25)	0.027 ± 0.009	26
	winter (15)	0.008 ± 0.003	82

From Table 4.1.1 it can be concluded that 4-chloroaniline is more reactive than 2,4-dichloroaniline. The rate constants in summer are higher than in winter. In estuary water the rate constants are higher than in distilled water.

Miille and Crosby (1983) studied the photochemical reaction of 3,4-dichloroaniline in seawater. They found no difference between the half-life for 3,4-dichloraniline in distilled water and in seawater (17.2 hours). The analyzed reaction products were the same as reported earlier in this chapter by Miller et al. (1979).

Yager and Yue (1988) found no significant difference between the degradation half-life of 3,4-dichloroaniline in experiments with sunlight and with a xenon lamp (6.01 ± 3.61 and 4.32 ± 0.48 hours, respectively).

No data were found on the chemical degradation of 3-chloroaniline, 2,3-, 2,5-, 2,6- and 3,5-dichloroaniline.

In Table 4.1.2 a summary is given of the data on the photochemical degradation of chloroanilines presented in this chapter.

Table 4.1.2: Photochemical degradation of chloroanilines.

Substance	Experimental conditions	Half-life (h)	Degradation rate (h^{-1})	ref.
2-chloroaniline	mercury lamp	6.5	0.107	1
4-chloroaniline	sensitizing with riboflavin	2.3	0.30	2
	direct	4.6	0.15	2
	distilled/outdoor	Table 4.1.1		
2,4-dichloroaniline	distilled/outdoor	Table 4.1.1		
3,4-dichloroaniline	direct	87-140	0.005-0.008	3
	outdoor ponds	98-151	0.005-0.007	3
	direct (UV)	0.77	0.9	4
	UV/carbonate radicals	0.4	1.7	4
	distilled and seawater	17.2	0.04	5
	sunlight	6.01	0.12	6
	xenon lamp	4.32	0.16	6

References:
1 Ishikawa et al. (1989)
2 Larson et al. (1989)
3 Wolff and Crossland (1985)
4 Larson and Zepp (1988)
5 Miille and Crosby (1983)
6 Yager and Yue (1988)

4.1.2 Conclusions

Limited information is available on the abiotic degradation of the chloroanilines in the aquatic environment. For some chloroanilines this may be caused by their low reactivity under environmental conditions. Furthermore, most of these substances will volatilize rapidly into the air because of the relatively high volatilization rate.
Because of the variable environmental conditions most of the presented data give only an indication that photo-degradation may occur. Under special circumstances, like a high concentration of radicals and a high dose of UV-light, the chloroanilines will break down rapidly. Under moderate conditions chloroanilines are more stable than under extreme test 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 chloroanilines.

4.2.1 Biodegradation in standard tests

Standardized 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 standardized methods. Therefore, an attempt has been 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.

The isomer 2-chloroaniline appeared to be not readily biodegradable (MITI, 1985; Painter and King, 1985; Steinhäuser et al., 1986). In the Closed Bottle Test, 4-chloroaniline, 3,4- and 3,5-dichloroaniline were not readily biodegradable (Janicke and Hilge, 1980).

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.
Information on the toxicity of chloroanilines for bacteria is mostly limited to Microtox data (*Photobacterium phosphoreum*), which range between 1 and 15 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 chloroanilines was shown in studies with adapted micro-organisms which had been exposed for longer periods.

4.2.2. Biodegradation in simulation tests

Many authors carried out experiments simulating field conditions. Only few were successful in degrading chloroanilines.
According to Janicke and Hilge (1980) 4-chloroaniline was degraded in the "Confirmatory Test" (simulated activated sludge procedure) to approximately 97% (mostly biodegradation) in 1 - 2 months after 10 to 16 days adaptation time, while both dichloroanilines were biodegraded less than 5% (initial concentration of test substances: 20 mg/l).
The biodegradability of 2-, 3- and 4-chloroaniline was examined with OECD TG 302B, the Zahn-Wellens test (Wellens, 1990). The three isomers gave a positive result in this type of test and may be classified as inherently biodegradable.
Pfarl et al. (1990) tested aerated soil columns (22 $\pm$ 2°C, pH 6.5) with respect to their suitability for degrading chlorinated anilines and for studying microbial degradation processes in soil. Up to 90% of each isomer of monochloroaniline (0.1 g/l) was degraded after 25 days by microbial activity as indicated by chloride release. After stepwise adaptation (by simultaneous addition of monochlorobenzenes and 3,4-dichloroaniline) for approximately 87 days, up to 85% of the available amount of chloride was released from 3,4-dichloroaniline (0.1 g/l). After stepwise adaptation to 3,4-dichloroaniline no secondary carbon sources were needed to maintain the degradative capability. Under identical conditions no degradation was observed for 2,4-dichloroaniline and 3,5-dichloroaniline as indicated by a lack of chloride-release within a period of 140 days.

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 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.

In experiments of Lyons et al. (1985) the persistence of aniline, 3-chloroaniline, 4-chloroaniline and 3,4-dichloroaniline in pond water and pond water with settled domestic sewage sludge (8 mg/l) as inoculum were compared (concentrations of 250 mg/l, 20°C, pH 6.9 - 7.1). Only 10% of the added aniline was recovered after 2 weeks of incubation in pond water. In sterile controls 86% of the aniline persisted, indicating that most of the removal was due to biodegradation. In contrast 3-, 4-chloroaniline and 3,4-dichloroaniline showed high persistence in pond water samples and pond water samples inoculated with sewage sludge.

According to Hwang et al. (1987) there was no measurable microbial degradation of 4-chloroaniline and 2,4-dichloroaniline at separate concentrations of 25 µg/l in estuarine water samples after 3 days of incubation at 13 - 25°C. However, after transformation of these compounds by photolysis, there was microbial mineralization of the photo-products.

Scheunert et al. (1986) studied the distribution and biodegradability of ^{14}C-residues bound in various soil fractions (33.6% lutum, 3.2% organic matter) under field conditions. After 7 weeks ^{14}C of 4-chloroaniline (2.25 mg/kg) was concentrated for 65% in the organic fraction (mostly in the humid acid fraction); 89% of the total radioactivity (^{14}C) applied was recovered.

The mineralization of "bound residues" was slightly higher under aerobic conditions than under anaerobic conditions and the bound radioactive residues were mineralized more slowly than the parent compounds. After 28 days approximately 1% of total, unextractable ^{14}C, during both aerobic and anaerobic degradation, was transformed into $^{14}CO_2$.

In another study of Scheunert et al. (1987) the formation of $^{14}CO_2$ from ^{14}C-labelled 4-chloroaniline (0.3 mg/kg) in aerobic and anaerobic suspended soil (17% lutum, 2.5% organic matter) was determined. After 56 days at 35°C, $^{14}CO_2$ was 3.0% and 2.3% of the ^{14}C initially applied, under aerobic and anaerobic conditions, respectively.

4.2.3 Biodegradation under experimental conditions

Aerobic, co-metabolic degradation of mono- and dichloroanilines has been described repeatedly in literature.
You and Bartha (1982) isolated *Pseudomonas putida* from activated sludge. This micro-organism was able to use aniline as the sole carbon and nitrogen source and could mineralize completely 3,4-dichloroaniline co-metabolically. In the presence of aniline (0.25 - 1.8 g/kg) the mineralization of 3,4-dichloroaniline in soil (0.2 - 100 mg/kg) was speeded up several times, even when 3,4-dichloroaniline was completely bound in the humid acid fraction of soil. *Alcaligenes faecalis* was also able to use aniline as the sole carbon and nitrogen source and could co-metabolically degrade mono- and dichloroanilines (Surovtseva et al., 1983; Vasil'eva and Anan'eva, 1983).

Only a few micro-organisms were found to be able to mineralize particular chloroaromatic compounds through chlorocatechols completely and to use them as sole carbon and energy sources for growth. These organisms were mostly Gram-negative bacteria. According to the experimental data provided by Knackmuss and his coworkers (Schmidt and Knackmuss, 1980, Schmidt et al., 1980), Zeyer et al. (1985) as well as Surovitseva et al. (1985a, 1986), the following requirements should be met for productive bacterial catabolism of chloroaromatics through chlorocatechols: (i) presence of broad-specificity "aromatic-ring" oxygenase(s), (ii) absence (or blockage, respectively) of the meta-pathway (which otherwise would yield halogenated dead-end or "suicide" metabolites), and (iii) presence of modified ortho-cleavage pathway, i.e. the maleylacetate pathway. The enzymes of the latter route are characterized by high affinities for chlorinated substrates while, in contrast, the "normal" ortho-cleavage in Gram-negative bacteria proved to be inefficient at processing chlorinated analogues due to a narrow substrate specificity of the respective catabolic enzymes. The capability of representatives of the actinomycete-genus *Rhodococcus* to catabolize quite different (unsubstituted) aromatic compounds via catechol and 3-ketoadipate has been well established (Kaminski et al., 1983; Janke et al., 1986, 1989). So far, however, no indication exists that enzymes of the ortho-cleavage pathway can be employed by rhodococci to bring about total degradation of chloroaromatics through chlorocatechols. According to the experimental data described above this failure seems primarily due to the absence in these organisms of a "modified" ortho-cleavage pathway (i.e. the maleylacetate pathway) (Janke et al., 1989).

Kaminski et al. (1983), and Janke et al. (1986, 1988) reported on aniline catabolism through catechol via the ortho-cleavage pathway by different aniline-assimilating *Rhodococcus* wildtype-strains. Typically, all of these strains failed to use any of the monochloroaniline isomers as sole carbon and energy source, although under co-metabolic conditions (i.e. in the obligate presence of glucose or other appropriate additional carbon substrates) resting aniline-grown cells mediated the turnover of 2- and 3-chloroaniline with considerable rates (Schukat et al. 1983; Janke et al. 1984[b], 1986, 1988). Interestingly, glucose did not stimulate turnover of the unsubstituted (growth-supporting) aniline as shown for *Rhodococcus* sp. An 117 and An 213 (Janke et al. 1988). It was concluded that the observed co-metabolic effect of the additional carbon substrate(s) was mainly due to provision of the co-metabolizing cells with energy and/or reducing power required for the initial oxigenative conversion of the monochloroaromatic non-growth substrates into chlorocatechols (Janke et al. 1984, 1988; Janke and Ihn, 1989).

Zeyer et al. (1985) isolated *Moraxella* sp. strain G from soil. This bacterium is able to utilize as the sole source of carbon and nitrogen: aniline, 2-, 3- and 4-chloroaniline but not 3,4-dichloroaniline. *Moraxella* sp. strain G was shown to degrade 4-chloroaniline to 4-chlorocatechol. An enzyme extract of induced cells metabolized catechol, chlorocatechol, and methylcatechol to the corresponding cis,cis-muconic acids. In addition, the extract converted cis,cis-muconic acid to the lactone. It is highly probable, therefore, that 4-chloroaniline is degraded through an ortho-cleavage pathway.

Surovtseva et al. (1985b, 1986) isolated *Pseudomonas diminuta* from soil. *Pseudomonas diminuta* was able to grow on 3- and 4-chloroaniline and 3,4-dichloroaniline as the sole source of carbon and nitrogen.

Through naturally occurring genetic recombination Latorre et al. (1984) developed a *Pseudomonas* strain capable of utilizing all monochloroanilines as the sole source of carbon and energy.

After enrichment in aerated soil columns, Loidl et al. (1990) isolated *Pseudomonas acidovorans* strain CA 28, which was able to use aniline, 3- and 4-chloroaniline as sole sources of carbon, nitrogen and energy.

Arjmand and Sandermann (1986) studied the metabolism of chloroanilines by the whiterot fungus *Phanerochaete chrysosporium* and concluded that 4-chloroaniline and 3,4-dichloroaniline were mineralized to carbondioxide. On the contrary, the detailed tests with *Phanerochaete chrysosporium* of Hallinger et al. (1988) did not confirm that the fungus was able to mineralize 3,4-dichloroaniline. In experiments with radioactive labelled 3,4-dichloroaniline, $^{14}CO_2$ could not be detected.

Few data are available on anaerobic degradation of chloroanilines.
Russel (1978) described the fermentation of mono- and dichloroanilines by *Paracoccus* species. The anaerobic fermentation was complete within a day.

Kuhn et al. (1989, 1990) studied the microbial metabolism of 2-, 3-, and 4-chloroaniline in slurries from an anoxic aquifer polluted by leachate from a municipal landfill. The three mono-chloroaniline isomers (50µM, 6.3 mg/l) were not significantly metabolized during an 8-month incubation period when methanogenic or sulphate reducing conditions prevail. 3,4-Dichloroaniline was, when used as a parent substrate at a concentration of approximately 50 µM, transformed after an adaptation period of 3 months to 3-chloroaniline in stoichiometric amounts by reductive dehalogenation under methanogenic conditions.

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

4.2.4 Conclusions

The report "Evaluation of the impact of chloroanilines and chloronitrobenzenes on the aquatic environment" (Cabridenc, 1984) concluded that chloroanilines can be partly metabolized by soil micro-organisms and consequently by pre-adapted aquatic micro-organisms, probably in the presence of co-metabolites. Chloroanilines were considered to be biodegradable only to a limited extent.

In the present evaluation no studies were found on the biodegradation of 2,3-dichloro-, 2,5-dichloro- and 2,6-dichloroaniline.

The three monochloroaniline isomers were shown to be inherently biodegradable, so biodegradation is possible but standard tests for degradation were negative.
Also 3,4-dichloroaniline may be classified as inherently biodegradable based on the 85% mineralisation in a soil column. Both 2,4-, and 3,5-dichloroaniline did not degrade under these conditions, nor in the activated sludge simulation test.

Monochloroanilines were completely degradable under anaerobic conditions by a *Paracoccus*, and also dichloroanilines were completely degradable under these conditions.

Table 4.2.1 Biodegradation of chloroanilines

Compound	Conditions	Results	Ref.
2-chloroaniline	OECD 301 (Screenings tests)	not readily biodegradable	1,2,3
	OECD 302B (Zahn-Wellens) activated sludge, adaptation	85% degradation (incl. 10% physical elimination): inherently biodegradable	4
	aerated soil columns (pH 6.5; 22°C), 0.1 g/l	up to 90% biodegradation after 25 d. (chloride release)	6
3-chloroaniline	OECD 302B (Zahn-Wellens) activated sludge, adaptation	100% degradation inherently biodegradable	4
	aerated soil columns (pH 6.5; 22°C), 0.1 g/l	up to 90% biodegradation after 25 d. (chloride release)	6
4-chloroaniline	OECD 301D (Closed Bottle Test)	not readily biodegradable	5
	OECD 302B (Zahn-Wellens)	97% degradation inherently biodegradable	4
	OECD 303A (Act. sl. simulation test)	97% degraded in 1-2 months after 10-16 days adaptation	5
	aerated soil columns (pH 6.5; 22°C), 0.1 g/l	up to 90% biodegradation after 25 d. (chloride release)	6
monochloroaniline	Alcaligenes faecalis	co-metabolic degradation	10, 11
	Paracoccus sp., anaerobic	complete mineralization within 1 day	12

References:
1. MITI, 1985; 2. Painter and King, 1985; 3. Steinhäuser et al., 1986;
4. Wellens; 5. Janicke and Hilge, 1980; 6. Pfarl et al., 1990;
7. You and Bartha, 1982; 8. Arjmand and Sandermann, 1986; 9. Hallinger et al., 1988;
10. Surovtseva et al., 1983; 11. Valsil'eva and Anan'eva, 1983; 12. Russel, 1978.

Table 4.2.1 Continued

Compound	Conditions	Results	Ref.
2,3-dichloroaniline			
2,4-dichloroaniline	aerated soil columns (pH 6.5; 22°C), 0.1 g/l	no degradation after 140 d.	6
2,5-dichloroaniline			
2,6-dichloroaniline			
3,4-dichloroaniline	OECD 301D (Closed Bottle Test)	not readily biodegradable	5
	OECD 303A (Act. Sl. Simulation test)	degradation <5%	5
	aerated soil columns (pH 6.5; 22°C), 0.1 g/l adapted	85% biodegradation after 87 days (chloride release) (inherently biodegradable)	6
	Pseudomonas putida, 0.2 mg/l	complete mineralization (co-metabolic)	7
	Phanerochaete chrysosporium	mineralization contradictory	8,9
3,5-dichloroaniline	OECD 301D (Closed Bottle Test)	not readily biodegradable	5
	OECD 303A (Act. Sl. Simulation test)	degradation <5%	5
	aerated soil columns (pH 6.5; 22°C), 0.1 g/l adapted	no degradation after 140 d.	6
dichloroanilines	Alcaligenes faecalis	co-metabolic degradation	10, 11
	Paracoccus sp., anaerobic	complete mineralization within a day	12

References:
1. MITI, 1985; 2. Painter and King, 1985; 3. Steinhäuser et al., 1986;
4. Wellens; 5. Janicke and Hilge, 1980; 6. Pfarl et al., 1990;
7. You and Bartha, 1982; 8. Arjmand and Sandermann, 1986; 9. Hallinger et al., 1988;
10. Surovtseva et al., 1983; 11. Valsil'eva and Anan'eva, 1983; 12. Russel, 1978.

5 DISTRIBUTION BETWEEN ENVIRONMENTAL COMPARTMENTS

The behaviour of a substance is not only dependant on degradation but also on a number of physical and chemical characteristics such as volatilization adsorption and accumulation.

5.1 Volatilization

In the previous evaluation for the EC, Cabridenc (1984) reported a low volatility for 1,4-dichloroaniline. Nothing was reported on the volatilization rate.

Hellman (1987) studied the vaporization behaviour of 4-chloroaniline and developed a model to quantify the volatilization rate in the environment. With his model he found a volatilization rate of $< 1.1 \cdot 10^{-3}$ min^{-1}.

No data were found on the volatilization of 2-, 3- and dichloroanilines.

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, such as water solubility, vapour pressure, water flow (1 m/s), air velocity (3 m/s), temperature (20°C) 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 chloroaniline.

Table 5.1.1 Calculated volatilization rate (standard half-life) for chloroanilines according to De Bruin (1985).

Substance	Half-life (h)
2-chloroaniline	200
3-chloroaniline	640
4-chloroaniline	47
2,3-dichloroaniline	95
2,4-dichloroaniline	91
2,5-dichloroaniline	170
2,6-dichloroaniline	270
3,4-dichloroaniline	330
3,5-dichloroaniline	270

Table 5.1.1 can be used for a proper comparison of the volatility of the substances, since those calculations are based on identical physical and chemical properties and assumptions.
In general it can be concluded that the substances will volatilize within a month out of the water into the air.

5.2 Sorption

For the fate of a substance in the environment, sorption can play an important role. Substances may (ad)sorb on suspended solids and 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" (K_{oc}).
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 calculated K_{oc} are presented for the chloroanilines.

Table 5.2.1 Calculated K_{oc}-values for chloroanilines (De Bruin, 1985)

Substance	log K_{oc}-value
2-chloroaniline	1.90
3-chloroaniline	1.88
4-chloroaniline	-
2,3-dichloroaniline	2.47
2,4-dichloroaniline	2.48
2,5-dichloroaniline	2.45
2,6-dichloroaniline	2.38
3,4-dichloroaniline	2.49
3,5-dichloroaniline	2.46

5.3 Bioaccumulation

5.3.1 Aquatic organisms

For both chloroanilines and dichloroanilines only few data were found on bioaccumulation. These data are presented in Table 5.3.1. 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 regarded to accumulate in the biomass. Whether accumulation actually occurs, depends among other things on the capacity of the organisms to metabolise or eliminate the substance.

A steady state in *Brachydanio rerio* for the uptake and elimination of 3,4-dichloroaniline was found within 24 h and 50 h respectively. Comparison of the BCF-values of 3,4-dichloroaniline in tap water and in river water revealed no difference. Both in tap water and river water 3,4-dichloroaniline was nearly completely eliminated within 48 h. Elimination kinetics indicated that the elimination of 3,4-dichloroaniline could be described best by a first order two compartment model (Ensenbach and Nagel, 1991).

As Table 5.3.1 shows, chloroanilines may accumulate in lower organisms, such as algae and bacteria, with BCF-values between 260 and 1300. However, the limited number of bioaccumulation factors that are available for fish show that accumulation of mono- and dichloroanilines is not important. Apparently fish are capable to eliminate or metabolize chloroanilines.

Table 5.3.1 Bioaccumulation factors for chloroanilines on different aquatic organisms

Compound/ test organisms	Expo/ depur.time	k_1/k_2	Expo.conc. (mg/l)	BCF[1]	Ref.
3-chloroaniline					
Algae					
Chlorella fusca	1 d		0.05	260[2]	Cabridenc, 1984
" "	-		0.05	1200[2]	" "
Fish					
Idus idus melanotus	1 d		0.05	< 20[2]	" "
4-chloroaniline					
activated sludge	5 d			1300	Freitag, 1982
Algae					
Chlorella sp.	24 h			260	" "
Leuciscus sp.	2 d			< 10	" "
3,4-dichloroaniline					
Fish					
Brachydanio rerio	24/50 h	78.6/3.0-0.056	0.015	30[3]	Kalsch, 1988
" "		1.87/54.7-0.045	"	36[3]	Ensenbach, 1991
" "		2.15/63.3-0.048	"	38[4]	" "
" "				34[4]	" "

k_1: uptake rate; k_2: elimination rate.
[1] Concentration fish / concentration water, calculated on basis of wet weight
[2] Unknown whether BCF-value is calculated on wet or dry weight basis
[3] Tap water
[4] River water

5.3.2 Terrestrial organisms

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

5.3.3 Biomagnification

No references were found on biomagnification of chloroanilines.

5.3.4 Conclusions

Only limited data on bioaccumulation of chloroanilines were found. Although the substances may sorb to sediment, bacteria, algae, the available data does not indicate accumulation in fish to be important. Therefore biomagnification in a foodchain fish-fisheater is not expected to occur.

5.4 Environmental distribution

Although only limited information is available, some generalizations on environmental distribution of chloroanilines can be made. Chloroanilines which are released into the aquatic environment will dissolve in water up to the maximal solubility between 6 g/l and 300 mg/l. On one hand, the substances will volatilize from the water compartment. On the other hand they will adsorb to organic matter in the sediment according partition-equilibrium.
Monochloroanilines photolyze in water with a half-life of several hours, whereas the rate for dichloroanilines is 10 times lower. As monochloroanilines and 3,4-dichloroanilines are inherently biodegradable, they will be degraded in the sediment within on to several months depending on the conditions. The other dichloroanilines are not expected to degrade in the sediment.

6 TOXICITY

6.1 Aquatic organisms

6.1.1 Chloroanilines

All toxicity data for chloroanilines are summarized in Tables 6.1.1 to 6.1.3. When data were available on freshwater as well as on marine organisms then these are reported in separate tables (a and b). The EC report of Cabridenc (1984) contains tables with E(L)C_{50}-data of 2-chloroaniline, 3-chloroaniline and 4-chloroaniline on aquatic organisms: bacteria, algae, crustaceans and fish; most of these data are included in the Tables.

Freshwater organisms

From the information presented in the previous report to EC (Cabridenc, 1984) it was concluded that there is no significant difference in toxic effects of 2-chloroaniline, 3-chloroaniline and 4-chloroaniline. This was confirmed by the additional data collected in the present study, although 4-chloroaniline seemed to be slightly more toxic than the other two isomers. For the chloroanilines the following ranges in acute toxicity were found:

For 2-chloroaniline (Table 6.1.1a):
EC_{50} (immobilization) of 0.46 mg/l for *Daphnia magna* to an EC_{50} of 160 mg/l for the ciliate *Tetrahymena pyriformis* (population growth) and for *Scenedesmus subspicatum* (population growth).
For 3-chloroaniline (Table 6.1.2a):
EC_{50} (immobilization) of 0.4 mg/l for *Daphnia magna* to an EC_{50} of 64 mg/l for the ciliate *Tetrahymena pyriformis* (population growth).
For 4-chloroaniline (Table 6.1.3a):
EC_{50} (immobilization) of 0.1 mg/l for *Daphnia magna* to an EC_{50} of 43 mg/l for the fish *Oryzias latipes* (mortality).

The lowest NOEC-values available from chronic toxicity tests range between 0.01 and less than 0.04 mg/l for *Daphnia magna* and the fish *Brachydanio rerio*, respectively, for all three isomers. *Daphnia magna* is the most sensitive species tested with chronic NOEC-values (reproduction and mortality) of 0.032, 0.013 and 0.010 mg/l for 2-chloroaniline, 3-chloroaniline and 4-chloroaniline, respectively (Kühn et al., 1989).

Noteworthy is a study performed by Bresh et al. (1990). In an experiment lasting 32 weeks in a flow through system 3 generations of the zebrafish *Brachydanio rerio* were exposed to 3 concentrations of 4-chloroaniline. Reduction in egg release by fish revealed to be the most sensitive parameter, being significantly lower at the lowest test concentration of 0.04 mg/l. Growth was inhibited under 1 mg/l.
4-Chloroaniline caused disorder of the fecundity of fish whose parents had already been raised under 4-chloroaniline, but not in fish which had previously been bred and kept in non-contaminated water and were exposed after having reached sexual maturity.
Apart from the reduction of eggs released, the lower 4-chloroaniline concentrations caused a higher weight of the fish as compared with the control.

Marine organisms

The data on the acute toxicity of chloroanilines to marine organisms are summarized in Tables 6.1.2b and 6.1.3b. For the crustacean *Crangon septemspinosa*

LC_{50}-values of 12.5 and 25 mg/l were found for 3-chloroaniline and 4-chloroaniline respectively. Microtox EC_{50}-data were 15 mg/l for both 2-chloroaniline and 3-chloroaniline and 5.1 mg/l for 4-chloroaniline. The limited data available did not indicate that the toxicity to marine organisms differs from that to freshwater organisms.

Data on chronic effects of chloroaniline on marine organisms were not available.

6.1.2 Dichloroanilines

All information on the effects of dichloroanilines to freshwater organisms is summarized in Tables 6.1.4 to 6.1.9. When data were available of both freshwater and marine organisms, these are reported in separate Tables.
Only 2,4-dichloroaniline and 3,4-dichloroaniline have been tested more extensively, whereas for most other dichloroanilines the toxicity data are rather limited.

Freshwater organisms

A summary of the acute toxicity data for freshwater organisms is given in Tables 6.1.4a to 6.1.9.a and 6.1.8c. Acute $E(L)C_{50}$ values for all substances varied between 0.14 and 18 mg/l.

Data on chronic toxicity were available for 2,4-dichloroaniline and 3,4-dichloroaniline, as presented in Tables 6.1.5a and 6.1.8c. *Daphnia magna* appeared to be the most sensitive species tested with a 21-days NOEC (reproduction and mortality) of 0.0065 mg/l for 3,4-dichloroaniline and a 16-days NOEC (growth) of 0.015 mg/l for 2,4-dichloroaniline. Highest NOEC-values were found for the insect *Chironomus pipiens* and the bacteria *Pseudomonas fluorescens*, both with a NOEC of 10 mg/l.

Marine organisms

Toxicity data on marine organisms were mostly restricted to 3,4-dichloroaniline presented in Table 6.1.8b. The lowest acute 4 days LC_{50}-values ranged from 1.3 mg/l for *Palaemonetes varians* to 9.5 mg/l for *Mytilus edulis*. Freshwater guppies were less sensitive to 3,4-dichloroaniline than saltwater guppies. Highest acute LC_{50}-values were found for the mollusc *Mytilus edulis* and the worm *Ophryotrocha diadema* ranging from 8 to 25 mg/l.
The crustacean *Crangon crangon* was tested for 2,6-dichloroaniline, 3,4-dichloroaniline and 3,5-dichloroaniline. Although the exposure time ranged from 2 to 7 days the LC_{50}-values for the different isomers varied only between 2.1 and 3.6 mg/l. Microtox data on *Photobacterium phosphoreum* were available for all dichloroanilines except 3,4-dichloroaniline, with EC_{50} (photoluminescence) values ranging from 1.7 to 10 mg/l. For 2,3- and 2,5-dichloroaniline no other data were available.

Data on chronic toxicity were only available for 3,4-dichloroaniline, as presented in Table 6.1.8d. The lowest NOEC-values varied between 0.0032 and 0.032 mg/l for the worm *Ophryotrocha diadema*, the crustaceans *Artemia salina, Chaetogammarus marinus* and the fish *Pleuronectes platessa*. The crustaceans *Neomysis inter* and *Palaemonetes varians* were less sensitive with NOEC-values of 0.48 to 0.49 mg/l.

Table 6.1.1a Single species toxicity data for 2-chloroaniline - 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
Bacteria												
Nitrifying bacteria	population	-	S	-	-	-	-	-	EC_{50} nitrifying inhibition	10	Cesarone, 1980 (1)	
Heterotrophic bacteria	population	-	S	-	-	-	-	-	Inhibition O_2 consumpt.	20-30	Cesarone, 1980 (1)	#3
Algae												
Scenedesmus pannonicus	-	A	-	>99.9%	-	-	-	4 d	EC_{50} growth	32	Canton et al., 1985	#2 OECD, 1979
Scenedesmus subspicatus	population	-	S	-	-	-	-	5 d	growth inhibition	160	(1)	#3
Ciliates												
Tetrahymena pyriformis	GL-C strain	N	S	≥95% DMSO	-	-	-	2 d	EC_{50} pop.growth	160	Schultz et al., 1989[a]	#2
Crustaceans												
Daphnia magna	24 h	N	R (2 d)	-	Enr. deionized water + Tapwater	8.0	250	21 d	NOEC repr. + mort.	0.032	Kühn et al., 1989	#2
Daphnia magna	-	A	-	>99.9%	-	-	-	2 d	EC_{50} immobility	0.46	Canton et al., 1985	#2 OECD, 1979
Daphnia magna	24 h	N	S	-	Enr. deionized water + Tapwater	8.0	250	1 d	EC_{50}	1.4	Kühn et al., 1989	#2
Fish												
Poecilia reticulata	-	A	-	>99.9%	-	-	-	4 d	LC_{50} EC_{50} behav.	32 3.2	Canton et al., 1985	#2 OECD, 1979

Table 6.1.1b Single species toxicity data for 2-chloroaniline - marine 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
Bacteria												
Photobacterium phosphoreum	-	-	Microtox	-	-	-	-	30 min	EC_{50} photoluminescense	15	Devillers et al., 1986	#2
Salmo salar	adult	-	S	-	-	-	-	4 d	LC_{50}	1.5	Tonagai, 1982 (1)	

Table 6.1.2a Single species toxicity data for 3-chloroaniline - 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
Bacteria												
Heterotrophic bacteria	population	-	S	-	-	-	-	-	Inhibition O_2 consumpt.	20-30	Cesarone, 1980 (1)	#3
Ciliates												
Tetrahymena pyriformis	GL-C strain	N	S	≥95% DMSO	-	-	-	2 d	EC_{50} pop.growth	64	Schultz et al., 1989[a]	#2
Crustaceans												
Daphnia magna	24 h	N	R (3-4 d)	-	Enr. deionized water + Tapwater	8.0	250	21 d	NOEC repr.	0.013	Kühn et al., 1989	#2
Daphnia magna	24 h	N	S	-	Enr. deionized water + Tapwater	8.0	250	24 h	EC_{50}	0.4	Kühn et al., 1989	#2
Fish												
Brachydanio rerio	ELS	N	R (2 d)	98%	Enr. groundwater	7.4-8.4	210	28 d	NOEC surv. + hatch + growth	1.0	Van Leeuwen et al., 1990	#2 Rem.1
								28 d	LC_{50}	6.8 (5.8-8.0)		
Brachydanio rerio	egg → larvae	N	R (2 d)	98%	DSW	7.4-8.4	210	28 d	NOEC hatch mortality growth def.	10 3.2 1.0 3.2	Adema, 1987	#1
Brachydanio rerio	adult	-	S	-	-	-	-	24 h	LC_{50}	10	(1)	

Rem. 1: Concentration remained constant during the test and deviated <10% from nom. conc.

Table 6.1.2b Single species toxicity data for 3-chloroaniline - 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	14	Devillers et al., 1986	#2
Crustaceans												
Crangon septemspinosa	6-8 cm 2-5 g	N	R (2 d)	-	Seawater	-	30 ‰	4 d	LC_{50} threshold	25	Mcleese et al., 1979	#2

Table 6.1.3a Single species toxicity data for 4-chloroaniline - 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
Bacteria												
Heterotrophic bacteria	population	-	S	-	-	-	-	-	Inhibition O_2 consumpt.	20-30	Cesarone, 1980 (1)	#3
Ciliates												
Tetrahymena pyriformis	GL-C strain	N	S	≥95% DMSO	-	-	-	2 d	EC_{50} pop.growth	5.4	Schultz et al., 1989[a]	#2
Rotifera												
Brachionus rubens	population	-	S	-	-	-	-	1 d	LC_{50}	1000	Halbach, 1983 (1)	
Crustaceans												
Daphnia magna	24 h	N	R (2 d)	-	Enr. deionized water + Tapwater	8.0	250	21 d	NOEC repr.	0.010	Kühn et al., 1989	#2
Daphnia magna	24 h	N	S	-	Enr. deionized water + Tapwater	8.0	250	24 h	EC_{50}	0.1	Kühn et al., 1989	#2

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

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
Fish												
Brachydanio rerio	F1 eggs-> adult	A	F	>99%	Tapwater	7.3	360	32 w	NOEC egg number NOEC fert. + def.	<0.04 0.2	Bresch et al., 1990	#1
Brachydanio rerio	F2 eggs-> adult	A	F	>99%	Tapwater	7.3	360	20 w	NOEC egg number NOEC fert. + def.	<0.04 0.2	Bresch et al., 1990	#1
Brachydanio rerio	F0 LC adult-> eggs	A	F 200 ml/min	>99%	Tapwater	7.3	360	17 w	NOEC repr. growth behav. appearance	>1	Bresch et al., 1990	#1
Oryzias latipes	adult	-	S	-	-	-	-	1 d	LC_{50}	43	(1)	
Pimephales promelas	-	-	S	-	-	-	-	4 d	LC_{50}	12	(1)	
Salmo gairdneri	30-120 g	A	F (D=0.6)	98%	Lakewater	7.2	46 (45-48)	4 d	LC_{50}	11.0 (9.7-12.5)	Hermens et al., 1990	#1
Salmo gairdneri	-	-	S	-	-	-	-	4 d	LC_{50}	14	(1)	
Amphibians												
Xenopus laevis	egg - fry	N	R (7 d)	-	n.m	-	30	90 d	NOEC dev.	0.1	Dumpert, 1987	#3 Rem. 1

Rem 1: 30% mortality at 0.001 mg/l; 0-15% mortality in all other groups

Table 6.1.3b Single species toxicity data for 4-chloroaniline - 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	5.1	Devillers et al., 1986	#2
Crustaceans												
Crangon septemspinosa	2-5 g 2-5 g	N	S	-	Seawater	-	30 ‰	10 h	LC_{50}	12.5	Mcleese et al., 1979	#2
Mya arenaria	5 cm 20 g	N	S	-	Seawater	-	30 ‰	29 h	LC_{50}	15.1	Mcleese et.al., 1979	#2
Fish												
Salmo salar	-	-	S	-	-	-	-	4 d	LC_{50}	7-10	Tonagai, 1982 (1)	

Table 6.1.4b Single species toxity data for 2,3-dichloroaniline - marine organisms

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Salinity or ‰	Expo time	Parameter	Results (mg/l) (95% C.V.)	Reference	Quality
Bacteria												
Photobacterium phosphoreum	-	-	Microtox	-	-	-	-	30 min	EC_{50} photoluminescense	2.8	Devillers et al., 1986	#2

Table 6.1.5a Single species toxity data for 2,4-dichloroaniline - freshwater organisms

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Hardness/ mg $CaCO_3$/l	Expo	Parameter time	Results (95% C.V.)	Reference (mg/l)	Quality
Bacteria												
Pseudomonas fluorescens	log phase	N	S	-	n.m.	-	-	0.3 d	NOEC growth rate	10	Slooff, 1983	#2 Rem. 1
Microcystis aeruginosa	log phase	N	S	-	n.m.	-	-	4 d	NOEC growth rate	1	Slooff, 1983	#2
Algae												
Scenedesmus pannonicus	log phase	N	S	-	n.m.	-	-	4 d	NOEC growth	3.2	Slooff, 1983	#2
Macrophyte												
Lemnae minor (M19)	-	N	S	-	n.m.	-	-	7 d	NOEC growth rate	1	Slooff, 1983	#2
Crustaceans												
Daphnia magna	< 1 d	N	R (2 d)	ethanol	DSW	8.0	210	16 d	NOEC growth EC10 growth	0.015 0.060	Deneer et al., 1988	#1 NEN 6502
Daphnia magna	0-24 h adult	A	IF	98% DMSO	Lakewater (filtered)	8.1	225	21 d 21 d	NOEC growth, surv. EC_{50} yield (0.1-0.16)	0.032 0.12	Van Leeuwen et al., 1987	#1
Daphnia magna	24 h	N	R	-	DSW	8.0	210	21 d	NOEC mortality reproduction	0.032	Slooff, 1983	#2
Insects												
Chironomus pipiens	1 st inst	N	R	-	DSW	8.0	210	25 d	NOEC mortality development	10 10	Slooff, 1983	#2
Hydrozoans												
Hydra oligactis	budless	N	R	-	DSW	8.0	210	21 d	NOEC growth rate	3.2	Slooff, 1983	#2

Table 6.1.5a Single species toxity data for 2,4-dichloroaniline - freshwater organisms - continued

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
Molluscs												
Lymnea stagnalis	5 mth	N	R	-	DSW	8.0	210	40 d	NOEC mortality reproduction	3.2 1	Slooff, 1983	#2
Lymnea stagnalis	eggs	N	R	-	DSW	8.0	210	7 d	NOEC hatching	3.2	Slooff, 1983	#2
Fish												
Gastrosteus aculeatus	ELS	N	R (2 d)	≥ 99%	DSW	8.2	200	35 d	NOEC growth	0.32	Van den Dikkenberg, 1989	#2
Gastrosteus aculeatus	ELS	N	R (2 d)	≥ 99%	DSW	8.2	200	4 d	LC_{50}	10	Van den Dikkenberg, 1989	#2
Oryzias latipes	eggs	N	R	-	DSW	8.0	210	40 d	NOEC mortality mortality + behav. hatch growth	0.32 0.32 3.2	Slooff, 1983	#2
Poecilia reticulata	3-4 wk	N	R	-	DSW	8.0	210	28 d	NOEC mortality mortality + behav. growth	3.2 1 1	Slooff, 1983	#2
Amphibians												
Xenopus laevis	< 2 d	N	R	-	DSW	8.0	210	100 d	NOEC mortality development growth	1 0.32 1	Slooff, 1983	#2

Rem. 1: Test was performed without light

Table 6.1.5b Single species toxity data for 2,4-dichloroaniline - marine organisms

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Hardness/ mg $CaCO_3$/l	Expo	Parameter time	Results (95% C.V.)	Reference (mg/l)	Quality
Bacteria												
Photobacterium phosphoreum	-	-	Microtox	-	-	-	-	30 min	EC_{50} photoluminescense	4.7	Devillers et al., 1986	#2

Table 6.1.6b Single species toxity data for 2,5-dichloroaniline - 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	3.8	Devillers et al., 1986	#2

Table 6.1.7b Single species toxity data for 2,6-dichloroaniline - 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	1.7	Devillers et al., 1986	#2
Crustaceans												
Crangon septemspinosa	4 cm 0.6 g 2-5 g	N	S	-	Seawater	-	30 ‰	2 d	LC_{50}	3.6	Mcleese et al., 1979	#2

Table 6.1.8a acute single species toxity data for 3,4-dichloroaniline - 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
Protozoa												
Tetrahymena pyriformis	-	N	S	-	-	-	-	2 d	EC_{50} pop.growth	6.8	Schultz et al., 1989[a]	#2
Molluscs												
Dreissena polymorpha	adult 1 cm	A	S	pure	Freshwater	8.0	hard	4 d	LC_{50}	22	Adema, 1981	#2
Lymnea stagnalis	egg-juv 1st cleavage	A	S	pure	Freshwater	8.0	hard	2 d	LC_{50}	>32	Adema, 1981	#2
Crustaceans												
Daphnia magna	Young 1-2 d	N	R (1 d)	ethanol	Art.seawater	8.3	3.3 ‰	4 d	LC_{50}	0.12	Van der Meer, et al., 1988	#2 Rem. 1
Daphnia magna	24 h	N	S	-	Enr. deionized water + Tapwater	8.0	250	1 d	EC_{50}	0.14	Kühn et al., 1989	#2
Daphnia magna	larvae, 1 mm	A	S	pure	Freshwater	8.0	hard	4 d	LC_{50}	0.16	Adema, 1981	#2
Daphnia magna	<24 h	N	-	acetone (0.5 ml/l)	Dechlor. Tap water	8.0	200 162-250	2 d	EC_{50} immobility	0.29 (0.21-0.40)	Crossland and Hillaby, 1985	#1 OECD, 1981
Daphnia magna	adult, 3 mm	A	S	pure	Freshwater	8.0	hard	4 d	LC_{50}	1.0	Adema, 1981	#2
Daphnia longispina	<24 h	N	-	acetone (0.5 ml/l	Dechlor. Tap water	8.0	200 162-250	2 d	EC_{50} immobility	0.44 (0.36-0.54)	Crossland and Hillaby, 1985	#1 OECD, 1981

Table 6.1.8a acute single species toxity data for 3,4-dichloroaniline - freshwater organisms continued

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
Fish												
Pimephales promelas	28-34 d 0.113 g	A	F (D=0.65)	98%	Lakewater	7.6	44	4 d	LC_{50}	6.99 (6.55-7.47)	Call et al., 1987	#1
Pimephales promelas	30-35 d	N	F	-	-	-	-	4 d	LC_{50}	7.0	Schultz et al., 1989	#2
Pimephales promelas	28-34 d 0.077 g	A	F (D=0.65)	98%	Dechlor wellwater	7.2	44	4 d	LC_{50}	7.70 (7.03-8.43)	Call et al., 1987	#1
Pimephales promelas	28-34 d 0.220 g	A	F (D=0.65)	98%	Lakewater	7.6	44	4 d	LC_{50}	8.02 (7.26-8.95)	Call et al., 1987	#1
Poecilia reticulata	young lab. culture	A	S	pure	Freshwater	8.0	hard	4 d	LC_{50}	8.7	Adema, 1981	#2

Rem. 1: 7% mortality in controls on day 26; 1 ‰salt solution was used.

Table 6.1.8b acute single species toxity data for 3,4-dichloroaniline - 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
Molluscs												
Mytilus edulis	adult 3 cm	A	S	pure	Seawater	8.0	-	4 d	LC_{50}	9.5	Adema, 1981	#2
Worms												
Ophryotrocha diadema	larvae 3 d	A	S	pure	Art.seawater	8.0	-	1 d	LC_{50}	25	Adema, 1981	#2
Crustaceans												
Artemia salina	larvae 3 d 1 mm	A	S	pure	Art.seawater	8.0	-	4 d	LC_{50}	5.5	Adema, 1981	#2
Artemia salina	adult, 1 cm	A	S	pure	Art.seawater	8.0	-	4 d	LC_{50}	14	Adema, 1981	#2
Chaetogammarus marinus	larvae, 4 mm	A	S	pure	Seawater	8.0	-	4 d	LC_{50}	3.2	Adema, 1981	#2
Chaetogammarus marinus	adult, 1 cm	A	S	pure	Seawater	8.0	-	4 d	LC_{50}	4.0	Adema, 1981	#2
Neomysis integer	adult	N	R (1 d)	ethanol	Art.seawater	8.3	3.3 ‰	4 d	LC_{50}	1.5	Van der Meer, et al., 1988	#2
Palaemonetes varians	larvae	N	R (1 d)	ethanol	Art.seawater	8.3	3.3 ‰	4 d	LC_{50}	1.3	Van der Meer, et al., 1988	#2
Palaemonetes varians	adult, 4 cm	A	S	pure	Seawater	8.0	-	4 d	LC_{50}	2.5	Adema, 1981	#2
Palaemonetes varians	larvae	N	R (1 d)	ethanol	Art.seawater	8.3	33 ‰	4 d	LC_{50}	3.2	Van der Meer, et al., 1988	#2
Palaemonetes varians	adult	N	R (1 d)	ethanol	Art.seawater	8.3	3.3 ‰	4 d	LC_{50}	6.5	Van der Meer, et al., 1988	#2

Table 6.1.8b acute single species toxity data for 3,4-dichloroaniline - marine organisms continued

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Salinity ‰	Expo time	Parameter	Results (mg/l) (95% C.V.)	Reference	Quality
Crangon crangon	adult, 4 cm	A	S	pure	Seawater	8.0	-	4 d	LC_{50}	2.3	Adema, 1981	#2
Fish												
Gobius microps	adult	A	S	pure	Seawater	8.0	-	4 d	LC_{50}	2.4	Adema, 1981	#2
Pleuronectes platessa	~ 10 cm	A	S	pure	Seawater	8.0	-	4 d	LC_{50}	4.6	Adema, 1981	#2
Poecilia reticulata	adult bought	A	S	pure	Seawater	8.0	-	4 d	LC_{50}	3.5	Adema, 1981	#2

Table 6.1.8c (semi)chronic single species toxicity data for 3,4-dichloroaniline - 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	-	A	-	pure	Enr.freshwater	8.0	hard	4 d	EC_{50} growth	3.2	Adema, 1981	#2
Scenedesmus quadricauda	-	A	-	pure	Enr.freshwater	8.0	hard	4 d	EC_{50} growth	2.2	Adema, 1981	#2
Molluscs												
Dreissena polymorpha	adult 1 cm	A	-	pure	Freshwater	8.0	hard	28 d	LC_{50}	15	Adema, 1981	#2
Lymnea stagnalis	egg-juv	A	-	pure	Freshwater	8.0	hard	16 d 16 d 16 d	NOEC hatch + def. EC_{50} hatch + def. LC_{50}	0.13 1.0 5.8	Adema, 1981	#2
Crustaceans												
Daphnia magna	larvae, 1 mm	A	-	pure	Freshwater	8.0	hard	21 d 21 d 21 d	NOEC repr. + mort. EC_{50} repr. LC_{50}	0.0065 0.01 0.10	Adema, 1981	#2
Daphnia magna	24 h	N	R (2 d)	-	Enr. deionized water + Tapwater	8.0	250	21 d	NOEC repr.	0.012	Kühn et al., 1989	#2
Daphnia magna	<24 h	N	R (1 d)	acetone (0.25 ml/l)	Dechlor. Tap water	7.7 8.4	200 162-250	21 d	NOEC repr.	0.010 (LOEC 0.020)	Crossland and Hillaby, 1985	#1 OECD, 1981
Daphnia magna	adult, 3 mm	A	-	pure	Freshwater	8.0	hard	7 d	LC_{50}	<0.58	Adema, 1981	#2

Table 6.1.8c (semi)chronic single species toxicity data for 3,4-dichloroaniline - freshwater organisms - continued

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
Fish												
Pimephales promelas	eggs-fry ELS	A	F (D=0.5)	98%	Lakewater	7.6	51	7 d	NOEC growth	0.0051 (LOEC 0.0071)	Call et al., 1987	#1
Poecilia reticulata	young lab.cult.	A	-	pure	Freshwater	8.0	hard	4 m 4 m 7 d	EC_{50} repr. LC_{50} LC_{50}	0.55 2.1 8.5	Adema, 1981	#2
Poecilia reticulata	young bought	A	-	pure	Freshwater	8.0	hard	7 d	LC_{50}	8.2	Adema, 1981	#2

Table 6.1.8d (semi)chronic single species toxicity data for 3,4-dichloroaniline - 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
Algae												
Phaeodactylum tricornutum	-	A	-	pure	Enr.seawater	8.0	-	4 d	EC_{50} growth	0.45	Adema, 1981	#2
Worms												
Ophryotrocha diadema	larvae, 3 d	A	-	pure	Art.seawater	8.0	-	31 d	NOEC repr.	0.0032	Adema, 1981	#2
								31 d	EC_{50} repr.	0.01	Adema, 1981	
								38 d	LC_{50}	>1	Adema, 1981	
Ophryotrocha diadema	adult, 4 w	A	-	pure	Art.seawater	8.0	-	7 d	LC_{50}	10.5	Adema, 1981	#2
Molluscs												
Crepidula fornicata	veliger	A	-	pure	Seawater	8.0	-	7 d	LC_{50}	18	Adema, 1981	#2
Mytilus edulis	adult 3cm	A	-	pure	Seawater	8.0	-	21 d	LC_{50}	6.5	Adema, 1981	#2
								7 d	LC_{50}	8.0		

Table 6.1.8d (semi)chronic single species toxicity data for 3,4-dichloroaniline - marine organims - continued

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Salinity ‰	Expo time	Parameter	Results (mg/l) (95% C.V.)	Reference	Quality
Crustaceans												
Artemia salina	larvae, 3 d, 1 mm	A	-	pure	Art.seawater	8.0	-	28 d 28 d 28 d	NOEC repr. + mort. EC_{50} repr. LC_{50}	0.032 0.1 5.0	Adema, 1981	#2
Artemia salina	adult, 1 cm	A	-	pure	Art.seawater	8.0	-	12 d 7 d	LC_{50} LC_{50}	8.0 10	Adema, 1981	#2
Chaetogammarus marinus	larvae, 4 mm	A	-	pure	Seawater	8.0	-	7 m 7 m 11 m	NOEC repr.+ mort. EC_{50} repr. LC_{50}	<0.032 0.045 0.4	Adema, 1981	#2
Chaetogammarus marinus	adult, 1 cm	A	-	pure	Seawater	8.0	-	14 d	LC_{50}	1.8	Adema, 1981	#2
Crangon crangon	adult, 4 cm	A	-	pure	Seawater	8.0	-	7 d	LC_{50}	2.1	Adema, 1981	#2
Daphnia magna	Young 1-2 d	N	R (1 d)	ethanol	Art.seawater	8.3	3.3 ‰	30 d 10 d	NOEC mort. LC_{50}	0.0049 0.042	Van der Meer, et al., 1988	#2 Rem. 2

Table 6.1.8d (semi)chronic single species toxicity data for 3,4-dichloroaniline - marine organims continued

Species	Lifestage age/size	A/N	Test system	Purity/ solvent	Testwater	pH	Salinity ‰	Expo time	Parameter	Results (mg/l) (95% C.V.)	Reference	Quality
Neomysis integer	adult	N	R (1 d)	ethanol	Art.seawater	8.3	3.3 ‰	14 d 10 d	NOEC mort. LC_{50}	0.48 1.0	Van der Meer, et al., 1988	#3 Rem. 1
Palaemonetes varians	adult, 4 cm	A	-	pure	Seawater	8.0	-	7 d	LC_{50}	2.1	Adema, 1981	#2
Palaemonetes varians	larvae (1 d)	N	R	ethanol	Art.seawater	8.3	33 ‰	30 d 10 d	NOEC mort., dev. LC_{50}	0.49 1.8	Van der Meer, et al., 1988	#2
Palaemonetes varians	adult	N	R (1 d)	ethanol	Art.seawater	8.3	3.3 ‰	30 d 10 d	NOEC mort. LC_{50}	1.6 3.2	Van der Meer, et al., 1988	#2
Palaemonetes varians	larvae	N	R (1 d)	ethanol	Art.seawater	8.3	3.3 ‰	30 d 10 d	NOEC mort. dev. LC_{50}	0.48 0.94	Van der Meer, et al., 1988	#2
Fish												
Gobius microps	adult	A	-	pure	Seawater	8.0	-	7 d	LC_{50}	2.2	Adema, 1981	#2
Pleuronectes platessa	egg → metam. larvae				Art.seawater	8.0	-	3 m 3 m	NOEC mort.,growth,def. LC_{50}	0.032 0.18	Adema, 1981	#2
Pleuronectes platessa	~ 10 cm	A	-	pure	Seawater	8.0	-	14 d	LC_{50}	1.1	Adema, 1981	#2
Poecilia reticulata	adult bought	A	-	pure	Seawater	8.0	-	7 d	LC_{50}	2.6	Adema, 1981	#2
Poecilia reticulata	young lab.cult.	A	-	pure	Seawater	8.0	-	7 d	LC_{50}	4.6	Adema, 1981	#2

Rem. 1: 15% mortality in controls on day 14;
Rem. 2: 7% mortality in controls on day 26.

Table 6.1.9a Single species toxity data for 3,5-dichloroaniline - 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
Fish												
Brachydanio rerio	ei → larvae	N	R (2 d)	> 97%	DSW	7.4-8.4	210	28 d	NOEC def. growth mortality hatch	0.32 1.0 3.2 3.2	Adema, 1987	#1
Brachydanio rerio	ELS	N	R (2 d)	>97%	Enr. ground-water	7.4-8.4	210	28 d	NOEC surv., hatch, growth LC_{50}	0.32 1.3 (1.0-1.8)	Van Leeuwen et al., 1990	#2 Rem. 1

Rem. 1: Concentration remained constant during the test and deviated <10% from nom. conc.

Table 6.1.9b Single species toxity data for 3,5-dichloroaniline - 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	10	Devillers et al., 1986	#2
Crustaceans												
Crangon septemspinosa	4 cm 0.6 g	N	R (2 d)	-	Seawater	-	30 ‰	4 d	LC_{50}	2.5	Mcleese et al., 1979	#2

Abbreviations:

A	Analyzed concentrations during the experiment
N	Nominal concentrations
S	Static system
R	Renewal system (at least once) (time interval)
F	Flow through system
IF	Intermittent flow
Purity	Purity of the test chemical
solvent	Solvent used to solve the test chemical
Dechlor.	Dechlorinated
Art.	Artificial
Enr.	Enriched
DSW	Dutch Standard Water
n.m.	nutrient medium

Parameters:

pop.growth	Population growth
repr.	Reproduction
mort.	Mortality
behav.	Behaviour
surv.	Survival
hatch	Hatching
fert.	Fertility
def.	Deformity
dev.	Development

ELS Early Life Stage test

Rem. Remark
(1) sited in EC report U/83/203, Cabridenc, 1984.

# 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 Quantitative structure activity relations (QSARs)

Based on experimental data quantitative structure activity relations can be established for substances with similar structures and working mechanisms. For narcotizing substances QSARs are often used for relations where toxicity is a function of their octanol-water partition coefficient. Chloroanilines have a higher, more specific toxicity than narcotizing substances, but as chloroaniline group QSARs with a high correlation can be derived for several species as presented in Table 6.1.4.

Table 6.1.4 QSARs for the chloroanilines

Organism	QSAR equations (µmol/l)	r	s	Ref.
Pimephales Poecilia reticulata	$\log 1/LC_{50} = 0.92 \log K_{ow} - 3.72$	0.946	0.27	1
Chlorella pyrenoidosa	$\log 1/EC_{50} = 0.82 \log K_{ow} - 3.61$	0.932	0.27	2
Photobacterium phosphoreum	$\log 1/EC_{50} = 0.70 \log K_{ow} - 3.18$	0.900	0.29	2
Brachydanio rerio	$\log 1/LC_{50} = 0.82 \log K_{ow} - 3.26$	0.983	0.27	3
Brachydanio rerio	$\log 1/NOEC = 0.66 \log K_{ow} - 2.05$	0.991	0.16	3

r=correlation coefficient and s=standard error of estimate

References:
1 Hermens et al. (1984)
2 Maas-Diepeveen and Van Leeuwen (1986)
3 Van Leeuwen et al. (1990)

6.2 Toxicity to terrestrial organisms

Data on the toxicity of chloroanilines and dichloroanilines to terrestrial organisms like plants, bacteria and invertebrates are summarized in Table 6.2.1. As lipophilic substances may strongly adsorb to organic matter in the soil, the bioavailability of the test substance for the test organism is strongly influenced by content of organic material in the soil. Therefore test concentrations are often recalculated and standardized for a so-called standard soil, which contains 10% of organic matter and 25% of clay. NOEC-values for chloroanilines and dichloroanilines, converted to standard soil conditions ranged from 12 to 380 mg/kg dry weight.

6.3. (semi)field studies

The effects of chloroanilines were studied in various types of multi-species systems. NOEC-values of ≥10 µg/l and ≥25 µg/l were reported for 2,4- and 3,4-dichloroaniline, respectively (Slooff et al., 1986). Okkerman estimated the NOEC from Experiments with 3,4-dichloroaniline carried out by Crossland and Hillaby (1985) at 12 µg/l. Slooff et al. (1991) cite a plankton community study by Ratte et al. (1990) with a NOEC-value of 20 µg/l.

Table 6.2.1 LC_{50}- and NOEC-values for chloroanilines derived from laboratory experiments with various soil organisms, converted into standard soil (organic matter (OM) 10%, clay content 25%) (Denneman and Van Gestel, 1990)

Compound\ test organism	Soil type	Soil properties pH	%OM	%clay	Expo. time	Criterion	Result (mg/kg)	Standard soil (mg/kg)	Ref.
2-chloroaniline									
Plant									
Lactuca sativa	OECD	7.8	2	12	14d	EC_{50} growth	33	165	1
						NOEC growth	10	50	
3-chloroaniline									
Plants									
Lactuca sativa	OECD	7.8	2	12	14d	EC_{50} growth	15	75	1
						NOEC growth	3.2	16	
Oligochaetes									
Eisenia andrei	-	-	10	-	14d	LC_{50}	448	448	2
4-chloroaniline									
Microbial processes									
ATP-content	agric	6.4	3.1	33.6	48d	NOEC	20	66	3
O_2-consumption	sandy loam	7.3	7.9	-	4h	NOEC	100	125	4
CO_2-production					4h	NOEC	10	12	
2,4-dichloroaniline									
Plants									
Lactuca sativa	OECD	7.8	2	12	14d	EC_{50} growth	29	145	1
					14d	NOEC growth	10	50	
Oligochaetes									
Eisenia andrei	humic sand	5.6	6.1	2.4	14d	LC_{50}	285	380	5
	humic sand	5.2	3.7	2	14d	LC_{50}	142	384	
	art.soil	7	7.7	10.4	14d	LC_{50}	319	413	
	peat	3.8	15.6	9	14d	LC_{50}	842	526	
Lumbricus	humic sand	5.6	6.1	2.4	14d	LC_{50}	304	400	5
rubellus	humic sand	5.2	3.7	2	14d	LC_{50}	201	441	
	art. soil	7	7.7	10.4	14d	LC_{50}	190	246	
	peat	3.8	15.6	9	14d	LC_{50}	580	600	
Eisenia andrei	-	6.0	10	20	21d	NOEC reprod.	56	56	2
3,4-dichloroaniline									
Microbial processes									
O_2-consumption	sandy loam	7.3	7.9	-	4h	EC_{20}	10	12	4
CO_2-production					4h	NOEC	300	380	
Nitrification	loam	7.2	3	-	>10d	NOEC	5	16	6
3,5-dichloroaniline									
Plants									
Lactuca sativa	OECD	7.8	1.4	12	14d	EC_{50} growth	13	65	1
						NOEC growth	3.2	16	

1 Adema and Henzen, 1990
2 Van Gestel, n.p.
3 Zelles et al., 1985
4 Semus and Ottow, 1985
5 Van Gestel and Ma, 1990

6.4.1 Toxicity to mammals and birds

Toxicity data available for chloroanilines are presented in Table 6.4.1. Most of the LD_{50}-values for oral administration vary between 100 and 2900 mg/kg body weight. The lower NOEC in a chronic test with oral exposure was 0.005 mg/kg body weight/day for guinea pig. Extrapolation from this value with a margin of safety of 100 results in a tentative "acceptable daily intake" for man at lifetime exposure to a value of 0.05 µg/kg body weight/day, equivalent to 3 µg/day for a 60 kg person (Slooff et al., 1991).

Table 6.4.1 Acute toxicity of chloroanilines and dichloroanilines to mammals and birds (Sax, 1989)

Compound\ test organism	Route of administration	Expo. time	Criteria	Result (mg/kg)	
2-chloroaniline					
mouse	oral		LD_{50}	256	
cat	skin		LD_{50}	222	
3-chloroaniline					
rat	oral	8 mth	NOEC	0.25	**
rat	oral		LD_{50}	256	
mouse	oral		LD_{50}	334	
guinea-pig	oral		LD_{50}	250	
4-chloroaniline					
guinea-pig	oral		LD_{50}	350	
guinea-pig	oral	7-8 mth	NOEC	0.005	
mouse	oral		LD_{50}	100	
quail	oral		LD_{50}	237	
rat	oral	8 mth	NOEC	0.01	**
rat	oral	78 w	TDLo	25	
mouse	oral	78 w	TDLo	590	
mouse	inhalation		LC12	250	*
rat	inhalation	chron.	NOEC	0.29	**
rat	skin		LD_{50}	3200	
cat	skin		LD_{50}	239	
rabbit	skin		LD_{50}	360	
2,5-dichloroaniline					
rat	oral		LD_{50}	2900	
3,4-dichloroaniline					
rat	oral		LD_{50}	648	
rat	oral	6 mth	NOEC	0.2	**
cat	skin		LD_{50}	700	

TDLo lowest dose that has induced toxicological reactions to test animals

* mg/m^3

** mg/kg body weight/day

6.5 Carcinogenic, mutagenic and teratogenic effects

Data on mutagenity, carcinogenity and teratogenity are evaluated by the Dutch National Institute of Public Health and Environmental Protection (RIVM) (Vermeire et al. 1991). Additional data were searched for in IARC (1987a; 1987b),

2-Chloroaniline

No data were available on carcinogenity. 2-Chloroaniline is considered to have no mutagenic properties, although in some experiments a positive response is found.

3-Chloroaniline

No data were available on carcinogenity. Like 2-chloroaniline, 3-chloroaniline is considered to have no mutagenic properties, although in some experiments a positive response is found.

4-Chloroaniline

In some carcinogenicity tests 4-chloroaniline responded positively, like the occurrence of haemangiosarcomas in mice and sarcomas in spleen and abdomal cavity in rats. This was, however, insufficient evidence to conclude that 4-chloroaniline is carcinogenic. It is assumed that 4-chloroaniline has carcinogenic potential (Koten-Vermeulen et al., 1989; BG chemie, 1988).
The Dutch National Cancer Institute has tested 4-chloroaniline on carcinogenicity, result "indefinite".

Dichloroanilines

In one study 3,4-dichloroaniline is found to stimulate back mutation to a significant degree (Prasad and Pramer, 1968).

No data on the teratogenity of chloroanilines are available.

7 ENVIRONMENTAL IMPACT ASSESSMENT

7.1 Comparison of exposure and effects

When chloroanilines are released into the aquatic environment, they will distribute among the environmental compartments. They will partly volatilize from the water into the air, where they may be degraded (photo-degradation). Another part will distribute between the water and sediment compartments.

Environmental concentrations for chloroanilines were just below 1 µg/l in some European rivers in 1979 (for individual isomers). These concentrations have decreased during the past ten years to values in the range of 0.05 µg/l. Concentrations in the sediment were in the range of 0.5 mg/kg d.w. in 1982.
The relatively low log K_{ow}-values (between 1.9 and 2.9) indicate that chloroanilines do not have strong bioaccumulative properties. Moreover, experimental data showed BCF-values in fish predicted on the basis of their lipophility (log K_{ow}). Yet low levels may be found in organisms.

The toxicity of these substances is well below their water solubility. Although for several isomers only a limited amount of data is available, it seems that the isomers of both mono- and dichloroanilines are about equally toxic to aquatic organisms. The lowest No Observed Effect Concentration from chronic tests vary between 3.2 and 40 µg/l with *Daphnia magna*, a fish and a marine worm as the most sensitive test species. Results from (semi)field tests indicate that no effect concentrations in aquatic ecosystems range between 10 and ≥25 µg/l. Comparison of these toxicity data with the above mentioned environmental levels leads to the conclusion that the distance between the actual exposure and the concentrations where effects are to be expected was very small in 1979. Moreover, if the additivity of the various isomers is taken into account, the summed concentration of all chloroanilines actually present in the river Rhine (0.4 µg/l) is still rather close to the lowest NOEC for the most sensitive species.

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 which protects the aquatic ecosystem (OECD, 1991). This 'safe level' may also be called maximal tolerable concentration or MTC. The 'modified US-EPA method' 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.
Another approach is to use the variability in the sensitivity among the various test species as a means to calculate a concentration that is expected to be safe for most (e.g. 95%) of the species in the aquatic ecosystem. In other words, a concentration is calculated that is hazardous for only a small number (5%) of species. Two calculation methods are available, which differ in their basic assumptions regarding the shape of the distribution curve for the species sensitivity. One method assumes a log-logistic distribution (Aldenberg and Slob, 1991), whereas the other assumes a log-normal distribution (Wagner and Løkke, 1991).

As the different chloroaniline isomers have similar working mechanisms and they are about equally toxic, the data for all isomers are grouped and the extrapolation methods are applied to derive a MTC for the sum of all chloroanilines. The results are:

Extrapolation method	MTC (µg/l)	Remarks
Modified EPA	0.32	lowest NOEC / 10
Aldenberg and Slob, 1991	5.5	95% protection level, (50% confidence,) 20 test species
Wagner and Løkke, 1991	4.8	

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. Chloroanilines 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 chloroanilines of 5 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) a maximal permissible concentration was proposed of 1 to 5 µg/l in both freshwater and marine water for all chloroanilines. This level was derived from the toxicity data available at the time, where the lowest LC_{50} was 1.5 mg/l.

When the proposed water quality standard is compared to the environmental levels actually found in the rivers Rhine, Meuse and Scheldt (see Table 3.3.1: (total chloroanilines) mean 0.15 and max. 0.4 µg/l in 1990), the proposed standard is not exceeded. Therefore it is concluded that chloroanilines do not pose a hazard to the aquatic environment of the river Rhine.

For chloroanilines standards were proposed by the Rhine Action Program (1991) of 0.1 µg/l for 2-, 3-, and 4-chloroaniline and for 3,4-dichloroaniline and 0.01 µg/l for 4-chloroaniline. For 2- and 3-chloroaniline 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. For 4-chloroaniline and 3,4-dichloroaniline the standards are based on the extrapolation of laboratory toxicity data of an algae, daphnia and/or fish, using extrapolation factors of 10, 100 or 1000 on the lowest toxicity test result.
When the proposed Rhine Action Program water standards for each substance are compared to the water quality standards for the sum of all chloroanilines as proposed here, it is concluded that these standards are an order of magnitude higher.

7.3 Human exposure

Exposure of man to substances in the aquatic environment may occur through oral intake from (drinking) water and from fish, shellfish or crayfish. Other possible exposure 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 negligible 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 chloroanilines in the water is assumed to be at the level of the proposed water quality standard: 5 µg/l. Assuming a daily water consumption of 2 litre, the oral intake of chloroanilines from the water will be 10 µg/day.
The concentration in fish is estimated from the bioconcentration factor (C_{fish}/C_{water} = 30) to be 150 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 15 µg/day.
The total oral intake of chloroanilines at the proposed water quality standard is estimated at 25 µg/day for a 60 kg person or 0.42 µg/kg body weight/day.

Comparison with the lowest chronic NOEC for 4-chloroaniline (5 µg/kg body weight/day) shows that toxic effects are expected at doses that are at least 10 times higher. The estimated oral intake at the water quality standard is about 10 times higher than the tentative "acceptable daily intake" (0.05 µg/kg body weight/day for 4-chloroaniline. The risk of human exposure to chloroanilines present in aquatic systems at a concentration level of 5 µg/l may be considerable. A more refined human risk assessment should therefore be made.

In the actual situation of the river Rhine in 1990 the maximum water concentration all isomers together may rise to 0.4 µg/l. This may result in a daily intake of 0.034 µg/kg body weight/day which is 2/3 of the tentative "acceptable daily intake", indicating that chloroanilines in the river Rhine do not cause direct danger to humans, but also that the water is not completely safe to drink unpurified.

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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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