Canadian Environmental Protection Act

Priority Substances List

Supporting Documentation - Environmental Sections

ANILINE

(Unedited Version)

Environment Canada

July 1993

DISCLAIMER

This is an unedited document made available for public information. A published assessment report is available under the title "Canadian Environmental Protection Act, Priority Substances List, Assessment Report, Aniline" from:

Commercial Chemicals Branch Environment Canada 14th Floor, Place Vincent Massey 351 St. Joseph Blvd. Hull, Québec K1A 0H3

Environmental Health Centre National Health and Welfare Canada Room 104 Tunney's Pasture Ottawa, Ontario K1A 0L2

TABLE OF CONTENTS

3

1.0	IDENTITY OF SUBSTANCE51.1Name of Substance51.2Characteristics of Substance51.3Analytical Methodology5
2.0	PHYSICAL AND CHEMICAL PROPERTIES
3.0	SOURCES AND RELEASES TO THE ENVIRONMENT53.1 Natural Sources53.2 Anthropogenic Sources53.2.1 Production and market trends53.2.2 Canadian consumption, imports and exports63.2.3 Manufacturing processes63.2.4 Uses63.2.5 Releases7
4.0	ENVIRONMENTAL TRANSPORT, TRANSFORMATION AND CONCENTRATIONS
	Media 9 4.1.1 Water 9 4.1.2 Air 9 4.1.3 Soil 9 4.1.4 Biota 10
	4.2Transformation104.2.1Biodegradation104.2.2Abiotic degradation124.2.3Predictions of environmental fate using computer modelling12
	4.3 Environmental Concentrations 13 4.3.1 Surface water 13 4.3.2 Groundwater 13 4.3.3 Air 14 4.3.4 Soil and sediment 14 4.3.5 Biota 14
5.0	<pre>POPULATION EXPOSURES (refer also to supporting documentation from Health and Welfare Canada) 14 5.1 Exposures of wildlife populations</pre>
6.0	TOXICOKINETICS AND METABOLISM (refer also to supporting documentation from Health and Welfare Canada)

cont'd on next page

TABLE OF CONTENTS, cont'd

Ì

ļ

Î

7.0	MAMMALIAN TOXICOLOGY (refer to supporting documentation from Health and Welfare Canada) 1	5
8.0	EFFECTS ON HUMANS (refer to supporting documentation from Health and Welfare Canada) 1	5
9.0	EFFECTS ON THE ECOSYSTEM19.1 Aquatic Toxicity19.2 Terrestrial Toxicity1	5 5 6
10.0	REFERENCES	7
	APPENDIX: LEVEL III FUGACITY MODELLING	9
·		
List (<u>oi figures</u>	•
Figure	e 1. Chemical structure of aniline 3	7
Figure	e A-1. Mass balance diagram for aniline in southern Ontario according to the level III fugacity model of Mackay and Paterson (1991) 4	2
<u>List c</u>	of Tables	
Table	1. Chemical and physical properties of aniline 2	7
Table	2. Imports of aniline and aniline hydrochloride into Canada	8
Table	3. Environmental occurrence of aniline 2	9
Table	4. Acute toxicity of aniline to aquatic organisms 3	1
Table	A-1. Summary of results for aniline in southern Ontario according to the level III fugacity model of Mackay and Paterson (1991) 4	1

1.0 Identity of substance

1.1 Name of substance

Aniline (Chemical Abstracts Service Registry Number 62-53-3) is the simplest of the primary aromatic amines, with a molecular formula of C_6H_7N . Its structure is shown in Fig. 1. Synonyms for aniline include benzenamine, phenylamine and aminobenzene. Aniline is also available as aniline hydrochloride ($C_6H_7N \cdot HCl$, Chemical Abstracts Service Registry Number 142-04-1, synonyms: aniline chloride, anilium, chloride, phenylamine hydrochloride).

1.2 Characteristics of substance

Aniline is a clear, colourless oily liquid at room temperature with a bluish fluorescence (Sax, 1968).

1.3 Analytical methodology

Aniline in water, sediment and tissues can be determined by standard techniques of extraction and gas chromatography, e.g., the U.S. Environmental Protection Agency base/neutral method (U.S. Environmental Protection Agency, 1984). Detection limits depend upon the detector used. For example, Jungclaus et al. (1978) detected aniline at 20 μ g/L in wastewater using gas chromatography-electron impact mass spectrometry.

2.0 Physical and chemical properties

Table 1 gives the physical and chemical properties of aniline.

3.0 Sources and releases to the environment

3.1 Natural sources

No natural sources of aniline have been identified.

3.2 Anthropogenic sources

3.2.1 Production and market trends

Aniline is not produced in Canada. Production in the United States in the period 1981-1983 varied from 250,000 to 300,000 tonnes (Northcott, 1978). Production in 1984 was 359,000 tonnes (U.S. Environmental Protection Agency, 1988), and production in 1986 and 1990 was 755,000 and 1,035,000 tonnes, respectively (U.S. Environmental Protection Agency, 1992). Demand for aniline in the U.S.A. for the production of diphenylmethane disocyanate (MDI) (the largest use of aniline in the U.S.A.) is growing as new capacity comes on stream to serve domestic and overseas markets. The largest use for MDI is in rigid urethane foams where applications include insulation for housing and refrigerators

(Corpus Information Services, 1990).

3.2.2 Canadian consumption, imports and exports

Aniline is not produced in Canada, although at one time Uniroyal Chemical Inc. did manufacture the chemical at Elmira, Ont. via the old batch process using iron filings to reduce nitrobenzene to aniline. The Elmira plant began operations in 1942 as Naugatuck Chemicals, to produce aniline for the war effort (Corpus Information Services, 1990). Aniline has not been produced at Elmira at least since 1971 (Corpus Information Services, 1979). Aniline and aniline hydrochloride are primarily imported from the U.S.A. into Ontario. Table 2 shows import figures for aniline and aniline hydrochloride in the period 1976-1991. Amounts imported by individual companies constitute confidential business information, and are not reported here.

3.2.3 Manufacturing processes

Aniline can be produced by the reduction of nitrobenzene with iron filings using hydrochloric acid as a catalyst, by the catalytic reaction of chlorobenzene and aqueous ammonia, and by the ammonolysis of phenol. However, it is usually manufactured by the catalytic reduction of nitrobenzene. In this process nitrobenzene vapour and hydrogen are passed over a catalyst at temperatures below 350 °C to obtain a 98% yield of aniline. Catalysts used include copper oxide, sulfides of nickel, molybdenum or tungsten, and palladium-vanadium/lithium-aluminum mixtures (Northcott, 1978)

3.2.4 Uses

The major uses of aniline in Canada are in the production of rubber chemicals and polymers, accounting for approximately 94% of the amount used in 1990 (Canada Department of the Environment, 1991). The largest use of aniline in Canada is in the production of several rubber chemicals (antioxidants, antidegradants and vulcanization accelerators), notably mercaptobenzothiazole, 2mercaptobenzothiazyl disulfide and zinc 2-mercaptobenzothiazole (Corpus Information Services, 1990). This use accounted for 62% of aniline use in Canada in 1990 (Canada Department of the Environment, 1991). It is anticipated that this main use will be curtailed soon since the company which imported most of the aniline produce the rubber chemicals intends to import other to intermediates instead (Corpus Information Services, 1990). In the polymer industry, aniline is used primarily for the manufacture of isocyanate intermediates in the synthesis of polyurethanes. This use accounted for 32% of aniline use in Canada in 1990 (Canada Department of the Environment, 1991). Aniline is also used for the production of phenolic-based resins (6% of aniline use in Canada in 1990), and on a very small scale in laboratories. It is a trace contaminant in some polymers imported into, as well as manufactured in, Canada.

The major uses of aniline in the United States are in the polymer, rubber, agricultural and dye industries. Demand in the dye industry decreased markedly in the United States in the 1970s because of the increased use of synthetic fabrics and environmental and occupational health and safety concerns. Estimated U.S. uses of aniline in 1975 were 50% for urethane polymers, 30% for rubber chemicals, 10% for pesticides, 5% for dyes, 2% for photographic chemicals, 1% for drugs and 2% for miscellaneous uses (Northcott, 1978). Aniline and its N-alkyl derivatives have also been used as antiknock compounds in leaded gasolines (Northcott, 1978; Ontario Ministry of the Environment, 1980).

3.2.5 Releases

Possible routes of entry of aniline and its salts to the Canadian environment are:

- (a) atmospheric and water-borne transport from other countries
- (b) losses during transportation
- (c) losses in manufacture of aniline-containing materials
- (d) losses in weathering or leaching of aniline-containing materials
- (e) losses of landfill-disposed aniline-containing materials, or losses from licensed waste disposal facilities of reaction tars containing aniline
- (f) losses by incomplete incineration of aniline-containing materials
- (g) losses through the breakdown of aniline-containing pesticides
- (h) discharges of coal oil (e.g., from the production of coke from coal)

Aniline has been detected but not quantitated in a sewage treatment plant influent and effluent in Ontario (Ontario Ministry of the Environment, 1982). The source was not identified. Aniline could also be produced in the environment through the reduction of nitrobenzene, but there is no information on the importance of this degradative route in Canada or elsewhere.

Route (c) would likely be the most important route of entry of aniline to the Canadian environment. Losses during production of aniline and its salts are not included on the above list because they are not produced in Canada. In polymers the residual aniline content is generally so low that loss from this source (route d) would not constitute a significant route of entry. It is likely that incineration of aniline-containing materials (route f) would also destroy unreacted aniline. Hazards associated with the introduction of aniline to the environment through the breakdown of aniline-containing pesticides (route g) would be dealt with under the Pest Control Products Act. [Aniline has been found to be a metabolite of a number of chemically related pesticides (Lyons et al., 1985a,b).]. In the U.S.A., aniline has been found in small quantities in coal tar (route h) (Northcott, 1978) and as a result

of coal gasification (Stuermer *et al.*, 1982) and shale oil retorting (Hawthorne and Sievers, 1984). It has also been found in limited studies of industrial effluents in the U.S.A. (Games and Hites, 1977; Jungclaus *et al.*, 1978; Ellis *et al.*, 1982), but quantitative information on releases to the environment from these sources was not identified.

There are few available data from any country which could be used to quantitate effluent or emission loadings of aniline from the above routes of entry with confidence. Releases of aniline to the U.S. environment in 1989 were estimated to be 47% by deep well injection, 26% to municipal sewage treatment plants, 20% "offsite", 4% to the air, and 1% "fugitive" (U.S. Environmental Protection Agency, 1991). The National Analysis of Trends in Emergencies System (Canada Department of the Environment, 1992) has on record one aniline spill in Canada for the period 1974 to 1984. The total amount involved was 0.1 tonne, but no other information is available. No other Canadian data on releases are available. Total industrial emissions of aniline to the environment in the U.S.A. in 1988 and 1989 were estimated to be 898 and 3182 tonnes, respectively (U.S. Environmental Protection Agency, 1990, 1991). For the purposes of estimation, if it is assumed that aniline use in the United States were 1,000,000 tonnes in 1989, losses would be If this figure were applied to Canadian uses 0.32% of total use. in 1989, for example, losses would be estimated as 1.13 tonne. It should be noted that production losses in the United States may have contributed to a higher loss rate than should have been applied to Canada, which does not produce aniline.

4.0 Environmental transport, transformation and concentrations

With regard to the behaviour of a chemical in the environment, it should be noted that there are many factors which influence its persistence, including its physical and chemical properties, and ecosystem-specific properties such as (for aquatic ecosystems) the nature and concentration of dissolved and suspended material, nature and concentration of microbial populations, temperature, degree of insolation, etc. Important physical, chemical and biological removal mechanisms for aquatic ecosystems, for example, are (i) volatilization and adsorption to suspended solids and (ii) chemical and photochemical degradation sediment, or (iii) uptake transformation transformation, and and by microorganisms, respectively. A more detailed description of the way in which physical-chemical properties and ecosystem-specific properties determine the fate of chemicals has recently been given by Howard (1989). It is expected that salts of the aromatic amines would have the same environmental fate as their parent compounds.

4.1 Transport and distribution between and within media

4.1.1 Water

The relatively low vapour pressure, high water solubility, and low octanol/water partition coefficient of aniline suggest that most aniline in the environment should be found in water. The Henry's Law constant (ratio of vapour pressure to aqueous solubility) for aniline calculated from the data in Table 1 is 1.78 torr L mole⁻¹, which indicates that it is a relatively lowvolatility compound as far as volatilization from water is concerned (Smith *et al.*, 1980; U.S. Environmental Protection Agency, 1985). Based on physical/chemical properties, the halflife for volatilization of aniline from surface water [1 m deep, flowing at 1 m/s, with wind velocity of 3 m/s, at 20 °C] to the atmosphere was estimated to be 359 hours, according to a method described by Thomas (1982).

4.1.2 Air

Because aniline is a relatively low-volatility compound which is expected to partition to water, it is not expected to contribute to phenomena such as ozone depletion or global warming, or groundlevel ozone formation.

4.1.3 Soil

The binding of aniline and substituted anilines to soils has been studied extensively (e.g., Hsu and Bartha, 1974; Moreale and Van Bladel, 1976; Parris, 1980a,b; Dao et al., 1986; Dao and Lavy, 1987). Although there have been correlations between the extent of binding and clay content and pH of the soil (the pK, of aniline is 4.63 - Weast et al., 1984), soil organic matter appears to play the major role in the adsorption of aniline. The binding may occur between the amino group of aniline and the carboxy and carbonyl groups on the humic acid [one of the two mechanisms suggested by Hsu and Bartha (1974), the other mechanism being a non-hydrolyzable association with heterocyclic rings and ether bonds]. Parris (1980b) showed that covalent binding (as inferred from lack of recoverability by simple organic solvent extraction) of aniline and ring-substituted anilines (including 2-, 3- and 4methylaniline) involves two different chemical reactions. When an aniline is mixed with humate, a reversible equilibrium is very rapidly established. This equilibrium is thought to represent reaction of the amino group with aldehyde and ketone groups in the humate to form imine linkages. The second reaction is very slow and not readily reversible. This slow reaction is thought to represent addition of the amines to quinoidal structures followed by oxidation of the product to a nitrogen-substituted quinoid ring. Subsequent to this initial addition, further reactions may occur to lock the amine moiety into the humate as part of a heterocycle.

4.1.4 Biota

Bioconcentration of aniline in aquatic biota does not appear to be a significant process. The uptake and metabolism of aniline by aquatic organisms has been studied by a number of investigators. Lu and Metcalf (1975) studied the fate of aniline in a model aquatic ecosystem consisting of phytoplankton, zooplankton, green filamentous algae (Oedogonium cardiacum), snails (Physa), water flea (Daphnia magna), mosquito larvae (fourth instar) (Culex quinquifasciatus) and mosquito fish (Gambusia affinis). After 2 days, the fish was the only species which retained small amounts of aniline with a bioconcentration factor of 6. Freitag et al. (1982) found a 1-d bioconcentration factor (BCF) of 4 for algae (Chlorella fusca), and a 3-d BCF of <10 for fish (golden orfe, Leuciscus idus melanotus). In contrast, Hardy et al. (1985) found that the alga Scenedesmus quadricauda had a BCF for aniline of 91; after 24 h, 52% of the parent compound remained unmetabolized. Dauble et al. (1986) reported apparent BCF values of 74 (uptake phase data) and 590 (elimination phase data) for Daphnia magna. The results of Hardy et al. (1985) and Dauble et al. (1986) suggest some potential for bioaccumulation of aniline by organisms which consume these organisms; however, significant bioaccumulation has not been observed, nor would it be expected for a chemical with a log octanol-water partition coefficient of 0.9.

No information was identified on the bioconcentration of aniline by terrestrial animals.

4.2 Transformation

The general conclusion from studies of the environmental persistence and fate of aniline is that it is relatively nonpersistent in the environment, and that overall half-lives in water, soil and air would be less than a few weeks (e.g., U.S. Environmental Protection Agency, 1985). Microbial degradation has been identified as the most significant process determining the persistence of aniline in water (Sanders, 1979; Lyons *et al.*, 1984; Howard, 1989). Photooxidation in surface waters can also be important, with a half-life of a few days. The formation of bound, unextractable, aniline residues in soils is a significant phenomenon.

4.2.1 Biodegradation

Aniline did not persist in pond water (70, 59 and 10% remaining after 4, 7 and 14 d, respectively) or pond water plus sewage sludge (8, 0 and 0% remaining after 4, 7 and 14 d, respectively) (Lyons *et al.*, 1984, 1985a). The major pathway of aniline biodegradation in pond water involved oxidative deamination to catechol (see also Paris and Wolfe, 1987), which was further metabolized through *cis,cis*-muconic, β -ketoadipic, levulinic and succinic acid intermediates to CO₂.

involved reversible acylation to acetanilide and formanilide, whereas N-oxidation resulted in small amounts of oligomeric condensation products. The relatively easy degradation of aniline by microorganisms has been confirmed by others (e.g., Malaney, 1960; El-Dib and Aly, 1976; Pitter, 1976; Baird et al., 1977; Gerike and Fischer, 1979; Calamari et al., 1980; Korte and Klein, Aoki et al., 1982; Subba-Rao et al., 1982; 1982; King and Painter, 1983; Demirjian et al., 1987; Patil and Shinde, 1988; Konopka et al., 1989; Liu and Liu, 1992). Means and Anderson (1981) found that aniline completely degraded in 1-7 d in the BOD, shake flask, CO₂ evolution and activated sludge tests. Brown and Laboureur (1983) found that aniline was > 90% microbiologically degraded in 7 d under aerobic conditions, although it was not degraded under anaerobic conditions. This lack of degradation under anaerobic conditions was also noted by Hallas and Alexander (1983), who demonstrated that acetanilide and 2-methylquinoline were products of degradation or transformation. The diazonium ion was a key intermediate in the degradation of aniline by E. coli. in the presence of nitrite ion (Lammerding et al., 1982). This was shown by the trapping of the diazonium ion with 2-naphthol.

In estuarine water, half-lives for the combined sunlight photolysis and microbial degradation of aniline were 1-8 d (Hwang et al., 1987).

The biological degradation of aniline is expected to be important in groundwater, although it will be slower than in surface water (Aelion *et al.*, 1987, 1989).

In soil, biological degradation, oxidation and binding to soil constituents are important (Parris, 1980a; see also section 4.1.3). Aniline is easily degraded by many common species of bacteria and fungi found in soil and silage (e.g., Alexander and Lustigman, 1966; Lyons et al., 1985b; Swindoll et al., 1988; Howard, 1989). In sterile soil aniline partially degraded in 3 d to azobenzene, azoxybenzene, phenazine, formanilide and acetanilide (Pillai *et al.*, 1982). Nitrobenzene, p-benzoquinone and unidentified species were possible products. Substantial bound residues may also have been formed. Soil-catalyzed conversion of aniline or [d_s]aniline was suggested by 6-24 times more product recovery in sterile soil than in sterile water alone, a process inhibited by sodium dithionite (suggesting that molecular oxygen is involved). Freundlich adsorption isotherms showed soil-binding strength in the order azobenzene > azoxybenzene > phenazine >> aniline. Although a variety of aniline transformation products was most of the added aniline was unaccounted for. identified, Inefficient extraction may have contributed to part of this discrepancy. It is believed that the isolated products indicate intermediate formation of reactive polar species that will, in large part, form higher molecular weight polymers or react with soil organic matter. This leads to formation of non-extractable soil-bound residues. Approximately 60% of [14C] aniline became bound

after 10 weeks in four non-sterile soils. These results suggest that chemical transformations may play a significant role in aniline bound residue production.

4.2.2 Abiotic degradation

Aniline is readily oxidized on exposure to air. The half-life for direct photolysis in air was estimated to be 2 d, and for reaction with photochemically-generated hydroxyl radicals in air was estimated to be 3 h (Howard, 1989).

Aniline photodegraded with a half-life of about 7 d in distilled water. This reaction was accelerated to a considerable degree by humic acids and aquatic humus, with near-surface halflives of 4 to 8 h in May sunlight at Athens, GA, U.S.A. Azobenzene was an identified product (but at only 0.2% yield) (Zepp et al., 1981). Green and blue-green algae, at concentrations of 1-10 mg of chlorophyll a/L, accelerated the sunlight photolysis of aniline and other compounds (Zepp and Schlotzhauer, 1983). Aniline reacted up to 12,000 times faster with some algal species than it did in distilled water. Reaction rates appeared to be unaffected by heatkilling the algae, in accord with earlier studies that substances released by algae can photosensitize a variety of reactions in Dark metabolism made little or no contribution to the water. In estuarine water, half-lives for the combined degradation. sunlight photolysis and microbial degradation of aniline were 1-8 Carbonate radicals generated by the (Hwang et al., 1987). d photolysis of hydrogen peroxide in water can react with aniline and substituted anilines such as 3-methylaniline (Larson and Zepp, 1988). Freitag et al. (1982) found that irradiation of aniline on silica gel for 17 h with 290 nm UV light resulted in the mineralization of 46% of the radiolabel to $^{14}CO_2$.

Amador et al. (1991) have shown that sunlight irradiation of an aniline-humic acid complex resulted in a loss of UV light absorbance and the formation of low molecular weight products. Both the sunlight-irradiated and the unirradiated aniline-humic acid complexes resisted microbial attack over 21 d in a soil suspension. This unexpected resistance was apparently not due to toxicity of the complex to degrading microorganisms. The resistance may be due to the formation of N-heterocycles between the aniline and quinone groups in the humic acid.

4.2.3 Predictions of environmental fate using computer modelling

Because of the lack of data on fate and concentrations in the Canadian environment, the distribution of aniline in the environment was estimated using the level III fugacity computer model for southern Ontario (Mackay and Paterson, 1991) (see Appendix 1). It was based on the 1989 estimate for imports into Canada and data on production and releases in the U.S.A. (U.S. Environmental Protection Agency, 1991, 1992), and it assumed that

all the aniline was imported for use only in southern Ontario and that it would be released into the water at a rate of 1.385 mol/h (estimated 1.13 tonne released in 1989). The results indicated that at steady-state, aniline would be found in the air (0.002%), surface water (99.98%), sediment (0.015%) and soil (< 0.001%). This would result in steady-state concentrations of 2.15x10⁻⁹ μ g/m³ in air, 8.74x10⁻³ ng/L in water, 4.6x10⁻⁹ μ g/g dry weight in sediment, and 2.7x10⁻¹² μ g/g dry weight in soil. It should be noted that this model does not address the possibility of formation of bound residues in sediment; consequently, concentrations in sediment may be underestimated, and concentrations in water may be overestimated.

4.3 Environmental concentrations

Table 3 shows the environmental occurrence of aniline. There are relatively few data on the environmental occurrence of such a widely used chemical. The few studies conducted on aniline have indicated that it is generally introduced to the environment in effluents from chemical plants and energy-related processes.

4.3.1 Surface water

No data were identified on the occurrence of aniline in surface water in Canada. Outside Canada, aniline has been found in rivers in the Netherlands, Germany and the U.S.A. at concentrations up to 13 μ g/L (Meijers and van der Leer, 1976; Neurath *et al.*, 1977; Wegman and De Korte, 1981a, 1981b; U.S. Environmental Protection Agency, 1988).

4.3.2 Groundwater

Aniline has been found at 10 μ g/L in groundwater in Ontario close to a landfill (Reinhard et al., 1984). Recently, aniline was found in monitoring wells beneath the Uniroyal Chemical Inc. site in Elmira, Ontario, at concentrations up to 300 mg/L (Lesage et al., 1990; CH2M Hill Engineering, 1991), and in the dense non-aqueous phase liquid beneath former containment areas on the same site at concentrations up to 2% (Dames & Moore Canada, 1992). The total amount of aniline in the groundwater and in the dense nonaqueous phase liquid at the Elmira site is not known. There are no water quality guidelines for aniline in groundwater. It is not known what concentrations of aniline result in the nearby Canagagigue Creek when the groundwater migrates to the surface. The chemical company is under a control order from the Ontario Ministry of the Environment to prevent contaminated groundwater from migrating off its property in any aquifer (Ontario Ministry of the Environment, 1991). The town of Elmira now obtains its drinking water by pipeline from nearby Kitchener.

Outside Canada, aniline has been found at 0.4 μ g/L in groundwater near an underground coal gasification site in Wyoming

(Stuermer et al., 1982), and at 705 μ g/L in groundwater contaminated by coal-tar wastes in Minnesota (Pereira et al., 1983).

4.3.3 Air

No data were identified on the occurrence of aniline in air in Canada. Concentrations of aniline in air in the U.S.A. were found in the range from non-detected to 33 μ g/m³ (Hawthorne and Sievers, 1984).

4.3.4 Soil and sediment

No data were identified on the occurrence of aniline in soil in Canada. In the U.S.A., aniline was found at 5 mg/kg dry weight in soil near a dump for a dye manufacturing plant (Nelson and Hites, 1980).

No data were identified on the occurrence of aniline in sediment in Canada or elsewhere.

4.3.5 Biota

No data were identified on the occurrence of aniline in biota in Canada or elsewhere.

5.0 Population exposures

Refer also to supporting documentation from Health and Welfare Canada.

5.1 Exposures of wildlife populations

No data were identified for the exposure of aniline to wild mammals, terrestrial organisms, birds, sediment or soil biota in Canada or elsewhere.

5.2 Exposures of the general human population

Refer to supporting documentation from Health and Welfare Canada.

6.0 Toxicokinetics and metabolism

Refer also to supporting documentation from Health and Welfare Canada.

The metabolism of aniline by aquatic organisms has been studied by a number of investigators. In a model ecosystem study, Lu and Metcalf (1975) found that aniline was rapidly detoxified by methylation, acetylation, hydroxylation and conjugation. Daphnia and snails were able to metabolize aniline completely to polar metabolites. N-Methylaniline and N,N-dimethylaniline transformation products were found in algae, mosquito larvae and fish. Almost equal amounts of o-, m- and p-aminophenols were found in fish. Acetanilide was found in fish and water extracts and was further metabolized to p-acetamidophenol, then conjugated.

Aniline has been found to be a metabolite of a number of chemically related herbicides derived from acetanilide, phenylurea, phenylcarbamate, and nitroaniline (e.g., Lyons et al., 1985a). The chemical is then free to be taken up by plant roots and translocated into the shoots. Aniline appears to bind rapidly and irreversibly to plant constituents.

The microsomal fraction of germinated pea seeds (*Pisum sativum*) has been shown to oxidize aniline to N-nitrosoaniline (Corbett and Corbett, 1983).

7.0 Mammalian toxicology

Refer to supporting documentation from Health and Welfare Canada.

8.0 Effects on humans

Refer to supporting documentation from Health and Welfare Canada.

9.0 Effects on the ecosystem

9.1 Aquatic toxicity

Table 4 shows the acute toxicity of aniline to a number of aquatic organisms. Aniline is not very toxic to most species tested, with the exception of *Daphnia* sp. The lowest 48-h LC_{50} value reported was 0.1 mg/L for *Daphnia pulex* (Sloof *et al.*, 1983). Although neither the clawed toad nor the axolotl species shown in Table 4 is native to Canada, they may well serve as surrogates for native toads and salamanders.

Daphnia magna is very sensitive to chronic exposure to aniline. Gersich and Milazzo (1988) estimated the 21-d LC_{50} as 47 μ g/L. Gersich and Milazzo (1990) later reported statisticallysignificant 14-d LOECs for mortality of 22 μ g/L, and for reproduction (mean total number of young per adult and mean brood size) and growth of 43.2 μ g/L. Tadokoro and Maeda (1988) reported the 14-d LOEC (immobilization) to be 98.8 μ g/L for Daphnia magna. Van Leeuwen et al. (1990) reported a 28-d LC_{50} value of 39 mg/L for larval and embryo life stages of zebra fish (Brachydanio rerio). The no-observed-lethality-concentration (NOLC) was 5.6 mg/L, and the no-observed-effects-concentration (NOEC) for hatching and growth was 1.8 mg/L.

Some other effects were noted in the acute studies shown in Davis et al. (1981) noted Table 4 and in other studies. teratogenic effects of aniline on the larvae of the clawed toad Xenopus laevis in the mid-blastulae stage: the 96-h EC₅₀ value was 370 mg/L. (The 96-h LC_{50} value for swimming stage larvae was 150 mg/L.) At concentrations as low as 1 mg/L, aniline inhibited embryonic development of Xenopus laevis, resulting in undersized toads; higher doses (20-40 mg/L) inhibited pigmentation (Dumpert, Birge et al. (1979), examining the effects of aniline on 1987). bass and goldfish ova, found evidence for teratogenicity and significant evidence for reduced hatching and survival in both species when exposed to high concentrations (on the order of 100 mg/L), and much less evidence for both phenomena at low concentrations (1 mg/L).

Baird et al. (1977) noted that aniline at 20 mg/L had some inhibitory effect on the respiration of organisms in activated sludge even while being degraded, which suggested that a metabolite or metabolites may have been responsible for the observed toxicity. Aniline was not mutagenic in the Ames test, even with activation by the S-9 enzyme mixture (Lyons et al., 1985a). However, unidentified transformation products after incubation with pond water and sewage sludge inoculum were mutagenic.

9.2 Terrestrial toxicity

In loblolly pines, exposure to 0.4-10 ppm of aniline in air damaged the needles after 21-35 d (Cheeseman *et al.*, 1980).

No data were identified on the toxicity of aniline to wild mammals, birds, sediment or soil biota.

10.0 References

- Abram, F.S.H. and Sims, I.R. (1982). The toxicity of aniline to rainbow trout. Water Res. 16: 1309-1312.
- Aelion, C.M., Dobbins, D.C. and Pfaender, F.K. (1989). Adaptation of aquifer microbial communities to the biodegradation of xenobiotic compounds: influence of substrate concentration and preexposure. *Environ. Toxicol. Chem.* 8: 75-86.
- Aelion, C.M., Swindoll, C.M. and Pfaender, F.K. (1987). Adaptation to and biodegradation of xenobiotic compounds by microbial communities from a pristine aquifer. Appl. Environ. Microbiol. 53: 2212-2217.
- Alexander, M. and Lustigman, B.K. (1966). Effect of chemical structure on microbial degradation of substituted benzenes. J. Agric. Food Chem. 14: 410-413.
 - Amador, J.A., Alexander. M. and Zika, R.G. (1991). Degradation of aromatic compounds bound to humic acid by the combined action of sunlight and microorganisms. *Environ. Toxicol. Chem.* 10: 475-482.
- Aoki, K., Shinke, R. and Nishira, H. (1982). Identification of aniline-assimilating bacteria. Agric. Biol. Chem. (Jap.) 46: 2563-2570.
- Baird, R., Carmona, L. and Jenkins, R.L. (1977). Behaviour of benzidine and other aromatic amines in aerobic wastewater treatment. J. Water Pollut. Contr. Fed. 49: 1609-1615.
- Batterton, J., Winters, K. and Van Baalen, C. (1978). Anilines: selective toxicity to blue-green algae. Science 199: 1068-1070.
- Birge, W.J., Black, J.A., Hudson, J.E. and Bruser, D.M. (1979). Embryo-larval toxicity tests with organic compounds, in <u>Aquatic Toxicology - Proc. 2nd Ann. Symp. Aquat. Toxicol.</u>, eds. L.L. Marking and R.A. Kimerle, American Society for Testing and Materials Special Tech. Publ. 667, Philadelphia, PA 19103, U.S.A., pp. 131-147.
- Bringmann, G. and Kuehn, R. (1977). Results of the damaging effect of water pollutants on Daphnia magna. Z. Wasser Abwasser Forsch. 10: 161-166.
- Bringmann, G. and Kuehn, R. (1982). Results of toxic action of water pollutants on *Daphnia magna* Straus tested by an improved standardized procedure. Z. Wasser Abwasser Forsch. 15: 1-6.

Brooke, L.T., Call, D.J., Geiger, D.L. and Northcott, C.E. (eds.)

(1984). Acute toxicities of organic chemicals to fathead minnows (*Pimephales promelas*). Report of the Center for Lake Superior Environmental Studies, University of Wisconsin-Superior, Superior, WI, U.S.A., 414+ pp.

- Brown, D. and Laboureur, P. (1983). The aerobic biodegradability of primary aromatic amines. *Chemosphere* 12: 405-414.
- Calamari, D., Da Gasso, R., Galassi, S., Provini, A. and Vighi, M. (1980). Biodegradation and toxicity of selected amines on aquatic organisms. *Chemosphere* 9: 753-762.
- Canada Department of the Environment (1991). Canadian Environmental Protection Act notice with respect to certain aromatic amine substances and their salts. Preliminary results of the aromatic amines notice. Use Patterns Section, Commercial Chemicals Branch, Environmental Protection, Ottawa, Ont. K1A 0H3, Canada.
- Canada Department of the Environment (1992). National Analysis of Trends in Emergencies System. Environmental Emergencies Branch, Conservation and Protection, Hull, Qué. K1A 0H3, Canada.
- Canton, J.H. and Adema, D.M.M. (1978). Reproducibility of shortterm and reproduction toxicity experiments with Daphnia magna and comparison of the sensitivity of Daphnia magna with Daphnia pulex and Daphnia cucullata in short-term experiments. Hydrobiol. 59: 135-140.
- CH2M Hill Engineering Ltd. (1991). Research and development of permanent onsite solutions for contamination of groundwater at waste disposal and industrial sites in Canada. Final report. A report to Supply and Services Canada in fulfilment of DSS Contract KE405-7-6557/01-SE. Suite 600, 180 King Street South, Waterloo, Ontario N2J 1P8.
- Cheeseman, J.M., Perry, T.O. and Heck, W.W. (1980). Identification of aniline as an air pollutant through biological assay with loblolly pine. *Environ. Pollut. 21*: 9-22.
- Chiou, C.T., Schmedding, D.W. and Manes, M. (1982). Partitioning of organic compounds in octanol-water systems. *Environ. Sci. Technol.* 16: 4-10.
- Corbett, M.D. and Corbett, B.R. (1983). Arylamine N-oxidation by the microsomal fraction of germinating pea seedlings (*Pisum* sativum). J. Agric. Food Chem. 31: 1276-1282.
- Corpus Information Services (1979). Chemical process industry product profile on aniline. Now Camford Information Services, 801 York Mills Road, Don Mills, Ont. M3B 1X7, Canada, 2 pp.

- Corpus Information Services (1990). Chemical process industry product profile on aniline. Now Camford Information Services, 801 York Mills Road, Don Mills, Ont. M3B 1X7, Canada, 2 pp.
- Dames & Moore, Canada (1992). Study of DNAPL occurrence beneath former operating ponds of Uniroyal Chemical Ltd., Elmira. A report prepared for Uniroyal Chemical Ltd. in compliance with Part IV, Section 6 of the Ministry of the Environment Amended Control Order (1991). Project 19377-013, 7560 Airport Road, Mississauga, Ontario L4T 2H5.
- Dao, T.H., Bouchard, D., Mattice, J. and Lavy, T.L. (1986). Soil sorption of aniline and chloroanilines: direct and indirect concentration measurements of the adsorbed phase", Soil Sci. 141: 26-30.
- Dao, T.H. and Lavy, T.L. (1987). A kinetic study of adsorption and degradation of aniline, benzoic acid, phenol and diuron in soil suspensions. *Soil Sci.* 143: 66-72.
- Dauble, D.D., Carlile, D.W. and Hanf, J.R.W. (1986). Bioaccumulation of fossil fuel components during singlecompound and complex-mixture exposures of Daphnia magna. Bull. Environ. Contam. Toxicol. 37: 125-132.
- Davis, K.R., Schultz, T.W. and Dumont, J.N. (1981). Toxic and teratogenic effects of selected aromatic amines on embryos of the amphibian Xenopus laevis. Arch. Environ. Contam. Toxicol. 10: 371-391.
- Demirjian, Y.A., Joshi, A.M. and Westman, T.R. (1987). Fate of organic compounds in land application of contaminated municipal sludge. J. Water Pollut. Contr. Fed 59: 32-38.
 - De Zwart, D. and Sloof, W. (1983). The Microtox as an alternative assay in the acute toxicity assessment of water pollutants. Aquat. Toxicol. 4: 129-138.
 - Dumpert, K. (1987). Embryotoxic effects of environmental chemicals: tests with the South African clawed toad (Xenopus laevis). Ecotoxicol. Environ. Safety 13: 324-338.
 - El-Dib, M.A. and Aly, O.A. (1976). Persistence of some phenylamide pesticides in the aquatic environment - III. Biological degradation. *Water Res.* 10: 1055-1059.
 - Ellis, D.D., Jone, C.M., Larson, R.A. and Schaeffer, D.J. (1982). Organic constituents of mutagenic secondary effluents from wastewater treatment plants. Arch. Environ. Contam. Toxicol. 11: 373-382.

Ewell, W.S., Gorsuch, J.W., Kringle, R.O., Robillard, K.A. and

Spiegel, R.C. (1986). Simultaneous evaluation of the acute effects of chemicals on seven aquatic species. *Environ. Toxicol. Chem.* 5: 831-840.

- Felice, L.J. (1982). Determination of alkyl anilines and alkyl pyridines in solvent refined coal distillates and aqueous extracts by gas chromatography/mass spectrometry. Anal. Chem. 54: 869-872.
- Franco, P.J., Daniels, K.L., Cushman, R.M. and Kazlow, G.A. (1984). Acute toxicity of a synthetic oil, aniline and phenol to laboratory and natural populations of chironomid (Diptera) larvae. Environ. Pollut. Ser. A. 34: 321-331.
- Freitag, D., Geyer, H., Kraus, A., Viswanathan, R., Kotzias, D., Attar, A., Klein, W. and Korte, F. (1982). Ecotoxicological profile analysis. VII. Screening chemicals for their environmental behaviour by comparative evaluation. Ecotoxicol. Environ. Safety 6: 60-81.
- Games, L.M. and Hites, R.A. (1977). Composition, treatment efficiency and environmental significance of dye manufacturing plant effluents. *Anal. Chem.* 49: 1433-1440.
- Gerike, P. and Fischer, W.K. (1979). A correlation study of biodegradability determinations with various chemicals in various tests. *Ecotoxicol. Environ. Safety* 3: 159-173.
- Gershon, H., McNeil, M.W., Parmegiani, R. and Godfrey, P.K. (1971). Antifungal activity of substituted nitrobenzenes and anilines. Appl. Microbiol. 22: 438-440.
- Gersich, F.M. and Mayes, M.A. (1986). Acute toxicity tests with Daphnia magna Straus and Pimephales promelas Rafinesque in support of national pollutant discharge elimination permit requirements. Water Res. 20: 939-941.
- Gersich, F.M. and Milazzo, D.P. (1988). Chronic toxicity of aniline and 2,4-dichlorophenol to Daphnia magna Straus. Bull. Environ. Contam. Toxicol. 40: 1-7.
- Gersich, F.M. and Milazzo, D.P. (1990). Evaluation of a 14-day static renewal toxicity test with Daphnia magna Straus. Arch. Environ. Contam. Toxicol. 19: 72-76.

Hardy, J.T., Dauble, D.D. and Felice, L.J. (1985). Aquatic fate of synfuel residuals: bioaccumulation of aniline and phenol by the freshwater phytoplankter *Scenedesmus quadricauda*. Environ. Toxicol. Chem. 4: 29-35.

- Hawthorne, S.B. and Sievers, R.E. (1984). Emission of organic air pollutants from shale oil wastewaters. Environ. Sci. Technol. 18: 483-490.
- Hodson, P.V., Dixon, D.G. and Kaiser, K.L.E. (1984). Measurement of median lethal dose as a rapid indication of contaminants toxicity to fish. *Environ. Toxicol. Chem.* 3: 243-254.
- Holcombe, G.W., Phipps, G.L., Sulaiman, A.H. and Hoffman, A.D. (1987). Simultaneous multiple species testing: acute toxicity of 13 chemicals to 12 diverse freshwater amphibian, fish and invertebrate families. Arch. Environ. Contam. Toxicol. 16: 697-710.
- Howard, P.H. (1989). Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Vol. I. Large Production and Priority Pollutants. Lewis Publ., Chelsea, MI 48118, U.S.A.
- Hsu, T.-S. and Bartha, R. (1974). Interaction of pesticide-derived chloroaniline residues with soil organic matter. *Soil Sci.* 116: 444-452.
- Hwang, H.-M., Hodson, R.E. and Lee, R.F. (1987). Degradation of aniline and chloroanilines by sunlight and microbes in estuarine water. *Water Res. 21*: 309-316.
- Juhnke, I. and Luedemann, D. (1978). Results of the study of 200 chemical compounds on acute fish toxicity using the golden orfe test. Z. Wasser Abwasser Forsch. 11: 161-164.
- Jungclaus, G.A., Lopez-Avila, V. and Hites, R.A. (1978). Organic compounds in an industrial wastewater: a case study of their environmental impact. *Environ. Sci. Technol.* 12: 88-96.
- King, E.F. and Painter, H.A. (1983). Ring-test programme 1981-82.
 Assessment of biodegradability of chemicals in water by manometric respirometry. Commission of the European Communities, Environment and Quality of Life Report EUR 8631, Bâtiment Jean Monnet, Luxembourg, ISBN 92-825-3864-8, 28+ pp.
- Konopka, A., Knight, D. and Turco, R.F. (1989). Characterization of a *Pseudomonas* sp. capable of aniline degradation in the presence of secondary carbon sources. Appl. Environ. Microbiol. 55: 385-389.
- Korte, F. and Klein, W. (1982). Degradation of benzene in the environment. *Ecotoxicol. Environ. Safety 6*: 311-327.
- Kwasniewska, K., Liu, D. and Strachan, W.M.J. (1980). The relative biological toxicity effectiveness of chemicals towards

microorganisms, in <u>Proc. 14th Ann. Conf. Trace Subs. Environ.</u> <u>Health</u>, D.D. Hemphill (ed.), University of Missouri-Columbia, Columbia, MO, U.S.A., pp. 470-477.

- Lammerding, A.M., Bunce, N.J., Merrick, R.L. and Corke, C.T. (1982). Structural effects on the microbial diazotization of anilines. J. Agric. Food Chem. 30: 644-647.
- Larson, R.A. and Zepp, R.G. (1988). Reactivity of the carbonate radical with aniline derivatives. *Environ. Toxicol. Chem.* 7: 265-274.
- Lesage, S., Ritch, J.K. and Treciokas, E.J. (1990). Characterization of groundwater contaminants at Elmira, Ontario, by thermal desorption, solvent extraction GC-MS and HPLC. Water Pollut. Res. J. Can. 25: 275-292.
- Liu, J. and Liu, H. (1992). Degradation of azo dyes by algae. Environ. Pollut. 75: 273-278.
- Lu, P.-Y. and Metcalf, R.L. (1975). Environmental fate and biodegradability of benzene derivatives as studied in a model aquatic ecosystem. *Environ. Health Perspect.* 10: 269-284.
- Lyons, C.D., Katz, S.E. and Bartha, R. (1984). Mechanisms and pathways of aniline elimination from aquatic environments. Appl. Environ. Microbiol. 48: 491-496.
- Lyons, C.D., Katz, S.E. and Bartha, R. (1985a). Persistence and mutagenic potential of herbicide-derived aniline residues in pond water. *Bull. Environ. Contam. Toxicol.* 35: 696-703.
- Lyons, C.D., Katz, S.E. and Bartha, R. (1985b). Fate of herbicidederived aniline residues during ensilage. *Bull. Environ. Contam. Toxicol.* 35: 704-710.
- Mackay, D. and Paterson, S. (1991). Evaluating the multimedia fate of organic chemicals: a level III fugacity model. Environ. Sci. Technol. 25: 427-436.
- Malaney, G.W. (1960). Oxidative abilities of aniline-acclimated activated sludge. J. Water Pollut. Contr. Fed. 32: 1300-1311.
- McLeese, D.W., Zitko, V. and Peterson, M.R. (1979). Structurelethality relationships for phenols, anilines and other aromatic compounds in shrimp and clams. *Chemosphere 8*: 53-57.
- Means, J.L. and Anderson, S.J. (1981). Comparison of five different methods for measuring biodegradability in aqueous environments. Water Air Soil Pollut. 16: 301-315.

Meijers, A.P. and van der Leer, R.C. (1976). The occurrence of

organic micropollutants in the River Rhine and the River Maas in 1974. Water Res. 10: 597-604.

- Moreale, A. and Van Bladel, R. (1976). Influence of soil properties on adsorption of pesticide-derived aniline and pchloroaniline. J. Soil. Sci. 27: 48-57.
- Nelson, C.R. and Hites, R.A. (1980). Aromatic amines in and near the Buffalo River. Environ. Sci. Technol. 14: 1147-1149.
- Neurath, G.B., Duenger, M., Pien, F.G., Ambrosius, D. and Schreiber, O. (1977). Primary and secondary amines in the human environment. Food Cosmet. Toxicol. 15: 275-282.
- Northcott, J. (1978). Amines, Aromatic Aniline and Its Derivatives, in <u>Kirk-Othmer Encyclopaedia of Chemical</u> <u>Technology, 3rd ed., Vol. 2</u>, H.F. Mark, D.F. Othmer, C.G. Overberger and G.T. Seaborg (eds.), John Wiley and Sons, Toronto, Ont., Canada, pp. 309-321.
- Ontario Ministry of the Environment (1980). Environmental aspects of selected aromatic amines and azo dyes in Ontario. MOE Report No. ARB-TDA-83-79, Toronto, Ont., Canada.
- Ontario Ministry of the Environment (1982). Monitoring of selected trace organics during biological wastewater treatment. MOE Research Report No. 82, 102+ pp., Toronto, Ont., Canada.
- Ontario Ministry of the Environment (1991). Amended order of the director to Uniroyal Chemical Co. Ontario Ministry of the Environment, Hamilton Regional Office, 12th Floor, 119 King Street West, Hamilton, Ont. L8N 3Z9, Canada.
- Paris, D.F. and Wolfe, N.L. (1987). Relationship between properties of a series of anilines and their transformation by bacteria. Appl. Environ. Microbiol. 53: 911-916.
- Parris, G.E. (1980a). Environmental and metabolic transformations of primary aromatic amines and related compounds. *Residue Rev.* 76: 1-30.
- Parris, G.E. (1980b). Covalent binding of aromatic amines to humates. 1. Reactions with carbonyls and quinones. *Environ. Sci. Technol.* 14: 1099-1106.
- Patil, S.S. and Shinde, V.M. (1988). Biodegradation studies of aniline and nitrobenzene in aniline plant waste water by gas chromatography. *Environ. Sci. Technol.* 22: 1160-1165.
- Pereira, W.E., Rostad, C.E., Garbarino, J.R. and Hult, M.F. (1983). Groundwater contamination by organic bases derived from coaltar wastes. *Environ. Toxicol. Chem. 2*: 283-294.

Pillai, P., Helling, C.S. and Dragun, J. (1982). Soil-catalyzed oxidation of aniline. *Chemosphere 11*: 299-317.

Pitter, P. (1976). Determination of biological degradability of organic substances. Water Res. 10: 231-235.

Reinhard, M., Goodman, N.L. and Barker, J.F. (1984). Occurrence and distribution of organic chemicals in two landfill leachate plumes. *Environ. Sci. Technol.* 18: 953-961.

- Ribo, J.M. and Kaiser, K.L.E. (1983). Toxicities of chloroanilines to Photobacterium phosphoreum and their correlations with effects on other organisms and structural parameters, in <u>OSAR</u> <u>in Environmental Toxicology - Proc. Workshop Quant. Struct.-</u> <u>Activ. Relation. (OSAR) Environ. Toxicol.</u>, McMaster Univ., Hamilton, Ont., Canada, Aug. 16-18, pp. 319-336.
- Sanders, W.M. (1979). Exposure assessment: a key issue in aquatic toxicology, in <u>Aquatic Toxicology - Proc. 2nd Ann. Symp.</u> <u>Aquat. Toxicol.</u>, eds. L.L. Marking and R.A. Kimerle, American Society for Testing and Materials Special Tech. Publ. 667, Philadelphia, PA 19103, U.S.A., pp. 271-283.
- Sax, N.I. (1968). Dangerous Properties of Industrial Materials, 3rd ed., Van Nostrand Reinhold Co., Toronto, Ont., Canada, 1251+ pp.
- Schultz, T.W., Kyte, L.M. and Dumont, J.N. (1978). Structuretoxicity correlations of organic contaminants in aqueous coalconversion effluents. Arch. Environ. Contam. Toxicol. 7: 457-463.
- Sloof, W., Canton, J.H. and Hermens, J.L.M. (1983). Comparison of the susceptibility of 22 freshwater species to 15 chemical compounds. Aquat. Toxicol. 4: 113-128.
- Smith, J.H., Bomberger, D.C., Jr. and Haynes, D.L. (1980). Prediction of the volatilization rates of high-volatility chemicals from natural water bodies. Environ. Sci. Technol. 14: 1332-1337.
- Statistics Canada (1990). Imports, merchandise trade commodity detail, various years. Ottawa, Ont., Canada.
- Stuermer, D.H., Ng, D.J. and Morris, C.J. (1982). Organic contaminants in groundwater near an underground coal gasification site in northeastern Wyoming. *Environ. Sci. Technol. 16*: 582-587.

Subba-Rao, R.V., Rubin, H.E. and Alexander, M. (1982). Kinetics and extent of mineralization of organic chemicals at trace levels in freshwater and sewage. Appl. Environ. Microbiol. 43: 1139-1150.

Swindoll, C.M., Aelion, C.M., Dobbins, D.C., Jiang, O., Long, S.C. and Pfaender, F.K. (1988). Aerobic biodegradation of natural and xenobiotic organic compounds by subsurface microbial communities. Environ. Toxicol. Chem. 7: 291-299.

Tadokoro, H. and Maeda, M. (1988). Evaluation of toxicity profiles of organic chemicals: usefulness of ecotoxicological basic test set of OECD, in <u>Toxic Contamination in Large Lakes. Vol.</u> <u>I. Chronic Effects of Toxic Contaminants in Large Lakes</u>, N.W. Schmidtke (ed.), Lewis Publ., Chelsea, MI, U.S.A., pp. 179-193.

Thomas, R.G. (1982). Volatilization, in <u>Handbook of Chemical</u> <u>Property Estimation Methods</u>, W.J. Lyman, W.F. Reehl and D.H. Rosenblatt (eds.), McGraw-Hill Book Co., New York, NY, U.S.A.

Tomkins, B.A. and Ho, C.-H. (1982). Determination of polycyclic aromatic amines in natural and synthetic crudes. Anal. Chem. 54: 91-96.

- Tonogai, Y., Ogawa, S., Ito, Y. and Iwaida, M. (1982). Actual survey on TLm (median tolerance limit) values of environmental pollutants, especially on amines, nitriles, aromatic nitrogen compounds and artificial dyes. J. Toxicol. Sci. 7: 193-203.
- Tonogai, Y., Ogawa, S., Ito, Y. and Iwaida, M. (1983). Studies on the syncopic effects of aniline derivatives on fish. I. The problem concerning the determination of median lethal concentrations in fish. *Eisei Kagaku 29*: 280-285.
- U.S. Environmental Protection Agency (1984). Guidelines establishing test procedures for the analysis of pollutants under the Clean Water Act. Fed. Registr. 49: 1-210.
- U.S. Environmental Protection Agency (1985). Health and environmental effects profile for aniline. EPA Report 600/X-85/356, Office of Research and Development, Cincinnati, OH 45268, U.S.A., 108+ pp.
- U.S. Environmental Protection Agency (1988). Testing consent orders on aniline and seven substituted anilines. U.S. Fed. Reg. 53: 31804-31813.
- U.S. Environmental Protection Agency (1990). Toxics release inventory - 1988. Washington, DC 20460, U.S.A.
- U.S. Environmental Protection Agency (1991). Toxics release inventory - 1989. Washington, DC 20460, U.S.A.
- U.S. Environmental Protection Agency (1992). Personal

communication, C.M. Auer, Existing Chemical Assessment Division, Washington, DC 20460, U.S.A.

- van Leeuwen, C.J., Adema, D.M.M. and Hermens, J. (1990). Quantitative structure-activity relationships for fish early life stage toxicity. Aquat. Toxicol. 16: 321-334.
- Weast, R.C., Astle, M.J. and Beyer, W.H. (eds.) (1984). CRC Handbook of Chemistry and Physics, 65th ed., Chemical Rubber Company Press Inc., Boca Raton, FL, U.S.A.
- Wegman, R.C.C. and De Korte, G.A.L. (1981a). The gas chromatographic determination of aromatic amines after bromination in surface waters. Inter. J. Environ. Anal. Chem. 9: 1-6.
- Wegman, R.C.C. and De Korte, G.A.L. (1981b). Aromatic amines in surface waters of the Netherlands. Water Res. 15: 391-394.
- Wellens, H. (1982). Comparison of the sensitivity of Brachydanio rerio and Leuciscus idus in the study of the toxicity to fish of chemical compounds and wastewaters. Z. Wasser Abwasser Forsch. 15: 49-52.
- Yount, J.D. and Shannon, L.J. (1987). Effects of aniline and three derivatives on laboratory microecosystems. *Environ. Toxicol. Chem.* 6: 463-468.
- Zepp, R.G., Baughman, G.L. and Schlotzhauer, P.F. (1981). Comparison of photochemical behavior of various humic substances in water: I. Sunlight-induced reactions of aquatic pollutants photosensitized by humic substances. Chemosphere 10: 109-117.
- Zepp, R.G. and Schlotzhauer, P.F. (1983). Influence of algae on photolysis rates of chemicals in water. Environ. Sci. Technol. 17: 462-468.

		· · · · · · · · · · · · · · · · · · ·
Property		Reference
molecular formula	C ₆ H ₇ N	· · · · · · · · · · · · · · · · · · ·
molecular weight	93.13	
appearance	clear, colourless oily liquid, bluish fluorescence	Sax (1968)
melting point	-6.3 °C	Weast et al. (1984)
boiling point	184-186 °C	Weast <i>et al</i> . (1984)
density	1.02173 g/cm³ at 20 °C	Weast et al. (1984)
viscosity	4.42-4.43 cP at 20 °C	Northcott (1978)
vapour pressure	1 mm Hg at 35 °C	Sax (1968)
aqueous solubility	3.5x10 ⁴ mg/L	Northcott (1978)
рК _а	4.63 at 20 °C	Weast et al. (1984)
log (octanol-water partition coefficient)	0.9	Chiou <i>et al</i> . (1982)

Table 1. Chemical and physical properties of aniline

Year	Amount	import	ed, tonnes	5	
1076		222		· · ·	· ,
1976		552	•		N
1977	•	560	. '		1
1978		334			ø
1979		679		-	
1980		544	•	•	
1981	•	.610			
1982		513		· · ·	
1983		1353			· · ·
1004		1000	· · ,		
1984		1239	N	•	
1985		879			
1986		620			
1987	•	570	•		•
1988	· · · · · · · · · · · · · · · · · · ·	677	(includes	4 for an	iline HCl)
1989	· ·	354	(includes	12 for a	niline HCl)
1000		221	(includes	0.5 for	aniline ·HCl)
		- 107	(includes	4 for or	11 inc huch
T99T		. TO V.	(includes	4 LOF an	TTTHE HCT)

Table 2. Imports of aniline and aniline hydrochloride into Canada*

*All data are from Statistics Canada (1990). Beginning in 1988 separate figures were kept for aniline and aniline hydrochloride.

Table 3. Environmental occurrence of aniline*

Medium	Concentration	Connent	Reference
air	n.d33 µg/m³	USA	Hawthorne and Sievers (1984)
groundwater	0.4 µg/L	near underground coal gasification site in Wyoming	Stuermer <u>et al.</u> (1982)
groundwater	10 µg/L	. close to a landfill in Ontario	Reinhard <u>et al.</u> (1984)
groundwater	33-300 mg/L	monitoring wells on property of Uniroyal Chemical Ltd., Elmira, Ont.	Lesage <u>et al.</u> (1990); CH2M Hill Engineering (1991)
groundwater	7 05 μg/L	contaminated by coal-tar wastes, Minnesota	Pereira <u>et al.</u> (1983)
DNAPL	up to 2%	beneath former containment area on property of Uniroyal Chemical Co., Elmira, Ont.	Dames & Moore Canada (1992)
Rhine River	3 μg/L (mean)	2- and 4-methylaniline also found at lower concentrations (Netherlands, 1978)	Wegman and De Korte (1981a)
Rhine River	≤ 12 µg/L	Lobith, Netherlands (1979) 2- and 4-methylaniline also found ≤ 2 µg/L	Wegman and De Korte (1981b)
German Rivers	0.5 - 3.7 μg/L		Neurath <u>et al.</u> (1977)
Dutch rivers	≤ 5.8 μg/L	:	Wegman and De Korte (1981b)
Waal River	detected	Netherlands, 1974	Meijers and van der Leer (1976)
U.S rivers	1 - 13 μg/L	mean 9.5 μ g/L	U.S. EPA (1988)
industrial effluent		dye manufacturing	Games and Hites
- raw wastewater	36 - 480 μg/L	plant (USA)	(1977)
- final effluent	10 - 96 μg/L		
industrial effluent	20 µg/L	chemical plant, USA	Jungclaus <u>et al.</u> (1978)
industrial effluents (secondary)	detected	industrial plants and STP in Illinois	Ellis <u>et al.</u> (1982)
STP influent and effluent	detected	Ontario; partially consumed in nitrification stage	Ontario Ministry of Environment (1982)
shale oil wastewaters	0.5 mg/L	USA	Hawthorne and Sievers (1984)

29

cont'd next page

age

e.

Table 3 cont'd

Medium	Concentration	Comment	Reference
coal oil reference standard	5 mg/kg	USA	Tomkins and Ho (1982)
solvent-refined coal distillates	≤ 2500 mg/L	USA; also found 2-, 3- and 4-methylaniline	Felice (1982)
SRC aqueous extracts	≤ 25 mg/L	USA	Felice (1982)
soil	5 mg/kg	near dump for a dye manufacturing plant, USA	Nelson and Hites (1980)

Abbreviations: DNAPL, dense non-aqueous phase liquid; STP, sewage treatment plant; SRC, solvent-refined coal. Concentrations in soil are by dry weight.

Table 4. Acute toxicity of aniline to aquatic organisms

ompound	Species	Size / øge	Static / flow-through	Temp. °C	Hardness mg/L	рН	Response	Conc. mg/L	Nominal / measured	Reference	•
·	bacteria Photobacterium phosphoreum		stat	15		•	5-30 min IC ₅₀ (light output)	65-70	n	Ribo and Kaiser (1983)	
	bacteria <u>Photobacterium</u> phosphoreum		stat	15			5-15 min IC ₅₀ (light output)	425-488	n	De Zwart and Sloof (1983)	1
	bacteria (mixed innocul	Lum)	stet	22			4-h IC ₅₀ (inhibition)	680	n	Kwasniewska <u>et al.</u> (1980)	,
·	alga <u>Selenastrum</u> capricornutum	· .	stat			•	96-h EC ₅₀ (growth)	19~	n .	Calamari <u>et al. (</u> 1980)	
	alga <u>Agmenellum</u> quedruplicatum		stat	30		•	3-7 d EC ₁₀₀ (growth)	0.5 est.	n	Batterton <u>et al.</u> (1978)	
	fungi, <u>Aspergillus nig</u> Aspergillus oryzøe, Tr viride, Myrothecium ve	<u>er.</u> ichoderma rrucaria and	støt				6-d EC ₁₀₀ (growth)	> 1000	n I	Gershon <u>et_al.</u> (1971)	
	Trichophyton mentagrop	hytes		· .			. ·				
	ciliate <u>Tetrahymena pyriformis</u>		stat	28	•		24-h LC ₁₀₀	2000	n	Schultz <u>et al.</u> (1978)	
	mosquito larvae <u>Aedes aegypti</u>	3rd instar	stat	26			48-h NOLC	75	n	Sloof <u>et al.</u> (1983)	
	mosquito larvae <u>Aedes aegypti</u>	3rd instar	stat	26	•		48-h LC ₅₀	155	n	Sloof <u>et al.</u> (1983)	
	mosquito larvae Culex pipiens	3rd instar	stət	26			48-h NOLC	- 58	ņ .	Sloof <u>et al.</u> (1983)	
	mosquito larvae <u>Culex pipiens</u>	3rd inster	Støt-	26			48-h LC ₅₀	94	n	Sloof <u>et al.</u> (1983)	

cont'd next page

. . 32

Table 4 cont'd

Compound	• •	Species	Size / age	Static / flow-through	°C	Hardness mg/L	рH	Response	Conc. mg/L	Nominal / measured	Reference
		pillbug Asellus_intermedius	• .	stat	20	130	7.4	96-h LC ₅₀	> 100	ń	Ewell <u>et al.</u> (1986)
	L	water flea <u>Daphnia magna</u>		stat		- ·		24-h IC_{50} (immobilization)	23	n	Calamari <u>et al.</u> (1980)
	·			stat			• .	24-h NOLC	0.13	n	Bringmann and Kuehn (1977)
۲.		•		stat				24-h LC ₅₀	0.5	n	Bringmann and Kuehn (1977)
		· · · ·		stat		· ,		24-h LC100	250	n .	Bringmann and Kuehn (1977)
· ·			•	stet				24-h NOEC (immobilization)	0.06	n,	Bringmann and Kuehn (1982)
				stat				24-h EC ₅₀ (immobilization)	0.6-70	י. חי	Bringmann and Kuehn (1982)
		<i>x</i>		stat				24-h EC ₁₀₀ (immobilization)	250-500	n,	Bringmann and Kuehn (1982)
ć .				stet	17	45	7. 4	48-h LC ₅₀	0.25	n	Holcombe <u>et al.</u> (1987)
		•	. •	stat			· •	48-h NOLC	0.34	'n	Sloof <u>et el.</u> (1983)
				stat	- *		·	48-h LC ₅₀	0.64	n	Sloof <u>et al.</u> (1983)
				stat	20	130	7.4	96-H LC50	0.21	n	Ewell <u>et al.</u> (1986)
м.	•	•	*	stat		Α.		48-H LC ₅₀	0.55	n	Canton and Adema (1978)
	`	·		stat	20	77 [.]	7.5-7.9	48-h LC ₅₀	0.17	'n	Gersich and Mayes (1986)
		water flea <u>Daphnia pulex</u>	-	stat				48-h NOLC	0.07	n ,	Sloof <u>et al.</u> (1983)
				stat				48-h LC ₅₀	0.1	n	Sloof <u>et_al.</u> (1983)
		water flea Daphnia cucullata	·	stat -	•			48-h LC ₅₀	0.68	n.	Sloof <u>et al.</u> (1983)

cont'd next page

· _ `i

Compound	Species	Size / age ·	Static / flow-through	Temp. °C	Hardness mg/L	рН	Response		Conc. mg/Ļ	Nominal / measured	Reference	•
	midge <u>Tanytarsus dissimilis</u>		stat	17	45	7.4	48-h LC ₅₀		> 220	n	Holcombe <u>et al.</u> (1987)	
	chironomid midge Chironomis tentans		stat	17			48-h LC ₅₀	•	400	n _.	Franco <u>et al.</u> (1984 <u>)</u>	
	chironomid midge Einfeldia natchitocheae	· .	stat	17		•	48-h LC ₅₀		428	n	Franco <u>et al.</u> (1984)	
	chironomid midge Chironomis pinguis		stat	17			48-h LC ₅₀		478	· n	Franco <u>et ml.</u> (1984)	
	chironomid midge Tanypus_neopunctipennis		stat ,	17			48-h LC ₅₀		272	n	Franco <u>et_al.</u> (1984)	
	amphipod <u>Gammarus fasciatus</u>		stat	20	130	7.4	96-H LC ₅₀	•	> 100	n	Ewell <u>et al.</u> (1986)	
	hydra Hydra oligactis	budless	stat	17			48-h NOLC		235	'n	Sloof <u>et al.</u> (1983)	
			• *				48-h LC ₅₀	· ·	406	n,	Sloof <u>et al.</u> (1983)	
	flatworm Dugesia tigrina		stat	20	130	7.4	96-H LC ₅₀		31.6	, n	Ewell <u>et_al.</u> (1986)	•
	segmented worm Lumbriculus variegatus		stat .	20	130	7.4	96-H LC ₅₀		> 100	n	Ewell <u>et al.</u> (1986)	` .
	snail Aplexa hypnorum		stat	17 .	45	7.4	96-h LC _{sò}		> 220	n	Holcombe <u>et al.</u> (1987)	
	snail <u>Helisoma_trivolvis</u>		stat	20	130	7.4	96-H LC ₅₀ -		100	n	Ewell <u>et al.</u> (1986)	
	mollusc Lymnaea stagnalis	3-4 wk	stat	20			48-h NOLC		560	n	Sloof <u>et al.</u> (1983)	

48-h LC₅₀

n

Sloof <u>et al.</u> (1983)

800

cont'd next page

Table 4 cont'd

.34

			·			•	•			-
Compound	Species	Size / age	Static / flow-through	°C	Hardness mg/L	рł	Response	Conc. mg/L	Nominal / measured	Reference
· ·	shrimp Crangon septemspinosa	· .	ren (2 d)	10	:		96-h lethal threshold	29,4	ņ	HcLeese <u>et al.</u> (1979)
•	clawed toad Xenopus_laevis	larvae	stat	25	102	•	96-h LC ₅₀	150	n	Davis <u>et al.</u> (1981)
	clawed toad Xenopus laevis		støt	x	·	ŝ	48-h NOLC	390	n +	-Sloof <u>et al.</u> (1983)
	·	. •					48-h LC ₅₀	560	, n	Sloof <u>et al.</u> (1983)
	axoloti Ambystoma mexicanum		stat				48-h NOLC	360	n	Sloof <u>et al.</u> (1983)
			•		~ .		48-h LC ₅₀	440	n '	Sloof <u>et al.</u> (1983)
ئر ب ب	fathead minnow <u>Pimephelas promelas</u>		stat	20			96-h LOEL	79	n •	Yount and Shannon (1987)
			stat	26	47	7.6	96-H LC50	134	. m	Brooke <u>et al.</u> (1984)
-		,	stát	20	130	7.4	96-H LC50	32	n	Ewell <u>et al.</u> (1986)
	· ·	0.3	flow	17	45	7.4	96-h LC ₅₀	78	n .	Holcombe <u>et al. (</u> 1987)
•		3-4 wk	flow	20		•	48-h NOLC	45	n .	Sloof <u>et al.</u> (1983)
	e e de la companya d		•				48-h LC ₅₀	65	n	Sloof <u>et al.</u> (1983)
.*	rainbow trout <u>Oncorhynchus mykiss</u>		flow	15	320		96-h LC ₅₀	41	'n	Calamari <u>et al. (</u> 1980)

20 96-h LC₅₀ Calamari et al. (1980) 20 n 96-h LC₅₀ 7.9 36 4.6-6.4 cm flow 15 m

cont'd next page

Hodson <u>et_al</u>, (1984)

	Size / age	Static / flow-through	Temp. ℃	Hardness mg/L	PH	Response	Conc. mg/L	Nominal / measured
		flow	, *			12-h LC ₅₀	46	n .
		flow				24-h LC ₅₀	31	n
•		flow				48-h LC _{s0}	28	n

			flow				24-h LC ₅₀		31	n	Abram and Sims (1982)
			flow				48-h LC ₅₀		28	n	Abram and Sims (1982)
· .		·	flow		•		96-h LC ₅₀		11	n	Abram and Sims (1982)
			flow		•		168-h LC ₅₀		8	n	Abram and Sims (1982)
		5-8 wk	•	15			48-h NOLC		36	n	Sloof <u>et al.</u> (1983)
							48-h LC ₅₀		43 .	n	Sloof <u>et al.</u> (1983)
		0.9 g	flow	17	45	7.4	96-h LC ₅₀		41	n -	Holcombe <u>et al.</u> (1987)
	guppy	3-4 wk	flow	24		·	48-h NOLC		52	n	Sloof <u>et al.</u> (1983)
							48-h LC ₅₀		100	n -	Sloof <u>et al.</u> (1983)
	medaka Oryzias latipes	4-5 wk	flow'	24		,	48-h NOLC		100	n	Sloof <u>et el.</u> (1983)
							48-h LC ₅₀		65	n	Sloof <u>et al.</u> (1983)
			stat	25			24-h LC ₅₀		74	n	Tonogai <u>et al.</u> (1982)
							48-h LC ₅₀		48 ·	n	Tonogai <u>et al.</u> (1982)
	golden orfe	•	flow				48-h LC ₅₀		49	n	Sloof <u>et al.</u> (1983)
	Leuciscus_idus_melano	tus				•			1		
							48-h LC ₅₀	· · · · ·	51-78	n	Wellens (1982)
							, 14 1		••		

48-h NOLC 48-h LC₅₀

20-51

61-65

Π.

n

Juhnke and Luedemann (1978) Juhnke and Luedemann (1978)

Reference

Abram and Sims (1982)

cont'd next page

Table 4 cont'd

Species

.

• Compound

36

Table 4 cont'd Conc. Nominal / Reference Static / Hardness Response Size / Temp. D Species Compound °C mg/L mg/L measured age flow-through . 92 48-h LC₁₀₀ Juhnke and Luedemann (1978) n 33 Wellens (1982) 96-h LC₅₀ n zebra fish Brachydanio rerio 49 n Holcombe et al. (1987) 45 96-h LC50 17 7.4 1.1 g flow bluegill Lepomis macrochirus 78 Holcombe et al. (1987) 17 45 7.4 96-h LC50 n 2.6 g flow white sucker Catostomus commersoni 127 Tonogai <u>et al.</u> (1983) 48-h LC50 m flow carp Cyprinus carpio 45 96-h LC₅₀ 187 n Holcombe et al. (1987) 17 7.4 4.4 g flow goldfish Carassius auratus 104 Tonogai <u>et al.</u> (1983) 48-H LCsn m flow Tonogai <u>et al.</u> (1983) 48-h LC₅₀ 115 m flow killifish Oryzias latipes

Abbreviations used: EC₅₀, IC₅₀ - concentration which effectively inhibits 50% of function/growth; LC₂₁ - concentration which kills xx% of test organisms; ren - renewal (tests solutions renewed at specified intervals, when given); NOLC - no-observed-lethality-concentration; NOEC - no-observed-effects-concentration.

Figure 1. Chemical structure of aniline.

NH₂

ANILINE

.

Appendix

Level III Fugacity Modelling

No data were identified on the concentrations of aniline in environmental media. This has necessitated the use of a modelling technique, namely the level III fugacity model of Mackay and Paterson (1991). The fugacity model for the region of southern Ontario accepts as input: the physical/chemical properties of the chemical, its transformation half-lives and emission rates into the environmental media of air, water, soil and sediment. It then calculates the prevailing steady state concentrations, amounts and rates of degradation, advective flow and intermedia transport. It should be noted that this model does not address the possibility of formation of bound residues in sediment. Consequently, sediment bė underestimated, and concentrations in may concentrations in water may be overestimated.

A brief account of the principal findings is presented below. It was assumed that all the aniline imported into Canada in 1989 was for use only in southern Ontario, and that it would be released into water at a rate of 1.385 mol/h (based on a loss of 1.13 tonne (see section 3.2.5). The following assumptions were entered into the model:

(1) The 1.13 tonnes/year of aniline is released into southern Ontario in the following proportions: air 0%, water 100% (1.385 mol/h) and soil 0%.

(2) The following estimated degradation rate constants were used in the model (from persistence section):

air: $k = 0.22 h^{-1}$ $(t_{1/2} = 3.1 h)$ water: $k = 0.0036 h^{-1}$ $(t_{1/2} = 193 h)$ soil: $k = 0.0036 h^{-1}$ $(t_{1/2} = 193 h)$

(3) Advective outflows in air and water were included corresponding to residence times in those media of 5 d and 500 days, respectively (i.e., air = 3.3×10^{12} m³/h and water = 3.3×10^{8} m³/h).

Table A-1 summarizes emissions, environmental distribution (%) and resulting concentrations. A mass balance diagram is shown in Figure A-1. Of the 1.385 mol/h entering the water compartment, 3.098×10^{-2} mol/h is advected out of the region, 2.125×10^{-3} mol/h enters the air, 2.026×10^{-4} mol/h enters the sediment, and 1.352mol/h reacts in the region. The amount in the water is 99.98% of the total amount of aniline present and corresponds to a concentration in water of 8.74×10^{-3} mg/L.

The amount in air of 0.0092 mol is about 0.002% of the total and corresponds to a concentration of $2.15 \times 10^{-9} \ \mu g/m^3$. Aniline,

entering the air reacts at a rate of 2.046×10^{-3} mol/h and is advected by a rate of 7.602×10^{-3} mol/h and enters the soil at a rate of 2.911×10^{-6} mol/h.

The concentration in soil is approximately $2.7 \times 10^{-12} \ \mu g/g$ and in sediment it is $4.6 \times 10^{-9} \ \mu g/g$.

It is apparent from the distribution model that it is the aquatic fate of aniline that is of primary concern. The prevailing concentrations will be highest when reaction rates are slow.

Table A-1. Summary of results for aniline in southern Ontario according to the level III fugacity model of Mackay and Paterson (1991).

Compartment	Emission mol/hour	Environmental distribution %	Concentrations
Air	0	0.002	2.15 X 10 ⁻⁹ μg/m ³
Water	1.385	99.98	8.74 X 10 ⁻³ ng/L
Soil	0	0.000	2.7 X 10 ⁻¹² µg/g
Sediment	0	0.015	4.6 X 10 ⁻⁹ μg/g

residence time 11.3 days reaction persistence 11.6 days

Figure A-1. Mass balance diagram for aniline in southern Ontario according to the level III fugacity model of Mackay and Paterson (1991).



Mass balance diagram for aniline in Southern Ontario