Canadian Environmental Protection Act

Priority Substances List

Supporting Documentation - Environmental Sections

3,3'-DICHLOROBENZIDINE

(Unedited Version)

Environment Canada

March 1993

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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

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1.0 Identity of substance

1.1 Name of substance

3,3'-Dichlorobenzidine (Chemical Abstracts Service Registry Number 91-94-1) is a chlorinated primary aromatic amine with a molecular formula of $C_{12}H_{10}N_2Cl_2$. Its structure is shown in Fig. 1. Synonyms for 3,3'-dichlorobenzidine include 4,4'-diamino-3,3'-dichlorobiphenyl, o,o'-dichlorobenzidine, 3,3'-dichlorobiphenyl-4,4'-diamine and 3,3'-dichloro-4,4'-diamino(1,1-biphenyl). 3,3'-Dichlorobenzidine is usually available as the dihydrochloride salt, 3,3'-dichlorobenzidine dihydrochloride ($C_{12}H_{10}N_2Cl_2 \cdot 2HCl$) (Chemical Abstracts Service Registry No. 612-83-9).

1.2 Characteristics of substance

3,3'-Dichlorobenzidine is a grey to purple crystalline solid at room temperature.

1.3 Analytical methodology

3,3'-Dichlorobenzidine in water, sediments and tissues can be determined by standard techniques of extraction and gas chromatography. Detection limits depend upon the detector used. For industrial and municipal wastewater discharges, the method detection limit by gas chromatography-mass spectrometry is 16.5 μg/L for a 1 L water sample (Clesceri et al., 1989).

2.0 Physical and chemical properties

Table 1 gives the physical and chemical properties of 3,3'-dichlorobenzidine.

3.0 Sources and releases to the environment

3.1 Natural sources

No natural sources of 3,3'-dichlorobenzidine have been identified.

3.2 Anthropogenic sources

3.2.1 Production and market trends

Production in the United States in 1972 was 2,650 tonnes. It was used almost exclusively in the manufacture of yellow, orange and red pigments (Ferber, 1978). Global production in 1983 was estimated as 8,200 tonnes (U.S. Agency for Toxic Substances and Disease Registry, 1988). No 3,3'-dichlorobenzidine was produced in the U.S.A. in 1986, but 640 tonnes were produced in 1990 (U.S. Environmental Protection Agency, 1992).

3.2.2 Canadian consumption, imports and exports

3,3'-Dichlorobenzidine is not produced in Canada (Canada Department of the Environment, 1990, 1991a,b). It was not reported on the Domestic Substances List of the Department of Environment, which designates chemicals in use in Canada in the period 1984-1986 (Canada Department of the Environment, 1990). However, 3,3'-dichlorobenzidine dihydrochloride was reported. Statistics Canada (1990) importation records are shown in Table 2. From 1978 to 1984 it was imported solely from the U.S.A. From 1985 to 1989 it was imported from India, Japan and South Korea, but not the U.S.A. The destinations in Canada are in general not known except for 1989, in which 80 of the 109 tonnes imported were to Ontario. Amounts imported by individual companies constitute confidential business information, and are not reported here.

3.2.3 Manufacturing processes

3,3'-Dichlorobenzidine can be produced by the alkaline reduction of o-chloronitrobenzene and rearrangement of the resulting hydrazo compound (Ferber, 1978).

3.2.4 Uses

3,3'-Dichlorobenzidine and some of its derivatives are used as intermediates in the manufacture of pigments for printing inks, textiles, paints, plastics and crayons. This is its primary use in Canada (Canada Department of the Environment, 1991a,b). It can also be used as a curing agent in polyurethane elastomers, and in the analytical determination of gold (Ferber, 1978; Budavari, 1989).

3.2.5 Releases

Possible routes of entry of 3,3'-dichlorobenzidine 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 3,3'-dichlorobenzidine-containing materials
(d) losses in weathering or leaching of 3,3'-dichlorobenzidine-containing materials
(e) losses of landfill-disposed 3,3'-dichlorobenzidine-containing materials, or losses from licensed waste disposal facilities of reaction tars containing 3,3'-dichlorobenzidine
(f) losses by incomplete incineration of 3,3'-dichlorobenzidine-containing materials

Route (c) would likely be the most important route of entry of 3,3'-dichlorobenzidine to the Canadian environment. Losses during production of 3,3'-dichlorobenzidine and its salts are not included

on the above list because they are not produced in Canada. In polymers the residual 3,3'-dichlorobenzidine content would be generally so low that loss from this source would not constitute a significant route of entry. It is possible that it could be released in the degradation of 3,3'-dichlorobenzidine-containing pigments. It is likely that incineration of 3,3'-dichlorobenzidine-containing materials would also destroy unreacted 3,3'-dichlorobenzidine. There are no available data from any country which could be used to quantitate effluent or emission loadings of 3,3'-dichlorobenzidine from the above routes of entry with any degree of confidence. However, 3,3'-dichlorobenzidine has been detected, albeit rarely, in industrial effluent samples (see Section 4.3.1). Total industrial emissions of 3,3'-dichlorobenzidine to the environment in the U.S.A. in 1988 were estimated to be 6 tonnes (U.S. Environmental Protection Agency, 1990). For the purposes of estimation, if it is assumed that 3,3'-dichlorobenzidine use in the United States were 5,000 tonnes in 1988, losses would be 0.1% of total use. If this figure were applied to Canadian uses in 1989, for example, losses would be estimated as 0.1 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 3,3'-dichlorobenzidine.

Although it is reasonable to assume that 3,3'-dichlorobenzidine and its salts may enter the Canadian environment *via* the routes described above, there are no effluent or emission data which demonstrate that they are doing so.

4.0 Environmental transport, transformation and concentrations

4.1 Transport and distribution between and within media

Adsorption to soil and sediment is expected to be a major pathway of distribution of 3,3'-dichlorobenzidine in the environment (Sikka *et al.*, 1978; Callahan *et al.*, 1979; Howard, 1989).

4.1.1 Water

The pK_a values for 3,3'-dichlorobenzidine are 4.5 and 3.3 (Korenman and Nikolaev, 1974). Therefore, dissolved 3,3'-dichlorobenzidine will be present almost entirely as the free base in most natural waters. The relatively low vapour pressure, low water solubility, and medium octanol/water partition coefficient of 3,3'-dichlorobenzidine suggest that most 3,3'-dichlorobenzidine in the environment should be found in water, with partitioning to sediment expected. Volatilization from water is not expected to be significant for such an involatile chemical with a Henry's Law constant value of 0.8 torr L mole^{-1} (Smith *et al.*, 1980). A calculation based on physical/chemical properties bears this out.

The half-life for volatilization of 3,3'-dichlorobenzidine from surface water [1 m deep, flowing at 1 m/sec, with wind velocity of 3 m/sec, at 20 °C] to the atmosphere was estimated to be 1725 hours, according to a method described by Thomas (1982), which indicates that it is a relatively low-volatility compound as far as volatilization from water is concerned.

4.1.2 Air

Because of the low volatility of 3,3'-dichlorobenzidine, significant concentrations are not expected to be found in air. Consequently, it is not expected to be a greenhouse gas, to contribute to stratospheric ozone depletion, or to contribute to the formation of ground level ozone.

4.1.3 Soil

The log K_{ow} value of 3.02 for 3,3'-dichlorobenzidine (Callahan et al., 1979) suggests considerable potential for binding to the organic part of sediment and soil.

4.1.4 Biota

The log K_{ow} value of 3.02 for 3,3'-dichlorobenzidine (Callahan et al., 1979) suggests considerable potential for bioaccumulation (Howard, 1989). Appleton and Sikka (1980) investigated the bioconcentration, elimination and metabolism of 3,3'-dichlorobenzidine in bluegill sunfish (Lepomis macrochirus). Uniformly ring-labelled [^{14}C]-3,3'-dichlorobenzidine was rapidly (i.e., over a few days) accumulated by the fish from water containing 5 μg/L or 0.1 mg/L of the chemical. Based on total ^{14}C residues, bioconcentration factors of 495-507 were observed in the whole fish with equilibria achieved in 96-168 hr. The ^{14}C residues were distributed in both the edible and non-edible portions. [^{14}C]-3,3'-dichlorobenzidine or its metabolites were not completely eliminated over 14 d upon transfer of the fish to water free of 3,3'-dichlorobenzidine. The only metabolite detected in fish was an acid-labile conjugate of 3,3'-dichlorobenzidine, which appeared to be an N-glucuronide.

Freitag et al. (1985) observed a 5-d bioaccumulation factor in activated sludge of 3100, a 1-d bioaccumulation factor in algae (Chlorella fusca) of 940, and a 3-d bioaccumulation factor in fish (golden ide, Leuciscus idus melanotus) of 610.

4.2 Transformation

In general, photooxidation and slow microbiological degradation (with very slow mineralization) are expected to be the main pathways of transformation of 3,3'-dichlorobenzidine in the environment (Sikka et al., 1978; Callahan et al., 1979; Howard,

1989). 3,3'-Dichlorobenzidine itself is not expected to be persistent (with overall half-lives in water, soil and air less than a few weeks) since strongly bound residues in soils and sediments are formed quickly, but the biological availability of such residues has not been investigated. In addition, products of degradation have not been well characterized.

4.2.1 Biodegradation

3,3'-Dichlorobenzidine was not significantly biodegraded by a sewage sludge inoculum over a 28 day period in the absence of added yeast extract (Brown and Laboureur, 1983). In the presence of high levels of yeast extract (100-200 mg/L) significant biodegradation was achieved over the same period. This may have been because the yeast extract provided growth factors necessary for the degradation of 3,3'-dichlorobenzidine, or that the yeast acted as a readily degradable food source and built up a large concentration of active bacteria which were then able to effect degradation of the 3,3'-dichlorobenzidine.

3,3'-Dichlorobenzidine was fairly resistant to degradation by naturally-occurring aquatic microbial communities with only minor losses over a 30-d period at 21 °C (Sikka *et al.*, 1978). Half-lives of 4-26 weeks, and 16-101 weeks, have been estimated for the biodegradation of 3,3'-dichlorobenzidine in surface water and anaerobic groundwater, respectively (Syracuse Research Corp., 1989).

In soil, 3,3'-dichlorobenzidine is mineralized very slowly under aerobic conditions (Boyd *et al.*, 1984), with 2% $^{14}CO_2$ production after 32 weeks at either 4 or 40 mg/kg. Thin layer chromatography of ethyl acetate-methanol soil extracts failed to reveal any major transformation products. There was very little $^{14}CO_2$ production in autoclaved soils under aerobic conditions. There was no production of $^{14}CH_4$ under anaerobic conditions over a period of one year. Total ^{14}C radioactivity in soil remained constant during the incubations, demonstrating that 3,3'-dichlorobenzidine and its decomposition products did not volatilize. 3,3'-Dichlorobenzidine was strongly bound to soil. After 32 weeks of incubation, 90% of the applied radioactivity could not be extracted with ethyl acetate and methanol. The loss of solvent-extractable 3,3'-dichlorobenzidine occurred mainly in the first several weeks of incubation and was accompanied by an increase in alkali-extractable residue. These data strongly suggest the formation of covalent linkages between 3,3'-dichlorobenzidine and soil humic components as the primary fate of the chemical in the soil studied. However, the ultimate fate and biological availability of these bound residues in soil are unknown. Chung and Boyd (1987) found that < 2% of added [^{14}C]-3,3'-dichlorobenzidine evolved as $^{14}CO_2$ from soil and sludge-amended soil during a 182-d incubation, and that it was highly immobile in soil. The half-life for the aerobic

degradation of 3,3'-dichlorobenzidine in soil has been estimated to range from 4 to 26 weeks (Syracuse Research Corp., 1989).

Demirjian *et al.* (1987) showed that 3,3'-dichlorobenzidine quickly became unextractable in soil after application in municipal sewage sludge, with none recovered by organic solvent extraction after 4 months. This may have been due to irreversible adsorption or transformation, perhaps to 2,2'-dichloroazobenzene via the 2-chloroaniline intermediate.

4.2.2 Abiotic degradation

3,3'-Dichlorobenzidine is very rapidly photodegraded in aqueous solution by sunlight (half-life of minutes) to give monochlorobenzidine, benzidine, and a number of brightly colored water-insoluble materials (Banerjee *et al.*, 1978). The mechanism of photodegradation appears to involve (at least) sequential dechlorination to benzidine which is relatively stable on the time scale of the the experiments performed (< 45 minutes). Disappearance quantum yields measured at 254 nm for 3,3'-dichlorobenzidine and 3-chlorobenzidine were 0.43 and 0.70, whereas that for benzidine was much lower (0.012). From an environmental viewpoint the photodegradation of 3,3'-dichlorobenzidine does not necessarily lead to detoxification since benzidine, a relatively photostable carcinogen, is one of the products. Freitag *et al.* (1985) found that irradiation of 3,3'-dichlorobenzidine on silica gel for 17 h with 290 nm UV light resulted in the mineralization of 41% of the radiolabel to $^{14}CO_2$.

By analogy with benzidine (Tennakoon *et al.*, 1974a,b; Callahan *et al.*, 1979), 3,3'-dichlorobenzidine may be oxidized by metal ions such as ferric ion in clays.

In air 3,3'-dichlorobenzidine is expected to photooxidize fairly rapidly (Howard, 1989). Half-lives of 1.5-5 minutes and 0.9-9 hours have been estimated for the photolysis and photooxidation of 3,3'-dichlorobenzidine, respectively (Syracuse Research Corp., 1989).

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 behaviour of 3,3'-dichlorobenzidine in the environment was studied using the level III fugacity computer model for southern Ontario of Mackay and Paterson (1991) (see the Appendix). Based on the estimate for import into Canada and data on releases in the U.S.A. (U.S. Environmental Protection Agency, 1990), it was assumed that all the 3,3'-dichlorobenzidine was imported in 1989 for use only in southern Ontario and it would be released into the water at a rate of 0.05 mol/h. The results indicated that at steady-state, 3,3'-dichlorobenzidine would be

found in the air (<0.001%), surface water (99.75%), sediment (0.254%) and soil (<0.001%). This would result in steady-state concentrations of $7.6x10^{-16}$ $\mu g/m^3$ in air, $3.44x10^{-7}$ ng/L in water, $1.1x10^{-16}$ $\mu g/g$ dry weight in soil, and $3.1x10^{-12}$ $\mu g/g$ dry weight in sediment. 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

4.3.1 Surface water

No data were identified on the occurrence of 3,3'-dichlorobenzidine in surface water in Canada. It was detected (but not quantitated) in 1% of 1239 industrial effluent samples, and in 0.1% of 863 natural water samples in the United States (Staples *et al.*, 1985).

4.3.2 Groundwater

No data were identified on the occurrence of 3,3'-dichlorobenzidine in groundwater in Canada or elsewhere.

4.3.3 Air

No data were identified on the occurrence of 3,3'-dichlorobenzidine in air in Canada or elsewhere. 3,3'-Dichlorobenzidine was not found in the ambient air surrounding two dyestuff production facilities, at the detection limits of 0.1 and 5 ng/m^3 (U.S. Agency for Toxic Substances and Disease Registry, 1989).

4.3.4 Soil and sediment

No data were identified on the occurrence of 3,3'-dichlorobenzidine in soil or sediment in Canada. It was not detected in any of 347 sediment samples in the United States (Staples *et al.*, 1985).

4.3.5 Biota

No data were identified on the occurrence of 3,3'-dichlorobenzidine in biota in Canada. In the United States it was not detected in any of 83 biota samples (Staples *et al.*, 1985).

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 3,3'-dichlorobenzidine 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 to supporting documentation from Health and Welfare Canada.

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

Few data were identified on the acute toxicity of 3,3'-dichlorobenzidine to aquatic organisms (see Table 3). It is very toxic to bacteria in the Microtox assay, with an IC_{50} value of 0.06 mg/L (Dutka and Kwan, 1981). It is also very toxic to bluegill sunfish (*Lepomis macrochirus*), and is eliminated only slowly. Sikka *et al.* (1978) found that the 48-h LC_{100} value for bluegill sunfish (*Lepomis macrochirus*) was 2 mg/L. At 0.5 mg/L between 96 and 120 h, one half of the test group died, and the survivors exhibited extreme toxic symptoms. After transfer to uncontaminated water the surviving fish eliminated 3,3'-dichlorobenzidine fairly rapidly in the first 24 h, but whole fish concentrations appeared fairly constant from 120 to 240 h. Kaiser (1992) estimated the following 96-h LC_{50} values: > 3 mg/L for fathead minnow (*Pimephales promelas*), 3 mg/L for rainbow trout (*Oncorhynchus mykiss*), and 1.5 mg/L for golden orfe (*Leuciscus idus melanotus*), based on quantitative structure-activity relationships.

No data were identified on the chronic toxicity of 3,3'-dichlorobenzidine to aquatic organisms.

9.2 Terrestrial toxicity

No data were identified for the acute or chronic toxicity of 3,3'-dichlorobenzidine to wild mammals, terrestrial organisms, birds, sediment or soil biota.

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Table 1. Chemical and physical properties of 3,3'-dichlorobenzidine

Property		Reference
molecular formula	$C_{12}H_{10}N_2Cl_2$	
molecular weight	253.13	
appearance	grey to purple crystalline solid	Banerjee et al. (1978)
melting point	133 °C	Ferber (1978)
boiling point	402 °C	Banerjee et al. (1978)
vapour pressure	10^{-5} mm Hg at 22 °C	Mabey et al. (1982)
aqueous solubility	4 mg/L (as dihydrochloride)	Banerjee et al. (1978)
pK_a	4.5, 3.3	Korenman and Nikolaev (1974)
log (octanol-water partition coefficient)	3.02	Callahan et al. (1979)

Table 2.   Importation of 3,3'-dichlorobenzidine into Canada[*]

| Year	Amount imported, tonnes
1978	82
1979	56
1980	53
1981	20
1982	5
1983	15
1984	25
1985	28
1986	21
1987	60
1988	not available
1989	109

[*]All data are from Statistics Canada (1990), and probably include derivatives of 3,3'-dichlorobenzidine.

Table 3. Acute toxicity of 3,3'-dichlorobenzidine to aquatic organisms[*]

Species	Size / age	Static / flow-through	Temp. °C	Hardness mg/L	pH	Response	Conc. mg/L	Nominal / measured	Reference
bacteria Photobacterium phosphoreum		stat	15			15-min IC_{50} (light output)	0.06	n	Dutka and Kwan (1981)
bluegill sunfish Lepomis macrochirus	5-8 cm	stat	21			48-h LC_{100}	2	n	Sikka et al. (1978)

[*]Abbreviations used: IC_{50} - concentration which effectively inhibits 50% of function/growth; LC_{100} - concentration which kills 100% of test organisms.

Figure 1. Chemical structure of 3,3'-dichlorobenzidine.
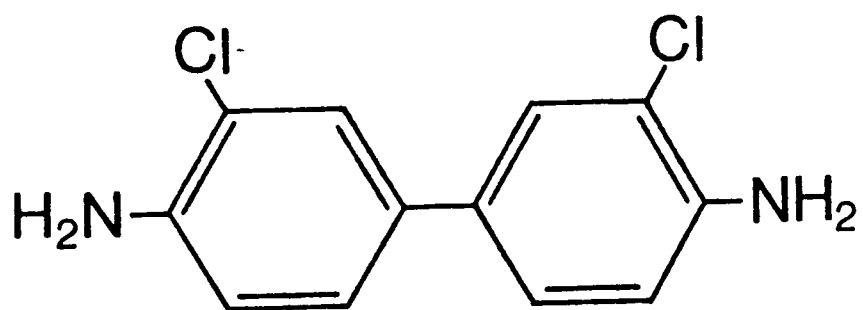
3,3'-DICHLOROBENZIDINE

Appendix

Level III Fugacity Modelling

No data were identified on the concentrations of 3,3'-dichlorobenzidine 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, concentrations in sediment may be underestimated, and concentrations in water may be overestimated.

A brief account of the principal findings is presented below. It was assumed that all the 3,3'-dichlorobenzidine imported into Canada in 1989 was for use only in southern Ontario, and that it would be released into water at a rate of 0.05 mol/h (based on a loss of 0.1 tonne (see section 3.2.5). The following assumptions were entered into the model:

(1) The 0.11 tonnes/year of 3,3'-dichlorobenzidine is released into southern Ontario in the following proportions: air 0%, water 100% (0.05 mol/h) and soil 0%.

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

air   – k = 9.2 h^{-1} ($t_{1/2}$ = 0.075 h)
water – k = 9.2 h^{-1} ($t_{1/2}$ = 0.075 h)
soil – k = 0.00016 h^{-1} ($t_{1/2}$ = 4320 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} m^3/h and water = 3.3×10^8 m^3/h).

Table A-1 summarizes emissions, environmental distribution (%) and resulting concentrations. A mass balance diagram is shown in Figure A-1. Of the 0.05 mol/h entering the water compartment, 4.5×10^{-7} mol/h is advected out of the region and 0.05 mol/h reacts in the region. There is a net outflow to other compartments of 1.3×10^{-8} mol/h and a net inflow from other compartments of 2.9×10^{-13} mol/h. The advective residence time is 12,100 h and the reaction half-life is 0.075 h. There is a total of 5.4×10^{-3} mol resident in the water, equivalent to an overall residence time of approximately

0.11 h. The amount in the water is 99.75% of the total amount of 3,3'-dichlorobenzidine present and corresponds to an average of concentration in water of 3.4×10^{-7} ng/L.

The amount in air of 1.2×10^{-9} mol is <0.001% of the total and corresponds to a concentration of 7.6×10^{-16} $\mu g/m^3$. 3,3'-Dichlorobenzidine entering the air reacts at a rate of 1.1×10^{-8} mol/h and is advected by a rate of 9.9×10^{-12} mol/h. The residence time in air is approximately 0.11 h.

The concentration in soil is approximately 1.1×10^{-16} $\mu g/g$ and in sediment it is 3.1×10^{-12} $\mu g/g$, both very low values.
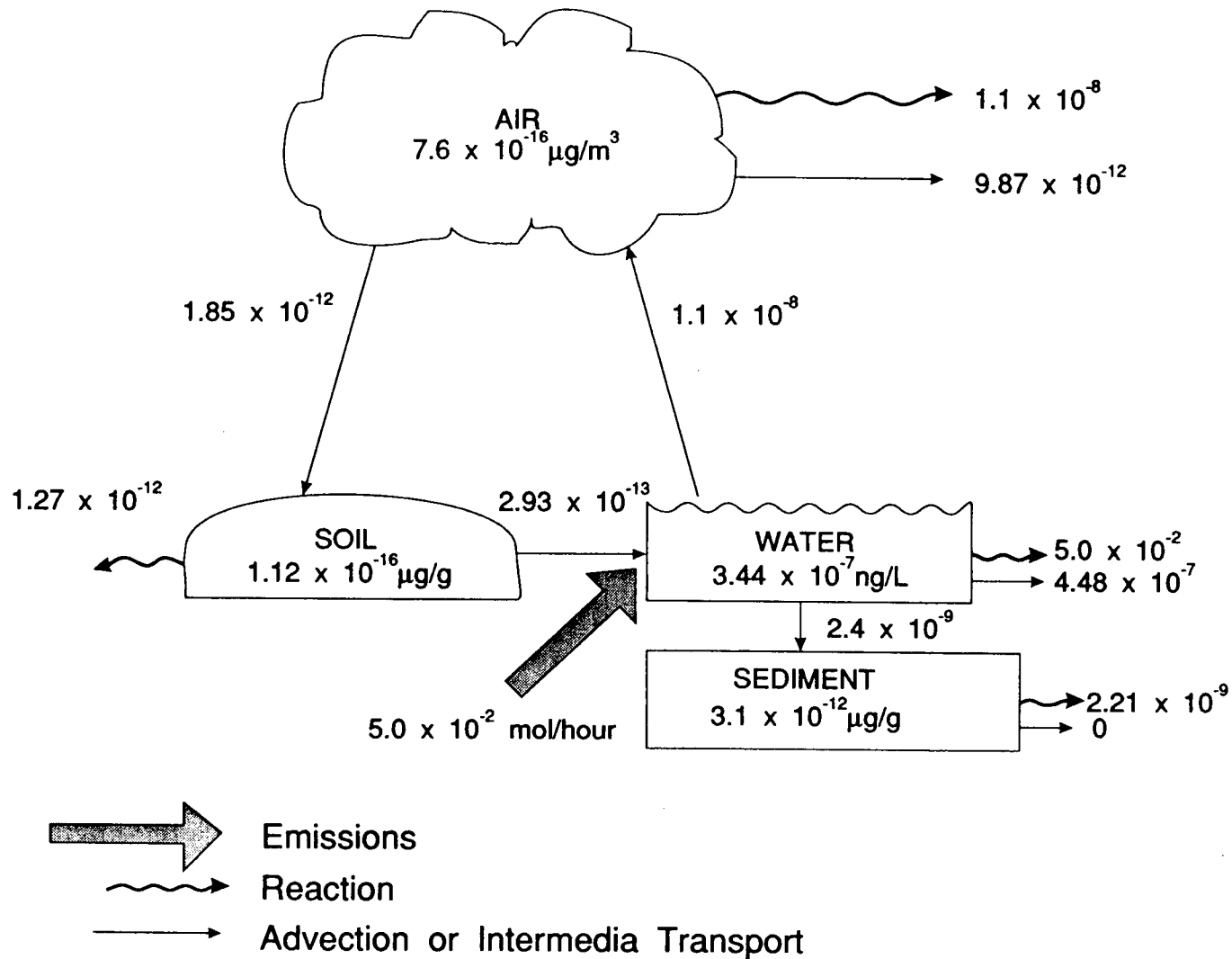
It is thus apparent from the results that it is the aquatic fate of 3,3'-dichlorobenzidine which is of primary concern. The prevailing concentrations will be highest when reaction rates are slow.

Table A-1.   Summary of results for 3,3'-dichlorobenzidine in
      southern Ontario according to the level III fugacity model of
      Mackay and Paterson (1991).

Compartment	Emission mol/hour	Environmental distribution %	Concentrations
Air	0	0.000	7.6×10^{-16} $\mu g/m^3$
Water	0.05	99.746	3.44×10^{-7} ng/L
Soil	0	0.000	1.1×10^{-16} $\mu g/g$
Sediment	0	0.254	3.1×10^{-12} $\mu g/g$

residence time 6.5 min
reaction persistence 6.5 min

Figure A-1.   Mass balance diagram for 3,3'-dichlorobenzidine in southern Ontario according to the level III fugacity model of Mackay and Paterson (1991).

AIR
$7.6 \times 10^{-16} \mu g/m^3$

1.1×10^{-8}

9.87×10^{-12}

1.85×10^{-12}

1.1×10^{-8}

1.27×10^{-12}

2.93×10^{-13}

SOIL
$1.12 \times 10^{-16} \mu g/g$

WATER
$3.44 \times 10^{-7} ng/L$

5.0×10^{-2}

4.48×10^{-7}

2.4×10^{-9}

5.0×10^{-2} mol/hour

SEDIMENT
$3.1 \times 10^{-12} \mu g/g$

2.21×10^{-9}

0

⇨ Emissions

⌇→ Reaction

→ Advection or Intermedia Transport

Mass balance diagram for 3,3'-dichlorobenzidine in Southern Ontario