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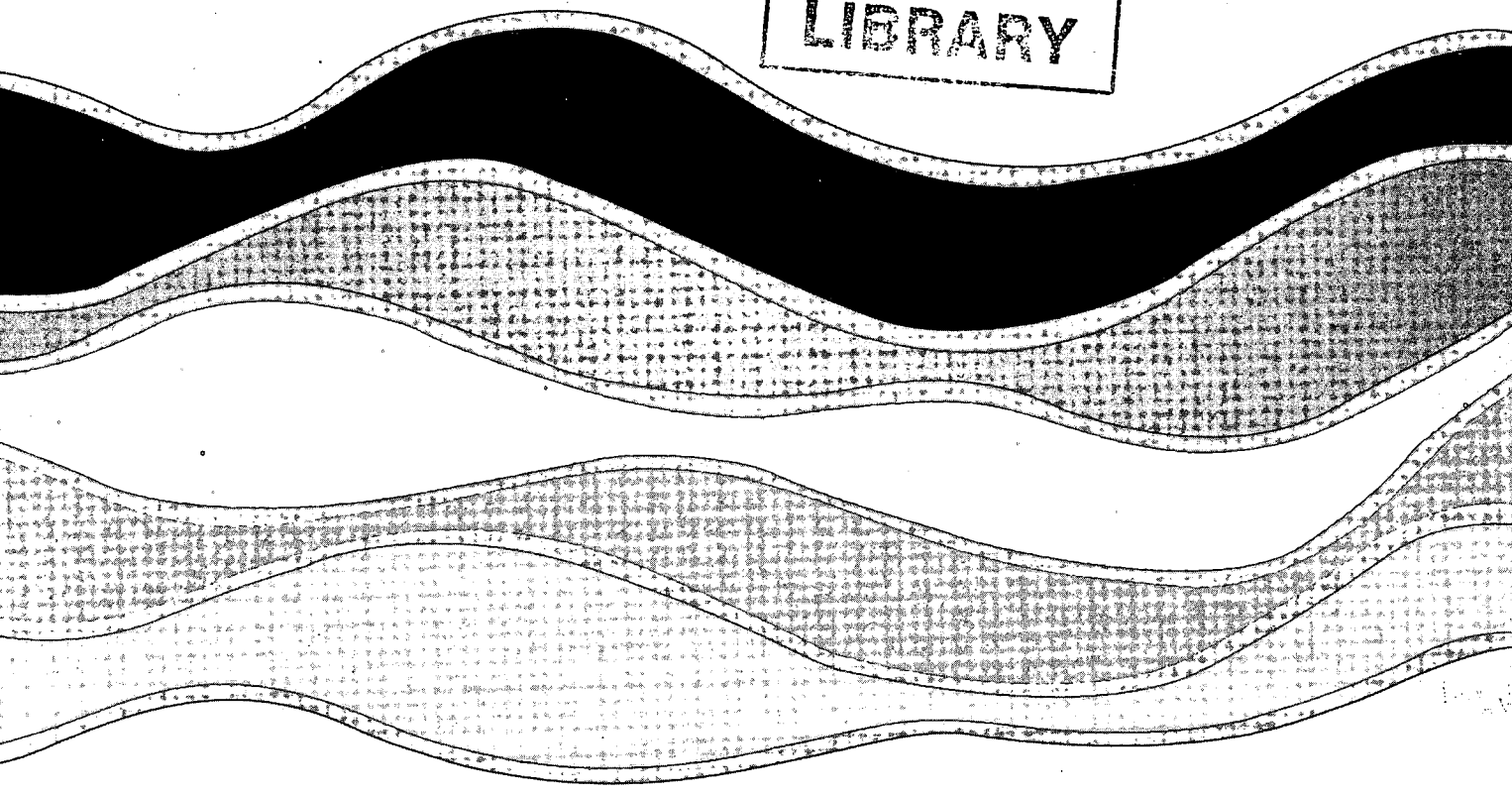

ENVIRONMENTAL CHEMISTRY OF THE FOUR AROMATIC AMINES TO BE ASSESSED UNDER THE CANADIAN ENVIRONMENTAL PROTECTION ACT: ANILINE, 3, 5-DIMETHYLANILINE, BENZIDINE AND 3, 3'-DICHLOROBENZIDINE

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MANAGEMENT PERSPECTIVE

The four aromatic amines aniline, 3,5-dimethylaniline, benzidine and 3,3'-dichlorobenzidine are on the Priority Substances List of the Canadian Environmental Protection Act. They must be assessed to determine whether they are toxic according to the definition specified in section 11 of the Act. This report is a review of the environmental chemistry of the four aromatic amines. This information will be combined with data on the toxicity and exposure patterns of the chemicals (currently being prepared by the Department of National Health and Welfare) to provide environmental and human health risk assessments of the four chemicals.

PERSPECTIVES DE GESTION

Les quatre amines aromatiques, l'aniline, la 3,5-diméthylaniline, la benzidine et la 3,3'-dichlorobenzidine figurent dans la Liste des substances prioritaires de la Loi canadienne sur la protection de l'environnement. Elles doivent être évaluées pour déterminer si elles sont toxiques en vertu de la définition précisée à l'article 11 de la loi. Le présent rapport est une étude de la chimie environnementale des quatre amines aromatiques. Ces données seront combinées avec l'information relative à la toxicité et aux divers modes d'exposition à ces produits chimiques (actuellement préparée par le ministère de la Santé et du Bien-être social) pour l'évaluation finale du risque que représentent les quatre produits pour la santé humaine.

ABSTRACT

A review was made of the environmental chemistry of the four aromatic amines (aniline, 3,5-dimethylaniline, benzidine and 3,3'-dichlorobenzidine) to be assessed under the Canadian Environmental Protection Act, and a number of important data gaps were identified. Aniline, benzidine and 3,3'-dichlorobenzidine do not appear to persist in the environment. It is likely that 3,5-dimethylaniline will also be relatively non-persistent. Overall half-lives appear to be less than a few weeks as far as the parent compounds are concerned, although there is some concern whether the fast and apparently irreversible binding to soils and sediments observed with many aromatic amines renders them permanently biologically unavailable. Summary statements for each chemical are given below.

The general conclusion from a number of studies of the environmental persistence and fate of **aniline** is that it is relatively non-persistent in the environment. Microbial degradation has been identified as the most significant process determining the persistence of aniline in water. Photooxidation in surface waters can also be important, with a half-life of a few days. Biological degradation will also be important in groundwater, although it will be slower. In soil, biological degradation, oxidation and binding to soil constituents are also

important. In air, aniline photodegrades with a half-life of a few hours.

There are only two reports in the literature which deal with the environmental persistence and fate of **3,5-dimethylaniline**. It is degraded by activated sludge about as quickly as aniline. There are no quantitative data on its aqueous and organic solvent solubility, vapour pressure and octanol-water partition coefficient to allow an estimate to be made of the relative importance of various pathways of distribution and transformation. However, by analogy with aniline it is anticipated that 3,5-dimethylaniline will be relatively non-persistent in the environment and that biological degradation will be a major (if not the major) process determining its persistence in the aquatic and soil environments. Sunlight photolysis may also be important in water and on soil. It is anticipated that sunlight photolysis will be important in air. The vapour pressure of 3,5-dimethylaniline will probably be less than that of aniline. Because of the electron-donating nature of the two methyl groups, the pK_a of 3,5-dimethylaniline will be higher than that of aniline, indicating that more of this chemical (relative to aniline) will be charged at environmental pH values. This may make binding to clays relatively more important compared to binding to soil organic matter.

In general, photochemical transformation, partitioning to sediment or soil and microbial degradation (with slow

mineralization) are expected to be the main pathways of distribution and transformation of the well-known carcinogen **benzidine** in the environment. Benzidine by itself is not expected to be persistent 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.

In general, photooxidation, adsorption to soil and sediment, and slow microbiological degradation (with very slow mineralization) are expected to be the main pathways of distribution and transformation of **3,3'-dichlorobenzidine** in the environment. It will bioconcentrate in fish and will probably be less biodegradable than benzidine. 3,3'-Dichlorobenzidine by itself is not expected to be persistent 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. One of the products is the carcinogen benzidine.

RÉSUMÉ

Une étude a été entreprise sur la chimie environnementale de quatre amines aromatiques (aniline, 3,5-diméthylaniline, benzidine et 3,3'-dichlorobenzidine) pour les évaluer selon la Loi canadienne sur la protection de l'environnement; on a ainsi pu mettre en évidence plusieurs importantes lacunes au niveau de l'information. L'aniline et la 3,3'-dichlorobenzidine ne semblent pas persister dans l'environnement. Il est probable que la 3,5-diméthylaniline est elle aussi relativement non persistante. Les demi-vies globales sont probablement inférieures à quelques semaines pour ce qui est des composés parents, mais on se demande si la fixation rapide et apparemment irréversible aux sols et aux sédiments, observée dans le cas de nombreuses amines aromatiques les rend biologiquement inaccessibles, et ce de façon permanente. On présente ci-dessous des descriptions sommaires pour chaque produit chimique.

Conclusion générale d'un certain nombre d'études sur la persistance et le devenir de l'aniline dans l'environnement : ce composé est relativement non persistant dans l'environnement. On a pu observer que la dégradation microbienne était le processus le plus significatif déterminant la persistance de l'aniline dans l'eau. La photo-oxydation dans l'eau de surface peut elle aussi être importante, avec une demi-vie de quelques jours. La dégradation biologique se révélera également significative dans l'eau souterraine, bien qu'elle y soit plus lente. Dans le sol, la dégradation biologique, l'oxydation et la fixation aux constituants du sol sont toutes importantes. Dans l'air, la photodégradation de l'aniline détermine une demi-vie de quelques heures.

Dans la documentation scientifique, seuls deux rapports traitent de la persistance et du devenir de la 3,5-diméthylaniline dans l'environnement. Elle est dégradée par les boues activées à peu près aussi rapidement que l'aniline. Il n'existe pas de données quantitatives sur sa solubilité dans l'eau et les solvants organiques, ni sur sa pression de vapeur et sur son coefficient de partage octanol/eau pour permettre une évaluation de l'importance relative des diverses voies de diffusion et de transformation. Cependant, par analogie avec l'aniline, on peut s'attendre à ce que la 3,5-diméthylaniline soit relativement non persistante dans l'environnement et que la dégradation biologique constituera un important (sinon le plus important) processus déterminant sa persistance dans les milieux aquatiques et dans le sol. On peut prévoir que la photolyse à la lumière solaire sera importante dans l'air. La pression de vapeur de la 3,5-diméthylaniline sera probablement inférieure à celle de l'aniline. En raison du rôle de donneurs d'électrons des deux groupes méthyle, le pK_a de la 3,5-diméthylaniline sera supérieur à celui de l'aniline, ce qui montre que davantage de ce composé (par rapport à l'aniline) s'accumulera aux valeurs de pH qui existent dans l'environnement. Cela peut rendre la fixation aux argiles plus importante, comparativement à la fixation aux matières organiques du sol.

De façon générale, la transformation photochimique, le partage entre les sédiments ou le sol et la dégradation microbienne (avec minéralisation lente) sont probablement les principales voies de diffusion et de transformation de la benzidine, agent cancérigène bien connu, dans l'environnement. La benzidine comme telle n'est sans doute pas persistante, du fait qu'il y a formation rapide de résidus

solidement fixés dans les sols et les sédiments, mais on n'a pas étudié l'accessibilité biologique de ces résidus. En outre, les produits de dégradation n'ont pas été caractérisés de façon satisfaisante.

En général, la photo-oxydation, l'adsorption par le sol et les sédiments, et la lente dégradation microbiologique (avec minéralisation très lente) sont probablement les principales voies de diffusion et de transformation de la 3,3'-dichlorobenzidine dans l'environnement. Il y aura bioconcentration de ce composé chez le poisson, mais sa biodégradation sera sans doute inférieure à celle de la benzidine. La 3,3'-dichlorobenzidine comme telle n'est sans doute pas persistante, du fait qu'il y a formation rapide de résidus solidement fixés dans les sols et les sédiments, mais on n'a pas étudié l'accessibilité biologique de ces résidus. En outre, les produits de dégradation n'ont pas été caractérisés de façon satisfaisante. L'un de ces produits est la benzidine cancérigène.

INTRODUCTION

The Canadian Environmental Protection Act (CEPA), proclaimed June 30, 1988, authorizes the Ministers of National Health and Welfare and of the Environment to conduct research and collect information on a wide variety of substances that may contaminate the environment and cause adverse effects on human health or the environment (Government of Canada, 1988). The term "substance" is defined in section 3 of CEPA and for the purposes of the Act includes chemicals in commerce, chemical contaminants in products or environmental media, and complex mixtures of substances in effluent streams and emissions. The estimated 30,000 to 40,000 chemicals that are manufactured in or imported into Canada and hundreds of effluent streams and emissions are candidates for assessment of their health and environmental impacts under CEPA. It is not possible to assess simultaneously all the substances that may pose a threat to health or the environment. Therefore it was necessary to select a manageable number that should be given priority for assessment, as required by subsection 12(1) of CEPA which states:

> "The Ministers shall compile and may amend from time to time a list known as the Priority Substances List, and the List shall specify substances in respect of which the Ministers are satisfied priority should be given in assessing whether they are toxic or capable of becoming toxic."

Substances that appear on the Priority Substances List must be assessed to determine whether they are toxic according to the definition specified in section 11 of the Act, which states, in part:

> "... a substance is toxic if it is entering or may enter the environment in a quantity or concentration or under conditions
>
> (a) having or that may have an immediate or long-term harmful effect on the environment;
>
> (b) constituting or that may constitute a danger to the environment on which human life depends; or
>
> (c) constituting or that may constitute a danger in Canada to human life or health."

In preparing the CEPA Priority Substances List for the first time, the Ministers of the Environment and of National Health and Welfare gave consideration to recommendations of academia, industry, environmental public interest groups and provincial governments, as provided for in subsection 12(3) of CEPA. A substance was selected for the List if it met at least one of the following three criteria:

(a) The substance causes or has the potential to cause adverse effects on human health or the environment.

(b) The substance accumulates or could accumulate to significant concentrations in air, water, soil, sediment or tissue.

(c) The substance is released or may be released into the environment in significant quantities or concentrations.

The CEPA Priority Substances List of February 11, 1989 (Canada Department of Environment, 1989) contains four aromatic amines which are the subject of this report:

Chemical	Chemical Abstracts Service Registry Number
aniline	62-53-3
3,5-dimethylaniline	108-69-0
benzidine	92-87-5
3,3'-dichlorobenzidine	91-94-1

The structures of these chemicals are shown in Figure 1. Although salts of these compounds were not specifically mentioned in the CEPA Priority Substances List, it is expected that such salts would

have the same environmental chemistry and fate as their parent compounds.

This report is a review of the environmental chemistry of the four aromatic amines. It is divided into four separate sections dealing with each chemical. The aim was to determine the hazard posed by the chemicals. The hazard posed by a chemical to an organism in any environmental "compartment" such as water, sediment or air may be viewed as a function of its toxicity, its concentration and its persistence. Although the toxicity of the four aromatic amines will be described briefly, this report is concerned mainly with the environmental occurrence and persistence of the chemicals. This report reviews available information on the uses, chemical and physical properties, environmental occurrence and environmental chemistry and fate of each of the four aromatic amines. This information will be combined with data on the toxicity and exposure patterns of the chemicals (currently being prepared by the Department of National Health and Welfare) to provide environmental and human health risk assessments of the four chemicals.

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 sediment, (ii) chemical and photochemical degradation or transformation, and (iii) uptake and transformation 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).

ANILINE

Production and Uses

Aniline is the simplest of the primary aromatic amines. It occurs in small quantities in coal tar. It 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, at present it is manufactured mainly 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 (Mark et al., 1978a). Some physical and chemical properties of aniline are shown in Table 1.

In the United States, aniline production in the period 1981 - 1983 varied from 2.5×10^5 to 3.0×10^5 tonnes. Industrial emissions to the environment in the U.S.A. in 1988 were estimated to be 900 tonnes (Croy and DeVoto, 1990a). Aniline is apparently not produced in Canada, but 300 tonnes were imported in 1989 (Statistics Canada, 1990). There is no information on releases to the Canadian environment.

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 (Mark et al., 1978a).

In the polymer industry aniline is used primarily for the manufacture of isocyanates to make polyurethanes. Aniline condenses with formaldehyde to give methylenedianilines and polymers which on phosgenation give methylenebis(phenyl isocyanates) and the polymeric isocyanates. The pure 1,1'-methylenebis(4-isocyanatobenzene) is used for the production of urethane elastomers.

In the rubber industry aniline is used in the manufacture of antioxidants, antidegradants and vulcanization accelerators such as mercaptobenzothiazoles, diphenylguanidine, diphenylthiourea and condensation products of aniline with various aldehydes. As rubber antioxidants, amines are used mostly in darker coloured rubbers where staining is not a problem. Conversely, phenolic stabilizers are used more in lighter coloured rubbers where aesthetics are more important. Consumer exposure to amine stabilizers will come from

contact with vehicle tires, V-belts and rubber hoses, foam rubber carpet backings, various sponge goods, padding, sporting goods and shoes. Normally the stabilizer is added in concentrations of 1-3% by weight (Ontario Ministry of Environment, 1980).

Important agricultural uses for aniline derivatives include herbicides, fungicides, insecticides, animal repellants and defoliants.

Aniline and its N-alkyl derivatives have been used as antiknock compounds in leaded gasolines. Mercaptobenzothiazole compounds find use as corrosion inhibitors for glycol antifreeze and in boiler feed water. Amine salts are used as motor fuel additives to prevent carburetor icing and as rust inhibitors.

In the pharmaceutical industry aniline is used in the manufacture of sulfa drugs, acetanilide and sweetening agents. Aniline is also used in the manufacture of hydroquinone, optical whitening agents, resins, marking inks, perfumes, shoe polishes, and many organic chemicals (Mark et al., 1978a; Ontario Ministry of Environment, 1980).

In Ontario in 1980 uses of all anilines were largely confined to the manufacture of rubber chemicals, as a hardener in industrial epoxies and as a corrosion inhibitor. About 900 tonnes were used,

and all of it was imported (Ontario Ministry of Environment, 1980).

Toxicity, Uptake and Metabolism

The most important action of aniline on the body is the formation of methemoglobin, with the resulting anoxemia and depression of the central nervous system. Aniline may also have a direct toxic action, resulting in a fall in blood pressure and cardiac arrhythmia. In acute exposures, which usually result from spilling the liquid on the skin and clothes, but which may also follow the inhalation of the vapour given off when aniline is heated, the signs are of methemoglobinaemia and anoxemia. In less acute exposure which has been prolonged over some weeks or months, there is usually hemolysis of the red blood cells, followed by stimulation of the bone marrow and attempts at regeneration. The red cells may show stippling; immature cells may be present. The white blood cells usually show little change either in number or in morphology. The liver may be affected, with production of jaundice. The urine is frequently dark brown or wine coloured, and may contain hemoglobin, hematoporphyrin, and, in some cases, excretion products of aniline, such as p-aminophenol. Long continued employment in the manufacture of aniline dyes has been associated with the development of papillomatous growths of the bladder, some of which became malignant. Aniline itself has not

been proven to be a carcinogen, but the intermediates benzidine and naphthylamines have been implicated (Sax, 1968).

Table 2 shows acute toxicities of aniline to a number of aquatic organisms. Aniline is not very toxic to most species tested, with the exception of Daphnia magna; one study showed a LC_{50} value of 0.25 mg/L (Holcombe et al., 1987). Although neither the clawed toad nor the axolotl species shown in Table 2 is native to Canada, they may well serve as surrogates for toads and salamanders that are native.

Some other effects were noted in the acute studies shown in Table 2 and in other studies. Davis et al. (1981) noted teratogenic effects of aniline on the larvae of the clawed toad Xenopus laevis in the mid-blastulae stage: the 96 hr EC_{50} value was 370 mg/L. At concentrations as low as 1 mg/L, aniline was found by Dumpert (1987) to inhibit embryonic development of X. laevis, resulting in undersized toads; higher doses (20-40 mg/L) inhibited pigmentation. Birge et al. (1979), examining the effects of aniline on 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).

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

Baird et al. (1977) noted that aniline at 20 mg/L had some inhibitory effect on the respiration of 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., 1985). However, unidentified transformation products after incubation with pond water and sewage sludge inoculum were mutagenic.

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). Aniline was rapidly detoxified by methylation, acetylation, hydroxylation and conjugation. Daphnia and snail were able to metabolize aniline completely to polar metabolites. N-Methyl- and N,N-dimethylaniline were found in algae and mosquito larvae, respectively. The fish was the only species which retained small amounts of aniline with a bioconcentration factor of 6, together with N-methylaniline and N,N-dimethylaniline and almost equal amounts of o-, m- and p-aminophenols. Acetanilide was found

in fish and water extracts and was further metabolized to p-acetamidophenol, then conjugated. Freitag et al. (1985) found a one-day bioconcentration factor (BCF) of 4 for algae (Chlorella fusca), and a 3-day BCF of <10 for fish (golden ide, 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 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 algae; however, significant bioaccumulation has not yet been observed, nor would it be expected for a chemical with a log octanol-water partition coefficient (log K_{OW}) of 0.98 (cf. Table 1).

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., 1985). 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.

Environmental Occurrence

Table 3 shows the environmental occurrence of aniline. There are relatively few data on the environmental occurrence of such a widely used chemical, possibly because its relatively short environmental persistence has made it a low priority for monitoring. Aniline apparently does not occur in nature, and its presence in the environment is largely due to effluents from chemical plants and energy-related processes. Concentrations in the Rhine River have been found in the 0 - 20 μg/L range (Wegman and De Korte, 1981a, 1981b). Concentrations in groundwater up to 700 μg/L have been found close to an underground coal gasification site, a shale oil retorting site and a landfill (Stuermer et al., 1982; Pereira et al., 1983; Reinhard et al., 1984). Concentrations were considerably higher in coal distillates and industrial effluents.

Persistence

The general conclusion from a number of studies of the environmental persistence and fate of aniline is that it is relatively non-persistent in the environment, and that overall half-lives in water, soil and air would be less than a few weeks. 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. Biological degradation will also be important in groundwater, although it will be slower (Aelion et al., 1987). In soil, biological degradation, oxidation and binding to soil constituents are also important. In air, aniline photodegrades with a half-life of a few hours (Howard, 1989).

Aniline did not persist in pond water (70, 59 and 10% remaining after 4, 7 and 14 days, respectively) or pond water plus sewage sludge (8, 0 and 0% remaining after 4, 7 and 14 days, respectively) (Lyons et al., 1984, 1985). The major pathway of aniline biodegradation in pond water involved oxidative deamination to catechol (cf. also Paris and Wolfe, 1987), which was further metabolized through cis,cis-muconic, β-ketoadipic, levulinic and succinic acid intermediates to CO_2. Minor biodegradation pathways 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., Baird et al., 1977; Calamari et al., 1980; Subba-Rao et al., 1982; Demirjian et al., 1987). Means and Anderson (1981) found that aniline completely degraded in 1 - 7 days in the BOD, shake flask, CO_2 evolution and activated sludge tests. Brown and Laboureur (1983) found that aniline was > 90% microbiologically degraded in 7 days 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.

Aniline photodegraded with a half-life of about 7 days in distilled water. This reaction was accelerated to a considerable degree by humic acids and aquatic humus, with near-surface half-lives of 4 to 8 hours 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 12000 times faster with some algal species than it did in distilled water. Reaction rates appeared to be unaffected by heat-killing the algae, in accord with earlier studies that substances released by algae can photosensitize a variety of reactions in water. Dark metabolism made little or no contribution to the degradation. In estuarine water, half-lives for the combined sunlight photolysis and microbial degradation of aniline were 1 - 8 days (Hwang et al., 1987). Carbonate radicals generated by the photolysis of hydrogen peroxide in water can react with aniline and substituted anilines such as 3-methylaniline (Larson and Zepp, 1988).

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 low-volatility compound as far as volatilization from water is concerned (Smith et al., 1980).

Aniline is also easily degraded by many common species of bacteria and fungi found in soil (Howard, 1989). In sterile soil aniline partially degraded in 3 days 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_5]aniline seems evidenced 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 identified, most of the added aniline was unaccounted for. Inefficient extraction may have caused 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 [^{14}C]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.

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, 1980). Although there have been correlations between the extent of binding and clay content and pH of the soil (the pK_a of aniline is 4.63), 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 (1980) showed that covalent binding (as inferred from lack of recoverability by simple extraction) of aniline and ring-substituted anilines (including 2-, 3- and 4-methylaniline) 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.

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

3,5-DIMETHYLANILINE

Production and Uses

3,5-Dimethylaniline is one of six isomeric dimethylanilines, or xylidines. It and other xylidine isomers are mainly used as intermediates in the manufacture of azo dyes (Mark et al., 1978a; Merck, 1989). It is also used in the manufacture of pharmaceuticals, curing agents, antioxidants and antiozonants, as well as in the manufacture of gasoline additives and detergents. It is used in organic synthesis in the preparation of wood preservatives, wetting agents for textiles, frothing agents for ore dressing, special lacquers and metal complexers.

3,5-Dimethylaniline can be produced by the reduction of 3,5-dinitroaniline by strong acid. Xylidine is a general term used to describe any or all of the six isomers of ar,ar-dimethylaniline. Physical and chemical properties are commonly reported for xylidine or xylidines, with no reference to any specific isomer. Table 4 gives some physical properties of 3,5-dimethylaniline.

There is no specific information on the production of 3,5-dimethylaniline in any country. Canada imported 354 tonnes of aniline derivatives in 1989 (Statistics Canada, 1990). There is no information on releases to the Canadian environment of 3,5-dimethylaniline or any other aniline derivative.

Toxicity, Uptake and Metabolism

With one minor exception there is no information in the literature on the toxic effects of 3,5-dimethylaniline. Baird et al. (1977) have shown that 3,5-dimethylaniline at 20 mg/L has some inhibitory effect on the respiration of activated sludge even while being degraded, which suggests that a metabolite or metabolites may be responsible for the observed toxicity.

Environmental Occurrence

There is no information on the environmental occurrence of 3,5-dimethylaniline or any other xylidine. As seen in the section on aniline, there are some data on the environmental occurrence of methylanilines.

Persistence

There are only two reports in the literature which deal with the environmental persistence and fate of 3,5-dimethylaniline. Baird et al. (1977) showed that 3,5-dimethylaniline was degraded by activated sludge about as quickly as aniline, and Lammerding et al. (1982) showed that the diazonium ion was a key intermediate in the

degradation of 3,5-dimethylaniline by E. coli in the presence of nitrite ion.

There are no quantitative data on the aqueous and organic solvent solubility, vapour pressure and octanol-water partition coefficient of 3,5-dimethylaniline to allow an estimate to be made of the relative importance of various pathways of distribution and transformation. However, by analogy with aniline it is anticipated that 3,5-dimethylaniline will be relatively non-persistent in the environment and that biological degradation will be a major (if not the major) process determining its persistence in the aquatic and soil environments. Sunlight photolysis may also be important in water and on soil. It is anticipated that sunlight photolysis will be important in air. The vapour pressure of 3,5-dimethylaniline will probably be less than that of aniline. Because of the electron-donating nature of the two methyl groups, the pK_a of 3,5-dimethylaniline will be higher than that of aniline, indicating that more of this chemical will be charged at environmental pH values. This may make binding to clays relatively more important compared to binding to soil organic matter.

BENZIDINE

Production and Uses

Benzidine and several of its derivatives were of commercial value primarily as intermediates in the manufacture of dyes and pigments. They were also used in minor amounts in inorganic qualitative and quantitative analysis for the determination of various cations and anions, in various phases of organic analyses, in the determination of blood in forensic and clinical medicine, and as stains in microscopy (Mark et al., 1978b; Merck, 1989). However, in recognition of its dangers to human health, many countries have prohibited or severely limited its production, use and importation.

Commercial manufacture of benzidine involved the alkaline reduction of nitrobenzene in either one stage to hydrazobenzene, or stepwise, changing conditions at the azoxybenzene or azobenzene stages. Zinc or sodium amalgams, iron and the electrolytic cathode have been used as reducing agents; however, powdered zinc or methanol was preferred. The hydrazobenzene was separated from the reaction mass and rearranged to benzidine and several by-products with hydrochloric acid. Some physical and chemical properties of benzidine are shown in Table 5.

Benzidine is no longer manufactured for sale in the United States or Japan (International Agency for Research on Cancer, 1982). One or more companies in South Korea and one company in France are believed still to produce benzidine dihydrochloride as a captive dye intermediate. Other countries that may also produce this intermediate are Argentina, Brazil, Mexico, China, Poland, Romania and the USSR (International Agency for Research on Cancer, 1982). Benzidine does not appear to be produced in Canada.

Although there are 254 dyes or pigments that can be produced from benzidine, in 1983 only 1 benzidine-based pigment and 16 benzidine-based dyes were in production (Croy and DeVoto, 1990b). Estimated U.S. production of benzidine-based dyes was 200 - 300 tonnes in 1983, but there have been no imports of benzidine for such syntheses in recent years (Croy and DeVoto, 1990b).

In Ontario in 1980 approximately 68 tonnes of benzidines were used by industry (Ontario Ministry of Environment, 1980). Approximately 900 tonnes of benzidine-related aromatic polyamines were imported into Canada in 1989 (Statistics Canada, 1989), most of it entering Ontario but some of it entering Quebec. It is not known whether benzidine itself is included in this group.

Toxicity, Uptake and Metabolism

Benzidine can cause damage to blood including hemolysis and bone marrow depression. On ingestion it causes nausea and vomiting which may be followed by liver and kidney damage. Benzidine is a recognized human carcinogen, and any exposure is considered extremely hazardous (Sax, 1968).

Table 6 shows the acute toxicity of benzidine to a number of aquatic organisms. Benzidine is toxic to some fish at concentrations as low as 5 mg/L.

Baird et al. (1977) noted that benzidine at 20 mg/L had some inhibitory effect on the respiration of activated sludge even while being degraded, which suggested that a metabolite or metabolites may have been responsible for the observed toxicity. Lu et al. (1977) showed that the accumulation and bioconcentration of benzidine in a laboratory model ecosystem was closely correlated with its octanol-water partition coefficient (log K_{ow} = 1.34). Biomagnification factors were 55 for fish, 293 for daphnia, 456 for mosquito, 645 for snail and 2617 for algae. Benzidine was fairly easily biodegradable. Degradative pathways were through N-demethylation and acetylation of amino groups.

Environmental Occurrence

There are few data on the environmental occurrence of benzidine. Benzidine was only detected in 1.1% of 1235 industrial effluent samples, and 0.1% of 879 natural water samples in the United States. It was not detected in any of 3240 sediment samples or 110 biota samples (Staples et al., 1985).

Persistence

In general, photochemical transformation, partitioning to sediment or soil and microbial degradation (with slow mineralization) are expected to be the main pathways of distribution and transformation of benzidine in the environment (Sanders, 1979; Callahan et al., 1979; Howard, 1989). Benzidine 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.

In water, although both oxidation (by hydroperoxyl radical or molecular oxygen) and photolysis may be significant processes, the most important process controlling the fate of benzidine appears to be oxidation by naturally-occurring metal cations, with a half-life of the order of a few hours (Callahan et al., 1979). Benzidine is

very rapidly oxidized by iron (III) and several other naturally-occurring cations (Lahav and Raziel, 1971) which are found in natural waters as solvated cations, complexes of fulvic acids, and as parts of the structure of microcrystalline clays (Gould, 1968). Little is known of the products of oxidation. Adsorption to clays with subsequent oxidation is very fast. For example, benzidine is oxidized by the iron (III) in montmorillonite clay to an intensely blue-coloured benzidine radical-cation (Tennakoon et al., 1974). Although the environmental fate of such complexes is not known with certainty, by analogy with other relatively easily oxidized semiquinone-like structures, it is assumed that further oxidation would be facile (Callahan et al., 1979). However, this has not been demonstrated.

The pK_a values for benzidine are 4.7 and 3.6. Therefore, dissolved benzidine will be present almost entirely as the free base in most natural waters. Volatilization from water is not expected to be significant for such an involatile chemical with a Henry's Law constant value of 0.2 torr L $mole^{-1}$. The relatively low log K_{ow} value of 1.34 for benzidine suggests only a modest potential for bioaccumulation and for binding to the organic part of sediment and soil.

Benzidine is relatively easily biodegraded in sewage treatment plants. Benzidine at 20 mg/L was readily degraded by activated sewage sludge (Baird et al., 1977). It had some inhibitory effect

on the respiration of activated sludge even while being degraded, which suggested that a metabolite or metabolites may be responsible for the observed toxicity. Tabak and Barth (1978) showed that acclimated extended aeration sludges could completely oxidize continuous doses of 1 mg/L benzidine in less than two weeks (controls indicated that the removal was not simply adsorption). Less complete oxidation occurred at higher dosage levels and intermediate oxidation products began to accumulate in the system. One of the products of chlorination of benzidine in a sewage treatment plant appeared to be a polymer (Ontario Ministry of Environment, 1982). No information was found on the biodegradation of benzidine in natural waters, but it is expected to occur.

The absorption maximum for benzidine in aqueous ethanol is at 287 nm with significant absorption in the ultraviolet region extending to 340 nm (Bilbo and Wyman, 1953), which indicates the possibility of sunlight photolysis (i.e., absorption at $\lambda > 290$ nm). However, there are no studies on the sunlight photolysis of benzidine. Larson and Zepp (1988) have shown that light of wavelength 313 nm directly photolyzed benzidine, with a half-life of < 60 min in the pH range 4.2 - 11.9. In addition, carbonate radicals generated by the photolysis of hydrogen peroxide at 313 nm in aqueous sodium bicarbonate (pH 8.3) or carbonate (pH 11.6) solution can react with benzidine. No products were identified in this study. Lu et al. (1977) found that the photolysis half-life of benzidine in methanol under 254 nm light was about 2 h. Within

0.5 h the colour of the solution changed from clear to red to brown. After 4 h 23% of the benzidine remained, with a number of unidentified degradation products. The formation of unidentified and polar degradation products was proportional to the length of the time of exposure to light.

In soil benzidine is strongly bound and subject to microbial degradation. Lu et al. (1977) found that benzidine was relatively biodegradable (compared to benzo(a)pyrene) in a Drummer soil, with only 21% remaining after 4 weeks. Methylated and acetylated metabolites were among those found. Graveel et al. (1986) studied the decomposition of ^{14}C-labelled benzidine in soil by monitoring $^{14}CO_2$ evolution over a 10 - 12 month period. More benzidine decomposition was observed in non-sterile soils than in sterile soils. After 1 year of incubation, 8-12% of the original benzidine was evolved as CO_2. Almost all the rest was residual activity in the soil, indicating no volatilization. Soil environmental conditions had only a limited effect on the decomposition of benzidine. Modifying soil environmental conditions such as water potential, temperature or addition of metabolizable organic substrates did not markedly affect the short-term rate of benzidine degradation to CO_2 in soils. Sorption experiments indicated that benzidine was strongly retained by all soils studied, and that minimal amounts of sorbed benzidine were desorbed by a neutral salt.

In air benzidine is expected to photooxidize fairly rapidly, with a half-life < 1 d (Howard, 1989).

3,3'-DICHLOROBENZIDINE

Production and Uses

3,3'-Dichlorobenzidine is used primarily as an intermediate in the manufacture of pigments for printing inks, textiles, plastics and crayons. It is also used as a curing agent in polyurethane elastomers, and in the determination of gold (Mark et al., 1978b; Merck, 1989).

3,3'-Dichlorobenzidine is manufactured by a process analogous to that of benzidine by alkaline reduction of o-chloronitrobenzene and rearrangement of the resulting hydrazo compound. 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 whose 1973 United States production was about 5,500 tonnes (Mark et al., 1978b). Industrial emissions to the environment in the U.S.A. in 1988 were estimated to be 6 tonnes (Croy and DeVoto, 1990c). Global production in 1983 was estimated as 8,200 tonnes (Croy and DeVoto, 1990c).

3,3'-Dichlorobenzidine is not manufactured in Canada. In 1980 90 tonnes were imported to produce 450 tonnes of pigments, the most important of which was Pigment Yellow 12. The largest consumers of these pigments were the paints and printing industries (Ontario Ministry of Environment, 1980). In 1989, Canada imported 109

tonnes of 3,3'-dichlorobenzidine, 80 tonnes from Japan and the rest from South Korea (Statistics Canada, 1989). All of it was imported into Ontario. There is no information on releases of this chemical to the Canadian environment. Some physical and chemical properties of 3,3'-dichlorobenzidine are shown in Table 7.

Toxicity, Uptake and Metabolism

There are very few data on the acute toxicity of 3,3'-dichlorobenzidine to aquatic organisms. It appears to be very toxic to one species of fish, 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.

The log K_{ow} value of 3.02 for 3,3'-dichlorobenzidine (cf. Table 7) suggests that, unlike benzidine, there is considerable potential for bioaccumulation. Appleton and Sikka (1980) investigated the bioconcentration, elimination and metabolism of 3,3'-dichlorobenzidine in bluegill sunfish (Lepomis macrochirum Raf.). 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 days 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 a fish (golden ide, Leuciscus idus melanotus) of 610.

Environmental Occurrence

There is very little information on the environmental occurrence of 3,3'-dichlorobenzidine. Staples et al. (1985) reported that it was only detected in 1.0% of 1239 industrial effluent samples and 0.1% of 863 natural water samples in the U.S.A. It was not detected in any of 347 sediment samples or 83 biota samples.

Persistence

In general, photooxidation, adsorption to soil and sediment, and slow microbiological degradation (with very slow mineralization) are expected to be the main pathways of distribution and transformation of 3,3'-dichlorobenzidine in the environment (Callahan et al., 1979; Howard, 1989). It will bioconcentrate in fish and will probably be less biodegradable than benzidine. 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. One of the products, benzidine, is of concern since it is a well-known carcinogen.

The pK_a values for 3,3'-dichlorobenzidine are 4.5 and 3.3. Therefore, dissolved 3,3'-dichlorobenzidine will be present almost entirely as the free base in most natural waters. 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 $mole^{-1}$. As stated above, the log K_{OW} value of 3.02 for 3,3'-dichlorobenzidine suggests considerable potential for bioaccumulation and for binding to the organic part of sediment and soil. By analogy with benzidine discussed above, 3,3'-

dichlorobenzidine may be oxidized by metal ions such as iron (III) in clays.

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 DCB and MCB are 0.43 and 0.70, whereas that for benzidine is 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.

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.

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.

Demirjian et al. (1987) showed that 3,3'-dichlorobenzidine quickly became unextractable in soil after application of 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.

In air 3,3'-dichlorobenzidine is expected to photooxidize fairly rapidly (Howard, 1989).

CONCLUSIONS AND RECOMMENDATIONS FOR RESEARCH

Aniline, benzidine and 3,3'-dichlorobenzidine do not appear to persist in the environment. It is likely that 3,5-dimethylaniline will also be relatively non-persistent. Overall half-lives appear to be less than a few weeks as far as the parent compounds are concerned, although there is some concern whether the fast and apparently irreversible binding to soils and sediments renders them permanently biologically unavailable.

Several major data gaps have been identified:

(1) Basic physical and chemical data are lacking for 3,5-dimethylaniline, let alone studies of its toxicity, uptake, metabolism and abiotic fate.

(2) The kinetics and products of sunlight degradation of benzidine should be characterized. In addition, the question of whether the formation of benzidine-clay complexes leads to further oxidation should be resolved, and products should be identified.

(3) For benzidine and 3,3'-dichlorobenzidine it is important to determine if the observed strong (perhaps covalent) binding to soils and sediments results in their biological unavailability, and is truly a detoxification process. The

proposed incorporation of aromatic amines into heterocyclic rings of soil (cf. aniline discussion) suggests that the residues will be biologically unavailable, but the definitive experiments have not been carried out.

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Table 1. Chemical and Physical Properties of Aniline*

CAS No. 62-53-3
molecular formula C_6H_7N
molecular weight 93.13
clear, colourless, oily liquid, bluish fluorescence
melting point -6.3 °C
boiling point 184-186 °C
density 1.022 at 20°C
refractive index 1.5845
viscosity at 20°C 4.42-4.43 cP
vapour pressure 0.67 mm Hg at 25 °C
solubility in water 3.5×10^4 mg/L
pK_a 4.63 at 20°C
log octanol-water partition coefficient 0.98

*References: Sax (1968); Mark et al. (1978a); Veith et al. (1979); Ontario Ministry of Environment, 1980; CRC Press (1984).

Table 2. Acute toxicity of aniline

Species	Exposure time	LC_{50}, mg/L	Comments	Reference
algae (Selenastrum capricornutum)	96 h	19	EC_{50}	Calamari et al. (1980)
protozoa (Paramecium caudatum)	24 h	10		Yount and Shannon (1987)
ciliate (Tetrahymena pyriformis)	24 h	2000		Schultz et al. (1978)
water flea (Daphnia magna)	24 h	23	IC_{50} immobilization	Calamari et al. (1980)
	48 h	0.25		Holcombe et al. (1987)
midge (Tanytarsus dissimilis)	48 h	> 220		Holcombe et al. (1987)
snail (Aplexa hypnorum)	96 h	> 220		Holcombe et al. (1987)
clawed toad larvae (Xenopus laevis)	96 h	150	teratogenic effects in mid-blastulae stage (96 h EC_{50} 370 mg/L)	Davis et al. (1981)
clawed toad (Xenopus laevis)	48 h	560		Sloof and Baerselman (1980)
axolotl (Ambystoma mexicanum)	48 h	440		Sloof and Baerselman (1980)
rainbow trout (Salmo gairdneri)	96 h	41	320 mg/L $CaCO_3$	Calamari et al. (1980)
	96 h	20	20 mg/L $CaCO_3$	Calamari et al. (1980)
	12 h	46		Abram and Sims (1982)
	24 h	30.5		Abram and Sims (1982)
	48 h	28.3		Abram and Sims (1982)
	96 h	10.6		Abram and Sims (1982)
	168 h	8.2		Abram and Sims (1982)
	96 h	40.5		Holcombe et al (1987)
fathead minnow (Pimephales promelas)	96 h	78		Holcombe et al. (1987)
bluegill (Lepomis macrochirus)	96 h	49		Holcombe et al. (1987)
white sucker (Catostomus commersoni)	96 h	78		Holcombe et al. (1987)
goldfish (Carassius auratus)	96 h	187		Holcombe et al. (1987)

Table 3. Environmental occurrence of aniline*

Medium	Concentration	Comment	Reference
industrial effluent		dye manufacturing plant (USA)	Games and Hites (1977)
- raw wastewater	36 - 480 µg/L		
- final effluent	10 - 96 µg/L		
wastewater	20 µg/L	chemical plant, USA	Jungclaus et al. (1978)
soil	5 mg/kg	near dump for a dye manufacturing plant, USA	Nelson and Hites (1980)
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)
Dutch rivers	≤ 5.8 µg/L		Wegman and De Korte (1981b)
STP influent and effluent	detected	Ontario; consumed in nitrification stage	Ontario Ministry of Environment (1982)
secondary effluents	detected	industrial plants and POTW in Illinois	Ellis et al. (1982)
groundwater	0.4 µg/L	near underground coal gasification site in Wyoming	Stuermer et al. (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)
coal oil reference standard	5 mg/kg	USA	Tomkins and Ho (1982)
groundwater	10 µg/L	close to a landfill in Ontario	Reinhard et al. (1984)
groundwater	705 µg/L	contaminated by coal-tar wastes, Minnesota	Pereira et al. (1983)
Waal River	detected	Netherlands, 1974	Meijers and van der Leer (1976)
shale oil wastewaters	0.5 mg/L	USA	Hawthorne and Sievers (1984)
air	n.d. - 33 µg/m^3	USA	Hawthorne and Sievers (1984)

*Abbreviations: STP, sewage treatment plant; POTW, publicly owned treatment works; SRC, solvent-refined coal.

Table 4. Chemical and Physical Properties of 3,5-Dimethylaniline*

CAS No. 108-69-0
molecular formula $C_8H_{11}N$
molecular weight 121.18
pale to yellow oily liquid
melting point 9.8 °C
boiling point 220 °C
density 0.97
refractive index 1.5581

*Reference: CRC Press (1984).

Table 5. Chemical and Physical Properties of Benzidine*

CAS No. 92-87-5
molecular formula $C_{12}H_{12}N_2$
molecular weight 184.24
white or slightly reddish crystals, powder or leaflets
melting point 127 °C
boiling point 400 °C
density 1.250 at 20 °C
solubility in water 500 mg/L
vapour pressure 5 x 10^{-4} mm Hg at 25°C
$pK_a(1)$ 4.66
$pK_a(2)$ 3.57
log octanol-water partition coefficient 1.34

*References: Bowman et al. (1976); Lu et al. (1977); Mark et al. (1978b); CRC Press (1984); Croy and DeVoto (1990b).

Table 6. Acute toxicity of benzidine*

Species	TL_{50}, mg/L			
	24 h	48 h	72 h	96 h
flagfish (Jordanella floridae)	> 50	32.5	25	16.2
fathead minnow (Pimephales promelas)	> 20	> 20	> 20	> 20
red shiner (Notropia lutrensis)	> 20	10	2.5	2.5
lake trout (Salvelinus namaycush)	8.7	5	4.4	4.4
rainbow trout (Salmo gairdneri)	> 20	14.1	10	7.4
emerald shiner (Notropis atherinoides)	n.t.	n.t.	n.t.	5
bluegill sunfish (Lepomis macrochirus)	n.t.	n.t.	n.t.	15
scud (Gammarus pseudolimnaeus)	> 20	> 20	> 20	> 20

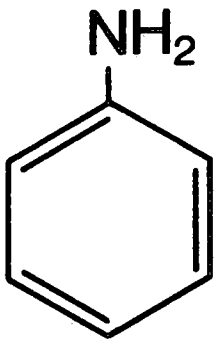
*TL_{50} refers to the threshold lethal value for 50% of the test species; n.t. means not tested. Reference: Croy and DeVoto (1990b).

Table 7. Chemical and Physical Properties of 3,3'-Dichlorobenzidine*

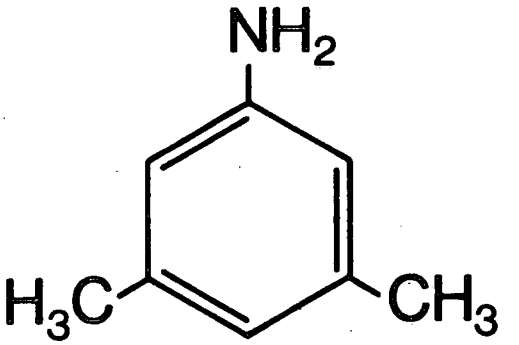
CAS No.	91-94-1
molecular formula	$C_{12}H_{10}N_2Cl_2$
molecular weight	253.13
	grey to purple crystalline solid
melting point	132-133 °C
boiling point	402 °C
vapour pressure	10^{-5} mm Hg at 22 °C
solubility in water	3.1 mg/L
$pK_a(1)$	4.5
$pK_a(2)$	3.3
log octanol-water partition coefficient	3.02

*References: Korenman and Nikolaev (1974): Mark et al. (1978b); CRC Press (1984); Banerjee et al. (1978, 1980); Croy and DeVoto (1990c).

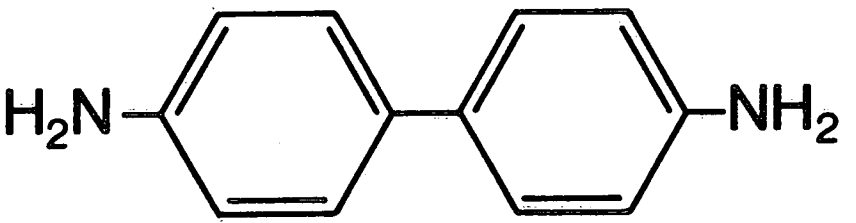
Figure 1. Chemical structures of aniline, 3,5-dimethylaniline, benzidine and 3,3'-dichlorobenzidine.



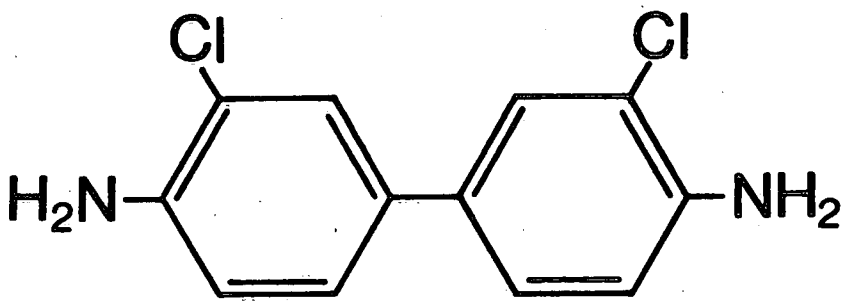
ANILINE



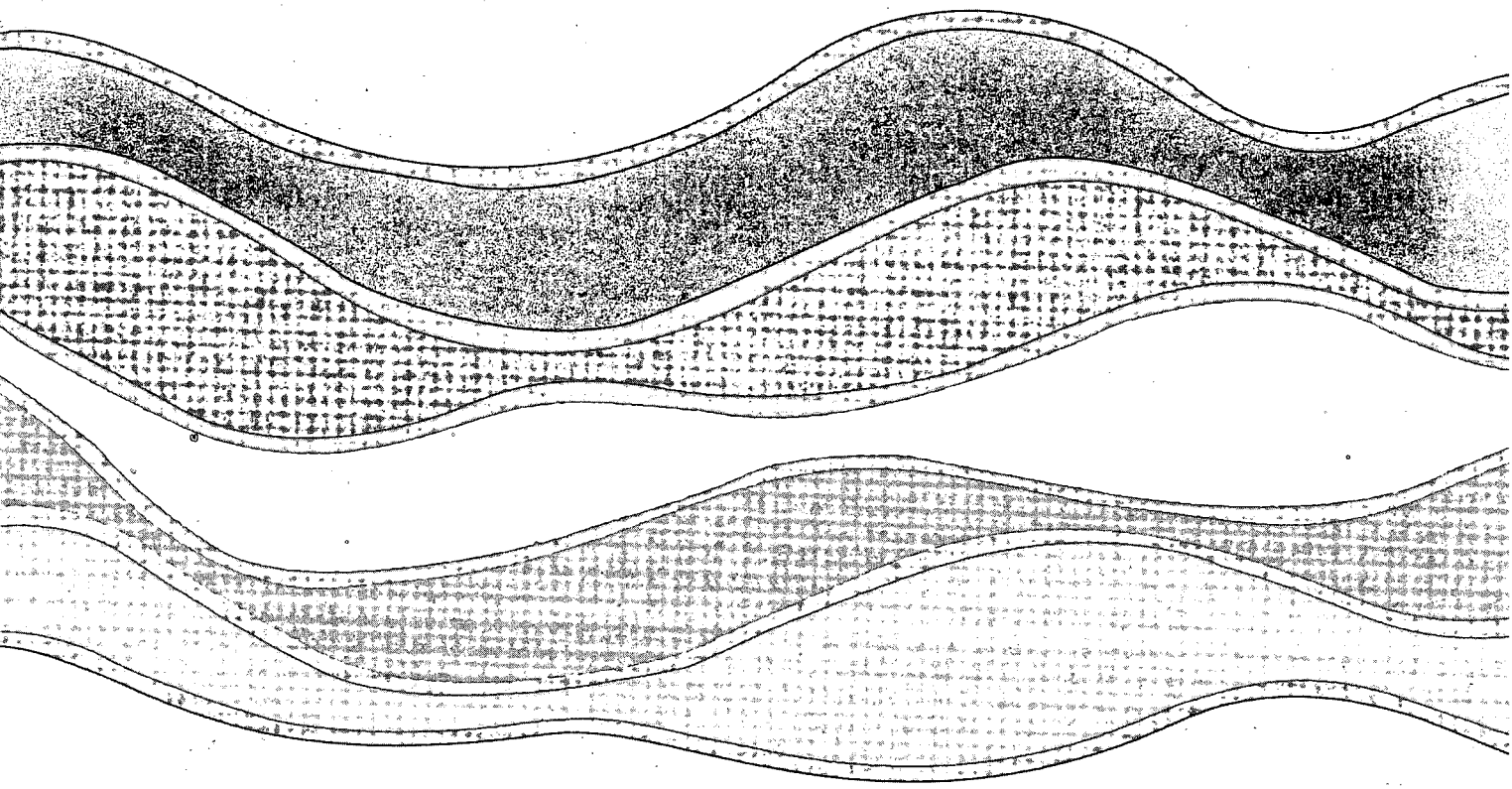
3,5-DIMETHYLANILINE



BENZIDINE



3,3'-DICHLOROBENZIDINE



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