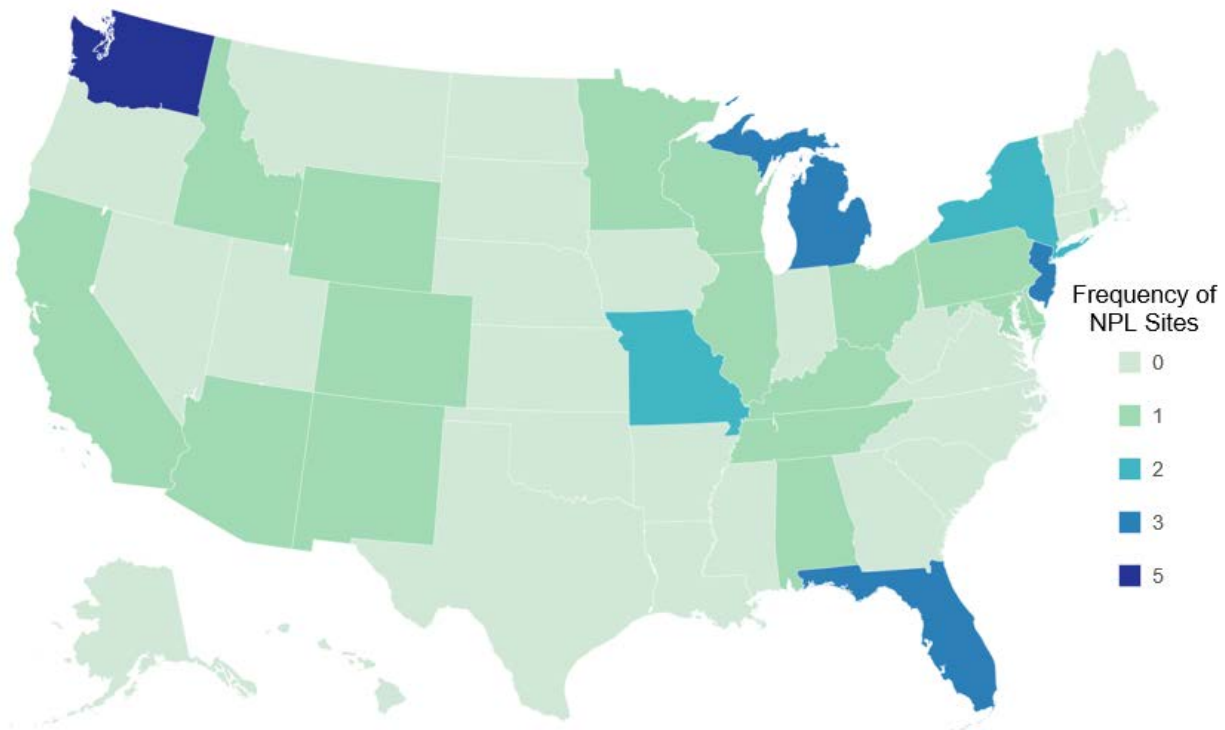


CHAPTER 5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

3,3'-Dichlorobenzidine has been identified in at least 35 of the 1,854 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (ATSDR 2019). However, the number of sites evaluated for 3,3'-dichlorobenzidine is not known. The number of sites in each state is shown in Figure 5-1.

Figure 5-1. Number of NPL Sites with 3,3'-Dichlorobenzidine Contamination



Source: ATSDR 2019

- Exposure to 3,3'-dichlorobenzidine primarily occurs in occupational settings by inhalation and dermal exposure in industries that manufacture or use the chemical.
- Communities near dye manufacturers, or hazardous waste sites, are most likely to be exposed to industrial wastewater effluents containing 3,3'-dichlorobenzidine.
- Human exposure can also occur from use of personal care products containing small amounts of 3,3'-dichlorobenzidine and through ingestion of paint chips containing 3,3'-dichlorobenzidine as a pigment.

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- 3,3'-Dichlorobenzidine is commercially produced for industrial use as a dye or pigment, primarily in ink, textile, rubber, and plastics industries. It enters the environment through industrial wastewater. It is not naturally occurring.
- The manufacturing of 3,3'-dichlorobenzidine has markedly decreased since 1986 in the United States, but large quantities are still imported into the United States and occupational exposure remains the major source of exposure.
- In the environment, 3,3'-dichlorobenzidine is primarily found in soils and sediments since it binds to sediments and has low mobility.
- Photodegradation is an important fate process in air, water, soil, and sediment, has been observed in controlled laboratory settings, and is expected to occur in the environment under natural sunlight.

5.2 PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.2.1 Production

3,3'-Dichlorobenzidine is a chlorinated primary aromatic amine (NTP 2016; WHO 1998). The primary anthropogenic source of 3,3'-dichlorobenzidine is pigments and dyes. 3,3'-Dichlorobenzidine is no longer used to manufacture dyes in the United States (CPMA 1998). 3,3'-Dichlorobenzidine is commercially produced by reduction of o-nitrochlorobenzene with zinc dust and sodium hydroxide solution, and the resulting hydrazobenzene derivative is rearranged with dilute hydrochloric acid or sulfuric acid to form 3,3'-dichlorobenzidine (DCMA 1989; Schwenecke and Mayer 2000). Commercial supplies are usually provided in the form of the dihydrochloride salt because of its greater stability.

In 1986, there were approximately 10 suppliers of the chemical listed in the United States (NTP 1991). 3,3'-Dichlorobenzidine was produced by 1 manufacturer in Europe in 2009; the hydrochloride was produced by 10 manufacturers (1 in Europe, 1 in China, 2 in East Asia, and 6 in India). There were 14 suppliers of 3,3'-dichlorobenzidine worldwide, including 8 in the United States (NTP 2016). The 2016 CDR reported the national aggregate production volume of the 3,3'-dichlorobenzidine dihydrochloride salt to be between 1,000,000 and 10,000,000 pounds in 2012, 2013, 2014, and 2015 (CDR 2016).

No information regarding facilities that produce, process or use 3,3'-dichlorobenzidine was reported to the EPA's Toxic Release Inventory (TRI) Program (TRI20 2021).

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5.2.2 Import/Export

According to the 2016 CDR, Flint Group in Plymouth, Michigan; Sumitomo Corporation of Americas in New York, New York; and Sun Chemical in Parsippany, New Jersey manufacture or import 3,3'-dichlorobenzidine dihydrochloride (CDR 2016). Activity at Sun Chemical is confidential, but Flint Group and Sumitomo report that the dihydrochloride is imported, although production volume for all three sites is withheld (CDR 2016). Imports of the dihydrochloride amounted to 5,773,111 pounds (2,618,639 kg) in 2018, and came from India and China (USITC 2021).

5.2.3 Use

3,3'-Dichlorobenzidine had been primarily used in the production of yellow, and some red and orange, pigments for the textile, paint, printing inks, paper, rubber, plastic, and pharmaceutical industries (EPA 2010; NLM 2019). Currently, use of 3,3'-dichlorobenzidine in the production of dyes has stopped, as dye production in the United States has largely ceased and has shifted abroad (Dapson 2009). 3,3'-Dichlorobenzidine has also been used as a curing agent for isocyanate-containing polymers and solid urethane plastics, and as a compounding ingredient for rubber and plastics (NLM 2019). The chemical can also be used to produce polybenzimidazole (Maner et al. 2009) or as a color test for the detection of gold (NLM 2019). 3,3'-Dichlorobenzidine has been detected in the wastewater of metal finishing operation facilities and oilfield operations (see Section 5.5), suggesting that it is used in these industries, but no specific information on its use is available. Additionally, the chemical is likely used in steam electric power generation based on its EPA regulatory limitation (EPA 2018a).

5.2.4 Disposal

Facilities that generate 3,3'-dichlorobenzidine-containing wastes, and owners and operators of hazardous waste treatment, storage, and disposal facilities, must also comply with regulations promulgated under the authority of the Resource Conservation and Recovery Act (RCRA) (EPA 2011, 2015).

Disposal of wastes containing 3,3'-dichlorobenzidine is controlled by a number of federal regulations (see Chapter 7). The standard treatment technologies specified for treating 3,3'-dichlorobenzidine-containing wastewaters prior to land disposal are wet air oxidization, chemical or electrolytic oxidation, carbon absorption, and incineration; for non-wastewater treatment, only incineration (EPA 2003).

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A 1986 health hazard evaluation report was conducted by the National Institute for Occupational Safety and Health (NIOSH) on a company that purchased 3,3'-dichlorobenzidine as the dihydrochloride salt in sealed fiber in drums. The report stated the company rinsed the empty drums with water, added the rinse water to the product stream, then sprayed the drums with a sodium hypochlorite bleach solution (converting the 3,3'-dichlorobenzidine to a less toxic quinone-type compound), and placed them in polyethylene bags for disposal (NIOSH 1986b).

5.3 RELEASES TO THE ENVIRONMENT

The Toxics Release Inventory (TRI) data should be used with caution because only certain types of facilities are required to report (EPA 2005). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the TRI only if they employ ≥ 10 full-time employees; if their facility is included in Standard Industrial Classification (SIC) Codes 10 (except 1011, 1081, and 1094), 12 (except 1241), 20–39, 4911 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4931 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4939 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4953 (limited to facilities regulated under RCRA Subtitle C, 42 U.S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited to facilities primarily engaged in solvents recovery services on a contract or fee basis); and if their facility produces, imports, or processes $\geq 25,000$ pounds of any TRI chemical or otherwise uses $> 10,000$ pounds of a TRI chemical in a calendar year (EPA 2005).

5.3.1 Air

No information regarding releases of 3,3'-dichlorobenzidine was reported to the U.S. EPA's TRI Program (TRI20 2021).

5.3.2 Water

There is no information on releases of 3,3'-dichlorobenzidine to water from manufacturing and processing facilities because these releases are not required to be reported (EPA 2005).

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The free base form of 3,3'-dichlorobenzidine is only slightly soluble in water, and will rapidly adsorb and bind to sediment and particulate matter (NTP 2016). It may also undergo photolysis in water exposed to sunlight. The solubility of 3,3'-dichlorobenzidine-2HCl in water is 4 mg/L at a pH of 6.9 (Banerjee et al. 1978). 3,3'-Dichlorobenzidine is primarily released into municipal sanitary sewer systems in wastewater generated by the production of dyes and pigments, including from tanneries (Cao et al. 2007; Lee et al. 2004). The EPA measured maximum 3,3'-dichlorobenzidine concentrations in wastewater of 0.07 ppb in metal finishing operations, 2 ppb in nonferrous metals manufacturing, 3 ppb in coal mining, and up to 10 ppb in paint and ink formulation operations (EPA 1980b).

The Massachusetts Water Resource Authority (MWRA) measured average influent concentrations of 3,3'-dichlorobenzidine of 2.13–2.25 µg/L, and average effluent concentrations of 2.18–2.28 µg/L, in two wastewater treatment plants (MWRA 2015).

5.3.3 Soil

There is no information on releases of 3,3'-dichlorobenzidine to soil from manufacturing and processing facilities because these releases are not required to be reported (EPA 2005).

3,3'-Dichlorobenzidine binds to soil, and volatilization from most soil surfaces is not expected (NLM 2019). Industrial wastewater entering aqueous environments contributes to the presence of 3,3'-dichlorobenzidine in soils, as it has been detected in surface water sediments (Nyman et al. 2004). No quantitative data could be located measuring environmental releases or off-sites transfers of 3,3'-dichlorobenzidine to soil or sediment.

5.4 ENVIRONMENTAL FATE

5.4.1 Transport and Partitioning

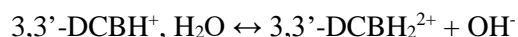
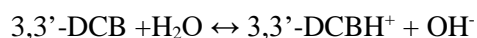
Air. 3,3'-Dichlorobenzidine is not a volatile chemical and has a low vapor pressure and Henry's law constant (see Table 4-2), suggesting that the atmosphere is not important in its environmental transport and partitioning (EPA 2015). Any 3,3'-dichlorobenzidine released to the air will adsorb to airborne dust particles or bind to particulate matter (NTP 2016). Suspended 3,3'-dichlorobenzidine is subject to atmospheric convection, dispersion, gravitational settling, and wash-out by rain. Particulate-phase 3,3'-dichlorobenzidine may be removed by wet and dry deposition (NLM 2019).

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Water. 3,3'-Dichlorobenzidine has low solubility in water, does not volatilize or hydrolyze, and may slowly oxidize in solution (Banerjee et al. 1978; EPA 1979, 1982). The Henry's law constant for a compound helps estimate the partitioning of the compound between its vapor phase and aqueous media. The estimated Henry's law constant for 3,3'-dichlorobenzidine of $2.8 \times 10^{-11} \text{ atm}\cdot\text{m}^3/\text{mole}$ suggests that 3,3'-dichlorobenzidine remains dissolved in water and does not volatilize from water to air (NLM 2019).

Use of Fenton's reagent ($\text{Fe(II)} + \text{H}_2\text{O}_2$) for treatment of wastes contaminated with various carcinogenic aromatic amines was investigated by Casero et al. (1997). Under laboratory conditions, 3,3'-dichlorobenzidine was converted to ring-cleavage products, with 99.9% efficiency after 1 hour of treatment at room temperature, demonstrating that this technology is potentially useful as a wastewater treatment technique (Casero et al. 1997).

Sediment and Soil. 3,3'-Dichlorobenzidine is moderately hydrophobic, and will bind to soil and sediments (Nyman et al. 1997). The chemical can exist as a weak base in water and exists in both neutral and cationic forms. Written as an acid-base reaction, the amine groups may be protonated as follows:



Values of pK_a reported for 3,3'-dichlorobenzidine vary. EPA (1978b) reported a pK_a of <4 , and Nyman et al. (1997) reported $\text{pK}_{a,1}$ and $\text{pK}_{a,2}$ values of 1.6 and 3.2, respectively. This indicates that the dominant state of 3,3'-dichlorobenzidine in water would be the non-ionic form. As pH increases, the proportion of cationic forms of 3,3'-dichlorobenzidine decreases. The extent of adsorption to sediments via Coulombic interactions will thus decrease, and adsorption should become dominated by hydrophobic interactions as pH increases. This expectation was demonstrated by EPA (1978b), who found that the adsorption constant (K_f) decreased with increasing pH; the decrease was more rapid in the range of pH 7–9. Boyd et al. (1984) concluded that non-protonated 3,3'-dichlorobenzidine is subject to hydrophobic bonding to some extent. However, no correlation has been found between K_f and the organic carbon content of sediment and soil (Boyd et al. 1984; EPA 1978b; Graveel et al. 1986).

Aromatic amines are also expected to bind to soils through irreversible covalent bonding, especially to soils containing large organic carbon content (Donaldson and Nyman 2005). 3,3'-Dichlorobenzidine covalently bonds with soil humic and fulvic components (Boyd et al. 1984; EPA 1978b; NLM 2019), and

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these bonds are often irreversible and immobile. Studies show that the extent of 3,3'-dichlorobenzidine desorption decreases with age of the sample, and that the adsorbed 3,3'-dichlorobenzidine is resistant to extraction. After 24 hours of 3,3'-dichlorobenzidine-sediment contact, only 36% of the parent compound could be extracted by methanol (Boyd et al. 1984; EPA 1978b). A result of this complex behavior is that adsorption constants (K_f) for 3,3'-dichlorobenzidine cannot be accurately predicted for a given soil based on a K_{oc} value alone.

K_{oc} values measured for 3,3'-dichlorobenzidine range from 721 to 47,000. The EPA's TRI Program reported a K_{oc} value of 47,000 (EPA 2014); K_{oc} values ranging from 721 to 3,965 were measured in sediment samples from Lake Macatawa in Michigan (Donaldson and Nyman 2005); EPA (1982) reported a K_{oc} value of 1,553. These relatively high values imply that 3,3'-dichlorobenzidine would exhibit low to no mobility in soil (see Roy and Griffin 1985). 3,3'-Dichlorobenzidine was highly immobile in soil column experiments (Chung and Boyd 1987). Water was passed through sandy soil (Entic Haplorthod) and 3,3'-dichlorobenzidine-contaminated sewage sludge samples. Only small amounts of radioactive 3,3'-dichlorobenzidine added to columns of sandy soil or sewage sludge were eluted with water over extended time periods. Extractable radioactivity from these soils and sludge samples decreased with time of chemical contact. There was greater adsorption of 3,3'-dichlorobenzidine to soil than to sludge as a result of the greater humus content of the soil samples, suggesting that the compound may favor migration from sludge to soil substrates (Chung and Boyd 1987).

3,3'-Dichlorobenzidine bound to sediment can be transported over relatively long distances, attributed to its hydrophobicity (Harden et al. 2005). An 11-year field study measured higher levels of 3,3'-dichlorobenzidine 6 km from its known source in Lake Macatawa, Michigan, than in the sediment immediately adjacent to that source. This transport likely occurred due to sediment resuspension events in the lake (Harden et al. 2005).

The Henry's law constant of 3,3'-dichlorobenzidine indicates that it is not expected to volatilize from moist soil surfaces. Volatilization from dry soil surfaces is also not expected due to the chemical's low vapor pressure (EPA 2015). Boyd et al. (1984) found no loss of 3,3'-dichlorobenzidine from soil due to volatilization during 32- and 52-week studies under aerobic and anaerobic conditions, respectively.

Other Media. Since 3,3'-dichlorobenzidine is moderately hydrophobic (see Table 4-2), it may be concentrated from aqueous media by aquatic organisms, and some bioaccumulation in aquatic organisms may occur (Law 1995). Bluegill sunfish were exposed to radiolabeled 3,3'-dichlorobenzidine in dynamic-

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flow experiments for 130–168 hours, and transferred to clean water free of the chemical (Appleton and Sikka 1980). The chemical and its metabolites showed some accumulation. They were not completely eliminated upon transfer, as residues remained after 14 days. Appleton and Sikka (1980) calculated moderately low bioconcentration factors (BCFs) of 495–507 for whole fish. The edible and non-edible portions of the fish had BCFs of 114–175 and 814–856, respectively. BCFs for golden ide fish of 610 and for green algae of 940 have been reported (Freitag et al. 1985). A BCF range of 43–213 was calculated for carp exposed to 3,3'-dichlorobenzidine over an 8-week period (NLM 2019). These BCF data suggest that the potential for bioconcentration in aquatic organisms is low to moderate.

Bioaccumulation by terrestrial animals has not been studied. Assuming a log K_{ow} range of 3.02–3.78 (DCMA 1989; EPA 1982), 3,3'-dichlorobenzidine is not likely to bioaccumulate in plants or terrestrial animals appreciably.

A BCF was estimated for 3,3'-dichlorobenzidine in fruits (oranges) of 1.77 L kg⁻¹ (Paraiba et al. 2006). The study applied Fruit Tree Model (FTM) to a hypothetical culture of orange orchards, and the BCF estimated by the model was considered applicable to other fruits. The study examined fruit from orange orchards cultivated in soils treated with sludge originating from sewage treatment plants (Paraiba et al. 2006).

5.4.2 Transformation and Degradation

Air. 3,3'-Dichlorobenzidine in sunlight in ambient air may react with photochemically-produced hydroxyl radicals and ozone with an estimated half-life of 10 hours (NLM 2019). This was calculated from an EPA-estimated hydroxyl radical reaction rate constant of 4×10^{-11} cm³/molecule-second at 25°C (EPA 2015). No other information on the fate of 3,3'-dichlorobenzidine in the atmosphere was located.

Water. 3,3'-Dichlorobenzidine was found to be extremely photolabile in water and is expected to be susceptible to photolysis in sunlit surface water, an important fate process (Banerjee et al. 1978; EPA 1978b). When exposed to laser radiation at wavelengths ranging from 300 to 360 nm in aqueous solutions, 3,3'-dichlorobenzidine photodechlorinated (Nyman et al. 2002). Chlorobenzidine was observed as an unstable intermediate, yielding benzidine as a stable photoproduct. Photochemical half-lives were calculated and ranged from 279 to 3,013 seconds for 3,3'-dichlorobenzidine (Nyman et al. 2002). When exposed to artificial light, 3,3'-dichlorobenzidine photolyzed yielding monochlorobenzidine, benzidine,

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and a number of colored, water-insoluble products. In natural sunlight, the half-life of 3,3'-dichlorobenzidine in water was determined to be approximately 90 seconds. While 3,3'-dichlorobenzidine is very rapidly photolyzed under environmental conditions, the process may yield benzidine (Banerjee et al. 1978).

Biodegradation of 3,3'-dichlorobenzidine is slow in water. When incubated in natural water from eutrophic and mesotrophic lakes, 25% of the chemical biodegraded within a month (Boyd et al. 1984).

The composition of the biological community was not described. Minor decreases in 3,3'-dichlorobenzidine concentrations were attributed to adsorption onto suspended sediment. Half-lives of 4–26 weeks and 16–101 weeks have been estimated for 3,3'-dichlorobenzidine biodegradation in surface water and anaerobic groundwater, respectively (Howard et al. 1991).

There are no data to suggest that the hydrolysis of 3,3'-dichlorobenzidine is significant (EPA 1979). In one study, no hydrolysis of 3,3'-dichlorobenzidine was observed after 5 days at elevated temperature (50°C) (NLM 2019). A half-life of 100 days was estimated based on surrogate substances (NLM 2019).

Several studies (Mizuno et al. 2007; Ohe et al. 2008) reported 3,3'-dichlorobenzidine contamination of the Waka River in Japan. Mizuno et al. (2007) detected high levels of 3,3'-dichlorobenzidine and 4-amino 3,3'-dichloro-5,4-dinitrobiphenyl (ADDDB), a mutagenic compound and endocrine disruptor, from samples collected at chemical plants' wastewater discharge into the river. ADDDB is formed by oxidation and nitration from 3,3'-dichlorobenzidine during the process of wastewater treatment of drainage. Mutagenicity of water samples was evaluated in the *Salmonella* assay using the O-acetyltransferase-overexpressing strain YG1024. Water samples from the discharge site showed stronger mutagenicity than water samples collected from upstream and downstream sites. Similarly, Ohe et al. (2008) identified two mutagenic fractions (YG1024 strain) in the water adsorbate, 3,3'-dichlorobenzidine, and a novel chemical, a 5-nitro derivative of 3,3'-dichlorobenzidine (4,4'-diamino-3,3'-dichloro-5-nitrobiphenyl), thought to be formed from 3,3'-dichlorobenzidine during the wastewater treatment process.

Sediment and Soil. Sediment/water mixtures spiked with 3,3'-dichlorobenzidine display evidence of the chemical's degradation (Nyman et al. 1997). Silty-clay to sandy sediments collected from a lake near Holland, Michigan, were spiked with 3,3'-dichlorobenzidine and incubated at 20°C for 12 months under anaerobic conditions. Time-course analysis of this mixture showed that dehalogenation of 3,3'-dichloro-

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benzidine to produce benzidine appears to take place through a transient intermediate, 3-monochlorobenzidine. Up to 80% of the 3,3'-dichlorobenzidine was transformed to benzidine over a 1-year incubation period. No metabolites were observed in autoclaved samples, suggesting that dehalogenation is mediated by microbial activity. The final product, benzidine, shows more affinity for the solution (aqueous) phase and thus has a greater potential for transport in the environment. A half-life of approximately 150 days was estimated for 3,3'-dichlorobenzidine in lake water and sediment mixes (Nyman et al. 1997).

The Japanese MITI test classified 3,3'-dichlorobenzidine as not readily biodegradable (NLM 2019). The chemical (at a concentration of 100 mg/L) was found to achieve 1% of its theoretical biological oxygen demand (BOD) in 4 weeks (NLM 2019). A summary of seven laboratory tests conducting aerobic biodegradation experiments with 3,3'-dichlorobenzidine concluded that while results showed its “inherent biodegradability,” the compound should not be classified as readily biodegradable (Brown and Laboureur 1983). There was a clear dependence of the extent of degradation on the concentration of yeast extract added to the batch containers. The role of the extract was uncertain, but without it, no degradation was detected. The study authors hypothesized that the yeast may be a food source to allow buildup of large concentrations of active bacteria that are able to break down the amines. Possible degradation mechanisms and degradation byproducts were not discussed (Brown and Laboureur 1983).

Laboratory experiments designed to probe biodegradation and photodegradation pathways showed that 3,3'-dichlorobenzidine undergoes sequential dehalogenation to yield 3-chlorobenzidine and then benzidine under exposure to microorganisms and under simulated tropospheric solar radiation (Nyman et al. 1999). Dechlorination is expected to yield higher total concentrations of aromatic amines in the solution (Nyman et al. 1999).

3,3'-Dichlorobenzidine degraded very little when incubated with soil. In a study by Boyd et al. (1984), a Brookston clay loam soil (a typical Argiaquoll fine loamy, mixed mesic) containing [^{14}C]-3,3'-dichlorobenzidine at concentrations of 40 and 4 mg/kg of dry soil was incubated aerobically and anaerobically in batch experiments (Boyd et al. 1984). Under aerobic conditions, 3,3'-dichlorobenzidine degradation occurred at a very slow rate; cumulative $^{14}\text{CO}_2$ production was approximately 2% after 32 weeks. Under anaerobic conditions, no gas evolution was detected after 1 year of incubation. The authors did not comment on the population or type of microorganisms in the soil sample (Boyd et al. 1984). Additional studies indicated that 3,3'-dichlorobenzidine was very persistent in soil and sludge-amended soil (Chung and Boyd 1987). Biodegradation of [^{14}C]-3,3'-dichlorobenzidine was evaluated over a 182-day

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incubation period in a sandy soil (Entic Haplorthod) amended with sewage sludge. The total amount of [^{14}C]-3,3'-dichlorobenzidine recovered as $^{14}\text{CO}_2$ was <2%. It should be noted that biodegradation when measured by $^{14}\text{CO}_2$ evolution may provide a conservative estimate of the extent of decomposition. This technique does not account for carbon that is incorporated into the biomass or into soil organic matter, or for the compound being only partially metabolized (Graveel et al. 1986). The disparity between the results of this work and the results of Nyman et al. (1997) was likely related to the nature of their respective biotic communities.

As previously discussed, in aqueous solutions 3,3'-dichlorobenzidine rapidly undergoes photolysis and strong absorption of light at relatively high wavelengths. This suggests that 3,3'-dichlorobenzidine may be susceptible to direct photolysis on soil surfaces exposed to natural sunlight (NLM 2019). Benzidine, as a product of 3,3'-dichlorobenzidine photolysis, has been found in sediment testing for 3,3'-dichlorobenzidine (Harden et al. 2005). The study found that environmental transformation to benzidine in the natural environment is of possible concern. No further information was located on this suggested transformation.

5.5 LEVELS IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to 3,3'-dichlorobenzidine depends, in part, on the reliability of supporting analytical data from environmental samples and biological specimens.

Concentrations of 3,3'-dichlorobenzidine in unpolluted atmospheres and in pristine surface waters are often so low as to be near the limits of current analytical methods. In reviewing data on 3,3'-dichlorobenzidine levels monitored or estimated in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable.

Table 5-1 shows the limit of detections typically achieved by analytical analysis of environmental media. 3,3'-Dichlorobenzidine has been detected in varying environmental media and products. An overview summary of the range of concentrations detected in environmental media is presented in Table 5-2.

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Table 5-1. Lowest Limit of Detection for 3,3'-Dichlorobenzidine Based on Standards

Media	Detection limit	Reference
Air	0.05 µg/sample	NIOSH 2020
Wastewater	0.01 µg/L	Lee et al. 2004
Surface water	0.05 µg/L	Vera-Avila et al. 2001
Drinking water	0.2 µg/L	Onuska et al. 2000
Sediment	15 µg/L	Armentrout and Cutie 1980; Harden et al. 2005
Fish tissue	<20 µg/L	Diachenko 1979
Human hemoglobin adducts	<0.1 ng/g	Joppich-Kuhn et al. 1997
Rat hemoglobin adducts	0.01 µg/L	Lee et al. 2003
Urine (dichlorobenzidine, mono- and di-acetyldichlorobenzidine)	525 to 600 µg/L	Bowman and Nony 1981; Nony and Bowman 1980; Nony et al. 1980
Urine	1.6 µg/L	Guerbet et al. 2007
Leather	<1 mg/kg	Sparr Eskilsson et al. 2002
Commercial dyestuff	0.9 µg/g	Wu and Huang 1998

^aDetection limits based on using appropriate preparation and analytics. These limits may not be possible in all situations.

Table 5-2. Summary of Environmental Levels of 3,3'-Dichlorobenzidine in the United States

Media	Low	High	For more information
Sediment (ppm)	Not detected	69.663	Section 5.5.3
Indoor air (ppbv)	Not detected	ND	Section 5.5.1
Surface water (ppm)	Not detected	26.8	Section 5.5.2
Groundwater (ppm)	<10	0.90	Section 5.5.2
Pore water (ppm)	6.53	8.71	Section 5.5.2
Soil	Not detected	Not detected	Section 5.5.3

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Table 5-3 shows the levels of 3,3'-dichlorobenzidine in environmental media at NPL sites.

Table 5-3. 3,3'-Dichlorobenzidine Levels in Water, Soil, and Air of National Priorities List (NPL) Sites

Medium	Median ^a	Geometric mean ^a	Geometric standard deviation ^a	Number of quantitative measures	NPL sites
Water (ppb)	8.00	22.4	9.03	3	2
Soil (ppb)	5,080	7,070	8.77	10	7
Air (ppbv)	NA	NA	NA	NA	NA

^aConcentrations found in ATSDR site documents from 1981 to 2019 for 1,854 NPL sites (ATSDR 2019). Maximum concentrations were abstracted for types of environmental media for which exposure is likely. Pathways do not necessarily involve exposure or levels of concern.

5.5.1 Air

3,3'-Dichlorobenzidine was not detected in ambient air of two dyestuff production plants at detection limits of 5 (Narang et al. 1982) and 0.1 ng/m³ (Riggin et al. 1983). Data on occupational exposure levels indicate the presence of levels ≤ 0.6 –2.5 $\mu\text{g}/\text{m}^3$ in 3,3'-dichlorobenzidine production and pigment manufacturing plants in Germany (DCMA 1989).

The concentration of 3,3'-dichlorobenzidine in the Canadian environment was estimated by Liteplo and Meek (1994) by applying the Level III Fugacity Computer Model of Mackay and Paterson (Mackay and Paterson 1991). The model assumed that 1% of the total amount produced in and imported to Canada was released into various media in proportions similar to those given in the U.S. TRI. The average concentration of 3,3'-dichlorobenzidine in air, as estimated by the model, was 7.6×10^{-16} $\mu\text{g}/\text{m}^3$ (Liteplo and Meek 1994).

5.5.2 Water

EPA's computerized water quality database (STORET) was used to determine the median concentration of 3,3'-dichlorobenzidine in surface water, groundwater, and municipal and industrial inflow and outflow (Staples et al. 1985). The median concentration of 3,3'-dichlorobenzidine detected in 12 of 1,239 samples of waste effluent, collected from about 1980 to 1984, was reported to be <10 $\mu\text{g}/\text{L}$. The median concentration of 3,3'-dichlorobenzidine in both surface water and groundwater was also reported to be

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<10 µg/L. The U.S. Geologic Survey measured 3,3'-dichlorobenzidine concentrations of 0.65–0.90 µg/L groundwater from wells of an oilfield service site in Oklahoma from 2005 to 2006 (USGS 2007).

EPA indicated that 3,3'-dichlorobenzidine concentrations in wastewater from metal finishing operations were ≤0.07 µg/L (EPA 1980b). Discharge concentrations from other industrial sources were ≤10 µg/L. Using a Fugacity Computer Model, Liteplo and Meek estimated the concentration of 3,3'-dichlorobenzidine in Canadian water to be 3.4×10^{-7} ng/L (Liteplo and Meek 1994). Because the model did not address the possibility of bound residue in sediment, the concentration in water is likely overestimated.

Onuska et al. (2000) extracted 3,3'-dichlorobenzidine from industrial effluent samples close to an industrial pigment site in Toronto, Canada. Water concentrations near the Toronto pigment site ranged from 2.60 to 654 µg/L. Lee et al. (2004) followed up testing at this site, and measured concentrations as low as 1.6 µg/L in 2001. This significant decrease from the 1996 concentrations measured by Onuska et al. (2000) (>600 µg/L) was attributed to stringent pollution control programs adopted by the company (Lee et al. 2004). Wastewater effluent from four metal plating companies showed that two companies had non-detectable amounts of 3,3'-dichlorobenzidine, and two companies had detectable trace levels of 3,3'-dichlorobenzidine of 0.013 and 0.032 µg/L (Lee et al. 2004). Non-detectable amounts of 3,3'-dichlorobenzidine were detected from the other two companies.

Harden et al. (2005) detected up to 26.8 µg/L of 3,3'-dichlorobenzidine in lake water and 6.53–8.71 µg/L in sediment pore water. 3,3'-Dichlorobenzidine concentrations tended to be higher in the pore water of silty clay sediments.

Capillary gas chromatography/mass spectrometry (GC/MS) was used to identify, but not quantify, 3,3'-dichlorobenzidine in the dissolved phase (that is, smaller particles and dispersed colloids not retained by the filter) of water concentrates from the Besos River in Spain (Grifoll et al. 1992). Valls et al. (1990) identified 3,3'-dichlorobenzidine in urban wastewater in the same region.

5.5.3 Sediment and Soil

The estimated median concentration of 3,3'-dichlorobenzidine in sediments in the United States has been reported to be <1 µg/kg on a dry sediment basis (Staples et al. 1985). Of the 347 sediment or soil measurements recorded in the STORET database, none of the samples contained detectable concentrations of 3,3'-dichlorobenzidine.

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Harden et al. (2005) measured concentrations of 3,3'-dichlorobenzidine from nondetectable up to 69.663 mg/kg-sediment near Lake Macatawa from 1993 to 2003. The highest level was found 6 km away from the single known source of 3,3'-dichlorobenzidine in the area (Harden et al. 2005). This finding was supported by the oscillatory pattern of 3,3'-dichlorobenzidine distribution within Lake Macatawa where sampling sites of nondetectable 3,3'-dichlorobenzidine concentrations were adjacent to sites of high concentrations. The pattern was explained by sediment resuspension and transport mostly due to wind-driven resonant motions (Nyman et al. 2003). 3,3'-Dichlorobenzidine levels of 0.01–0.04 mg/kg were detected in Canadian agricultural soils (NLM 2019).

5.5.4 Other Media

The estimated median concentration of 3,3'-dichlorobenzidine in biota in the United States has been reported to be <2.5 mg/kg wet (Staples et al. 1985). Of the 83 biota measurements recorded in the STORET database, none of the samples contained detectable concentrations of 3,3'-dichlorobenzidine.

There is a potential for 3,3'-dichlorobenzidine to occur in wastewater sludges and industrial solid wastes. A 3,3'-dichlorobenzidine concentration of 16 ppm in municipal sludge from Michigan has been reported (Chung and Boyd 1987). 3,3'-Dichlorobenzidine was detected at concentrations of 3.13 mg/kg dry sewage sludge in two of a total of 253 sewage treatment plants examined (Fricke et al. 1985). These plants were all in the United States (Arizona, Indiana, Michigan, Missouri, New Mexico, New York, and Texas). Concentrations up to 535 µg/L were detected in a communal sewage treatment plant (Lopez-Avila et al. 1981). The chemical was detected at 8.55 mg/kg in sewage sludge of an aeration basin in Muskegon, Michigan (Demirjian et al. 1984).

BCFs for 3,3'-dichlorobenzidine were measured for orange orchards cultivated in soils treated with sludge originating from sewage treatment plants (Paraiba et al. 2006). The study did not provide the concentration of 3,3'-dichlorobenzidine found in soil or orange orchards, but suggests that 3,3'-dichlorobenzidine can occur in produce grown in contaminated soils (Paraiba et al. 2006).

[¹⁴C]-3,3'-Dichlorobenzidine was found to rapidly accumulate in bluegill sunfish as a result of their exposure to water in which either 5 or 100 µg/L of the chemical was intentionally added. Residues were

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distributed in both the edible and nonedible portions (Appleton and Sikka 1980). However, 3,3'-dichlorobenzidine was not detected in fish samples obtained from rivers near nine textile dyestuff manufacturers known to use 3,3'-dichlorobenzidine-based pigments (Diachenko 1979).

In cosmetic products, 3,3'-dichlorobenzidine has been detected in concentrations as low as 0.14 mg/kg in skin oils, and as high as 2.05 mg/kg in hair gels (Hailong et al. 2014). Cosmetic samples were taken from commercial products in China, and 3,3'-dichlorobenzidine was also detected in trace amounts in hair dye, talcum powder, facial skin care mask, and facial cream. The study did not comment on possible dermal absorption to humans but suggests that 3,3'-dichlorobenzidine and other aromatic amines can be found in trace amounts in consumer cosmetic products (Hailong et al. 2014).

5.6 GENERAL POPULATION EXPOSURE

The greatest chance of exposure to 3,3'-dichlorobenzidine by the general public is from its persistence in the environment attributed to improper land disposal of compounds. The importance of this exposure source can only be evaluated on a site-by-site basis, but the potential for nonindustrial exposure via air, soil, or water is expected to be negligible. 3,3'-Dichlorobenzidine is no longer used to manufacture soluble dyes in the United States (CPMA 1998). Previously benzidine and its congeners such as 3,3'-dichlorobenzidine were likely to only be found in the vicinity of pigment plants (EPA 1978a, 1980a, 1980b) where wastes may escape or be discharged. 3,3'-Dichlorobenzidine was also found in locations where it was used to formulate other products such as rubber and plastic (NLM 2019).

In the past, the general public may have been exposed to minute amounts of 3,3'-dichlorobenzidine during the use of pressurized spray containers of paints, lacquers, and enamels containing traces of benzidine yellow, a pigment derived from 3,3'-dichlorobenzidine (EPA 1978a). Exposure of the general population, primarily children, may occur through ingestion of paint chips containing 3,3'-dichlorobenzidine as a pigment.

3,3'-Dichlorobenzidine-based pigments have been used in printing ink applications; their use in paints is rare and, thus, its presence in present-day pressurized paint spray would not be expected (CPMA 1998).

Trace amounts of 3,3'-dichlorobenzidine have been detected in various consumer cosmetics products sold abroad, including facial skin care masks, skin oils, talcum powder, hair gel, and hair dye (Hailong et al. 2014). While 3,3'-dichlorobenzidine is not directly used in the production of cosmetic products, the

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decomposition of azo dyes used in cosmetic colorants can result in the presence of aromatic amines (Hailong et al. 2014).

3,3'-Dichlorobenzidine has been identified as a degradation product in pigments, commonly used in tattooing, exposed to sunlight and laser irradiation (Hauri and Hohl 2015). Irradiation by laser of C.I. Yellow Pigment 14, C.I. Yellow Pigment 83, and C.I. Orange Pigment 13 resulted in 3,3'-dichlorobenzidine as a degradation product. Irradiation by different sunlight sources of C.I. Yellow Pigment 14, C.I. Orange Pigment 13, and C.I. Orange Pigment 34 also resulted in 3,3'-dichlorobenzidine as a degradation product (Hauri and Hohl 2015). These results suggest that skin tattoos using pigments containing azo dyes may yield 3,3'-dichlorobenzidine.

Occupational exposure to 3,3'-dichlorobenzidine is most likely to occur in the synthesis of pigments, the compounding of lead iodide, and the garment, leather, printing, paper, and homecraft industries where benzidine-based pigments are used. Since 1974, Occupational Safety and Health Administration (OSHA) regulations have set strict standards for worker protection, required the use of closed manufacturing vessels, and prescribed methods to chemically destroy residues. Nevertheless, 3,3'-dichlorobenzidine has been detected in urinary samples collected from workers of facilities where the chemical had been used. Less than 0.2 µg/L of 3,3'-dichlorobenzidine was detected in urine samples of 36 workers exposed to pigments derived from the compound (Hatfield et al. 1982). 3,3'-Dichlorobenzidine levels of 0.006–0.281 ppm were measured in the urine of workers of a manufacturing plant producing the chemical, and in some of their family members (ATSDR 1996).

In Canada, the estimated daily intake of 3,3'-dichlorobenzidine by various segments of the population has been calculated. The calculations are based on the predicted levels of 3,3'-dichlorobenzidine in air, water, and soil, as well as on the estimated daily intake of each (air, water, soil) by Canadians (Government of Canada 1993). The predicted concentrations or human intake levels were not measured values but rather predicted values based on output from mathematical models using worst-case assumptions that did not take into consideration removal mechanisms such as photolysis, oxidation, or irreversible binding to substrates. The total intake by adults (≥ 20 years of age) was predicted to be 7.4×10^{-9} ng/kg body weight/day. For infants up to 6 months of age (the group with the greatest predicted exposure based on body weight), the total intake was estimated at 3.6×10^{-8} ng/kg-body weight/day. A study by Paraiba et al. (2006) calculated a BCF for 3,3'-dichlorobenzidine in fruits. Average daily intake values were not measured in this study, but the BCF calculated makes calculations of average daily intake values possible.

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The study suggests that consumer exposure to 3,3'-dichlorobenzidine through fruit consumption is possible (Paraiba et al. 2006).

5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

In addition to individuals who are occupationally exposed to 3,3'-dichlorobenzidine (see Section 5.6) there are other groups whose levels are above those of the general population. These groups include individuals living in proximity to sites where 3,3'-dichlorobenzidine was produced or sites where 3,3'-dichlorobenzidine was disposed of, and individuals living near one of the NPL hazardous waste sites where 3,3'-dichlorobenzidine has been detected in some environmental media (ATSDR 2019). Harden et al. (2005) found 3,3'-dichlorobenzidine and its degradation product, benzidine, present in sediment samples up to 6 km from its primary source indicating the chemical can be transported long distances. This suggests that the chemical and its products may be in local soils and sediments at elevated levels.