UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

July 12, 2007

MEMORANDUM

SUBJECT: Summary Review of Available Literature for Hydrogen Peroxide and Peroxyacetic Acid for New Use to Treat Wastewater

DP Barcode: D340077 **Reregistration Case No.: 4072**

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Chemical Names Hydrogen Peroxide/Peroxyacetic Acid
PC Codes 000595, 063201
CAS Nos. 7722-84-1, 79-21-0

PEROXY COMPOUNDS:
HYDROGEN PEROXIDE AND PEROXYACETIC ACID
ENVIRONMENTAL FATE SCIENCE CHAPTER

EXECUTIVE SUMMARY

The Antimicrobial Division (AD) has received a request to add the outdoor wastewater treatment use for hydrogen peroxide and peroxyacetic acid. AD conducted a review of the available literature on environmental fate for these compounds to determine if guideline studies would be required from this outdoor use. Based on the limited persistence of both compounds, AD does not believe that significant environmental exposure is likely from this use and therefore no additional environmental fate data are needed at this time.

The transformation products of hydrogen peroxide are water and oxygen. The primary transformation products of peroxyacetic acid are acetic acid, water, and oxygen. Acetic acid is rapidly metabolized to carbon dioxide and water by ambient aerobic microorganisms. Hydrogen peroxide and peroxyacetic acid are inherently unstable species due to the peroxide bond (O-O bond). At typical pesticide concentrations, peroxides degrade rapidly.

HYDROGEN PEROXIDE

Under abiotic conditions, hydrogen peroxide does not appear to be hydrolytically or photolytically stable. The half-life in water under abiotic conditions has not been determined absolutely, but it varies with concentration. In seawater, the DT20 of hydrogen peroxide was 25-35 minutes. The half-life of hydrogen peroxide (90% purity) was 8.3 days in the presence of sunlight in the UV range. Hydrogen peroxide is not expected to pose any concerns for surface water run off.

Under aerobic aquatic metabolism conditions, hydrogen peroxide degrades with half-lives of 1.1-5.3 hours in non-sterile conditions, and *ca.* 80 hours in sterile conditions. Under anaerobic soil metabolism conditions, hydrogen peroxide degrades with a half-life of *ca.* 4 hours in samples of nine petroleum-contaminated surface soils from five different states. The texture and pH of the soil, as well as the experimental temperature, did not affect the degradation process; however, the organic carbon content of the soil did affect the degradation. Under aerobic soil metabolism conditions, hydrogen peroxide degrades with a half-life of *ca.* 1.4 hours in diluted test solutions. This half-life value was extrapolated to *ca.* 7 hours for concentrated test solutions.

There is no data on the mobility of hydrogen peroxide in regards to either adsorption/desorption (to determine K_d) with various soils or soil column leaching. However, it is assumed that, since hydrogen peroxide has physical properties that are similar to water, hydrogen peroxide will not bind to soils.

The Agency does not have data on hydrogen peroxide bioaccumulation in aquatic organisms. However, hydrogen peroxide is not expected to bioaccumulate due to its low octanol-water partition coefficients (0.40).

The average degradation half-life for hydrogen peroxide in the atmosphere is 24 hours. The average overall release rate of hydrogen peroxide from NO FOUL-WB paint was 0.0013 $mg/cm^2/day$ in synthetic seawater at 24 ± 1°C.

PUBLISHED LITERATURE ON HYDROGEN PEROXIDE

Several articles discuss the fate of hydrogen peroxide in conjunction with the use of peroxy compounds as wastewater treatment disinfectants utilized in Mexico (Diaz-Avelar et al, 2004), the United Kingdom (Booth and Lester, 1995), Italy (Lubello et al., 2004), and Canada (Wagner et al, 2002); hydrogen peroxides reactivity with transition metals (e.g. cadmium, copper, iron, phosphorous; Chaco-Rivero and Suidan, 2006; Liao et al, 2005; Mercier et al, 2002; Moffett and Zika, 1987; Yoshizaki and Tomida, 2000) and other chemicals (e.g. creosote, benzene, trichloroethylene, BTX, cyanide, PAHs, and phenols; Flotron et al, 2005; Fraser and Sims, 1984; Lodaya et al, 1991), environmental occurrence in air (Sakugawa et al, 1990, 1992; Gunz and Hoffman, 1990; Heikes et al, 1987; Claiborn and Aneja, 1993; Hwang and Dasgupta, 1985; Yoshizumi et al, 1984) or environmental occurrence aqueous media (Sakugawa et al, 1990, 1992; Gunz and Hoffman, 1990; Heikes et al, 1991; Jacob et al, 1990; Kieber and Helz, 1995; Yoshizumi et al, 1983; Moffett and Zika, 1987). Hydrogen peroxide is a naturally occurring chemical; therefore, occurrence data does not suggest anthropogenic sources. H_2O_2 concentrations are influenced by concentrations of primary air pollutants, such as NOx, volatile organic compounds (VOCs), and carbon monoxide, and increase with rising air temperature, solar intensity, and water vapor concentrations (Sakugawa et al, 1990, 1992).

Atmospheric Occurrence and Fate of Hydrogen Peroxide

Hydroxyl radical, ozone, and hydrogen peroxide are the primary endogenous oxidants in the atmosphere. Photochemical processes are mainly responsible for atmospheric hydrogen peroxide concentrations and aqueous-phase reactions, and are the dominant pathways for atmospheric consumption of hydrogen peroxide (Sakugawa et al., 1990, 1992). Reported concentrations of gas phase hydrogen peroxide ranged from 0.01-7.0 ppb in Los Angeles (Sakugawa et al., 1992). Field measurements of atmospheric hydrogen peroxide from various locations in North America, Europe, Brazil, and Japan revealed concentrations of 0.001-5 ppb (Gunz and Hoffman, 1990). Diurnal variation is also seen with gaseous hydrogen peroxide concentrations, with peaks between 2-5 PM (Sakugawa et al., 1992). However, measurements taken at high elevation sites displayed the inverse relationship with highest concentrations at night due to tropospheric interactions (Heikes et al., 1987; Sakugawa et al., 1990, 1992). Tropospheric concentrations have been measured from 0.5-5 ppb (Claiborn and Aneja, 1993). Tropospheric concentrations have been measured between from 0.02-4.1 ppbv in the Eastern United States, with maximum concentrations just above cloud tops (Claiborn and Aneja, 1993; Heikes et al., 1987). Hydrogen peroxide concentrations are influenced by concentrations of

primary air pollutants, such as NOx, volatile organic compounds (VOCs), and carbon monoxide, and increase with rising air temperature, solar intensity, and water vapor concentrations (Sakugawa et al., 1990, 1992).

Concentrations of hydrogen peroxide in cloudwater have been reported at 247 μM (Gunz and Hoffman, 1990), with rainwater concentrations of 10 nM-100 μM (Sakugawa et al, 1990). Cloud hydrogen peroxide is removed from the atmosphere by wet deposition, including rain, fog, and mist droplet scavenging (Sakugawa et al, 1990, 1992), and dry deposition onto surfaces, including foliage uptake by trees (Sakugawa et al, 1990, 1992; Claiborn and Aneja, 1993). Hydrogen peroxide has a fairly high Henry's law constant in comparison to other oxidants (e.g., O_3, O_2, NO_2), with a value around 10^5 M/atm (Claiborn and Aneja, 1993; Gunz and Hoffman, 1990; Hwang and Dasgupta, 1985; Yoshizumi et al., 1984).

Aqueous Occurrence and Fate of Hydrogen Peroxide

Generally, hydrogen peroxide is unreactive with organic compounds, but this reactivity is increased in the presence of transition metals (e.g. iron, copper, chromium), due to the formation of free-radical intermediates (Moffett and Zika, 1987). Much of the hydrogen peroxide concentrations in natural waters are attributed to a photochemical formation of the chemical (Cooper and Zika, 1983, Cooper et al., 1987, 1988, 1989, Cooper and Zepp, 1990; Draper and Crosby, 1983; Johnson et al., 1989; Kieber and Helz, 1995; Moffett and Zika, 1987; Sakugawa et al., 1992; Yoshizumi et al., 1983). In addition, the photodecomposition of solutes, such as tryptophan, tyrosine, and humic substance continuously produce hydrogen peroxide in sunlight (Draper and Crosby, 1983). It is thought that the superoxide anion is also a precursor in the sunlight-induced production of hydrogen peroxide in natural waters and that both hydrogen peroxide and O_2. are important in the maintenance of the redox potential of natural waters high in organic matter (Cooper and Zika, 1983; Johnson et al., 1989).

Summertime concentrations have been found mid-day in southeastern U.S. surface and groundwaters from 3- 67 E^{-6} mol/liter hydrogen peroxide and $6.5E^{-8}$-1.00 E^{-5}, respectively, and 800 nM in Ontario (Cooper and Zika, 1983, Cooper and Lean, 1989). These concentrations were also correlated to the amount of TOC in the water samples; with increasing hydrogen peroxide as TOC rises in both types of water (Cooper and Zika, 1983; Wagner et al., 2002). In the mid-Atlantic, February-September concentrations ranged from 11-350 nM in estuarine waters (Kieber and Helz, 1995). In Canada, lake water hydrogen peroxide formation rates ranged from 81-2,120 nM/hour (Scully et al., 1996). The vertical variation of the rates of formation of hydrogen peroxide depends on UV light penetration, with dark decay rates dependant upon the concentration of algae and bacteria in the water (Cooper et al., 1988, 1989; Herrmann and Herrmann, 1994; Johnson et al, 1989). Pico plankton may be partially responsible for the biological component of hydrogen peroxide decay (Cooper and Lean, 1989). In the Mediterranean, hydrogen peroxide formation rates ranged from 0-3.6 μmol/l-h (Herrmann and Herrmann, 1994), with the higher rates near the surface of the water (Herrmann and Herrmann, 1994; Johnson et al., 1989).

First-order hydrogen peroxide decay in soil suspensions is at least one order of magnitude faster than in distilled water, with a half-life of between 2.1-5.6 hours, which is attributed to microbial decay processes in the soils, in conjunction with the catalytic action of soil-associated peroxidases (Cooper and Zepp, 1990). Dark decay of hydrogen peroxide in the Great Lakes region, which followed first order kinetics, revealed half-lives of 10-22 hours (Cooper et al., 1989).

Hydrogen peroxide levels are also thought to decrease slightly during rain storms (Cooper and Lean, 1989), as well as with increasing altitude, due to lower humidity (Jacob et al., 1990). Summer time measurements from rainwater in Tokyo revealed hydrogen peroxide levels of approximately 1000 μg/L (Yoshizumi et al., 1983). In tropical regions, such as Brazil, H_2O_2 concentrations in rainwater ranged from 0.1-6.8 ppbv (Jacob et al., 1990). Rain is also a significant source of hydrogen peroxide in the surface ocean (Cooper et al., 1987).

Terrestrial Occurrence and Fate of Hydrogen Peroxide

Hydrogen peroxide has been used to oxidize and recover various contaminants in soils, including chromium, creosote, trifluralin, trichloroethylene (TCE), and polycyclic aromatic hydrocarbons (PAHs) (Atagana, 2003; Baciocchi et al., 2004; Bermond and Benzineb, 1991; Conte et al., 2001; Paoli et al., 1991; Rock et al., 2001). In chromium-enriched soils, H_2O_2 additions produce rapid, dose-dependent increases in soluble Cr(VI) in the uppermost, peaty horizon (Rock et al, 2001). The half-life of hydrogen peroxide in chromium-enriched soils is less than 48 hours, but between can vary between 8 minutes to 153 hours in TCE-contaminated soils, depending on the TOC content of the soils, the levels of metal oxides in the soils, and whether or not a stabilizer is used in conjunction with hydrogen peroxide (Baciocchi et al., 2004; Rock et al, 2001). The ability for hydrogen peroxide to readsorb heavy metals in sewage treated soils depends on the pH of the extractant (Bermond and Benzineb, 1991).

Anaerobic Degradation

Hydrogen peroxide photolysis has proven to be useful for the destruction of hazardous organic substances in water and sludge, including benzene, BTX, cyanide, PAHs, and phenols (Flotron et al., 2005; Fraser and Sims, 1984; Lodaya et al., 1991), with oxidation products generally low molecular weight oxygenated compounds that are easily biodegradable (Lipczynska-Kochany, 1993). It has also been used to remove heavy metals from sewage sludge and wastewater, such as cadmium, copper, iron, phosphorous (Chaco-Rivero and Suidan, 2006; Liao et al., 2005; Mercier et al., 2002; Moffett and Zika, 1987; Yoshizaki and Tomida, 2000).

Through advanced oxidation methods, such as Fenton's oxidation, when hydrogen peroxide is combined with ferrous ions or another ferrous complex at a low pH, Fe^{2+} catalyzes the decomposition of hydrogen peroxide into Fe^{3+} and the hydroxyl radical, which has an extremely high oxidation potential and can decompose organic compounds in a very short time (Aggarwal, 1991; Baciocchi et al., 2004; Flotron et al., 2005; Fraser and Sims., 1984; Kotsou et al., 2004; Kwon et al., 2004; Lau et al., 2002; Neyens et al., 2003; Ntampegliotis et al., 2006; Rock et al., 2001; Tekin et al., 2006). Catalase is one of the strongest catalysts in decomposing

peroxide (Aggarwal, 1991; Lodaya et al., 1991; Patel et al., 2005).

PEROXYACETIC ACID

Peroxyacetic acid is expected to easily degraded in air, water and soil and does not persist or accumulate in the environment. The half-lives/DT50s for peroxyacetic acid are 48 hours at pH 4 and 7, and 3.6 hours at pH 9. In water containing 0.01 mol/L, the half-lives were 107, 109, and 112 hours for pH values of 4, 7,a nd 9, respectively. For solutions containing 0.001 mol/L, the half-lives were 3.5, 3.5, and 0.3 hours, respectively. In seawater, the DT50 of peroxyacetic acid was 7-20 minutes. Only a minor portion (<1%) of peroxyacetic acid, which is released into the environment, will remain in the atmosphere, where it is rapidly degraded (half-life of 22 minutes). Peroxyacetic acid will not partition into sediment, suspended matter, or biota. In the OECD Closed Bottle Test with adapted bacteria, peroxyacetic acid (initial concentration of 2-5 mg/L) was highly biodegradable (>79%).

The hydrolysis products of peroxyacetic acid (acetic acid and hydrogen peroxide) are readily biodegradable. The biodegradation/DT50 of peroxyacetic acid is rapid (not defined). The ready biodegradation of peroxyacetic acid is >70%. In soil, diluted peroxyacetic acid is rapidly and easily degraded via hydrolysis and instantaneously degraded via transition metal decomposition. At low concentrations, biodegradation could contribute to the degradation in soils. After *ca.* 20 minutes, 99.2% of the peroxyacetic acid (1.1% solution) had degraded in dried soil (not specified) following extraction with demineralized water.

The soil column leaching of peroxyacetic acid was studied in an unspecified soil. At 5 minutes post-treatment, 21.5% of the peroxyacetic acid was recovered, along with 42% of hydrogen peroxide, at a soil depth of 25 mm. The recovery of peroxyacetic acid decreased to 3.2% at 50 mm, 0.3% at 100 mm, and <0.2% at 150 mm. At 150 mm, 10% of hydrogen peroxide was present. At 10 minutes post-treatment, the column washing yielded only 8.7% recovered peroxyacetic acid at the 25-mm depth. Peroxyacetic acid is not expected to bioaccumulate due to its low octanol-water partition coefficients (0.30). Peroxyacetic acid and its transformation products, hydrogen peroxide and acetic acid, are of low molecular weight, high water solubility, low fat solubility, and have no tendency to bioaccumulate.

No photodegradation in water, photodegradation in air, anaerobic soil metabolism or accumulation studies in aquatic non-target organisms information was found for peroxyacetic acid.

PUBLISHED LITERATURE ON PEROXYACETIC ACID

Treatment of final sewage effluent with 6 or 30 mg/L PAA rapidly produces monosubstituted chlorophenols (2-, 3-, and 4-chlorophenol), with by-product formation independent of temperature or reaction time, but rather dependent on pH of the effluent, PAA dosage, chlorine content, and concentration of organic and mineral constituents in the final effluent (Booth and Lester, 1995). The concentration never exceeded 100 ng/L.

PAA is a powerful oxidizer of bromide to hypobromous acid and can form brominated organics (2- and 4-bromophenol) (Booth and Lester, 1995; Wagner et al, 2002), but it cannot oxidize chloride to hypochlorous acid and subsequently chlorinated organics (Booth and Lester, 1995). PAA treatment also can also generate free chlorine and bromine radicals (Booth and Lester, 1995). An addition of 5 mg/L PAA to wastewater increases the amount of total organic carbon (TOC) by a factor of 1.5, and 10 mg/L triples the TOC level (Wagner et al., 2002; Profazier et al., 1997). When used as a disinfectant, PAA decomposes to hydrogen peroxide in an initially rapid process, but measurable residuals can last up to two hours (Wagner et al., 2002).

I. Environmental Fate Assessment

A. Abiotic

Hydrogen peroxide is an unstable substance in water with abiotic conditions. It is highly miscible in water and continuously autoionizes, which water does as well. The autoionization generates free radicals or odd electron molecules or ions, all of which are also unstable. Hydrogen peroxide in water has a natural low tendency to ionize/decompose to HO^{2-} and H^{+} ions in abiotic or biotic systems. The rate of this ionization/decomposition increases with increasing pH (in homogeneous or heterogeneous systems) and in the presence of transition metal ions and other elements, organic matter, dust, enzymes, dilution, and heterogeneous surfaces. The half-life in water under abiotic conditions has not been determined absolutely, but it varies with concentration. The half-life/DT50 for hydrogen peroxide is variable, but short at pH 7. The rate of degradation increases as the pH/alkalinity increases. In seawater, the DT20 of hydrogen peroxide was 25-35 minutes. In seawater samples from the Bay of Biscayne (filtered 0.2 μm, initial concentration 3.4 μg/L), the half-life of hydrogen peroxide was 60 hours. In the seawater samples from the Mediterranean shallow lagoon Etang de Tau (filtered 0.2 μm), the half-life was 50-70 hours.

The half-lives/DT50s for peroxyacetic acid are 48 hours at pH 4 and 7, and 3.6 hours at pH 9. In seawater, the DT50 of peroxyacetic acid was 7-20 minutes. The rate of hydrolysis of peroxyacetic acid is accelerated by increasing pH and, to a lesser extent, temperature. Hydrolysis half-lives at 20°C were *ca.* 1 week at pH 4.4 and <1 day at pH 7 for a 2% peroxyacetic acid solution. In distilled water at pH 2, the degradation of peroxyacetic acid was 18 and 19 days, respectively, for initial test concentrations of 95 and 748 mg/L. Peroxyacetic acid degraded in synthetic seawater with a half-life of 2 minutes at 2% and 3.3% salinity, and an initial concentration of 52.5 mg/L of peroxyacetic acid. When the initial concentration of peroxyacetic acid was doubled to 105 mg/L, the half-lives were 7 minutes at 3.3% salinity, and 20 minutes at 2% salinity. Based on these results, it was concluded that increased salinity increased the rate of degradation of peroxyacetic acid. At acidic pH, the half-life of peroxyacetic acid is *ca.* 7-12 days; at neutral or alkaline pH, the half-life is <1 day. In seawater, the half-life is expected to be even more rapid (≤1 hour).

Hydrogen peroxide is an unstable molecule under photolytic, abiotic conditions. The half-life of hydrogen peroxide (90% purity), was 8.3 days in the presence of sunlight in the UV range. This rate is 70 times greater than in the absence of radiation. Hydrogen peroxide degrades to two OH free radicals, while peroxyacetic acid degrades to acetic acid and hydrogen peroxide. Direct photolysis in water of hydrogen peroxide is not expected to be an important degradation process. Photodegradation in water information was not reported for peroxyacetic acid.

The average degradation half-life for hydrogen peroxide in the atmosphere (from different atmospheric conditions) is 24 hours. The direct photolysis degradation of hydrogen peroxide to generate two hydroxyl radicals occurs with a half-life of 2.14 days. However, this direct photolysis degradation is estimated to form 10% of the total hydroxyl radical daytime concentration. The major route of hydrogen peroxide degradation in air is expected to be by indirect photolysis, which is the reaction of hydrogen peroxide with hydroxyl radical to produce water and a hydroperoxide radical. The overall photolysis rate has been difficult to quantify, but one study at a high-elevation site (1,689 m) showed that the *ca.* 25% of hydrogen peroxide decomposed in unpolluted air at nighttime over 8-10 hours (half-life extrapolated to 16-20 hours), assuming nighttime production rate of hydrogen peroxide is low or negligible.

Peroxyacetic acid released in the environment will partition almost exclusively (>99%) to the water compartment. Only a minor portion (<1%) will remain in the atmosphere, where it is rapidly degraded with a half-life of 22 minutes. In the presence of air, peroxyacetic acid degrades to acetic acid, which then degrades to carbon dioxide and water.

B. Biotic

The aerobic aquatic metabolism of hydrogen peroxide degraded with half-lives of 1.1-5.3 hours under unsterile conditions, and *ca.* 80 hours under sterile conditions. Hydrogen peroxide is degraded in biologically active systems due to the fact that aerobic bacteria product catalase enzymes that converts hydrogen peroxide to water and oxygen. The degradation rate is dependent on the microbial population size. The half-life is between minutes and hours in municipal wastewater ($>10^6$ cells/mL), only a few seconds in sludge (10^8-10^{10} cells/mL) and from hours to a few days in natural waters ($\leq 10^3$ cells/mL). The degradation of hydrogen peroxide is assumed to follow first-order kinetics at low concentrations and non-first-order kinetics with a slower rate at higher concentrations (≥100 µg). Hydrogen peroxide is expected to degrade rapidly in sediment due to the normal high concentrations of catalytic abiotic and biotic material.

Four aerobic aquatic studies were performed with natural waters. In the first study, the summer time degradation rate of hydrogen peroxide was studied at 3.4 µg/L (natural concentration) in lake water (pH 7.2, DOC 6 mg/L) from Jacks Lake, Ontario. The dark decay of hydrogen peroxide followed first-order kinetics with half-lives of 7.8 hours (unfiltered lake water), 8.6 hours (filtered, 5 µm), 31 hours (filtered, 1 µm) and >24 hours (filtered, 0.45 µm). Based on these results, it was concluded that the picoplancton (defined as 0.2-2 µm) contains the major portion of the biological agent responsible for hydrogen peroxide degradation. In the

second study, hydrogen peroxide decay in Lake Ontario was measured as 14.7-21.6 hours for water samples at depths and initial concentrations of 0 m with 112 nM, and 10 m with 44 nM. When the samples were filtered through 0.45 μm membrane filters, no degradation of hydrogen peroxide was observed after 7 hours. Based on these results, it was concluded that bacteria and/or algae are responsible for the degradation of hydrogen peroxide. In the third study, the degradation of hydrogen peroxide was measured at 90-150 nmol/L (3-5 μg/L) in seawater at room temperature in the dark. The measured degradation rate was 3.8 nmol/L/h (0.13 μg/L) with hydrogen peroxide concentrations reaching zero after 23-39 hours. In the fourth study, the degradation of hydrogen peroxide was studied in water from the River Saone at initial concentrations of 100, 250, 500, 1000, and 10000, mg/L. The half-lives were first-order and measured as 20.1 days, 15.2 ± 2.5 days (higher values for filtered samples), 8.2 ± 2 days (higher values for filtered samples), 8.1 days and 2.5 days for the initial concentrations of 100, 250, 500, 1000, and 10000 mg/L, respectively. Based on these results, it was concluded that the filtering of particles >0.2 μm had little effect on degradation, and the degradation of hydrogen peroxide was slower at initial concentrations <500 mg/L. Also, studies, which were similar to this third study, but using de-ionized water containing 500 mg/L of hydrogen peroxide, showed an increase in concentration which was probably due to light reactions. Hydrogen peroxide is considered "readily biodegradable" based on the results of these four studies. In the natural environment, many more catalase active microbes are present versus the concentration of hydrogen peroxide; however, if the concentration of hydrogen peroxide increases substantially, then the degradation rates will be slower because of the toxicity of hydrogen peroxide.

Peroxyacetic acid will not partition into sediment, suspended matter or biota. In the OECD Closed Bottle Test, peroxyacetic acid (initial concentration of 2-5 mg/L) was not readily biodegradable. However, when adapted bacteria derived from a Zahn-Wellens Test (unreported amount) were included in the same test procedure, peroxyacetic acid was highly biodegradable (>79%).

The aerobic soil metabolism of hydrogen peroxide occurred with a half-life of *ca.* 1.4 hours for diluted non-sterile test solutions. This half-life value was extrapolated to *ca.* 7 hours for concentrated non-sterile test solutions. Hydrogen peroxide degrades rapidly in soil due to the high concentrations of catalytic materials, such as transition metals, enzymes, easily oxidized/reduced organic substances and living microbes. Observed half-lives of hydrogen peroxide vary from 15 hours in soil without microbiological activity and few minerals to several minutes in soils with 10^8-10^9 cells/g total solids and minerals like iron and manganese. The average half-life is estimated as 12 hours.

The biodegradation/DT50 of peroxyacetic acid is 'rapid' (not defined). The ready biodegradation of peroxyacetic acid is >70%. In soil, diluted peroxyacetic acid is rapidly and easily degraded via hydrolysis and instantaneously degraded via transition metal decomposition. At low concentrations, biodegradation could contribute to the degradation in soils. The hydrolysis products of peroxyacetic acid (acetic acid and hydrogen peroxide) are readily biodegradable.

The anaerobic soil metabolism of hydrogen peroxide occurred with a half-life of *ca.* 4 hours in samples of nine petroleum-contaminated surface soils from five different states. Hydrogen peroxide degraded from 42-83% in *ca.* 6 hours. The texture and pH of the soil, as well as the experimental temperature, did not affect the degradation process; however, the organic carbon content of the soil did affect the degradation.

No adsorption/desorption or leaching data have been submitted to the Agency for hydrogen peroxide. However, it was proposed that since hydrogen peroxide is similar to water in its physical characteristics, hydrogen peroxide is mobile but unstable in soils. Also, due to its high polarity, it was proposed that hydrogen peroxide is unlikely to bind with soils. The sorption of hydrogen peroxide and peroxyacetic acid are very low.

Peroxyacetic acid will not partition into sediment, suspended matter or biota. After *ca.* 20 minutes, 99.2% of the peroxyacetic acid (1.1% solution) had degraded in dried soil (not specified) following extraction with demineralized water. The soil column leaching of peroxyacetic acid was studied with an unspecified soil. At 5 minutes post-treatment, 21.5% of the peroxyacetic acid was recovered, along with 42% of hydrogen peroxide, at a soil depth of 25 mm. The recovery of peroxyacetic acid decreased to 3.2% at 50 mm, 0.3% at 100 mm, and was <0.2% at 150 mm. At 150 mm, 10% of hydrogen peroxide was present. At 10 minutes post-treatment, the column washing yielded only 8.7% recovered peroxyacetic acid at the 25-mm depth.

The Agency does not have data on hydrogen peroxide bioaccumulation in aquatic organisms. However, based on its characteristics, hydrogen peroxide is unlikely to bioaccumulate in aquatic and other organisms. Bioconcentration factors (BCF) have not been reported; however, hydrogen peroxide and peroxyacetic acid are not expected to bioaccumulate due to their low octanol-water partition coefficients (0.30 for peroxyacetic acid and 0.40 for hydrogen peroxide). Peroxyacetic acid and its transformation products, hydrogen peroxide and acetic acid, are of low molecular weight, high water solubility, low fat solubility and have no tendency to bioaccumulate.

The release rate of hydrogen peroxide from NO FOUL-WB paint was studied in synthetic seawater at 24 ± 1°C. At 42, 66, 100, and 190 hours after addition of the test cylinder, the hydrogen peroxide concentrations were 0.5, 0.8, 1.3, and 1.2 mg/L, respectively. These levels corresponded to average release rates of 0.0015, 0.0014, 0.0015, and 0.0008 mg/cm^2/day for 42, 66, 100 and 190 hours after addition of the test cylinder, respectively. The average release rate was constant for the first 100 hours after addition of the test cylinder, and then declined by approximately half at 190 hours addition of the test cylinder. The average overall release rate was 0.0013 mg/cm^2/day. This study (MRID 426862-03) has not been reviewed by the Agency.

APPENDIX

Environmental Fate Assessment:

Hydrogen peroxide and peroxyacetic acid are not bioaccumlative (log K_{ow} values are *ca.* -1.5 to *ca.* -0.5). A bioconcentration factor (BCF) was not reported, however hydrogen peroxide and peroxyacetic acid are not expected to be a concern for bioconcentration in aquatic organisms. Hydrogen peroxide and peroxyacetic acid are highly soluble in water, and hydrogen peroxide is too unstable in water to determine an absolute half-life. Peroxyacetic acid has half-lives of 48 hours at pH 4 and 7, and 3.6 hours at pH 9. Hydrogen peroxide is expected to volatize from dry soil surfaces based upon an estimated vapor pressure of 300 Pa. Peroxyacetic acid is not expected to volatize from dry soil surfaces based upon an estimated vapor pressure of 1.1×10^{-5} Pa. The log K_{ow} and vapor pressure of potassium peroxymonosulfate sulfate were not reported, but it is 25.6% soluble in water at room temperature.

Environmental Fate Science Chapter for Peroxy compounds:

Hydrogen peroxide (PC code 000595) and peroxyacetic acid (PC code 063201) are registered as active products and used as disinfectants (bacteriocide/germicide), fungicides/fungistats (trycophyton), general and medical disinfectants, sanitizer, sterilizers/sporicides, tubercolocides and virucides (antimicrobial). Hydrogen peroxide is also used as an algaecide. The following fate properties were obtained from EPA internal environmental fate documents and databases, and open literature. Table 1 below contains the chemical, physical, and environmental fate data for hydrogen peroxide, and Table 2 contains same information for Peroxyacetic acid.

Table 1. Properties for Hydrogen Peroxide

Property	Value	Comment
Vapor Pressure	300 Pa	
Henry's Law	4.5×10^{-6}	Atm m^3 mol^{-1}
pKa	11.62	
Koc	Not reported	
Hydrolysis half-life	Unstable	Coluld not be determined
Water Solubility	Miscible	
Log Kow	0.4	Bioaccumulation not expected
Physical state	Clear, colorless, slightly pungent liquid	
Specific gravity/ density	1.438 g/ml	20 °C
Melting point	-0.40 °C	

Boiling point	150 °C	
DT_{20} in seawater	25-35 minutes	
DT_{50} in seawater	60 hours	Bay of Biscayne
	50-70 hours	Mediterranean shallow lagoon
DT_{50} in water	8.3 days	Abiotic and UV light
DT_{50} in atmosphere	24 hours	Average from different atmospheric conditions
	2.14 days	Degradation to form 2 hydroxy radicals 10 % of total hydroxyl radicals in air
	16-20 hours	Unpolluted air, high altitude
Aerobic aquatic metabolism	1.1-5.3 hours	unsterile
	80 hours	Sterile
	7.8 hours	Dark decay in unfiltered lake water
	8.6 hours	Filtered, 5 um
	31 hours	Filtered, 1 um
	>24 hours	Filtered 0.45 um
	3.8 nMol/L/H	Degradation rate in seawater
	2.5-20.1 days	Half-lives for concentrations of 100-10,000 ppm
Aerobic soil metabolism	1.4 hours	Diluted, non-sterile solutions
	7 hours	Concentrated, non-sterile solutions
	15 hours	Soil w/o microbial activity and few minerals
	Several minutes	Microbes present and minerals
	12 hours	Average half-life
Anaerobic soil metabolism	4 hours	Average OC content of soil affected half-life
Release rate from paint	0.0013 $mg/cm^2/day$	Average release rate

Hydrogen peroxide

1. Vapor Pressure: 300 Pa.
2. Henry law Constant (air/water partition coefficient): 4.5×10^{-6}.
3. pKa: 11.62.
4. K_{oc} (organic carbon ratio in soil): Not reported.
5. Log K_{ow} (octanol/water partition coefficient): -1.5.
6. The hydrolysis rate: Unstable, could not be determined.
7. Hydrogen peroxide is highly miscible with water.
8. Log BCF: Not reported; BCF: Not reported.
9. Physical state: clear, colorless, rather unstable, slightly pungent liquid.
10. Specific gravity/density: 1442.5 kg/m^3 (relative) OR 1.40 g/mL OR 1.438 at 20°C.
11. Melting point: -0.40°C; boiling point 150°C

Peroxyacetic acid (PAA)

1. Vapor Pressure: 1.1×10^{-5} Pa.
2. Henry law Constant (air/water partition coefficient): 5×10^{-12} OR 0.22 Pa m^3/mol at 25°C.
3. pKa: 8.2 at 20°C.
4. pH <1 OR 2-3.
5. K_{oc} (organic carbon ratio in soil): Not reported.
6. Log K_{ow} (octanol/water partition coefficient): -0.52 (calculated).
7. The hydrolysis rates: 48 hours at pH 4 and 7, and 3.6 hours at pH 9.
8. Water solubility is 1000 g/L OR 1000 g/kg at 20°C.
9. Log BCF: Not reported; BCF: Not reported.
10. Physical state: clear, colorless liquid which is odorless at low concentrations, but quite pungent when present at 40% or higher concentrations.
11. Specific gravity/density: 1150 kg/m^3 (relative) OR 1.13 kg/m^3.
12. Melting point: -50°C; boiling point >60°C OR 103°C.
13. Flash point: 96°C; autoignition temperature: 265°C.

Table 2. Properties for Peroxyacetic Acid

Property	Value	Comment
Vapor Pressure	1.1 x 10^{-5} Pa	
Henry's Law	5 x 10^{-12}	Atm m^3 mol^{-1}
pKa	8.2	20 °C
Koc	Not reported	
Hydrolysis half-life	48 hours	pH 4 and 7
	3.6 hours	pH 9
	7 days	pH 4.4
	<1 day	pH 7
	18-19 days	pH 2
	2-7 minutes	Synthetic seawater
	7-12 days	Acid pH
	<1 day	Neutral or Alkaline pH
	>90 % degradation by 1 day	Drinking water and seawater
	DT50 >4 days	Demineralized water
Water Solubility	1000 g/L	20 °C
Log Kow	-0.52	Calculated
Physical state	Clear colorless liquid	
Specific gravity/ density	1.13 kg/m^3	
Melting point	-50 °C	
Flash point	96 °C	
DT_{50} in seawater	7-20 minutes	
DT_{50} in atmosphere	22 minutes	
Aerobic aquatic metabolism	Not readily biodegradable	OECD closed bottle test
	Readily biodegradable (>79 % degradation)	Presence of adapted bacteria
Aerobic soil metabolism	Readily biodegradable	>70 %
Anaerobic soil metabolism	No data	
Sorption to soil, sediment, or biota	Not sorbed	
Release rate from paint	No data	

Hydrogen peroxide is unstable in water, while peroxyacetic acid has half-lives of ≤2 days, depending on the pH. The Henry's Law constants for hydrogen peroxide and peroxyacetic acid (PAA) indicate that they are expected to be essentially nonvolatile from water surfaces. Mobility in soil (K_{oc}) was not reported for hydrogen peroxide and peroxyacetic acid; however, hydrogen peroxide is mobile but unstable in soils. The log K_{ow} values for hydrogen peroxide and peroxyacetic acid (*ca.* -1.5 to *ca.* -0.5) indicate that bioaccumulation in aquatic organisms like fish is not likely and that the soil/sediment adsorption coefficients will be low. Hydrogen peroxide is highly miscible with water. Peroxyacetic acid is highly soluble in water (1×10^3 g/L). Hydrogen peroxide (vapor pressure 300 Pa) is expected to volatize from dry soil surfaces, while peroxyacetic acid (vapor pressure 1.1×10^{-5} Pa) is not expected to volatize from dry soil surfaces.

Surface Water and Ground Water Contamination:

Although no data were available, due to their high solubility in water, hydrogen peroxide and peroxyacetic acid may reach surface or ground waters but are expected to be unstable and readily biodegrade; hydrogen peroxide may also volatize. Also, the use sites of hydrogen peroxide and peroxyacetic acid are all indoor sites, except for the aquatic non-food residential (swimming pool and hot tub use) use site for hydrogen peroxide. The use of hydrogen peroxide in residential swimming pools and hot tubs is not expected to come into contact with environmental waters.

Environmental Fate Data for Hydrogen Peroxide and Peroxyacetic acid

A. <u>Environmental Fate Guideline Studies</u>

Studies reviewed by the Agency under specific guidelines were generally not submitted unless otherwise specified. However, assorted documentation provided by the Agency was used to assess the environmental fate of hydrogen peroxide and peroxyacetic acid as it relates to each guideline.

1. Hydrolysis (OPP Guideline Number 161-1; R2025084, Memorandum, November 13, 2000; European Union Risk Assessment, Hydrogen Peroxide, Volume 38; Peracetic Acid and its Equilibrium Solutions, European Centre for Ecotoxicology and Toxicology of Chemicals, JACC No. 40, Brussels, January 2001; Marine Environmental Protection Committee, 53rd Session, April 15, 2005, MEPC 53/2/12; Marine Environmental Protection Committee, 54th Session, February 28, 2006, MEPC 54/2/12; R2025101, Data Package Record, Bean Sheet, March 21, 1995, DP Barcode: D213339, Case: 0408841)

Hydrogen peroxide in water has a natural low tendency to ionize/decompose to HO^{2-} and H^+ ions in abiotic or biotic systems. The rate of this ionization/decomposition increases with increasing pH (in homogeneous or heterogeneous systems) and in the presence of transition metal ions and other elements, organic matter, dust, enzymes, dilution and heterogeneous surfaces. The half-life/DT50 for hydrogen peroxide is variable, but short at pH 7. The rate of degradation increases as the pH/alkalinity increases. In seawater, the DT20 of hydrogen

peroxide was 25-35 minutes. In seawater samples from the Bay of Biscayne (filtered 0.2 μm, initial concentration 3.4 μg/L), the half-life of hydrogen peroxide was 60 hours. In the seawater samples from the Mediterranean shallow lagoon Etang de Tau (filtered 0.2 μm), the half-life was 50-70 hours. The natural levels of hydrogen peroxide in the freshwater, surface seawater, deep seawater and rainwater are 50-3200 nM (*ca.* 0.1 ppm), 100-300 nM (*ca.* 0.01 ppm), <5 nM, and 8000-80000 nM (*ca.* 2.7 ppm). In seawater, it is partly produced from the reaction of light with molecular oxygen, dissolved organic chromophores and transition metal ions.

The half-lives/DT50s for peroxyacetic acid are 48 hours at pH 4 and 7 and 3.6 hours at pH 9. In seawater, the DT50 of peroxyacetic acid was 7-20 minutes. The rate of hydrolysis of peroxyacetic acid is accelerated by increasing pH and, to a lesser extent, temperature. Hydrolysis half-lives at 20°C were *ca.* 1 week at pH 4.4 and <1 day at pH 7 for a 2% peroxyacetic acid solution. In distilled water at pH 2, the degradation of peroxyacetic acid was 18 and 19 days, respectively, for initial test concentrations of 95 and 748 mg/L. The degradation of peroxyacetic acid was studied at 10 and 20 mg/L in demineralised water (pH 5), drinking water (pH 6) and seawater (pH 7) at 20°C. Peroxyacetic acid degraded by >90% after 1 day in the drinking water and seawater at both concentrations. In the demineralised water, the 50% degradation occurred after >4 days. The degradation of peroxyacetic acid was studied in synthetic seawater with a 15% peroxyacetic acid solution at an unreported temperature and pH. For an initial concentration of 52.5 mg/L of peroxyacetic acid, the half-life was 2 minutes at 2% and 3.3% salinity. When the initial concentration of peroxyacetic acid was doubled to 105 mg/L, the half-lives were 7 minutes at 3.3% salinity and 20 minutes at 2% salinity. Based on these results, it was concluded that increased salinity increased the rate of degradation of peroxyacetic acid. At acidic pH, the half-life of peroxyacetic acid is *ca.* 7-12 days; at neutral or alkaline pH, the half-life is ≤1 day. In seawater, the half-life is expected to be even more rapid (<1 hour). Most studies were performed with levels of peroxyacetic acid which would be detrimental to the aquatic organisms; however, in lower environmental concentrations from normal use of peroxyacetic acid, the biotic degradation by algae and microorganisms could significantly increase the rate of degradation. Peroxyacetic acid released in the environment will partition almost exclusively (>99%) to the water compartment. Only a minor portion (<1%) will remain in the atmosphere, where it is rapidly degraded (half-life of 22 minutes).

2. Photodegradation in Water (OPP Guideline No. 161-2; R2025084, Memorandum, November 13, 2000; European Union Risk Assessment, Hydrogen Peroxide, Volume 38;)

A 90% hydrogen peroxide sample without inhibitors was irradiated with 100 W at 320-380 nm UV from a mercury lamp emitting 2.2 W of radiation. The half-life of the 90% hydrogen peroxide sample was estimated to be 200 hours (8.3 days) based on the observed 0.25%/hr decomposition rate. This rate is 70 times greater than in the absence of radiation. For dilute to moderately concentrated solutions of hydrogen peroxide (up to 0.20M) at a moderate intensity of absorbed radiation, the rate of photolytic decomposition is directly related to the concentration of the hydrogen peroxide and inversely related to the square root of the intensity of the radiation. Several photolytic decomposition reactions have been identified. Hydrogen

peroxide degrades to two OH free radicals, while peroxyacetic acid degrades to acetic acid and hydrogen peroxide.. Direct photolysis in water of hydrogen peroxide is not expected to be an important degradation process.

No photodegradation in water information was reported for peroxyacetic acid.

3. Photodegradation in Air (OPP Guideline No. 161-4; European Union Risk Assessment, Hydrogen Peroxide, Volume 38; R2025088, Hydrogen Peroxide RED, November 13, 1993, EPA 738-R-93-030; Peracetic Acid and its Equilibrium Solutions, European Centre for Ecotoxicolgy and Toxicology of Chemicals, JACC No. 40, Brussels, January 2001)

The average degradation half-life for hydrogen peroxide in the atmosphere (the average from the different atmospheric conditions) is 24 hours. The direct photolysis degradation of hydrogen peroxide to generate two hydroxyl radicals occurs with a half-life of 2.14 days. It is a slow and minor process which does not occur with exposure to light at >380 nm wavelength. However, this direct photolysis degradation is estimated to form 10% of the total hydroxyl radical daytime concentration. The major route of hydrogen peroxide degradation in air is expected to be by indirect photolysis which is the reaction of hydrogen peroxide with hydroxyl radical to produce water and a hydroperoxide radical. Daytime values of hydrogen peroxide were seen to exceed nighttime values by 26% in gas-phase, cloud and rainwater measurements at a high-elevation site (1,689 m). The half-lives of hydrogen peroxide in polluted urban air are measured as a few hours (not further specified). The overall photolysis rate has been difficult to quantify, but one study at the high-elevation site (1,689 m) showed that the *ca.* 25% of hydrogen peroxide decomposed in unpolluted air at nighttime during 8-10 hours (half-life extrapolated to 16-20 hours). For that study it was assumed that the nighttime production rate of hydrogen peroxide is low or negligible.

In the presence of air, peroxyacetic acid degrades to acetic acid, which then degrades to carbon dioxide and water. Peroxyacetic acid released in the environment will partition almost exclusively (>99%) to the water compartment. Only a minor portion (<1%) will remain in the atmosphere, where it is rapidly degraded (half-life of 22 minutes).

4. Aerobic Soil Metabolism (OPP Guideline No. 162-1; European Union Risk Assessment, Hydrogen Peroxide, Volume 38; Peracetic Acid and its Equilibrium Solutions, European Centre for Ecotoxicology and Toxicology of Chemicals, JACC No. 40, Brussels, January 2001; R2025084, Memorandum, November 13, 2000; Marine Environmental Protection Committee, 54th Session, February 28, 2006, MEPC 54/2/12)

Hydrogen peroxide was added to sterilized and nonsterilized ground water/soil samples. Half-lives were *ca.* 1.4 hours for the diluted nonsterilized samples, *ca.* 7 hours for the concentrated nonsterilized samples (estimated by extrapolation) and non-detectable for the sterilized samples. The conclusion of the study was that the rate of decomposition of hydrogen peroxide was highly dependent on the presence of microbes. The biodegradation/DT50 of hydrogen peroxide is 21 hours to 5 days (ready biodegradation was not performed). Hydrogen peroxide degrades rapidly in soil due to the high concentrations of catalytic materials, such as transition metals, enzymes, easily oxidized/reduced organic substances and living microbes. Observed half-lives of hydrogen peroxide vary from 15 hours in soil without microbiological activity and few minerals to several minutes in soils with 10^8-10^9 cells/g total solids and minerals like iron and manganese. The average half-life is estimated as 12 hours.

The ready biodegradation and biodegradation of peroxyacetic acid was >70% and rapid. In soil, diluted peroxyacetic acid is rapidly and easily degraded via hydrolysis and instantaneously degraded via transition metal decomposition. At low concentrations, biodegradation could contribute to the degradation in soils.

5. Anaerobic Soil Metabolism (OPP Guideline No. 162-1; R2025084, Memorandum, November 13, 2000)

A 0.1% hydrogen peroxide solution was added to nine petroleum-contaminated top soils from the following locations: Concord, Nebraska; Farmington, Minnesota; Genoa, Ohio; Rochelle (high pH), Illinois; Sandusky, Ohio; Stine, Delaware; Rochelle (low pH), Illinois; Waterville, Ohio; and Woodville, Ohio. All of the top soils contained organic matter 5-6% and a high concentration of microorganisms. Hydrogen peroxide decomposed from 42%-83% in six hours with varied rates of decomposition. The decomposition was not dependent on soil pH, microbial population, the nature or texture of soil. The organic carbon content of the soil was the critical factor in determining the rate of decomposition, but this was weakly correlated in the study. Similar tests were performed with subsoil samples from six states. The rates of decomposition were much more varied for the subsoils: 100% decomposition was observed in an hour for soils with high microorganism content and up to 10% decomposition was observed in soils with low microorganism content.

No information on the anaerobic soil metabolism of peroxyacetic acid was reported.

6. Anaerobic Aquatic Metabolism (OPP Guideline No. 162-3)

No data have been submitted to the Agency.

7. Aerobic Aquatic Metabolism (OPP Guideline No. 162-4; European Union Risk Assessment, Hydrogen Peroxide, Volume 38; Peracetic Acid and its Equilibrium Solutions, European Centre for Ecotoxicolgy and Toxicology of Chemicals, JACC No. 40, Brussels, January 2001; R2025084, Memorandum, November 13, 2000)

The degradation of hydrogen peroxide was studied in sterilized and unsterilized water samples from the Beaver Dam Lake, Canada and Bar-H Lake, Canada. For the unsterilized samples, the half-lives for hydrogen peroxide were 5.3 hours and 1.1 hours in the Beaver Dam Lake and Bar-H Lake waters, respectively. For the sterilized samples, the half-lives for hydrogen peroxide were over 80 hours for both systems. Hydrogen peroxide is degraded in biologically active systems due to the fact that aerobic bacteria product catalase enzymes that converts hydrogen peroxide to water and oxygen. The degradation rate is dependent on the microbial population size. The half-life is between minutes and hours in municipal wastewater ($>10^6$ cells/mL), only a few seconds in sludge (10^8-10^{10} cells/mL) and from hours to a few days in natural waters ($\leq 10^3$ cells/mL). The degradation of hydrogen peroxide is assumed to follow first-order kinetics at low concentrations and non-first-order kinetics with a slower rate at higher concentrations (≥100 µg). Hydrogen peroxide is expected to degrade rapidly in sediment due to the normal high concentrations of catalytic abiotic and biotic material.

Four studies were performed with natural waters. In the first study, the summer time degradation rate of hydrogen peroxide was studied at 3.4 µg/L (natural concentration) in lake water (pH 7.2, DOC 6 mg/L) from Jacks Lake, Ontario (site location 44° 41' N, 78° 02" W). The dark decay of hydrogen peroxide followed first-order kinetics with half-lives of 7.8 hours (unfiltered lake water), 8.6 hours (filtered, 5 µm), 31 hours (filtered, 1 µm), and >24 hours (filtered, 0.45 µm). Based on these results, it was concluded that the picoplancton (defined as 0.2-2 µm) contains the major portion of the biological agent responsible for hydrogen peroxide degradation. In the second study, hydrogen peroxide decay in Lake Ontario was measured as 14.7-21.6 hours for water samples at depths and initial concentrations of 0m with 112 nM and 10m with 44 nM. When the samples were filtered through 0.45 µm membrane filters, no degradation of hydrogen peroxide was observed after 7 hours. Based on these results, it was concluded that bacteria and/or algae are responsible for the degradation of hydrogen peroxide. In the third study, the degradation of hydrogen peroxide was measured at 90-150 nmol/L (3-5 µg/L) in seawater at room temperature in the dark. The measured degradation rate was 3.8 nmol/L/h (0.13 µg/L) with hydrogen peroxide concentrations reaching zero after 23-39 hours. In the fourth study, the degradation of hydrogen peroxide was studied in water from the River Saone at initial concentrations of 100, 250, 500, 1000, and 10000 mg/L. The half-lives were first-order and measured as 20.1 days, 15.2 ± 2.5 days (higher values for filtered samples), 8.2 ± 2 days (higher values for filtered samples), 8.1 days and 2.5 days for the initial concentrations of 100, 250, 500, 1000, and 10000 mg/L, respectively. Based on these results, it was concluded that the filtering of particles >0.2 µm had little effect and the degradation of hydrogen peroxide was slower at initial concentrations <500 mg/L. Also, studies, which were similar to this third study, but using de-ionized water containing 500 mg/L of hydrogen peroxide, showed an increase in concentration which was probably due to light reactions. Hydrogen peroxide is considered "readily biodegradable" based on the results of these four studies. In the natural environment, many more catalase active microbes are present versus the concentration of

hydrogen peroxide; however, if the concentration of hydrogen peroxide increases substantially, then the degradation rates will be slower because of the toxicity of hydrogen peroxide.

Peroxyacetic acid will not partition into sediment, suspended matter or biota. In the OECD Closed Bottle Test, peroxyacetic acid (initial concentration of 2-5 mg/L) was not readily biodegradable. However, when adapted bacteria derived from a Zahn-Wellens Test (unreported amount) were included in the same test procedure, peroxyacetic acid was highly biodegradable (>79%). The hydrolysis products of peroxyacetic acid (acetic acid and hydrogen peroxide) are readily biodegradable.

8. Adsorption/Desorption (OPP Guideline No. 163-1; Peracetic Acid and its Equilibrium Solutions, European Centre for Ecotoxicology and Toxicology of Chemicals, JACC No. 40, Brussels, January 2001; R2025084, Memorandum, November 13, 2000; Marine Environmental Protection Committee, 54th Session, February 28, 2006, MEPC 54/2/12)

It was proposed that since hydrogen peroxide is similar to water in its physical characteristics, hydrogen peroxide is mobile but unstable. Also, due to its high polarity, it was proposed that hydrogen peroxide is unlikely to bind with soils. The sorption of hydrogen peroxide and peroxyacetic acid are very low.

Peroxyacetic acid will not partition into sediment, suspended matter or biota. The degradation of peroxyacetic acid (1.1% solution) was studied on dried soil (not specified), then extracted using demineralized water. After *ca.* 20 minutes, 99.2% of the peroxyacetic acid had degraded.

a. Soil Column Leaching (OPP Guideline No. 163-1; Peracetic Acid and its Equilibrium Solutions, European Centre for Ecotoxicology and Toxicology of Chemicals, JACC No. 40, Brussels, January 2001)

The soil column leaching of peroxyacetic acid was studied by applying 1 mL of a *ca.* 2000 mg/L peroxyacetic acid solution to soil column (soil not specified). At 5 minutes postapplication, each column was washed with 100 mL of demineralized water. At a soil depth of 25 mm, 21.5% of the peroxyacetic acid was recovered, along with 42% of hydrogen peroxide. The recovery of peroxyacetic acid decreased to 3.2% at 50 mm to 0.3% at 100 mm to <0.2% at 150 mm. At 150 mm, 10% of hydrogen peroxide was present. At 10 minutes postapplication, the column washing yielded only 8.7% recovered peroxyacetic acid at the 25-mm depth.

No information on the soil column leaching of hydrogen peroxide was reported.

9. Field dissipation study on soil (OPP Guideline No. 164-1)

No data have been submitted to the Agency.

10. Aquatic field dissipation study (OPP Guideline No. 164-2)

No data have been submitted to the Agency.

11. Long-term study on accumulation on soil (OPP Guideline No. 164-5)

No data have been submitted to the Agency.

12. Bioaccumulation in Fish (OPP Guideline No. 165-4; Peracetic Acid and its Equilibrium Solutions, European Centre for Ecotoxicology and Toxicology of Chemicals, JACC No. 40, Brussels, January 2001; Marine Environmental Protection Committee, 53rd Session, April 15, 2005, MEPC 53/2/12; Marine Environmental Protection Committee, 54th Session, February 28, 2006, MEPC 54/2/12)

There is no bioconcentration of hydrogen peroxide and peroxyacetic acid. Hydrogen peroxide and peroxyacetic acid are not considered to bioaccumulate due to their low octanol-water partition coefficients (0.30 for peroxyacetic acid and 0.40 for hydrogen peroxide).

Peroxyacetic acid and its transformation products, hydrogen peroxide and acetic acid, are of low molecular weight, high water solubility, low fat solubility and have no tendency to bioaccumulate.

13. Accumulation Studies in Aquatic Non-target Organisms (OPP Guideline No. 165-5; MRID No. 426862-03 (R2054586))

This study has not been reviewed by the Agency.

The release rate of hydrogen peroxide from NO FOUL-WB paint was studied in synthetic seawater at 24 ± 1°C. The NO FOUL-WB paint was stored at room temperature for 1 to 3 months prior to testing in typical storage conditions (sealed in a retail container and held at 20-30°C). The synthetic seawater was prepared in accordance with ASTM D 1141 (Section 6). Test cylinders, which were polycarbonate pipes (*ca.* 6.4 cm x 12.5 cm), were coated with a 10-cm band circumference of antifouling paint, which produced *ca.* 200 cm^2 of paint film exposed surface and a minimum dry film thickness of 100 µm. The paint was allowed to dry for 7 + 1 days at 23-27°C. The bottom 1-2 cm of the test cylinder was not coated with paint and sealed with a polycarbonate disc via polycarbonate cement. The test cylinders were long enough to prevent seawater from entering the test cylinder. The test container was a polycarbonate container (2-L capacity) with three polycarbonate rods (*ca.* 6 mm), which served as baffles, and fitted with a polycarbonate cover, which had a polyurethane line through it for aerating the synthetic seawater with air from an air pump. The test container was filled with 1 L of the synthetic seawater and the test cylinder. At 42, 66, 100, and 190 hours after addition of the test cylinder, one 25-mL aliquot of the test seawater was collected and analyzed for hydrogen peroxide immediately or stored at 4°C prior to analysis. The hydrogen peroxide concentration was determined by potassium permanganate titration of triplicate 5-mL samples of each 25-mL

aliquot. The samples were acidified to pH 4 using drops of 10% sulfuric acid, then titrated to endpoint using 0.002N $KMnO_4$. A series of hydrogen peroxide standards of 3, 5 and 7 ppm were prepared using a 3.3 mg/mL hydrogen peroxide stock solution with synthetic seawater. These standards were used to standardize the potassium permanganate titration.

At 42, 66, 100 and 190 hours after addition of the test cylinder, the hydrogen peroxide concentrations were 0.5, 0.8, 1.3, and 1.2 mg/L, respectively. These levels corresponded to average release rates of 0.0015, 0.0014, 0.0015, and 0.0008 mg/cm^2/day for 42, 66, 100, and 190 hours after addition of the test cylinder, respectively. So, the average release rate was constant for the first 100 hours after addition of the test cylinder, and then declined by approximately half at 190 hours addition of the test cylinder. The average overall release rate was 0.0013 mg/cm^2/day.

Field testing for aquatic organisms was not reported for peroxyacetic acid.

14. Photolysis Rate on Surface of Soil (OPP Guideline No. 161-3)

No data have been submitted to the Agency.

15. Ready Biodegradability (CO_2 Evolution Test) (OECD Procedure 301 B)

No data have been submitted to the Agency.

16. Aqueous Availability (Leachability) (American Wood-Preservers' Association Standard Method E11-97 "Standard Method for Determining the Leachability of Wood Preservatives)

No data have been submitted to the Agency.

B. Published Literature

Several articles discuss the fate of hydrogen peroxide in conjunction with the use of peroxy compounds as wastewater treatment disinfectants utilized in Mexico (Diaz-Avelar et al., 2004), the United Kingdom (Booth and Lester, 1995), Italy (Lubello et al., 2004), and Canada (Wagner et al., 2002); hydrogen peroxides reactivity with transition metals (e.g. cadmium, copper, iron, phosphorous; Chaco-Rivero and Suidan, 2006; Liao et al., 2005; Mercier et al., 2002; Moffett and Zika, 1987; Yoshizaki and Tomida, 2000) and other chemicals (e.g. creosote, benzene, trichloroethylene, BTX, cyanide, PAHs, and phenols; Flotron et al., 2005; Fraser and Sims, 1984; Lodaya et al., 1991), environmental occurrence in air (Sakugawa et al., 1990, 1992; Gunz and Hoffman, 1990; Heikes et al., 1987; Claiborn and Aneja, 1993; Hwang and Dasgupta, 1985; Yoshizumi et al., 1984) or environmental occurrence aqueous media (Sakugawa et al., 1990, 1992; Gunz and Hoffman, 1990; Heikes et al., 1991; Jacob et al., 1990; Kieber and Helz, 1995; Yoshizumi et al., 1983; Moffett and Zika, 1987). Hydrogen peroxide is a naturally occurring chemical; therefore, occurrence data does not suggest anthropogenic sources. H_2O_2

concentrations are influenced by concentrations of primary air pollutants, such as NOx, volatile organic compounds (VOCs), and CO, and increase with rising air temperature, solar intensity, and water vapor concentrations (Sakugawa et al., 1990, 1992).

Atmospheric Occurrence and Fate of Hydrogen Peroxide

Hydroxyl radical, ozone, and hydrogen peroxide are the primary endogenous oxidants in the atmosphere. Photochemical processes are mainly responsible for atmospheric H_2O_2 concentrations and aqueous-phase reactions, and are the dominant pathways for atmospheric consumption of H_2O_2 (Sakugawa et al., 1990, 1992). Reported concentrations of gas phase H_2O_2 ranged from 0.01-7.0 ppb in Los Angeles (Sakugawa et al., 1992). Field measurements of atmospheric H_2O_2 from various locations in North America, Europe, Brazil, and Japan revealed concentrations of 0.001-5 ppb (Gunz and Hoffman, 1990). Diurnal variation is also seen with gaseous H_2O_2 concentrations, with peaks between 2-5 PM (Sakugawa et al., 1992). However, measurements taken at high elevation sites, such as the San Bernadino mountains and Mauna Loa, displayed peak concentrations at night, which may be attributed to long-range transport of H_2O_2 by vertical/horizontal movement of air masses at night, when higher elevations are exposed to free troposphere (Heikes et al, 1987; Sakugawa et al., 1990,1992). Tropospheric concentrations have been measured from 0.5-5 ppb (Claiborn and Aneja, 1993). H_2O_2 concentrations are influenced by concentrations of primary air pollutants, such as NOx, volatile organic compounds (VOCs), and CO, and increase with rising air temperature, solar intensity, and water vapor concentrations (Sakugawa et al., 1990, 1992).

Concentrations of H_2O_2 in cloudwater have been reported at 247 μM (Gunz and Hoffman, 1990), with rainwater concentrations of 10 nM-100 μM (Sakugawa et al., 1990). Cloud H_2O_2 is removed from the atmosphere by wet deposition, including rain, fog, and mist droplet scavenging (Sakugawa et al., 1990, 1992), and dry deposition onto surfaces, including foliage uptake by trees (Sakugawa et al, 1990,1992; Claiborn and Aneja, 1993). Wet deposition of H_2O_2 has been found at 0.43 kg/hayr, assuming an annual H_2O_2 concentration of 4.4 μM in rainwater and 290 millimeters of rain annually (Sakugawa et al., 1992). Dry deposition rates are about six times that of wet deposition (Sakugawa et al., 1992). H_2O_2 has a fairly high Henry's law constant in comparison to other oxidants (e.g., O_3, O_2, NO_2), with a value around 10^5 M/atm (Claiborn and Aneja, 1993; Gunz and Hoffman, 1990; Hwang and Dasgupta, 1985; Yoshizumi et al., 1984).

Aqueous Occurrence and Fate of Hydrogen Peroxide

The main precursors of H_2O_2 are hydroxyl and hydroperoxyl radicals from the reaction of ozone with water (Gunz and Hoffman, 1990; Hwang and Dasgupta, 1985). Generally, H_2O_2 is unreactive with organic compounds, but this reactivity is increased in the presence of transition metals (e.g. iron, copper, chromium), due to the formation of free-radical intermediates (Moffett and Zika, 1987). Seasonal and diurnal variations have been seen in H_2O_2 concentrations throughout the world (Gunz and Hoffman, 1990; Heikes et al., 1991; Jacob et al., 1990; Kieber and Helz, 1995; Sakugawa et al., 1992; Yoshizumi et al., 1983). Much of the H_2O_2 concentrations in natural waters are attributed to a photochemical formation of the chemical

(Cooper and Zika, 1983, 1988; Draper and Crosby, 1983; Johnson et al., 1989; Kieber and Helz, 1995; Moffett and Zika, 1987; Sakugawa et al., 1992; Yoshizumi et al., 1983). In addition, the photodecomposition of solutes, such as tryptophan, tyrosine, and humic substance continuously produce H_2O_2 in sunlight (Draper and Crosby, 1983). It is thought that the superoxide anion is also a precursor in the sunlight-induced production of H_2O_2 in natural waters and that both H_2O_2 and O_2- are important in the maintenance of the redox potential of natural waters high in organic matter (Cooper and Zika, 1983; Johnson et al., 1989).

Summertime concentrations have been found mid-day in southeastern U.S. surface and groundwaters from 3- 67 E^{-6} mol/liter H_2O_2 and 6.5E^{-8}-1.00 E^{-5}, respectively, and 800 nM in Ontario (Cooper and Zika, 1983, Cooper and Lean, 1989). These concentrations were also correlated to the amount of TOC in the water samples; with increasing hydrogen peroxide as TOC rises in both types of water (Cooper and Zika, 1983; Wagner et al, 2002). In the mid-Atlantic, February-September concentrations ranged from 11-350 nM in estuarine waters (Kieber and Helz, 1995). In Canada, lake water hydrogen peroxide formation rates ranged from 81-2,120 nM/hour (Scully et al, 1996). The vertical variation of the rates of formation of hydrogen peroxide depends on UV light penetration, with dark decay rates dependant upon the concentration of algae and bacteria in the water (Cooper et al., 1988; Herrmann and Herrmann, 1994; Johnson et al, 1989). Picoplankton may be partially responsible for the biological component of hydrogen peroxide decay (Cooper et al., 1989). In the Mediterranean, hydrogen peroxide formation rates ranged from 0-3.6 µmol/l-h (Herrmann and Herrmann, 1994), with the higher rates near the surface of the water (Herrmann and Herrmann, 1994; Johnson et al., 1989).

H_2O_2 levels are also thought to decrease slightly during rain storms (Cooper et al., 1989), as well as with increasing altitude, due to lower humidity (Jacob et al., 1990). Summer time measurements from rainwater in Tokyo revealed H_2O_2 levels of approximately 1000 µg/L (Yoshizumi et al, 1983). In tropical regions, such as Brazil, hydrogen peroxide concentrations in rainwater ranged from 0.1-6.8 ppbv (Jacob et al, 1990).

Aqueous fluorescence and chemiluminescence are the most common methods (Heikes et al., 1991; Jacob et al., 1990; Sakugawa et al., 1992) used to measure H_2O_2 in natural waters and the atmosphere, with the chemiluminescence method about two orders of magnitude more sensitive than the fluorescence method (Heikes et al., 1991).

Terrestrial Occurrence and Fate of Hydrogen Peroxide

Hydrogen peroxide has been used to oxidize and recover various contaminants in soils, including chromium, creosote, trichloroethylene (TCE), and polycyclic aromatic hydrocarbons (PAHs) (Atagana, 2003; Baciocchi et al., 2004; Bermond and Benzineb, 1991; Conte et al., 2001; Rock et al., 2001). In chromium-enriched soils, hydrogen peroxide additions produce rapid, dose-dependent increases in soluble Cr(VI) in the uppermost, peaty horizon (Rock et al., 2001). The half-life of hydrogen peroxide in chromium-enriched soils is less than 48 hours, but between can vary between 8 minutes to 153 hours in TCE-contaminated soils, depending on the TOC content of the soils, the levels of metal oxides in the soils, and whether or not a stabilizer is used in conjunction with hydrogen peroxide (Baciocchi et al., 2004; Rock et al., 2001). The

ability for hydrogen peroxide to readsorb heavy metals in sewage treated soils depends on the pH of the extractant (Bermond and Benzineb, 1991).

Anaerobic Degradation

Hydrogen peroxide is commonly used for municipal, industrial, and pharmaceutical waste degradation (Chaco-Rivero and Suidan, 2006; Fraser and Sims, 1984; Friedman, 1970; Glaze, 1991; Hoffmann, 1977; Kwon et al., 2004; Pamukoglu and Kargi, 2006; Tekin et al., 2006; U.S EPA, 1973; Wong et al., 2006) It is used to treat odorous pollutants in sewage and sludge, landfill leachates, industrial effluents, such as hydrogen sulfide, by oxidizing H_2S and the hydrosulfide ion into sulfur and sulfate in aqueous solution (Charron et al., 2004; Costle, 1977; Fraser and Sims, 1984; Hoffmann, 1977; McConkey et al., 2002; Shepard and Hobbs, 1973). H_2O_2 may also be used in combination with ozone or UV for disinfection of wastewater and sludge (Glaze, 1991; Kosaka et al., 2004; Li, 1996) or in conjunction with aerating treatments (Friedman, 1970; U.S. EPA, 1973) to oxidize contaminants.

H_2O_2 photolysis has proven to be useful for the destruction of hazardous organic substances in water and sludge, including benzene, BTX, cyanide, PAHs, and phenols (Flotron, 2005; Fraser and Sims, 1984; Lodaya et al., 1991), with oxidation products generally low molecular weight oxygenated compounds that are easily biodegradable (Lipczynska-Kochany, 1993). It has also been used to remove heavy metals from sewage sludge and wastewater, such as cadmium, copper, iron, phosphorous (Chaco-Rivero and Suidan, 2006; Liao et al., 2005; Mercier et al., 2002; Moffett and Zika, 1987; Yoshizaki and Tomida, 2000).

Through advanced oxidation methods, such as Fenton's oxidation, when H_2O_2 is combined with ferrous ions or another ferrous complex at a low enough pH, Fe^{2+} catalyzes the decomposition of H_2O_2 into Fe^{3+} and the hydroxyl radical, which has an extremely high oxidation potential and can decompose organic compounds in a very short time (Aggarwal, 1991; Baciocchi et al., 2004; Flotron et al., 2005; Fraser and Sims 1984; Kotsou et al., 2004; Kwon et al., 2004; Lau et al., 2002; Neyens et al., 2003; Ntampegliotis et al., 2006; Rock et al., 2001; Tekin et al., 2006). Catalase is one of the strongest catalysts in decomposing peroxide (Aggarwal, 1991; Lodaya et al., 1991; Patel et al., 2005).

Peroxyacetic Acid Published Literature

The vapor pressure of peroxyacetic acid with hydrogen peroxide is high and expected to be in vapor phase at ambient conditions. Treatment of final sewage effluent with 6 or 30 mg/L PAA rapidly produces monosubstituted chlorophenols (2-, 3-, and 4-chlorophenol), with by-product formation independent of temperature or reaction time, but rather dependent on pH of the effluent, PAA dosage, chlorine content, and concentration of organic and mineral constituents in the final effluent (Booth and Lester, 1995). The concentration never exceeded 100 ng/L. Electrophilic substitution was not the primary halogenation mechanism because all three monosubstituted chlorophenol isomers were present in treated sewage effluent. Based on the byproducts PAA is considered to promote the generation of halogenated products through a reaction of PAA-induced free chlorine radicals and organic matter present in sewage effluents.

Furthermore, PAA treatment of phenol and chloride enriched analytical grade water demonstrated that halogenated phenols are not generated as a consequences of PAA electrochemically oxidizing chloride to hypochlorous acid and subsequently forming organochlorine derivatives (Booth and Lester, 1995).

PAA is a powerful oxidizer of bromide to hypobromous acid and can form brominated organics (2- and 4-bromophenol) (Booth and Lester, 1995; Wagner et al., 2002), but it cannot oxidize chloride to hypochlorous acid and subsequently chlorinated organics (Booth and Lester, 1995). When the H_2O_2/O_3 mole ratio of injection was above 0.5 and the dissolved ozone concentration was below 0.1 mg/L, bromate ion formation was controlled, and treatment purposes such as the reduction of estrogenic activity or organic matter were completed (Kim et al., 2007). PAA treatment also can also generate free chlorine and bromine radicals (Booth and Lester, 1995). An addition of 5 mg/L PAA to wastewater increases the amount of total organic carbon (TOC) by a factor of 1.5, and 10 mg/L triples the TOC level (Wagner et al., 2002; Profazier et al., 1997). When used as a disinfectant, PAA decomposes to hydrogen peroxide in an initially rapid process, but measurable residuals can last up to two hours (Wagner et al., 2002).

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Figure 1: Structure of Hydrogen peroxide (PC code 000595)

Hydrogen peroxide

IUPAC Name: Hydrogen peroxide.
CAS Name: Not reported.
CAS Number: 7722-84-1.
SMILES String:

Figure 2: Structure of Peroxyacetic acid (PC code 063201)

Peroxyacetic acid

IUPAC Name: Peroxyethanoic acid.
CAS Name: Peroxyacetic acid.
CAS Number: 79-21-0.
SMILES String: