



THE DOW CHEMICAL COMPANY

1 45725
CONTAINS NO CBI

January 20, 1989

2030 WILLARD H. DOW CENTER
MIDLAND, MICHIGAN 48674

EPA-OTS



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8918-0189-0761 Sup.
PROCESS-890000006
89-890000079

Document Processing Center (TS-790)
Office of Toxic Substances
Environmental Protection Agency
401 M. Street, S.W.
Washington, DC 20460

ATTN: 8(e) Coordinator
8EHQ-1088-0761

Dear Sir/Madam:

Gelman Sciences has recently submitted information to the Environmental Protection Agency (EPA) on 1,4 dioxane pursuant to section 8(e) of the Toxic Substances Control Act (TSCA). In this letter, The Dow Chemical Company (Dow) is providing additional information concerning 1,4 dioxane. It should be noted, however, that we believe that none of this information constitutes section 8(e) information and that we are submitting it for your information.

Attached please find the following:

- ✓(1) a table of analyses of polyethylene glycol for 1,4 dioxane.
- ✓(2) a letter from Union Carbide on 1,4 dioxane in their polyethylene glycol.
- ✓(3) two letters written by Charles Gelman to Dr. Winifred Oyen, dated October 6, 1988 and October 17, 1988.
- ✓(4) A reprint of a published study entitled "Removal of 1,4-Dioxane From Wastewater" and a copy of the underlying internal report.
- ✓(5) A reprint of a published study entitled "Pharmacokinetics of 1,4-Dioxane in Humans."

The polyethylene glycol analyses in attachment 1 were done as part of an analytical development project using a cryogenic-focusing, headspace, capillary gas chromatographic method using flow programming.

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January 20, 1989
Page 2

We routinely analyze production lots of polyethylene glycol prior to shipment for 1,4-dioxane using a different gas chromatographic method. The 1,4-dioxane level is less than 3 ppm.

We have not identified any analyses by Dow of ethylene glycol or diethylene glycol products for 1,4 dioxane. However, we are attempting to develop an analytical method to determine what level of 1,4 dioxane, if any, is in these chemicals.

We trust that the information we are submitting will be useful to EPA.

Sincerely,



J. E. LeBeau, Director
Health & Environmental Sciences
1803 Building

dhr

attachments

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TABLE 2
Results of PCB Analyses

PEG-1450 ANALYSES

Lot #	Ethylene Oxide	1,4-Dioxane
	<u>Conc. ng/g</u>	<u>Conc. ng/g</u>
TB881003KIA	28	657**
TB880808	N.D.*	80
TB840824	688	811
TB881006KIA	8	690
TB841108	8	200
TB880903 (powdered)	N.D.	N.D.
TB880903 (solid)	N.D.	121
BASF WWH	N.D.	N.D.
ESF WPDH	N.D.	N.D.

PEG-3350 ANALYSES

Lot #	Ethylene Oxide	1,4-Dioxane
	<u>Conc. ng/g</u>	<u>Conc. ng/g</u>
TB881209A1H	N.D.	189
TB880819A1H	N.D.	25
TB880819A1H	N.D.	147
TB881008A1H	N.D.	22
TB881022A1H	N.D.	71

* N.D. = Non detectable. Limit of detection for EO and dioxane is 0.1 ng/g and 4.8 ng/g, respectively.

** Assuming linearity above 18 ng/g EO and 208 ng/g 1,4-dioxane and below 4 ng/g EO and 52 ng/g 1,4-dioxane.

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work group
Ref to



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UNION CARBIDE CORPORATION 39 OLD RIDGEBURY ROAD, DANBURY, CT 06817-0001
INDUSTRIAL CHEMICALS DIVISION

December, 1988

Dear Union Carbide Customer,

The purpose of this letter is to advise you that our CARBOWAX® Polyethylene Glycols above the molecular weight of 200 do not contain toxic chemicals in quantities subject to the reporting requirements of Section 313 of Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA) and 40 CFR Part 372. However, our CARBOWAX® Polyethylene Glycols do contain trace amounts of materials which are included on the State of California's list of carcinogens and reproductive toxicants under the provisions of the Safe Drinking Water and Toxic Enforcement Act of 1986, also known as Proposition 65.

The following chart outlines the CARBOWAX® Polyethylene Glycols manufactured by Union Carbide and the typical maximum levels of the trace "Proposition 65" materials contained within each product.

	TYPICAL MAXIMUM LEVELS (PPM)			
	ETHYLENE OXIDE	DIOXANE	FORMALDEHYDE	ACETALDEHYDE
CARBOWAX(R) Methoxy Polyethylene Glycols 350 to 5000	5	5	4	6
CARBOWAX(R) Polyethylene Glycols 300 to 8000	5	5	4	6
CARBOWAX(R) SENTRY(R) Polyethylene Glycols 300 to 8000	5	5	4	6
Polyethylene Glycol Compound 20M	5	5	4	6
CARBOWAX(R) TPEG 990	5	5	4	6

Please be aware that Ethylene Oxide has been listed by the State of California as a carcinogen and reproductive toxicant. Dioxane, Formaldehyde, and Acetaldehyde have been listed as carcinogens.

We are in the process of updating our Material Safety Data Sheets (MSDSs) to reflect this (and other) right-to-know information, and plan to have these available and distributed within the first quarter of 1989. In the meantime, please add a copy of this letter to each of the MSDSs for those products listed which you have received from us.

Should you have any questions on this information we would be happy to address them. Thank you for your continued business.

Very truly yours,
Union Carbide Corporation
Industrial Chemicals Division

Patricia L. Cody
Product Safety Manager

PLC/cw
22380
MS-0009

600 South Wagner Road
Ann Arbor, MI 48106 U.S.A.
Telex: 810-223-6036
Fax: 313-761-1208
(313) 665-0651

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MIDLAND COUNTY HEALTH DEPT.
MIDLAND, MI



October 6, 1988

Dr. Winifred A. Oyen
Director
Midland Co. Health Dept.
125 W. Main St.
Midland, MI 48640

Dear Dr. Oyen:

We sent you information about 1,4-dioxane contamination at rest stops. Since the date of that communication, we have discovered that 3,000 parts per billion of 1,4-dioxane is present in aircraft deicing fluids. In scanning through the Act 307 list of the DNR, we find that a number of airports and military bases around the state have been cited by the DNR as causing groundwater contamination. With the additional knowledge that the ethylene glycol contains 1,4-dioxane, the problem may be more serious than originally anticipated.

We suggest you contact your state health department to immediately start taking well samples of any wells surrounding sources of known ethylene glycol contamination to determine whether 1,4-dioxane is present. It would also be appropriate for you to alert the DNR office within your area to make them aware of this situation and alert them to contamination at airports, military bases and at rest stops. We have not alerted local DNR officials about the rest stop situation.

Sincerely yours,

A handwritten signature in cursive script that reads "Charles Gelman".

Charles Gelman
Chairman and
Chief Executive Officer

CG/dr

/0546G(1)

600 South Wagner Road
Ann Arbor, MI 48106 U.S.A.
Telex: 810-223-6036
Fax: 313-761-1208
(313) 665-0651

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OCT 19 1988

MIDLAND COUNTY HEALTH DEPT.
MIDLAND, MI

 **Gelman Sciences**

October 17, 1988

Dr. Winifred A. Oyen
Director
Midland Co. Health Dept.
125 W. Main St.
Midland, MI 48640

Dear Dr. Oyen:

We recently discovered that fresh ethylene glycol in auto radiators and deicing fluids contained as much as 20,000 parts per billion of 1,4-dioxane.

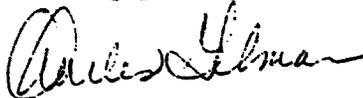
One potential situation of public health significance has been brought to our attention. At the end of the summer season, people who own summer cottages or lakeside cottages usually fill their pipelines and toilet systems with ethylene glycol. 1,4-dioxane from these summer cottages would go directly into septic fields and then into the drinking water supply.

Presently, the Michigan Department of Health sets a groundwater risk appraisal level of one part per billion of 1,4-dioxane.

We believe the same problem exists with state, county and local parks. RV vehicles and large boats follow the same practice.

You should inform your constituents of any public health risks from this practice.

Sincerely yours,



Charles Gelman
Chairman and
Chief Executive Officer

/0565G(/0566G)

Enclosures

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OCT 19 1988

ROBERT W. LE
County Health DE.
Rolf Hartung, Ph.D., D.A.B. JOZLAND, MI
Consultant in Environmental Toxicology
Professor of Environmental Toxicology
University of Michigan
3125 Fernwood Ave.
Ann Arbor, Michigan 48108-7155
(313) 971-9690

October 11, 1988

Michigan Department of Public Health
Lansing, Michigan

It is becoming evident that the chemical 1,4-dioxane is much more widely distributed in the environment than had previously been suspected. 1,4-Dioxane has been found to be a common contaminant of antifreeze fluids. 1,4-Dioxane moves readily into groundwater, and is not retarded significantly as the groundwater moves through various soils, so that it can spread readily from its sources of origin.

The assessment of potential risks is hampered by the fact that to date no maximum contaminant levels have been established for 1,4-dioxane by the U.S. EPA Office of Drinking Water, although a health advisory document exists. The Michigan Department of Public Health has also developed a very conservative risk assessment document.

In addition, an extensive Draft Health and Environmental Effects Assessment for 1,4-Dioxane (R. Hartung, Sept. 23, 1987) exists. That document has been widely circulated and has received extensive peer review. That document provides a variety of limiting concentrations for drinking water, using various methods which use a variety of assumptions, for the derivation of such values. Although 1,4-dioxane is carcinogenic to laboratory animals at extremely high dose levels, the available information strongly supports the existence of a threshold for toxic effects for this compound. The most sensitive effects found were non-cancer effects in liver and kidneys in lifetime exposures to rats, and a drinking water criterion was based on the absence of those effects, using a 100-fold safety factor. The resulting reference dose (RfD) was 0.096 mg/kg/day for a life time. The resulting drinking water limit was 3.36 mg/L, which could be rounded off to 3 mg/L.

To this date, this particular risk assessment is most strongly supported by the existing scientific data on 1,4-dioxane. The additional conservatisms used by the Michigan Department of Public Health appear to be founded largely on the desire to incorporate conservative risk management perspectives into the risk assessment process.

At this time it is becoming increasingly important to collect all of the environmental and health related information on 1,4-dioxane, assess it, expose the assessment to the broadest possible peer review, and then develop the appropriate management for 1,4-dioxane.

Sincerely,


Rolf Hartung

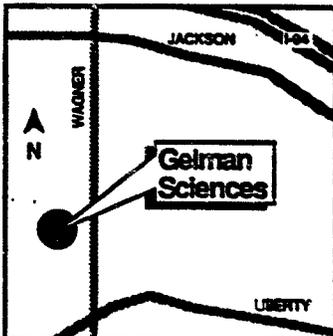
Gelman cites other dioxane sources

By PAUL JUDGE
NEWS BUSINESS REPORTER

□ Gelman sales up, C1

Gelman Sciences Inc., facing a court challenge to clean up soil and groundwater pollution around its Wagner Road plant, is claiming "the government and other individuals" may be polluting drinking water with the same chemical solvent the company is charged with releasing into the environment.

In a state hearing in Lansing Tuesday to consider changes to Michigan rules governing public water supply, a Gelman Sciences attorney claimed that the state has ignored the potential for groundwater contamination from puddles of antifreeze in the parking lots of rest areas along Michigan highways.



NEWS MAP

Robert Reichel, an assistant attorney general representing the state in its suit against Gelman, dismissed the company's statements as "a smoke screen and an attempt by Gelman to divert attention from the very significant, thoroughly documented contamination problem emanating from Gelman Sciences' facility."

The Department of Natural Resources has charged Gelman Sciences with polluting soil, surface water and groundwater near the company's plant on Wagner Road in Scio Township, just west of Ann Arbor.

The pollutant, a solvent called 1,4-dioxane, has been detected in more than 50 commercial and resi-

dential wells in Scio Township. The DNR is suing Gelman to restore the groundwater to its original purity.

The company and others, including Midland-based Dow Chemical Co., are also defendants in a separate civil lawsuit brought by homeowners seeking damages from the dioxane contamination.

In Tuesday's hearing, Gelman Sciences said the presence of dioxane is "statewide and of a much more extensive nature than originally assumed." The company's attorney called on the state to come up with "more realistic drinking water standards" that would classify dioxane as a less harmful pollutant.

The company claimed that research it has conducted as a result of the lawsuits shows that drinking water is tainted by dioxane from a variety of sources, including automotive coolant, de-icing fluid for airplanes, shampoo and cosmetics.

Specifically, Gelman officials released findings from samples of radiator boil-over pools it collected from the pavement in highway rest areas during August and September. According to a listing of "partial results" released by the company, the samples showed concentrations of dioxane in the puddles ranging from 2,300 parts per billion in the Clare area off US-27 to less than 10 parts per billion in the Ann Arbor area along I-94.

The state standard for safe levels of dioxane in drinking water is 2 parts per billion.

"This makes every service station, garage, parking lot and rest stop as well as homes in the state possible sources of 1,4-dioxane contamination," said Gelman Sciences' attorney Edward J. Levitt.

But Reichel, the state's leading attorney in its case against Gelman Sciences, said the claims by the company have no bearing on contamination around the plant site in Scio Township.

"I'm not aware of any data that attributes contamination near the Gelman Sciences' facility to some source of antifreeze leaks or radiator boil-overs," Reichel said.

DNR enforcement division official David Rymph said the depart-

ment was "aware of the potential for contamination from 1,4-dioxane in antifreeze prior to the Gelman study." The state departments of Natural Resources, Public Health and Transportation have each assigned a person to review the study provided by Gelman Sciences and consider what action, if any, to take on the matter of antifreeze boil-over in rest areas, Rymph said.

Levitt said the company has commissioned studies "to determine what is a safe level of dioxane in drinking water."

"Undoubtedly, results of this investigation may have an impact favorable to Gelman in the case," Levitt said. "But it wasn't done to avoid our responsibilities."

The full extent of those responsibilities for cleaning up pollution around the company's Scio Township plant is the subject of the court case brought against Gelman by the DNR.

According to company financial statements, Gelman Sciences spent \$1.2 million through the end of July on pollution-containment efforts, including fees paid to 11 scientists and consultants investigating the potential effect of dioxane on humans.

Levitt could not supply a figure for the amount the company spent on the sampling survey of radiator boil-over at Michigan highway rest areas.

To date, however, the company has not completed the hydro-geological survey of the plant site requested in 1986 by the Department of Natural Resources, according to Rymph.

#114

REMOVAL OF 1,4-DIOXANE FROM WASTEWATER

G.M. KLEČKA* and S.J. GONSIOR

*Environmental Chemistry Research Laboratory, Dow Chemical U.S.A., Midland,
MI 48674 (U.S.A.)*

(Received June 1, 1985; accepted in revised form September 10, 1985)

Summary

Chemical methods were evaluated for the treatment of 1,4-dioxane in industrial process wastewaters. The compound was rapidly oxidized by a combination of hydrogen peroxide and ferrous iron, although the rate of organic carbon removal was considerably slower than the disappearance of 1,4-dioxane from solution. Chlorine oxidation at 75°C was also found to be highly effective. The rate of the reaction was greatest at pH 5.2, suggesting that hypochlorous acid was the preferred oxidant. 1,4-Dioxane appeared to be completely oxidized during chlorination, although the removal of organic carbon was somewhat slower than the disappearance of the parent compound.

Introduction

1,4-Dioxane (1,4-diethylene dioxide) is used for a variety of industrial applications including, as a solvent for cellulose and a wide range of organic products, a wetting and dispersing agent for textile processing and printing, and as a stabilizer in certain chlorinated solvents. Process waters arising from these operations may contain 1,4-dioxane as a result of spills or through the routine discharge of wastes. Although the levels of 1,4-dioxane present in plant effluents are likely to be low, under certain conditions it may be desirable to pretreat more concentrated process waste streams to remove the compound. However, methods for the removal of 1,4-dioxane from such wastewaters have not been described.

1,4-Dioxane is generally considered to be nonbiodegradable. Results of the biochemical oxygen demand test for 1,4-dioxane indicate that negligible oxygen is consumed over a 20-day test period [1]. Mills and Stack [2] have also noted that degradation of the compound was not observed in cultures of sewage microorganisms exposed for 1 year to wastewater treatment plant effluents adjusted to contain 1,4-dioxane at concentrations ranging from 100 to 900 mg/L. Thus, it appears unlikely that significant removal of 1,4-dioxane will occur in conventional biological treatment systems.

*To whom correspondence should be addressed.

As an alternative to biological treatment, physical or chemical methods can be considered for the removal of 1,4-dioxane from industrial process wastes. However, in view of the infinite water solubility and low vapor pressure (30 mm at 20°C) [3] of the compound, physical treatment by air-stripping or activated carbon adsorption is not likely to be highly effective. Preliminary studies conducted in our laboratory have indeed confirmed this observation. As a result, the present study was conducted to evaluate chemical methods, including chlorine and hydrogen peroxide oxidation for the treatment of industrial wastewaters containing 1,4-dioxane.

Experimental

The oxidation of 100 mg/L of 1,4-dioxane by hydrogen peroxide in combination with a ferrous iron salt (Fenton's reagent) [4] was examined in aqueous solutions containing 115, 230 and 465 mg/L of H_2O_2 . These levels correspond to H_2O_2 :dioxane molar ratios of 3:1, 6:1 and 12:1, respectively. Reaction mixtures were prepared by combining the appropriate amount of a 30% H_2O_2 solution with distilled water, and adjusting the pH of the solution to $pH\ 5.5 \pm 0.2$. Test reaction mixtures were supplemented with 200 mg/L of $FeSO_4 \cdot 7H_2O$. Control reaction mixtures were prepared as above, except that the ferrous iron was omitted. Solutions (final volume of 200 mL) were transferred to amber bottles and incubated at an ambient temperature (25°C). Reactions were initiated by the addition of 20 mg of 1,4-dioxane (neat). Samples were removed periodically, diluted with an equal volume of 60 mM Na_2SO_3 to quench the reaction, and analyzed as described below.

Chlorine oxidation of 100 mg/L of 1,4-dioxane was initially examined in water solutions containing 1000 mg/L of NaOCl (corresponds to NaOCl:dioxane molar ratio of 12:1). Reaction mixtures were prepared by combining the appropriate amount of a 5% NaOCl solution with distilled water, and adjusting portions of the mixture to a pH of 2, 6 and 11. Test solutions (final volume of 200 mL) were transferred to amber bottles and incubated at an ambient temperature (25°C) or in a water bath at 75°C. Reactions were initiated by the addition of 20 mg of 1,4-dioxane (neat). Samples were removed periodically, diluted with an equal volume of 60 mM Na_2SO_3 to quench the reaction, and analyzed as described below.

The effect of pH on the oxidation of 1,4-dioxane by aqueous chlorine was examined in reaction mixtures prepared using 1.0 M NaH_2PO_4 buffers adjusted to a pH ranging from 5 to 6.5. Portions of the appropriate buffer were transferred to amber bottles and supplemented with 100 mg/L of 1,4-dioxane and 2000 mg/L of NaOCl. Reaction mixtures (final volume of 200 mL each) were incubated in a water bath at 75°C.

1,4-Dioxane was analyzed by gas chromatography by direct injection of aqueous samples. Chromatography was performed using a Hewlett-Packard model 5730 gas chromatograph with a flame ionization detector. The analytical column (glass; 10 ft. \times 0.25 in.) was packed with Tenax GC (Supelco,

Inc., Bellefonte, PA). Compounds were eluted from the column isothermally at an oven temperature of 150°C with a helium carrier gas at a flow rate of 30 mL/min. Output of the flame ionization detector was connected to a Hewlett-Packard model 3380 recording integrator. All values were calculated from peak height measurements by comparison with an external standard of 1,4-dioxane prepared in water.

Total organic carbon was determined using either a Beckmann model 915B or Dohrmann model 80 total carbon analyzer. Total organic carbon concentrations were calculated from the difference of the total carbon and inorganic carbon concentrations of a sample. The instruments were calibrated using potassium biphthalate and sodium carbonate as standards.

Results and discussion

1,4-Dioxane was rapidly degraded by a combination of hydrogen peroxide and ferrous iron, as shown in Fig. 1. No degradation was observed in the control. The compound was rapidly oxidized during the first hour in all test solutions; however, the rate of the reaction decreased thereafter in reaction mixtures containing 3 or 6 moles H_2O_2 per mole 1,4-dioxane. Complete removal of the compound occurred within 10 h in test solutions containing 12 moles H_2O_2 per mole 1,4-dioxane. During incubation, the pH of all test solutions rapidly decreased from pH 5.7 to pH 2.9 due to acid formation during the reaction. These conditions are within the optimum range (pH 2.5–4.0) reported for the oxidation of organic compounds by Fenton's reagent [5].

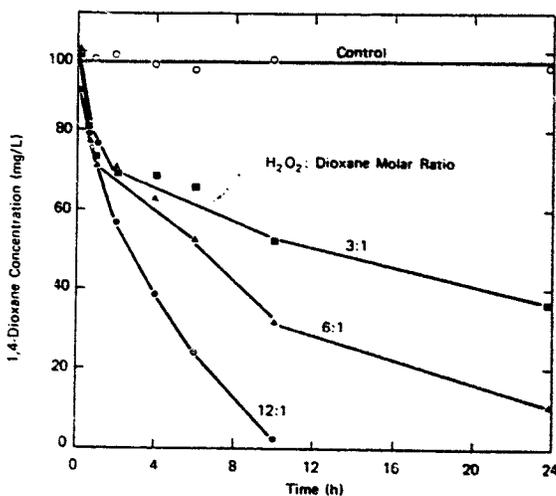


Fig. 1. Oxidation of 1,4-dioxane by a combination of hydrogen peroxide and ferrous iron.

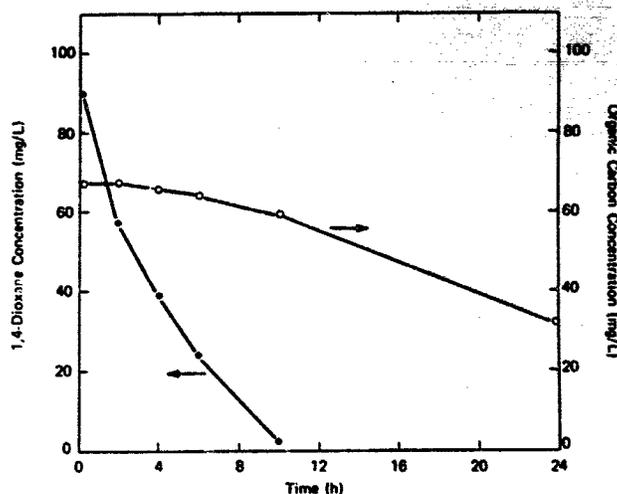


Fig. 2. Removal of 1,4-dioxane and organic carbon during hydrogen peroxide oxidation.

To determine whether 1,4-dioxane was completely oxidized during the reaction, samples of the test solution containing 12 moles H_2O_2 per mole compound were periodically analyzed for the concentration of organic carbon remaining in solution. As shown in Fig. 2, the rate of organic carbon removal was considerably slower than the disappearance of 1,4-dioxane from solution. After 10 h of incubation, removal efficiencies were 97% and 10.5% for 1,4-dioxane and organic carbon, respectively. Following 24 h of incubation, the organic carbon concentration of the reaction mixture was decreased by 48%.

The stoichiometry calculated for the oxidation of 1,4-dioxane,



suggests that 10 mol hydrogen peroxide are required for the complete degradation of 1 mol 1,4-dioxane. While removal of the parent compound occurred rapidly in test solutions containing a 12:1 molar ratio of H_2O_2 to 1,4-dioxane, the oxidation of the residual organic carbon was considerably slower. The incomplete oxidation of organic compounds by a combination of hydrogen peroxide and ferrous iron has been previously described [6], and appears to be due to the formation of low molecular weight organic aldehydes and acids which are resistant to further chemical oxidation. However, such products are known to be readily removed by conventional biological treatment processes.

A series of experiments were also conducted to examine the chlorine oxidation of 1,4-dioxane in aqueous solution. Preliminary studies indicated that the compound was not degraded at 25°C in reaction mixtures prepared at a

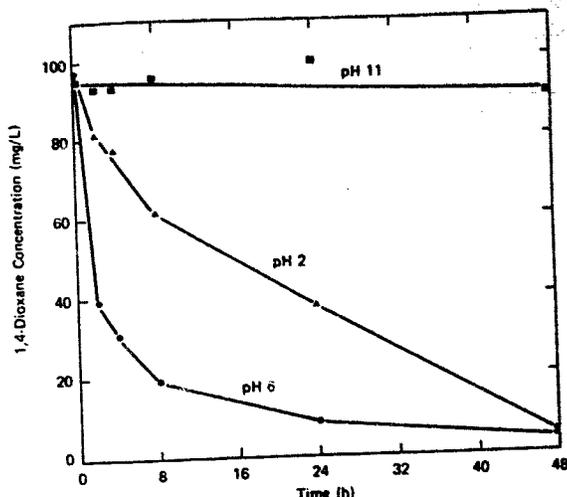


Fig. 3. Chlorine oxidation of 1,4-dioxane in water at 75°C.

pH of 2, 6 or 11. However, when solutions containing 100 mg/L of 1,4-dioxane and 1000 mg/L of NaOCl were adjusted to pH 2 or pH 6 and incubated at 75°C, the compound was rapidly degraded as shown in Fig. 3. The rate of the reaction at pH 6 changed with time. This was presumably due to a decrease in the pH of the solution from pH 6 to pH 2.8 as a result of acid formation during the reaction. The rate of oxidation was negligible in test solutions prepared at pH 11.

The effect of pH on the oxidation of 1,4-dioxane by aqueous chlorine at 75°C was subsequently examined in reaction mixtures prepared using 1.0 M NaH_2PO_4 buffers over the range from pH 5.2 to 6.5. Results of the study are shown in Fig. 4. Destruction of 1,4-dioxane at 75°C proceeded rapidly at pH 5.2, with an initial removal rate of approximately 32.6 mg of 1,4-dioxane consumed per hour. The rate of oxidation decreased as the pH of the reaction mixture was increased, and was negligible at a pH of 6.5 (see Inset, Fig. 4).

To determine whether 1,4-dioxane was completely oxidized during the reaction with chlorine, samples of the reaction mixture prepared at pH 5.2 were periodically analyzed for the concentration of organic carbon remaining in solution. As shown in Fig. 5, the rate of organic carbon removal was somewhat slower than the disappearance of 1,4-dioxane from solution. After 8 h of incubation, removal efficiencies were 97% and 70% for 1,4-dioxane and organic carbon, respectively. Following 24 h, the organic carbon concentration of the reaction mixture was decreased by 85%.

Chlorine oxidation was found to be highly effective for the removal of 1,4-dioxane from water, although the reaction rates were shown to be

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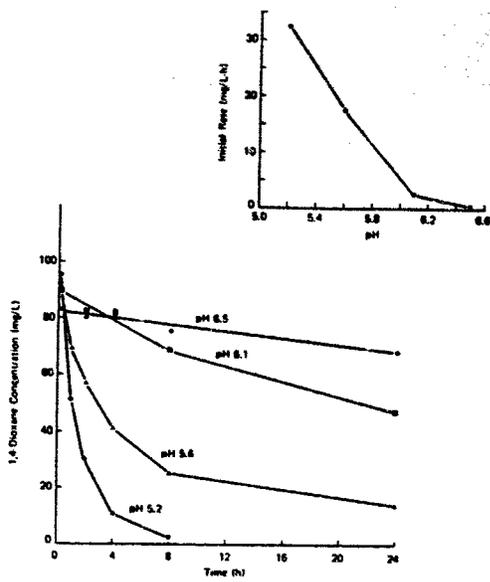


Fig. 4. Effect of pH on the oxidation of 1,4-dioxane by aqueous chlorine in 1.0 M NaH_2PO_4 buffer at 75°C.

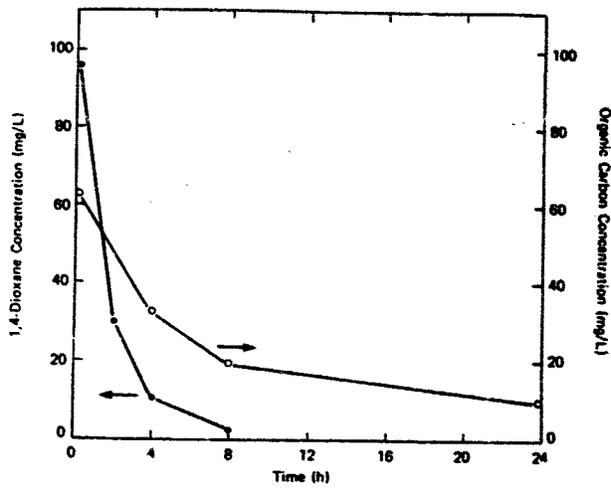
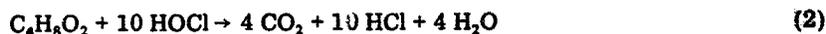


Fig. 5. Removal of 1,4-dioxane and organic carbon during chlorine oxidation chlorination at pH 5.2 at 75°C.

strongly influenced by temperature and pH. The effect of pH is reasonable in view of the chemistry of chlorine [7]. In aqueous solution, chlorine can exist as molecular chlorine (Cl_2), hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) depending on the pH of the system. Preliminary studies conducted with unbuffered solutions adjusted to pH 2 or pH 6 indicated that molecular chlorine and hypochlorous acid were capable of oxidizing 1,4-dioxane. No reaction was observed with hypochlorite ion at a pH 11. Oxidation of the compound was fastest at pH 6; however, in unbuffered mixtures the rate of the reaction rapidly decreased with time, presumably due to a decrease in the pH of the solution from pH 6 to pH 2.8 as a result of acid formation during the reaction. This observation suggests that hypochlorous acid is the preferred oxidant.

The stoichiometry of the reaction of 1,4-dioxane with hypochlorous acid is given by the following equation:



1,4-Dioxane appeared to be completely oxidized during the reaction, although the removal of organic carbon from solution was not as fast as the disappearance of the parent compound. However, the formation of intermediate degradation products was not detected during gas chromatographic analysis of test solutions for 1,4-dioxane.

In an attempt to optimize the reaction with respect to pH, the oxidation of 1,4-dioxane by chlorine was examined in solutions buffered with 1 M NaH_2PO_4 . Note that since phosphate buffers are not highly effective over the range from pH 5 to 6.5 ($\text{p}K_a = 7.2$), solutions had to be strongly buffered to prevent changes in pH during the reaction. The rate of the reaction was greatest at pH 5.2, which approximately corresponds to the maximum dissociation of chlorine to hypochlorous acid [7]. Further attempts to study the reaction at lower pH using an acetate buffer system ($\text{p}K_a = 4.76$) were unsuccessful due to the competitive reaction of available chlorine with acetate. However, in view of the fact that the rate of the reaction with molecular chlorine at pH 2 (unbuffered reactions) was slower than the reaction with hypochlorous acid at pH 5.2 (buffered solutions), the oxidation of 1,4-dioxane is likely to be optimal under conditions which favor the dissociation of chlorine to hypochlorous acid.

Conclusions

In contrast to biological or physical methods, chemical treatment can be used effectively for the removal of 1,4-dioxane from industrial process wastewaters. Oxidation of the compound by a combination of hydrogen peroxide and ferrous iron occurs within 10 h, and requires greater than a 10-fold molar excess of hydrogen peroxide. Chlorine oxidation of 1,4-dioxane proceeds rapidly at 75°C in the presence of a 12-fold molar excess of hypochlorous acid. The reaction was optimal under conditions favoring the dissociation of chlorine to hypochlorous acid.



THE DOW CHEMICAL COMPANY

January 20, 1989

2030 WILLARD H. DOW CENTER
MIDLAND, MICHIGAN 48674

EPA-OTS



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89-89-076/ Sup.
PROBS-89000006
89-89000079

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Office of Toxic Substances
Environmental Protection Agency
401 M. Street, S.W.
Washington, DC 20460

ATTN: 8(e) Coordinator
8EHQ-1088-0761

89 JAN 23 AM 10:06
OTS DOCUMENT CONTROL
OFFICE

Dear Sir/Madam:

Gelman Sciences has recently submitted information to the Environmental Protection Agency (EPA) on 1,4 dioxane pursuant to section 8(e) of the Toxic Substances Control Act (TSCA). In this letter, The Dow Chemical Company (Dow) is providing additional information concerning 1,4 dioxane. It should be noted, however, that we believe that none of this information constitutes section 8(e) information and that we are submitting it for your information.

Attached please find the following:

- ✓(1) a table of analyses of polyethylene glycol for 1,4 dioxane.
- ✓(2) a letter from Union Carbide on 1,4 dioxane in their polyethylene glycol.
- ✓(3) two letters written by Charles Gelman to Dr. Winifred Oyen, dated October 6, 1988 and October 17, 1988.
- ✓(4) A reprint of a published study entitled "Removal of 1,4-Dioxane From Wastewater" and a copy of the underlying internal report.
- ✓(5) A reprint of a published study entitled "Pharmacokinetics of 1,4-Dioxane in Humans."

The polyethylene glycol analyses in attachment 1 were done as part of an analytical development project using a cryogenic-focusing, headspace, capillary gas chromatographic method using flow programming.

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References

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- 2 E.T. Mills, Jr. and V.T. Stack, Jr., Biological oxidation of synthetic organic chemicals, *Proc. 8th Industrial Waste Conference, Purdue Univ., Eng. Ext. Ser.*, 83 (1954) 492.
- 3 K. Verschueren, *Handbook of Environmental Data on Organic Chemicals*, 2nd edn, Van Nostrand Reinhold, New York, 1983, p. 579.
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17 CONTAINS NO CBI

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TITLE EVALUATION OF METHODS FOR THE TREATMENT OF WASTEWATERS CONTAINING
1,4-DIOXANE

44
PAGES
IN FULL
REPORT

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This report is: INTERIM FINAL
and mainly: NEW REVIEW

DESCRIPTIVE SUMMARY WITH CONCLUSIONS:

1,4-Dioxane (1,4-diethylenedioxiide) is frequently used as a stabilizer in certain chlorinated solvents, such as 1,1,1-trichloroethane. Following some solvent recovery operations, 1,4-dioxane may be found in aqueous waste streams. A variety of biological, physical and chemical methods were evaluated for the treatment of these process wastes.

The biodegradation of 1,4-dioxane was examined in laboratory systems designed to simulate both municipal and industrial activated sludge treatment processes. Biodegradation of the compound was not observed during 28 days of operation. Volatility studies indicated that 1,4-dioxane is removed slowly from water, with 53% of the chemical remaining after 4 days of aeration at 25°C. Carbon adsorption was also found to be an ineffective means for treatment, as a 100-fold excess of activated carbon was required for the complete removal of 100 or 1000 mg/L of 1,4-dioxane from water. In contrast, a number of chemical treatment methods were found to be highly effective for the removal of 1,4-dioxane from aqueous solution. The compound was rapidly degraded by hydrogen peroxide in combination with a ferrous iron salt (Fenton's reagent), with a half-time for the reaction of approximately 3 hours. Chlorination at 75°C was also effective for the treatment of 1,4-dioxane in solution. Half-times for the reaction at pH 6 and pH 2 were 2 hours and 16 hours, respectively.

ARE MATERIALS DESCRIBED IN THIS REPORT ON TSCA INVENTORY?
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INTRODUCTION

1,4-Dioxane (1,4-diethylenedioxiide) is frequently used as a stabilizer in certain chlorinated solvents, such as 1,1,1-trichloroethane. Following some solvent recovery operations, low levels of 1,4-dioxane may be found in aqueous waste streams. For example, 1,4-dioxane may be present at low levels in the vapor phase over solvent degreasing systems. The vapor phase, containing solvent, stabilizer and water vapor, is commonly processed by initially passing it through a condenser, and the condensate is then transferred to a solvent-water separator. The organic layer is returned to the degreasing bath, leaving an aqueous waste stream which may contain low levels of 1,4-dioxane. Alternatively, organic vapors from degreasing operations may be treated by activated carbon adsorption. During steam regeneration of the carbon beds, 1,4-dioxane may enter the aqueous waste stream.

Relatively little is known about the biological treatability of 1,4-dioxane. Results of the biochemical oxygen demand test for 1,4-dioxane indicate that negligible oxygen is consumed over a 20-day test period (1,2). Mills and Stack (3) have also noted that degradation of the compound was not observed in suspended cultures of sewage microorganisms exposed for 1 year to wastewater treatment plant effluents containing 1,4-dioxane at concentrations ranging from 100 to 900 mg/L. However, Stack (4) has noted that 1,4-dioxane may be oxidized by specifically acclimated cultures of sewage microorganisms. Thus, biodegradation may contribute to the removal of the compound in some wastewater treatment plants.

The present study was conducted to investigate the fate of 1,4-dioxane in laboratory systems designed to simulate both municipal and industrial wastewater treatment facilities. Experiments were conducted to examine the importance of volatilization and biodegradation for the removal of 1,4-dioxane from activated sludge. Additional studies were performed to evaluate alternative physical and chemical methods for the treatment of aqueous wastes containing 1,4-dioxane.

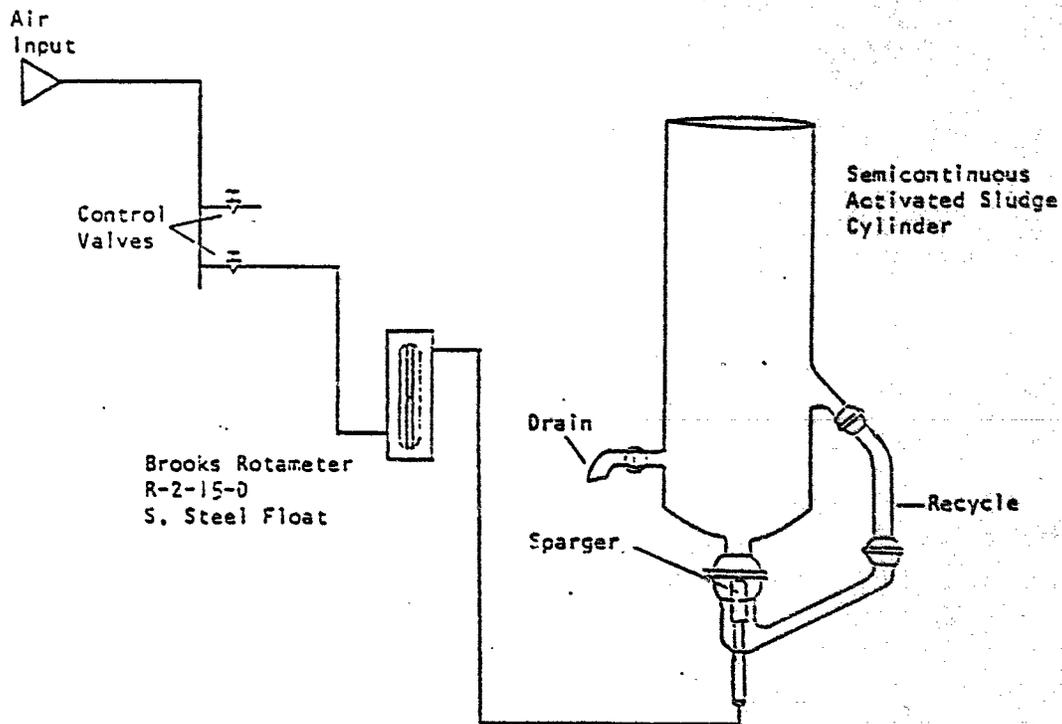


Figure 1. Laboratory-Scale Semicontinuous Activated Sludge Cylinder Used to Simulate Municipal Wastewater Treatment Systems.

settle and the upper 1-liter of waste liquor was removed and replaced with 1 liter of neutralized (pH 7.5) primary effluent. The cylinders were aerated at a rate of 500 mL/min and incubated at ambient temperature ($25\pm 3^\circ\text{C}$).

During operation, the laboratory activated sludge cylinders were supplemented daily as follows: a) Unit A did not receive 1,4-dioxane, and served as a control to detect the presence of components which might interfere with the analysis of 1,4-dioxane, b) Unit B was supplemented daily with 1,4-dioxane to achieve a nominal concentration of 100 mg/L, and c) Unit C was supplemented daily with 100 mg/L of 1,4-dioxane in addition to 100 mg/L of each of the following substrate analogs: diethyleneglycol ethyl ether, bis(2-ethoxyethyl)-ether, bis(2-methoxyethyl)ether, and 1,2-dimethoxyethane. Samples were removed periodically from the systems, filtered through 0.45 μm Acrodisc membrane filters and analyzed as described below.

Volatilization

The volatilization of 1,4-dioxane from activated sludge was examined using 9-liter activated sludge cylinders as previously described (5). Activated sludge was obtained from the Midland Municipal Wastewater Treatment Plant. Two systems were established with 8.5 liters each of activated sludge adjusted to contain 2500 ± 500 mg/L of mixed liquor suspended solids. The activated sludge was treated with mercuric chloride (200 mg/L) to inhibit biological activity, and supplemented with 1,4-dioxane at nominal concentrations of 10 and 100 mg/L. The cylinders were aerated at a rate of 500 mL/min and incubated for 24 hours at ambient temperature (22°C). Samples were removed periodically from the systems, filtered through 0.45 μm Acrodisc membrane filters and analyzed as described below.

The air-water partition coefficient for 1,4-dioxane was determined as previously described (8,9). A 1-liter aqueous solution containing 100 mg/L (nominal) of 1,4-dioxane was transferred to the aeration apparatus (Figure 3) and aerated at a rate of 700 mL/min for 4 days at 25°C . Samples were removed

periodically and analyzed for 1,4-dioxane as described below. The air-water partition coefficient was calculated from the slope of the line from a plot of the log of the concentration remaining versus the volume of air passed through the solution.

Activated Carbon Adsorption

The adsorption of 1,4-dioxane from water by activated carbon was determined in batch experiments. Aliquots (100 mL) of stock solutions containing either 100 mg/L or 1000 mg/L (nominal) of 1,4-dioxane were transferred to 4 or 8 oz. glass bottles containing various quantities of activated carbon (1.0 mg to 10.0 g). The bottles were sealed with aluminum-foil lined caps. Equilibrium in the solutions was achieved by agitating the bottles for 3 days on a reciprocating shaker. Due to the heat generated by the shaker, the temperature of the sample solutions was approximately 35°C. Samples were removed periodically, filtered through 0.45 μ m Acrodisc membrane filters and analyzed as described below.

Results of the experiment were used to prepare a Freundlich isotherm (10). The empirical equation for the isotherm is

$$\frac{X}{M} = kC^{1/n}$$

where X/M is the amount of chemical adsorbed per unit weight of carbon, C is the equilibrium concentration of the chemical in solution, k is an empirical constant equal to the intercept at C = 1, and 1/n is the slope of the line on a log-log plot.

Oxidation with Hydrogen Peroxide

Studies were conducted to examine the oxidation of 1,4-dioxane by hydrogen peroxide in combination with a ferrous iron salt (Fenton's reagent; 11). The effect of hydrogen peroxide concentration on the oxidation of 100 mg/L of

Analytical Methods

Concentration of 1,4-dioxane was determined by gas chromatography by direct injection of aqueous samples. Chromatography was performed using a Hewlett-Packard model 5730 gas chromatograph with a flame ionization detector. The analytical column (glass; 10 ft x 0.25 in) was packed with Tenax GC (Supelco, Inc., Bellefonte, PA). Compounds were eluted from the column isothermally at an oven temperature of 150°C with a helium carrier gas at a flow rate of 30 mL/min. Output of the flame ionization detector was connected to a Hewlett-Packard model 3380 recording integrator. All values were calculated from peak height measurements by comparison with an external standard of 1,4-dioxane prepared in water. The detector response was linear over the concentration range of interest (0.1 to 1000.0 mg/L) with a detection limit of approximately 0.05 mg/L.

Total organic carbon was determined using either a Beckman model 915B or a Dormann model 80 total carbon analyzer as previously described (12). Total organic carbon concentrations were calculated from the difference of the total carbon and inorganic carbon concentrations of a sample. The instruments were calibrated using potassium biphthalate and sodium carbonate as standards.

Concentration of activated sludge, mixed liquor suspended solids was determined by gravimetric analysis as previously described (13).

Chemicals

1,4-Dioxane (Distilled in Glass grade) was purchased from Burdick and Jackson Laboratories, Inc., Muskegon, MI. Nutrient broth was obtained from Difco Laboratories, Detroit, MI. Diethylene glycol ethyl ether, bis(2-methoxyethyl)ether, 1,2-dimethoxyethane and hydrogen peroxide solution (30%) were from Fisher Scientific Co., Fairlawn, NJ. Bis(2-ethoxyethyl)ether was from the Eastman Chemical Co., Rochester, NY. Activated carbon (Grade 718; 12 x 30 mesh) was obtained from the Witco Chemical Corp., New York, NY. Sodium hypochlorite solution (5.25%; Clorox bleach) was from the Clorox Co., Oakland, CA. All other chemicals were reagent grade (Appendix I).

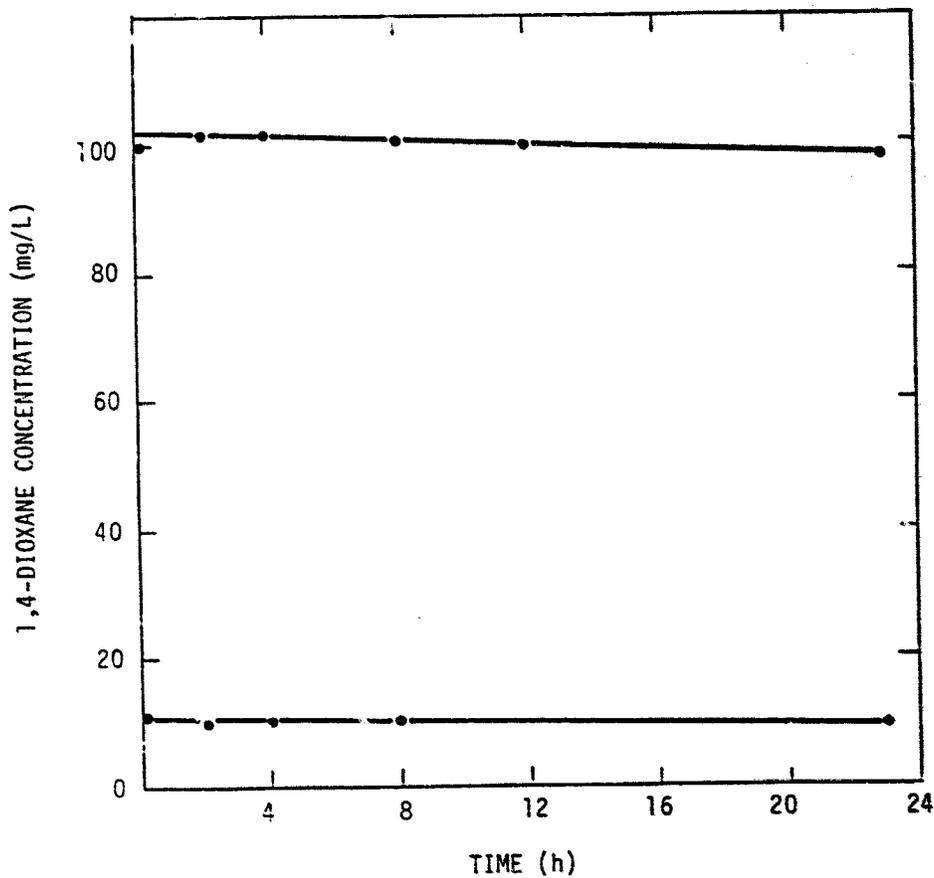


Figure 4. Volatilization of 1,4-Dioxane from Activated Sludge

Cylinders containing 8.5 liters of municipal activated sludge (treated with 200 mg/L of mercuric chloride) were supplemented with 1,4-dioxane at nominal concentrations of 10 and 100 mg/L. The systems were aerated at a flow rate of 500 mL/min at ambient temperature (22°C).

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Table 2. Fate of 100 mg/L of 1,4-Dioxane in Municipal Activated Sludge

Day	Initial [Dioxane] mg/L	Final [Dioxane] mg/L	% Removed
1	101.0	100.0	1.0
2	102.0	101.0	1.0
3	103.0	99.0	3.9
4	103.5	96.5	6.8
5	103.0	101.0	1.9
6	108.0	95.4	11.7
7	103.0	94.3	8.4
8	105.0	95.2	9.3
9	103.0	95.3	7.5
10	106.0	92.2	13.0
11	102.0	92.0	9.8
12	103.0	105.0	0.0
13	100.0	92.2	7.8
14	101.0	93.3	7.6
15	102.0	93.3	8.5
16	102.0	94.4	7.5
17	102.0	92.3	9.5
18	102.5	92.3	9.6
19	100.0	89.9	10.1
20	101.0	92.4	8.5
21	101.0	93.6	7.3
22	101.0	93.5	7.3
23	100.0	91.2	8.8
24	100.0	91.9	8.1
25	105.0	94.2	10.3
26	101.0	89.7	11.2
27	99.7	95.8	3.9
28	105.0	95.0	9.5
29	101.0	89.5	11.4

Laboratory-scale activated sludge cylinders (9-liter) were operated on a daily fill and draw cycle with synthetic municipal sewage supplemented with 100 mg/L of 1,4-dioxane. The systems were aerated at a rate of 500 mL/min and incubated at ambient temperature ($23 \pm 1^\circ\text{C}$).

Table 3. Fate of 100 mg/L of 1,4-Dioxane in Industrial Activated Sludge

Day	Initial [Dioxane] mg/L	Final [Dioxane] mg/L	% Removed
1	104.0	87.9	15.4
2	102.0	97.0	4.9
3	104.0	92.8	10.8
4	106.0	92.9	12.4
5	104.0	95.1	8.6
6	103.0	95.4	7.4
7	95.4	92.9	2.6
8	97.2	94.8	2.5
9	101.0	89.7	11.2
10	97.1	91.1	6.2
11	98.8	88.9	10.0
12	101.0	88.6	12.3
13	96.0	89.1	7.2
14	94.4	93.8	0.6
15	102.0	89.1	12.6
16	99.0	95.3	3.7
17	97.5	87.5	10.3
18	101.0	92.5	8.4
19	102.0	92.7	9.1
20	96.7	88.9	8.0
21	99.5	92.5	7.0
22	96.5	84.9	7.4
23	94.6	87.2	7.8
24	100.0	90.0	10.0
25	98.0	89.0	9.1
26	95.4	90.3	5.3
27	102.0	95.3	6.6

A laboratory-scale activated sludge cylinder (Unit B; 2.5-liter) was operated on a daily fill and draw cycle with authentic industrial sewage supplemented with 100 mg/L of 1,4-dioxane. The system was aerated at a rate of 500 mL/min and incubated at ambient temperature (25±3°C).

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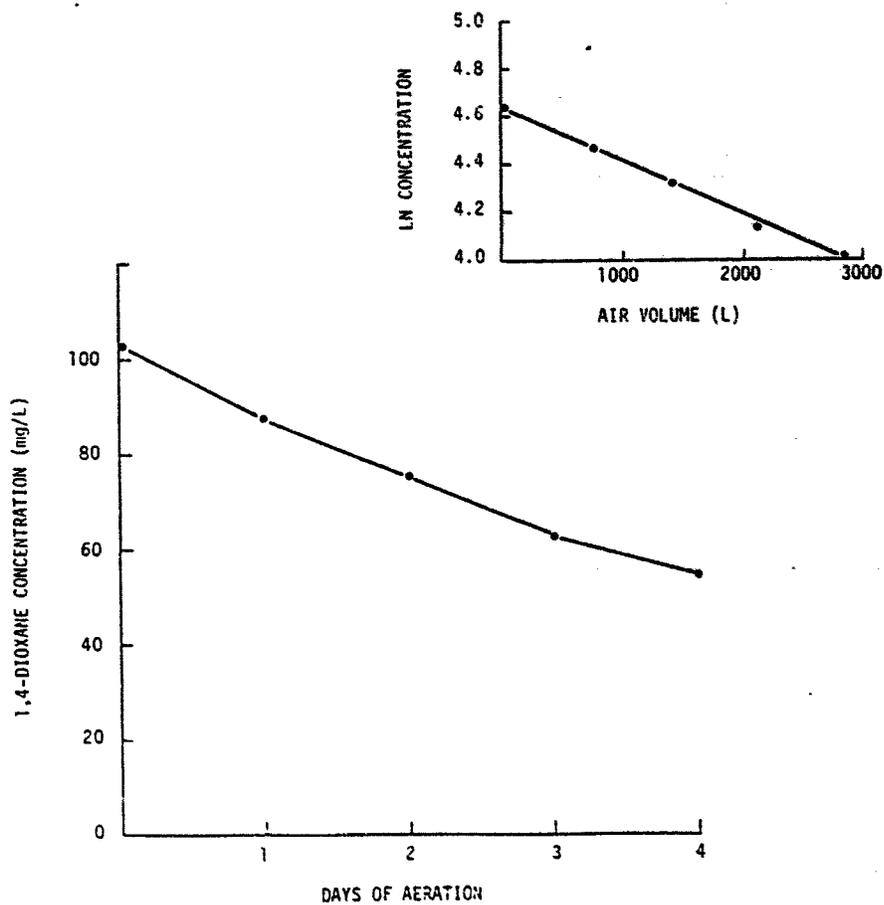


Figure 5. Volatilization of 1,4-Dioxane from Water

A 1-liter solution containing 100 mg/L of dioxane was aerated at a rate of 700 mL/min for 4 days at 25°C. The air-water partition coefficient was calculated from the slope of the line from the plot of the log of the concentration remaining versus the volume of air passed through the solution (see inset).

Table 5. Adsorption of 1,4-Dioxane on Activated Carbon

Initial Dioxane Concentration (mg/L)	Carbon Load (mg/L)	Final Dioxane Concentration ^a (mg/L)	Adsorbability	
			<u>g Dioxane</u> <u>g Carbon</u>	% Reduction
104	0	104.0	-	0
104	10	100.0	0.4	3.8
104	100	98.2	0.058	5.6
104	1,000	73.9	0.03	28.9
104	10,000	13.2 ^b	0.009	87.3
104	100,000	ND ^b	0.001	100.0
1067	0	1067	-	0
1067	10	1067	0	0
1067	100	1067	0	0
1067	1,000	985	0.082	7.7
1067	10,000	423	0.064	60.4
1067	100,000	9	0.0106	99.2

^aConcentration of 1,4-dioxane in solution at equilibrium at 35°C

^bNondetectable

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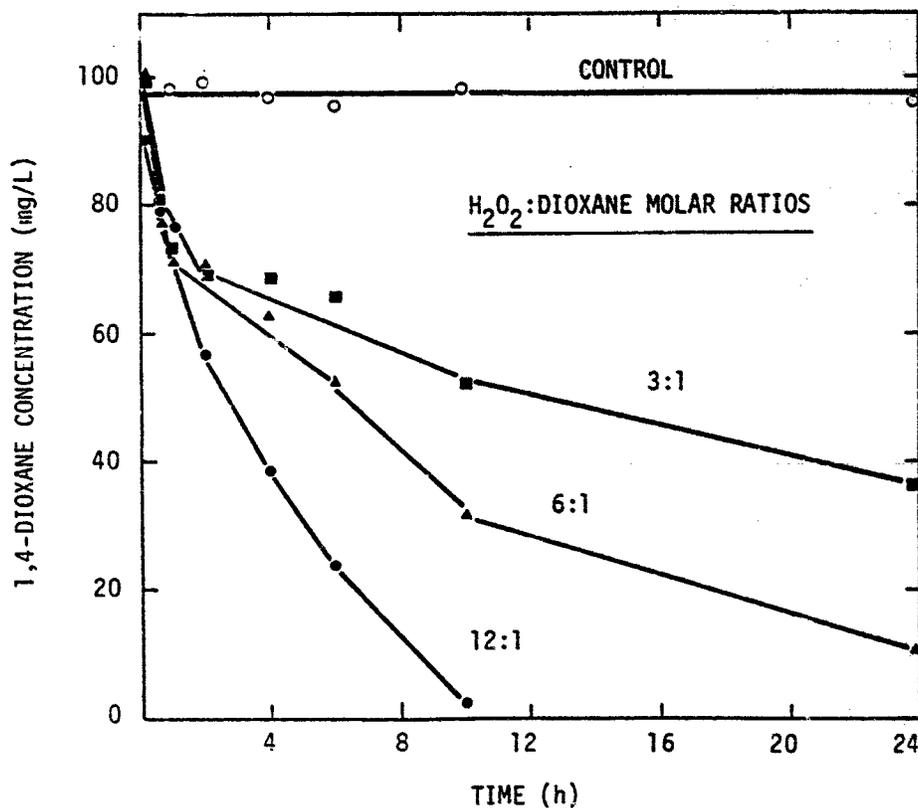


Figure 7. Effect of Hydrogen Peroxide Concentration on the Oxidation of 1,4-Dioxane by Fenton's Reagent

Reaction mixtures (200 mL) contained 100 mg/L of 1,4-dioxane, 200 mg/L of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and varying concentrations of H_2O_2 (116.3-465.1 mg/L). The control reaction mixture contained 100 mg/L of 1,4-dioxane and 232.6 mg/L of H_2O_2 . Solutions were incubated at ambient temperature (25°C).

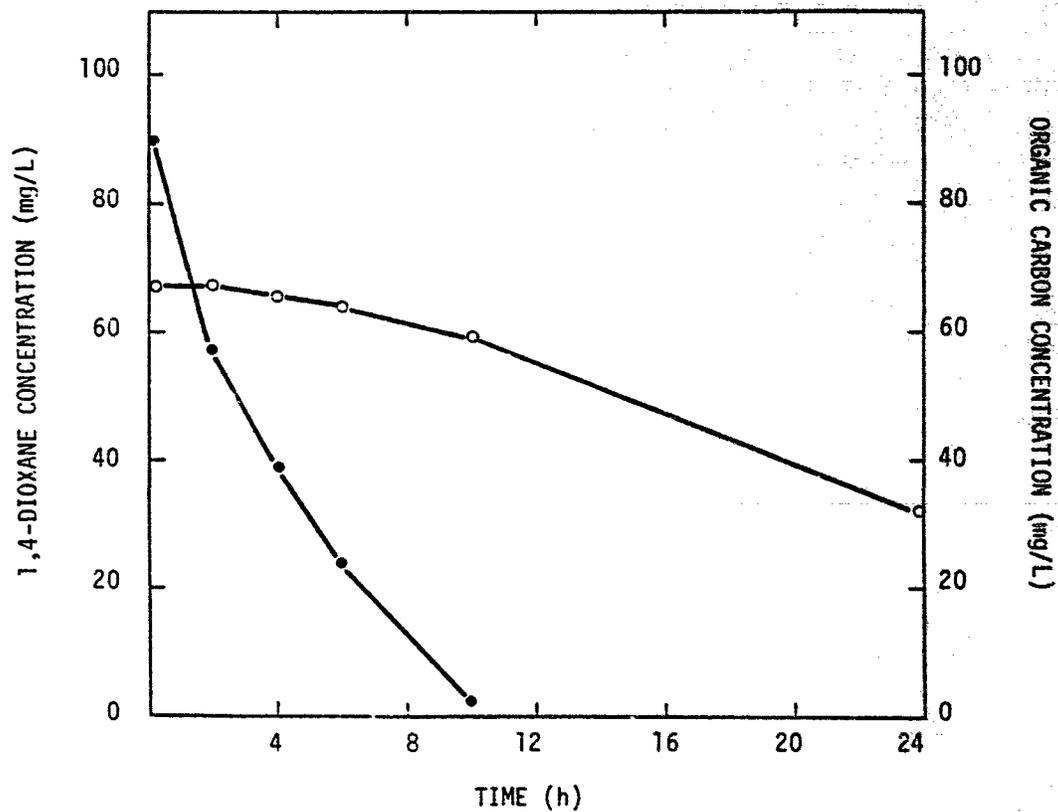


Figure 8. Oxidation of 1,4-Dioxane by Fenton's Reagent

The reaction mixture (200 mL) contained 100 mg/L of 1,4-dioxane, 200 mg/L of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 465.1 mg/L of H_2O_2 . The solution was incubated at 25°C and analyzed periodically for the concentration of 1,4-dioxane (●) and total organic carbon (○) as described in Materials and Methods.

The effect of pH on the chlorination of 1,4-dioxane at 75°C was subsequently examined in reaction mixtures prepared using 1.0 M NaH_2PO_4 buffers over the range from pH 5.2 to 6.5. Results of the study are shown in Figure 10. The chlorination of 1,4-dioxane at 75°C proceeded rapidly at pH 5.2, with an initial removal rate estimated to be 32.6 mg of 1,4-dioxane consumed per hour. The rate of chlorination decreased as the pH of the reaction mixture was increased, and was negligible at a pH of 6.5 (see inset, Figure 10).

To determine whether 1,4-dioxane was completely oxidized during chlorination, samples of the reaction mixture prepared at pH 5.2 were periodically analyzed for the concentration of organic carbon remaining in solution. As shown in Figure 11, the rate of organic carbon removal was somewhat slower compared to the disappearance of 1,4-dioxane from the solution. After 8 hours of incubation, removal efficiencies were 97% and 70% for 1,4-dioxane and organic carbon, respectively. Following 24 hours, the organic carbon concentration of the reaction mixture was decreased by 85%. The formation of intermediate degradation products was not detected during gas chromatographic analysis of the reaction mixture for 1,4-dioxane.

Temperature was also shown to influence the chlorination of 1,4-dioxane. As previously noted, the removal of the compound from water was not observed at 25°C. Consequently, the effect of temperature on the chlorination of 1,4-dioxane was examined in reaction mixtures prepared in 1.0 M NaH_2PO_4 buffer, pH 5.2. Results of the study are shown in Figure 12. The initial rate of the reaction was 3.4 fold greater at 75°C (32.6 mg of 1,4-dioxane consumed per hour) than at 50°C (9.7 mg of 1,4-dioxane consumed per hour).

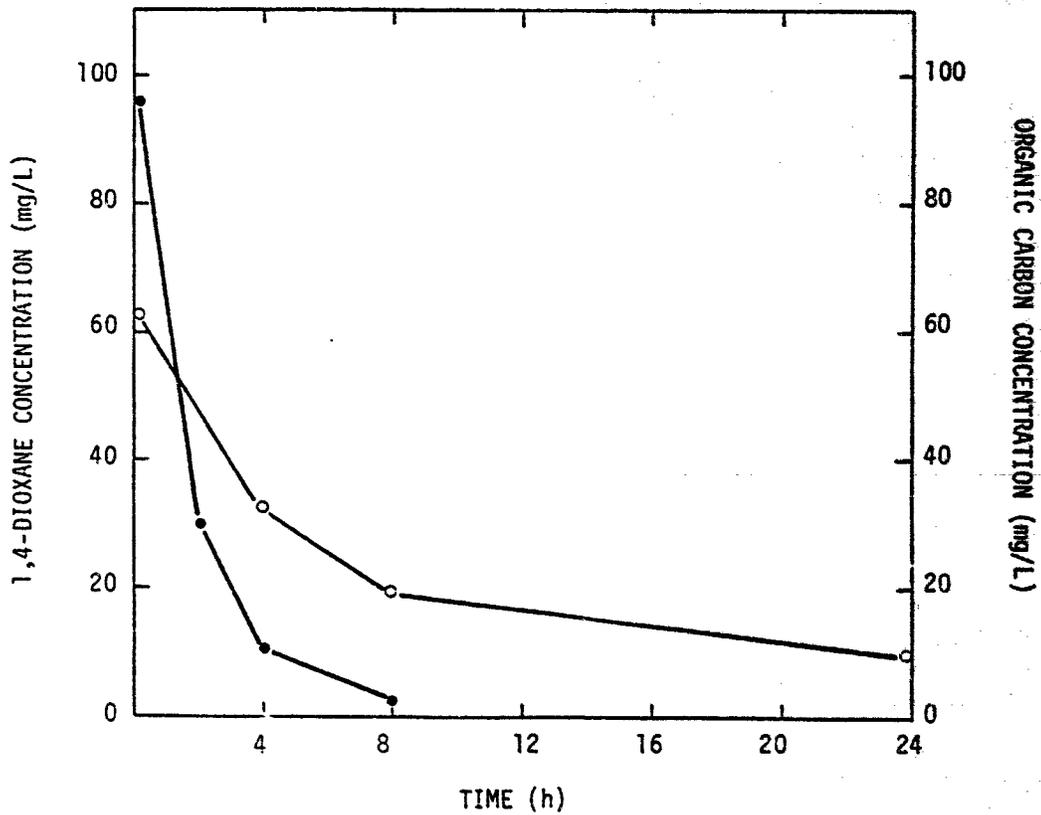


Figure 11. Oxidation of 1,4-Dioxane During Chlorination at pH 5.2 at 75°C

A reaction mixture containing 100 mg/L of 1,4-dioxane and 2000 mg/L of NaOCl was prepared in 1.0 M NaH_2PO_4 buffer, pH 5.2. The solution was incubated at 75°C and analyzed periodically for the concentration of 1,4-dioxane (●) and total organic carbon (○) as described in Materials and Methods.

DISCUSSION

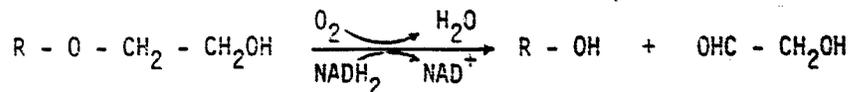
Biological Treatment of 1,4-Dioxane

Microorganisms present in either municipal or industrial activated sludge were unable to degrade 1,4-dioxane during 28 days of continuous exposure to concentrations ranging from 10 to 100 mg/L. These results are consistent with the previous report of Mills and Stack (3) who noted the inability of suspended sewage microorganisms to degrade 1,4-dioxane over 1 year of exposure to wastewater treatment plant effluents containing 100 to 900 mg/L of 1,4-dioxane. Since volatilization contributes only a 5 to 10% reduction of the compound from water over a 24 hour period, it appears unlikely that significant removal of 1,4-dioxane will occur in conventional biological treatment systems. As a result, alternative methods may be required for the treatment of wastewaters containing 1,4-dioxane.

The ether linkage has long been recognized as contributing to the resistance of organic molecules to biological attack (15). In addition to cyclic ethers such as 1,4-dioxane, simple alkyl ethers do not appear to be readily degraded in conventional wastewater treatment systems. For example, Ellis *et al* (16) have noted the presence of a number of alkyl ethers in biological treatment plant effluents.

Studies of the microbial degradation of strictly aliphatic ethers have not been extensive, and the mechanisms involved in the cleavage of such ether bonds are as yet unclear. However, Cain (17) has recently described several mechanisms which may be responsible for the biological cleavage of ether bonds, including:

(i) Oxygenative cleavage of the ether by a monooxygenase



Physical Treatment of 1,4-Dioxane

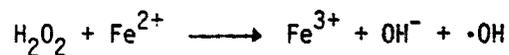
A variety of physical methods were evaluated for the treatment of aqueous wastes containing 1,4-dioxane. The physical properties of the compound are summarized in Table 6. In view of the extremely high water solubility and relatively low vapor pressure, very little of the compound would be expected to volatilize from water. These observations are consistent with the experimental results, as greater than 50% of the compound remained in solution after 4 days of aeration. The air-water partition coefficient was estimated to be 2.3×10^{-4} g/L of air per g/L of water, which is in the range for compounds generally considered to be nonvolatile from aqueous solution (23).

Carbon adsorption was also found to be an ineffective means for treatment, which is consistent with the infinite water solubility of the compound. Complete removal of 1,4-dioxane from aqueous solutions containing 100 or 1000 mg/L required greater than a 100-fold excess of activated carbon. Furthermore, based on the adsorption isotherm, the ultimate capacity of a system treating wastewaters containing 1000 mg/L of 1,4-dioxane would be approximately 0.09 grams of 1,4-dioxane per gram of activated carbon.

As an alternative to air-stripping or activated carbon adsorption, distillation can also be considered for the removal of 1,4-dioxane from dilute aqueous solution. Although not examined in the present study, 1,4-dioxane is reported to form a low boiling azeotrope with water (87.8°C at 760 mm Hg; 25), yielding a distillate containing 82% 1,4-dioxane by weight. Thus, careful fractional distillation could be used to remove the compound from dilute aqueous solutions, and the concentrated organic distillate could be recycled or disposed of by suitable means (e.g. incineration).

Chemical Treatment of 1,4-Dioxane

In contrast to biological or physical methods, chemical treatment was found to be highly effective for the removal of 1,4-dioxane from aqueous solution. The compound was rapidly degraded by hydrogen peroxide in combination with a ferrous iron salt (Fenton's reagent; 11). Fenton's reagent is reported to function as an oxidizing agent through the formation of free hydroxyl radicals ($\cdot\text{OH}$).



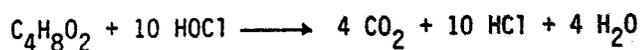
Hydroxyl radicals generated in this manner have been reported to oxidize a wide variety of organic compounds (14). Based on the stoichiometry calculated for the oxidation of 1,4-dioxane,



it appears that 10 moles of hydrogen peroxide are required for the complete degradation of one mole of dioxane. Studies conducted with a 12:1 molar ratio of hydrogen peroxide to 1,4-dioxane indicated that the parent compound was removed rapidly from solution, while the removal of the remaining organic carbon was considerably slower. The incomplete oxidation of organic molecules by hydrogen peroxide in combination with ferrous iron has been previously reported (26), and appears to be due to the formation of low molecular weight organic acids and aldehydes which are resistant to further chemical oxidation. However, such products are known to be readily removed by conventional biological treatment processes.

Chlorination was also found to be highly effective for the removal of 1,4-dioxane from aqueous solution, although the reaction rates were shown to be strongly influenced by temperature and pH. The effect of pH is reasonable in view of the chemistry of chlorine (27). In aqueous solution, chlorine can exist as free chlorine (Cl_2), hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) depending on the pH of the system (Figure 13). Preliminary studies conducted with unbuffered solutions adjusted to pH 2 and 6 indicated that free

chlorine and hypochlorous acid were capable of oxidizing 1,4-dioxane. No reaction was observed with hypochlorite ion at pH 11. The chlorination of 1,4-dioxane was fastest at pH 6. However, in unbuffered systems the rate of the reaction decreased with time, presumably due to a decrease in the pH of the solution from pH 6 to pH 2.8 as a result of acid formation during the reaction. This observation suggests that hypochlorous acid is the preferred oxidant. The stoichiometry of the reaction is given by the following equation.



1,4-Dioxane appeared to be completely oxidized during the reaction with hypochlorous acid, although the disappearance of organic carbon from the solution did not occur as fast as the removal of the parent compound.

In an attempt to optimize the reaction with respect to pH, the chlorination of 1,4-dioxane was examined in solutions buffered with 1 M NaH_2PO_4 . Note that since phosphate buffers are not highly effective over the range from pH 5 to 6.5 ($\text{pK}_a = 7.2$), solutions had to be strongly buffered to prevent changes in pH. The rate of the reaction was greatest at pH 5.2 which approximately corresponds to the maximum dissociation of chlorine to hypochlorous acid. Attempts to study the reaction using an acetate buffer system, which would be more effective in controlling pH at this range ($\text{pK}_a = 4.76$), were unsuccessful due to the competitive reaction of available chlorine with acetate. However, in view of the simplicity of an unbuffered system and the fact that the reaction does occur at low pH, the use of unbuffered reactions may be preferred for the small scale treatment of aqueous wastes containing 1,4-dioxane.

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TITLE OF STUDY: EVALUATION OF METHODS FOR THE TREATMENT OF WASTEWATERS
CONTAINING 1,4-DIOXANE

In compliance with Good Laboratory Practice Regulations, this study was inspected by the Quality Assurance Unit, and the results of these inspections reported to Management and the Study Director on the dates listed below. The report accurately reflects the data generated in accordance with the regulations and the standard operating procedures of the Laboratory. All data and the reports are located at the submitting laboratory.

Study Started: 02/21/84

Dates of Inspection: 10/24/84
02/01/85

Report Issued Date: 02/11/85

W. M. McCarty 2/16/85

W. M. McCarty
Quality Assurance
Health and Environmental Sciences
1702 Building
Dow Chemical U.S.A.
Midland, MI 48640

To John Gray
Legal,

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PHARMACOKINETICS OF 1,4-DIOXANE IN HUMANS

J. D. Young, W. H. Braun, L. W. Rampy

Toxicology Research Laboratory, The Dow Chemical Company, Midland, Michigan

M. B. Chenoweth

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G. E. Blau

Physical Research Laboratory, The Dow Chemical Company, Midland, Michigan

The pharmacokinetics and metabolism of 1,4-dioxane were determined in four healthy male volunteers exposed to 50 ppm dioxane vapor for 6 hr. Samples of blood and urine collected during and after the exposure were analyzed for dioxane and its metabolite β -hydroxyethoxyacetic acid (HEAA) by gas chromatography-mass spectrometry. A pharmacokinetic model with associated parameters was constructed to describe the fate of dioxane and HEAA in humans. The model was compared to a model constructed previously for dioxane in rats. This comparison facilitates assessment of the hazard to humans of dioxane exposure by extrapolation of toxicological information obtained in rats.

The dynamics of dioxane uptake and elimination in humans could be described by a one-compartment open-system model with zero-order uptake and first-order elimination. The half-life for elimination of dioxane was 59 ± 7 min; 99.3% of the elimination was by metabolism of dioxane to HEAA, and 0.7% was by excretion of dioxane in the urine. Dioxane and HEAA were detectable in the urine until 6 and 18 hr after cessation of exposure, respectively. The total absorbed dose of dioxane during the 6 hr period was 5.4 ± 1.1 mg/kg, although the maximum amount of dioxane in the body at any one time was 1.2 ± 0.2 mg/kg and occurred at the end of the exposure. At 6 hr the amount of dioxane in the body had reached over 99% of the steady-state amount. A simulation of repeated daily exposures to 50 ppm dioxane for 8 hr/day indicated that dioxane would never accumulate to concentrations above those attained after a single 8 hr exposure as long as the exposure concentration of dioxane was 50 ppm or less. Lack of accumulation of dioxane on repeated exposure is a critical point since saturation of the metabolism of dioxane at high dosage levels to rats has been shown to lead to toxicity. The results of the study conducted in human volunteers support the conclusion that exposure to the current threshold limit value of 50 ppm dioxane in the workplace will not cause adverse effects, even when the exposure is on a continuous or repeated basis.

The authors would like to acknowledge the following individuals for providing assistance with various portions of the study: M. J. McKenna, P. J. Brownson, D. J. Ducommun, W. A. Fishback, and R. W. Slaughter.

Requests for reprints should be sent to J. D. Young, Toxicology Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640.

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threshold limit value of 50 ppm dioxane vapor (ACGIH, 1976) produces blood levels of dioxane that are eliminated by first-order processes, and whether repeated exposures to 50 ppm would cause accumulation of dioxane in the body to levels that might saturate its pathway for metabolism and detoxification. To determine the pharmacokinetics of dioxane in humans, four volunteers were exposed to 50 ppm dioxane for 6 hr, and samples of blood plasma and urine were analyzed for dioxane and HEAA.

METHODS

Test Material

The 1,4-dioxane used in this study was obtained from The Dow Chemical Company, Freeport, Texas. The material used was within the specifications for sales grade dioxane, and was determined to be more than 99% pure by gas chromatography.

Conditions of the Study

The protocol of this study was approved by a seven-member Human Research Review Committee of The Dow Chemical Company and was followed rigorously. The four volunteer subjects were Caucasian males drawn from a group of scientists and businessmen aware of the toxicity of dioxane. They were fully advised of the details of the study and gave written informed consent to participate.

Prior to the study the subjects (Table 1) provided a complete history and underwent an extensive physical examination by a physician, including a chest X-ray if none had been taken during the prior 12 months, a 12-lead electrocardiogram, respiratory function tests, a conventional battery of 12 blood chemistry tests plus triglyceride and creatinine determinations, and complete hematological and urinary analyses.

TABLE 1. Characteristics of the Subjects

Parameter	Values for individuals				Mean \pm SD
	P	T	C	G	
Age, yr	46	49	40	40	44 \pm 5
Weight, kg	84	77	74.5	100.75	84.1 \pm 11.8
Height, cm	182	172.5	175.5	183	178.3 \pm 5.1
Plasma creatinine, ^a μ g/ml	12.25	8.50	13.75	11.75	11.56 \pm 2.21
Urine flow rate, ^b ml/min	2.58	1.14	1.62	2.74	2.02 \pm 0.77

^aValues are the average creatinine concentrations in four samples of blood per subject taken on the day of the study.

^bCalculated from the total urine volume from 0-24 hr.

ppm 1,4-dioxane. The chamber was monitored throughout the exposure with the infrared analyzer.

Analyses

Samples of blood plasma and urine were analyzed directly for dioxane using a Finnigan GC/MS/CI, model 3200, in the selected ion monitoring mode; HEAA was methylated before analysis by the method of Braun (1977) with the following modification. The injection port (310°C) was filled with copper filings to catalyze the cyclization of HEAA to dioxanone. The *m/e* 103 peak was monitored to quantify HEAA. This modification helped to partially eliminate an interfering peak encountered with human plasma. The detection limits were 0.1 µg dioxane/ml plasma, 2-10 µg HEAA/ml plasma, 0.2 µg dioxane/ml urine, and 1 µg HEAA/ml urine.

Creatinine was determined in blood plasma and urine by using a standard AutoAnalyzer method.

Statistics

After preliminary estimates were obtained by curve stripping procedures, nonlinear parameter estimation techniques were used to generate statistically meaningful estimates for the one-compartment model characterizing the plasma dioxane concentration time data (Gehring et al., 1976). The analytical variability in the data was characterized by a statistical "heteroscedasticity" parameter, which was then used to properly weight the data and to assess any lack of fit of the model to the data (Biau et al., 1977).

Model parameters and other characterizing parameters were obtained for each subject. The means and standard deviations of the individual values were used in this report to reflect the human population.

RESULTS

Chamber Dioxane Concentration

The nominal concentration of 1,4-dioxane vapors in the chamber was 53.9 ppm (0.19 mg/liter). The analytical concentration was quite uniform and within the range 48-52 ppm. Thus, a time-weighted average concentration was not calculated. Distribution was checked at three locations in the breathing zone of the subjects during the exposure and was found to be uniform.

Clinical Observations

Eye irritation was a frequent complaint throughout the exposure. Perception of the odor of dioxane diminished with time. Two of the subjects could not perceive the odor after 4 and 5 hr in the chamber,

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TABLE 2. Excretion of Dioxane and HEAA in Urine of Human Volunteers (P, T, C, and G) Exposed to 50 ppm Dioxane Vapor for 6 hr

Time (hr)	Urinary excretion (µg)				Mean ± SD
	P	T	C	G	
	Dioxane				
0-6	3,785	2,574	2,643	2,574	2,894 ± 595
6-8	460	98	147	416	280 ± 184
8-10	40	33	45	88	52 ± 25
10-12	2 ^d	7 ^d	10 ^d	5 ^d	6 ± 3 ^d
0-12 ^b	4,287	2,715	2,845	3,083	3,233 ± 719
	HEAA				
0-6	369,963	224,730	225,498	351,000	292,798 ± 78,538
6-8	127,758	114,402	108,810	121,590	118,140 ± 8,275
8-10	82,998	82,228	122,750	128,079	104,014 ± 24,809
10-12	46,652	48,178	28,809	80,750	51,097 ± 21,636
12-14	38,640	36,487	16,128	52,800	36,014 ± 15,103
14-16	17,748	15,295	10,530	20,040	15,803 ± 4,073
16-24	5,690	1,814	nil ^d	6,696	3,550 ± 3,167
0-24 ^c	689,449	523,134	512,525	760,955	621,516 ± 123,310

^aValues were obtained at a signal-to-noise ratio <2, and are therefore of doubtful accuracy.

^bNo dioxane was detectable beyond 12 hr.

^cNo HEAA was detectable beyond 24 hr.

^dLess than 203 µg (detection limit 1 µg/ml, urine volume 203 ml).

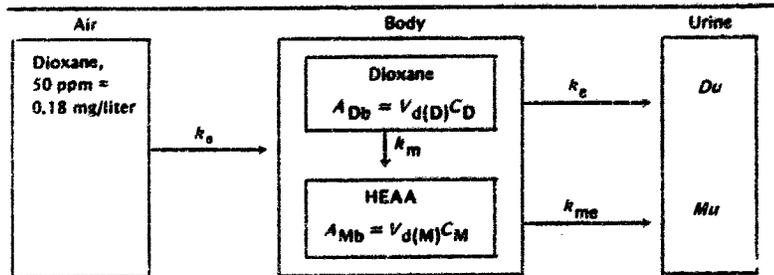
Plasma HEAA

The concentration of HEAA in plasma was measured in only two to three of the four subjects because of an interference from which HEAA could not always be separated. Therefore, the values shown in Fig. 1 are averages of the successful measurements. The concentration of HEAA in plasma reached a peak at approximately 7 hr and thereafter decreased at an apparently linear rate. After the exposure period concentrations of HEAA were higher than concentrations of dioxane.

Dioxane Excretion in Urine

The amounts of dioxane excreted into the urine during the exposure period (0-6 hr) and at 2 hr intervals after the exposure are shown in Table 2. Ninety percent of the total dioxane excreted was recovered in the 0-6 hr sample of urine, and none was detectable after 12 hr. In a one-compartment open-model system, the rate of elimination of the parent compound in the urine can be used to estimate the overall elimination rate. The half-life for elimination calculated from urinary excretion data was 48 ± 17 min. There is no significant difference between this value and

TABLE 3. One-Compartment Open-System Model for Dioxane in Humans Exposed to 50 ppm Dioxane Vapor for 6 hr



- k_a Zero-order uptake rate constant, mg/hr
- k_e First-order excretion rate constant for dioxane into urine, hr^{-1}
- k_{me} First-order excretion rate constant for HEAA into urine, hr^{-1}
- k_m First-order metabolic rate constant for dioxane to HEAA, hr^{-1}
- A_{Db} Amount of dioxane in the body, mg
- A_{Mb} Amount of HEAA in the body, mg
- $V_{d(D)}$ Volume of distribution of dioxane, ml
- $V_{d(M)}$ Volume of distribution of HEAA, ml
- C_D Concentration of dioxane in plasma, $\mu g/ml$
- C_M Concentration of HEAA in plasma, $\mu g/ml$
- Du Cumulative amount of dioxane excreted, μg
- Mu Cumulative amount of HEAA excreted, μg

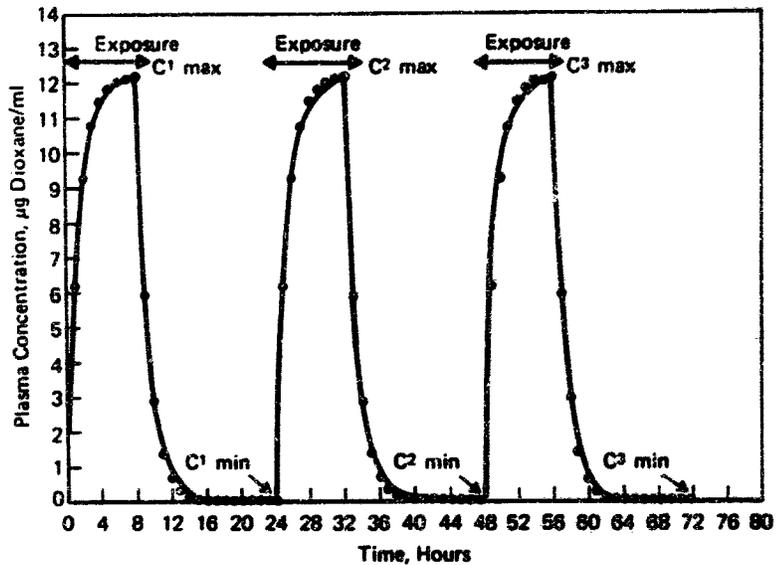


FIGURE 2. Simulated plasma concentration-time curve for humans exposed to 50 ppm dioxane for 8 hr/day. Parameters used for the simulation were obtained in the 6 hr exposure. Parameter values are shown in Table 6.

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was poorly eliminated by the kidneys. The metabolic clearance of dioxane was 75 ml/min. Thus, metabolism of dioxane to HEAA increased the rate of removal of dioxane from 0.34 to 121 ml/min.

DISCUSSION

The fate of dioxane in humans after exposure to 50 ppm for 6 hr was determined in order to provide a rationale for extrapolating extensive toxicological information obtained with rats under a variety of conditions and dosages. This would allow us to assess the hazard of dioxane exposures to humans in the workplace. The pharmacokinetic profile of dioxane in humans was essentially as predicted from previous studies conducted in rats. Dioxane was eliminated from the body primarily by metabolism to HEAA, which was subsequently eliminated rapidly in the urine. The half-life value for overall elimination of dioxane in humans was approximately 1 hr; in rats given single intravenous doses the half-life value was dependent on the dosage level, but the lower doses of 3 and 10 mg/kg had half-life values of 1.1 and 1.5 hr, respectively (Kociba et al., 1975).

The elimination of dioxane in humans after a 6 hr exposure was linear when the logarithm of concentration was plotted against time (Fig. 1), indicating that the metabolism of dioxane was a first-order process not saturated by the dosage. Since the toxicity of dioxane was observed in rats only at dosages higher than those that saturated the metabolism of dioxane to HEAA (Kociba et al., 1975; Young et al., 1976a), and since this study shows that the detoxification of dioxane in humans exposed to 50 ppm is not saturated, it is concluded that exposure to 50 ppm dioxane in the workplace will not cause adverse effects.

The pharmacokinetic model for dioxane in humans, Table 3, can be used to make predictions of the concentrations or amounts of dioxane or HEAA in the body at various times after any dosage regimen, assuming that the pharmacokinetic constants do not change with dose level and duration of dosage. The overall elimination rate equation, $K C_D$, is actually an approximation of the Michaelis-Menten form of the rate equation, $V_m C_D / [K_m + C_D]$, where the concentration of dioxane (C_D) is small relative to the Michaelis constant (K_m), and thus the equation becomes $V_m / K_m = K$. At higher dosages, C_D becomes large enough to make the approximation $V_m / K_m = K$ invalid, and the pharmacokinetics of dioxane become nonlinear. In humans the values for V_m and K_m are not known, and thus predictions of the fate of dioxane in humans at dosages above 50 ppm cannot be made. However, at concentrations of 50 ppm or less the elimination of dioxane can be predicted because $V_m / K_m = K$ will remain constant, and the pharmacokinetics will be linear. It is therefore important that 99% of the steady-state plasma concentration was attained in the 6 hr exposure, since further exposure to dioxane would have led to less than

TABLE 6. Parameters Used to Simulate Repeated Exposures to 50 ppm Dioxane Vapor

Definitions															
t^0	Time to reach a given fraction of steady state plasma concentration of dioxane.														
C_{\max}^1	Maximum plasma concentration of dioxane after the first dose.														
C_{\min}^1	Minimum plasma concentration of dioxane after the first dose and just prior to the second dose.														
C_{\max}^{∞}	Maximum plasma concentration of dioxane at steady state.														
C_{\min}^{∞}	Minimum plasma concentrations of dioxane at steady state, just prior to the next dose.														
Equations															
t^0	$= -\ln(1 - P)/K$, where P is the fraction of steady state.														
C_{\max}^1	$= R_0 [1 - e^{-KT}] / V_d K$, where T is the exposure time and other constants are defined in Table 3.														
C_{\max}^{∞}	$= C_{\max}^1 / [1 - e^{-K\tau}]$, where τ is the interval between the starts of successive exposures.														
C_{\min}^1	$= C_{\max}^1 [e^{-K(\tau - T)}]$.														
C_{\min}^{∞}	$= C_{\min}^1 / [1 - e^{-K\tau}]$.														
$C_{\max}^{\infty} / C_{\min}^{\infty}$	$= C_{\max}^1 / C_{\min}^1 = 1 / [1 - e^{-K\tau}]$.														
Simulation															
Parameters:	<table border="0"> <tr> <td>$R_0 = 76.1$ mg/hr (50 ppm)</td> <td>$C_{\max}^1 = 12.165$ μg/ml</td> </tr> <tr> <td>$V_d = 8746$ ml</td> <td>$C_{\max}^{\infty} = 12.165$ μg/ml</td> </tr> <tr> <td>$K = 0.7129$ hr$^{-1}$</td> <td>$C_{\min}^1 = 0.00013$ μg/ml</td> </tr> <tr> <td>$T = 8$ hr</td> <td>$C_{\min}^{\infty} = 0.00013$ μg/ml</td> </tr> <tr> <td>$\tau = 24$ hr</td> <td>$C_{\max}^{\infty} / C_{\min}^{\infty} = C_{\max}^1 / C_{\min}^1 = 1.00$</td> </tr> <tr> <td></td> <td>$t_{50}^0 = 3.2$ hr</td> </tr> <tr> <td></td> <td>$t_{90}^0 = 6$ hr</td> </tr> </table>	$R_0 = 76.1$ mg/hr (50 ppm)	$C_{\max}^1 = 12.165$ μ g/ml	$V_d = 8746$ ml	$C_{\max}^{\infty} = 12.165$ μ g/ml	$K = 0.7129$ hr $^{-1}$	$C_{\min}^1 = 0.00013$ μ g/ml	$T = 8$ hr	$C_{\min}^{\infty} = 0.00013$ μ g/ml	$\tau = 24$ hr	$C_{\max}^{\infty} / C_{\min}^{\infty} = C_{\max}^1 / C_{\min}^1 = 1.00$		$t_{50}^0 = 3.2$ hr		$t_{90}^0 = 6$ hr
$R_0 = 76.1$ mg/hr (50 ppm)	$C_{\max}^1 = 12.165$ μ g/ml														
$V_d = 8746$ ml	$C_{\max}^{\infty} = 12.165$ μ g/ml														
$K = 0.7129$ hr $^{-1}$	$C_{\min}^1 = 0.00013$ μ g/ml														
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	$t_{50}^0 = 3.2$ hr														
	$t_{90}^0 = 6$ hr														

dioxane will not accumulate in the body after continuous or repeated exposures. The pharmacokinetic profile of dioxane reported herein together with toxicological data and industrial experience suggests that a limit of 50 ppm dioxane provides a safe working environment.

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Document Processing Center
January 20, 1989
Page 2

We routinely analyze production lots of polyethylene glycol prior to shipment for 1,4-dioxane using a different gas chromatographic method. The 1,4-dioxane level is less than 3 ppm.

We have not identified any analyses by Dow of ethylene glycol or diethylene glycol products for 1,4 dioxane. However, we are attempting to develop an analytical method to determine what level of 1,4 dioxane, if any, is in these chemicals.

We trust that the information we are submitting will be useful to EPA.

Sincerely,



J. E. LeBeau, Director
Health & Environmental Sciences
1803 Building

dhr

attachments

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CONTAINS NO CBI

TABLE 2
Results of PCB Analyses

PCB-1450 ANALYSES

<u>Lot #</u>	<u>Ethylene Oxide Conc. ng/g</u>	<u>1,4-Dioxane Conc. ng/g</u>
TB861003K1A	26	987**
TB860608	N.D.*	80
TB840824	682	811
TB861006K1A	8	630
TB841103	8	200
TB850903 (powdered)	N.D.	N.D.
TB850903 (solid)	N.D.	121
BASF W8WE	N.D.	N.D.
BSP WPDH	N.D.	N.D.

PCB-3350 ANALYSES

<u>Lot #</u>	<u>Ethylene Oxide Conc. ng/g</u>	<u>1,4-Dioxane Conc. ng/g</u>
TB861209A1H	N.D.	159
TB860819A1H	N.D.	26
TB860819A1H	N.D.	147
TB851006A1H	N.D.	22
TB861022A1H	N.D.	71

* N.D. = Non detectable. Limit of detection for EO and dioxane is 0.1 ng/g and 4.6 ng/g, respectively.

** Assuming linearity above 18 ng/g EO and 206 ng/g 1,4-dioxane and below 4 ng/g EO and 52 ng/g 1,4-dioxane.

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UNION CARBIDE CORPORATION 39 OLD RIDGEBURY ROAD, DANBURY, CT 06817-0001
INDUSTRIAL CHEMICALS DIVISION

December, 1988

Dear Union Carbide Customer,

The purpose of this letter is to advise you that our CARBOWAX® Polyethylene Glycols above the molecular weight of 200 do not contain toxic chemicals in quantities subject to the reporting requirements of Section 313 of Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA) and 40 CFR Part 372. However, our CARBOWAX® Polyethylene Glycols do contain trace amounts of materials which are included on the State of California's list of carcinogens and reproductive toxicants under the provisions of the Safe Drinking Water and Toxic Enforcement Act of 1986, also known as Proposition 65.

The following chart outlines the CARBOWAX® Polyethylene Glycols manufactured by Union Carbide and the typical maximum levels of the trace "Proposition 65" materials contained within each product.

	TYPICAL MAXIMUM LEVELS (PPM)			
	ETHYLENE OXIDE	DIOXANE	FORMALDEHYDE	ACETALDEHYDE
CARBOWAX(R) Methoxy Polyethylene Glycols 350 to 5000	5	5	4	6
CARBOWAX(R) Polyethylene Glycols 300 to 8000	5	5	4	6
CARBOWAX(R) SENTRY(R) Polyethylene Glycols 300 to 8000	5	5	4	6
Polyethylene Glycol Compound 20M	5	5	4	6
CARBOWAX(R) TPEG 990	5	5	4	6

Please be aware that Ethylene Oxide has been listed by the State of California as a carcinogen and reproductive toxicant. Dioxane, Formaldehyde, and Acetaldehyde have been listed as carcinogens.

We are in the process of updating our Material Safety Data Sheets (MSDSs) to reflect this (and other) right-to-know information, and plan to have these available and distributed within the first quarter of 1989. In the meantime, please add a copy of this letter to each of the MSDSs for those products listed which you have received from us.

Should you have any questions on this information we would be happy to address them. Thank you for your continued business.

Very truly yours,
Union Carbide Corporation
Industrial Chemicals Division

Patricia L. Cody
Patricia L. Cody
Product Safety Manager

PLC/cw
22380
MS-0009

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Ann Arbor, MI 48108 U.S.A.
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(313) 685-0651

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313-761-1208
OCT - 7 1988
MIDLAND COUNTY HEALTH DEPT.

5

 **Gelman Sciences**

October 6, 1988

Dr. Winifred A. Oyen
Director
Midland Co. Health Dept.
125 W. Main St.
Midland, MI 48640

Dear Dr. Oyen:

We sent you information about 1,4-dioxane contamination at rest stops. Since the date of that communication, we have discovered that 3,000 parts per billion of 1,4-dioxane is present in aircraft deicing fluids. In scanning through the Act 307 list of the DNR, we find that a number of airports and military bases around the state have been cited by the DNR as causing groundwater contamination. With the additional knowledge that the ethylene glycol contains 1,4-dioxane, the problem may be more serious than originally anticipated.

We suggest you contact your state health department to immediately start taking well samples of any wells surrounding sources of known ethylene glycol contamination to determine whether 1,4-dioxane is present. It would also be appropriate for you to alert the DNR office within your area to make them aware of this situation and alert them to contamination at airports, military bases and at rest stops. We have not alerted local DNR officials about the rest stop situation.

Sincerely yours,



Charles Gelman
Chairman and
Chief Executive Officer

CG/dr

/0546G(1)

600 South Wagner Road
Ann Arbor, MI 48108 U.S.A.
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(313) 665-0651

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MICHIGAN COUNTY HEALTH DEPT.

 **Gelman Sciences**

October 17, 1988

Dr. Winifred A. Oyen
Director
Midland Co. Health Dept.
125 W. Main St.
Midland, MI 48640

Dear Dr. Oyen:

We recently discovered that fresh ethylene glycol in auto radiators and deicing fluids contained as much as 20,000 parts per billion of 1,4-dioxane.

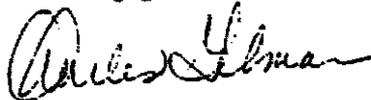
One potential situation of public health significance has been brought to our attention. At the end of the summer season, people who own summer cottages or lakeside cottages usually fill their pipelines and toilet systems with ethylene glycol. 1,4-dioxane from these summer cottages would go directly into septic fields and then into the drinking water supply.

Presently, the Michigan Department of Health sets a groundwater risk appraisal level of one part per billion of 1,4-dioxane.

We believe the same problem exists with state, county and local parks. RV vehicles and large boats follow the same practice.

You should inform your constituents of any public health risks from this practice.

Sincerely yours,



Charles Gelman
Chairman and
Chief Executive Officer

/0565G(/0566G)

Enclosures

7
OCT 19 1988

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COUNTY HEALTH DE-
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Michigan Department of Public Health
Lansing, Michigan

It is becoming evident that the chemical 1,4-dioxane is much more widely distributed in the environment than had previously been suspected. 1,4-Dioxane has been found to be a common contaminant of antifreeze fluids. 1,4-Dioxane moves readily into groundwater, and is not retarded significantly as the groundwater moves through various soils, so that it can spread readily from its sources of origin.

The assessment of potential risks is hampered by the fact that to date no maximum contaminant levels have been established for 1,4-dioxane by the U.S. EPA Office of Drinking Water, although a health advisory document exists. The Michigan Department of Public Health has also developed a very conservative risk assessment document.

In addition, an extensive Draft Health and Environmental Effects Assessment for 1,4-Dioxane (R. Hartung, Sept. 23, 1987) exists. That document has been widely circulated and has received extensive peer review. That document provides a variety of limiting concentrations for drinking water, using various methods which use a variety of assumptions, for the derivation of such values. Although 1,4-dioxane is carcinogenic to laboratory animals at extremely high dose levels, the available information strongly supports the existence of a threshold for toxic effects for this compound. The most sensitive effects found were non-cancer effects in liver and kidneys in lifetime exposures to rats, and a drinking water criterion was based on the absence of those effects, using a 100-fold safety factor. The resulting reference dose (RfD) was 0.096 mg/kg/day for a life time. The resulting drinking water limit was 3.36 mg/L, which could be rounded off to 3 mg/L.

To this date, this particular risk assessment is most strongly supported by the existing scientific data on 1,4-dioxane. The additional conservatisms used by the Michigan Department of Public Health appear to be founded largely on the desire to incorporate conservative risk management perspectives into the risk assessment process.

At this time it is becoming increasingly important to collect all of the environmental and health related information on 1,4-dioxane, assess it, expose the assessment to the broadest possible peer review, and then develop the appropriate management for 1,4-dioxane.

Sincerely,


Rolf Hartung

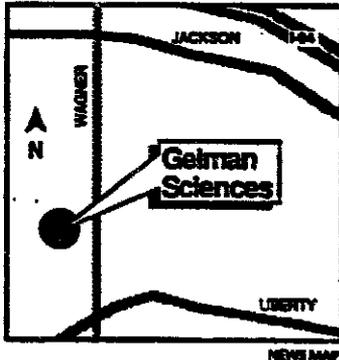
Gelman cites other dioxane sources

By PAUL JUDGE
NEWS BUSINESS REPORTER

□ Gelman sales up, C1

Gelman Sciences Inc., facing a court challenge to clean up soil and groundwater pollution around its Wagner Road plant, is claiming "the government and other individuals" may be polluting drinking water with the same chemical solvent the company is charged with releasing into the environment.

In a state hearing in Lansing Tuesday to consider changes to Michigan rules governing public water supply, a Gelman Sciences attorney claimed that the state has ignored the potential for groundwater contamination from puddles of antifreeze in the parking lots of rest areas along Michigan highways.



NEWS MAP

Robert Reichel, an assistant attorney general representing the state in its suit against Gelman, dismissed the company's statements as "a smoke screen and an attempt by Gelman to divert attention from the very significant, thoroughly documented contamination problem emanating from Gelman Sciences' facility."

The Department of Natural Resources has charged Gelman Sciences with polluting soil, surface water and groundwater near the company's plant on Wagner Road in Scio Township, just west of Ann Arbor.

The pollutant, a solvent called 1,4-dioxane, has been detected in more than 50 commercial and resi-

dential wells in Scio Township. The DNR is suing Gelman to restore the groundwater to its original purity.

The company and others, including Midland-based Dow Chemical Co., are also defendants in a separate civil lawsuit brought by homeowners seeking damages from the dioxane contamination.

In Tuesday's hearing, Gelman Sciences said the presence of dioxane is "statewide and of a much more extensive nature than originally assumed." The company's attorney called on the state to come up with "more realistic drinking water standards" that would classify dioxane as a less harmful pollutant.

The company claimed that research it has conducted as a result of the lawsuits shows that drinking water is tainted by dioxane from a variety of sources, including automotive coolant, de-icing fluid for airplanes, shampoo and cosmetics.

Specifically, Gelman officials released findings from samples of radiator boil-over pools it collected from the pavement in highway rest areas during August and September. According to a listing of "partial results" released by the company, the samples showed concentrations of dioxane in the puddles ranging from 2,300 parts per billion in the Clare area off US-27 to less than 10 parts per billion in the Ann Arbor area along I-94.

The state standard for safe levels of dioxane in drinking water is 2 parts per billion.

"This makes every service station, garage, parking lot and rest stop as well as homes in the state possible sources of 1,4-dioxane contamination," said Gelman Sciences' attorney Edward J. Levitt.

But Reichel, the state's leading attorney in its case against Gelman Sciences, said the claims by the company have no bearing on contamination around the plant site in Scio Township.

"I'm not aware of any data that attributes contamination near the Gelman Sciences' facility to some source of antifreeze leaks or radiator boil-overs," Reichel said.

DNR enforcement division official David Rymph said the depart-

ment was "aware of the potential for contamination from 1,4-dioxane in antifreeze prior to the Gelman study." The state Departments of Natural Resources, Public Health and Transportation have each assigned a person to review the study provided by Gelman Sciences and consider what action, if any, to take on the matter of antifreeze boil-over in rest areas. Rymph said.

Levitt said the company has commissioned studies "to determine what is a safe level of dioxane in drinking water."

"Undoubtedly, results of this investigation may have an impact favorable to Gelman in the case," Levitt said. "But it wasn't done to avoid our responsibilities."

The full extent of those responsibilities for cleaning up pollution around the company's Scio Township plant is the subject of the court case brought against Gelman by the DNR.

According to company financial statements, Gelman Sciences spent \$1.3 million through the end of July on pollution-containment efforts, including fees paid to 11 scientists and consultants investigating the potential effect of dioxane on humans.

Levitt could not supply a figure for the amount the company spent on the sampling survey of radiator boil-over at Michigan highway rest areas.

To date, however, the company has not completed the hydro-geological survey of the plant site requested in 1986 by the Department of Natural Resources, according to Rymph.

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REMOVAL OF 1,4-DIOXANE FROM WASTEWATER

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Summary

Chemical methods were evaluated for the treatment of 1,4-dioxane in industrial process wastewaters. The compound was rapidly oxidized by a combination of hydrogen peroxide and ferrous iron, although the rate of organic carbon removal was considerably slower than the disappearance of 1,4-dioxane from solution. Chlorine oxidation at 75°C was also found to be highly effective. The rate of the reaction was greatest at pH 5.2, suggesting that hypochlorous acid was the preferred oxidant. 1,4-Dioxane appeared to be completely oxidized during chlorination, although the removal of organic carbon was somewhat slower than the disappearance of the parent compound.

Introduction

1,4-Dioxane (1,4-diethylene dioxide) is used for a variety of industrial applications including, as a solvent for cellulose and a wide range of organic products, a wetting and dispersing agent for textile processing and printing, and as a stabilizer in certain chlorinated solvents. Process waters arising from these operations may contain 1,4-dioxane as a result of spills or through the routine discharge of wastes. Although the levels of 1,4-dioxane present in plant effluents are likely to be low, under certain conditions it may be desirable to pretreat more concentrated process waste streams to remove the compound. However, methods for the removal of 1,4-dioxane from such wastewaters have not been described.

1,4-Dioxane is generally considered to be nonbiodegradable. Results of the biochemical oxygen demand test for 1,4-dioxane indicate that negligible oxygen is consumed over a 20-day test period [1]. Mills and Stack [2] have also noted that degradation of the compound was not observed in cultures of sewage microorganisms exposed for 1 year to wastewater treatment plant effluents adjusted to contain 1,4-dioxane at concentrations ranging from 100 to 900 mg/L. Thus, it appears unlikely that significant removal of 1,4-dioxane will occur in conventional biological treatment systems.

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As an alternative to biological treatment, physical or chemical methods can be considered for the removal of 1,4-dioxane from industrial process wastes. However, in view of the infinite water solubility and low vapor pressure (30 mm at 20°C) [3] of the compound, physical treatment by air-stripping or activated carbon adsorption is not likely to be highly effective. Preliminary studies conducted in our laboratory have indeed confirmed this observation. As a result, the present study was conducted to evaluate chemical methods, including chlorine and hydrogen peroxide oxidation for the treatment of industrial wastewaters containing 1,4-dioxane.

Experimental

The oxidation of 100 mg/L of 1,4-dioxane by hydrogen peroxide in combination with a ferrous iron salt (Fenton's reagent) [4] was examined in aqueous solutions containing 115, 230 and 465 mg/L of H_2O_2 . These levels correspond to H_2O_2 :dioxane molar ratios of 3:1, 6:1 and 12:1, respectively. Reaction mixtures were prepared by combining the appropriate amount of a 30% H_2O_2 solution with distilled water, and adjusting the pH of the solution to $pH\ 5.5 \pm 0.2$. Test reaction mixtures were supplemented with 200 mg/L of $FeSO_4 \cdot 7H_2O$. Control reaction mixtures were prepared as above, except that the ferrous iron was omitted. Solutions (final volume of 200 mL) were transferred to amber bottles and incubated at an ambient temperature (25°C). Reactions were initiated by the addition of 20 mg of 1,4-dioxane (neat). Samples were removed periodically, diluted with an equal volume of 60 mM Na_2SO_3 to quench the reaction, and analyzed as described below.

Chlorine oxidation of 100 mg/L of 1,4-dioxane was initially examined in water solutions containing 1000 mg/L of NaOCl (corresponds to NaOCl:dioxane molar ratio of 12:1). Reaction mixtures were prepared by combining the appropriate amount of a 5% NaOCl solution with distilled water, and adjusting portions of the mixture to a pH of 2, 6 and 11. Test solutions (final volume of 200 mL) were transferred to amber bottles and incubated at an ambient temperature (25°C) or in a water bath at 75°C. Reactions were initiated by the addition of 20 mg of 1,4-dioxane (neat). Samples were removed periodically, diluted with an equal volume of 60 mM Na_2SO_3 to quench the reaction, and analyzed as described below.

The effect of pH on the oxidation of 1,4-dioxane by aqueous chlorine was examined in reaction mixtures prepared using 1.0 M NaH_2PO_4 buffers adjusted to a pH ranging from 5 to 6.5. Portions of the appropriate buffer were transferred to amber bottles and supplemented with 100 mg/L of 1,4-dioxane and 2000 mg/L of NaOCl. Reaction mixtures (final volume of 200 mL each) were incubated in a water bath at 75°C.

1,4-Dioxane was analyzed by gas chromatography by direct injection of aqueous samples. Chromatography was performed using a Hewlett-Packard model 5730 gas chromatograph with a flame ionization detector. The analytical column (glass; 10 ft. \times 0.25 in.) was packed with Tenax GC (Supelco,

Inc., Bellefonte, PA). Compounds were eluted from the column isothermally at an oven temperature of 150°C with a helium carrier gas at a flow rate of 30 mL/min. Output of the flame ionization detector was connected to a Hewlett-Packard model 3380 recording integrator. All values were calculated from peak height measurements by comparison with an external standard of 1,4-dioxane prepared in water.

Total organic carbon was determined using either a Beckmann model 915B or Dohrmann model 80 total carbon analyzer. Total organic carbon concentrations were calculated from the difference of the total carbon and inorganic carbon concentrations of a sample. The instruments were calibrated using potassium biphthalate and sodium carbonate as standards.

Results and discussion

1,4-Dioxane was rapidly degraded by a combination of hydrogen peroxide and ferrous iron, as shown in Fig. 1. No degradation was observed in the control. The compound was rapidly oxidized during the first hour in all test solutions; however, the rate of the reaction decreased thereafter in reaction mixtures containing 3 or 6 moles H_2O_2 per mole 1,4-dioxane. Complete removal of the compound occurred within 10 h in test solutions containing 12 moles H_2O_2 per mole 1,4-dioxane. During incubation, the pH of all test solutions rapidly decreased from pH 5.7 to pH 2.9 due to acid formation during the reaction. These conditions are within the optimum range (pH 2.5–4.0) reported for the oxidation of organic compounds by Fenton's reagent [5].

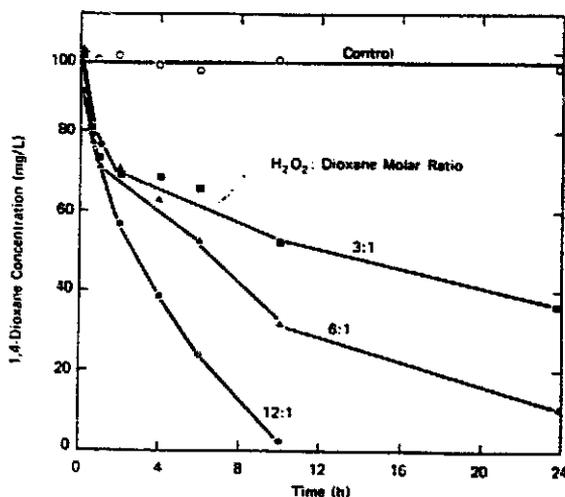


Fig. 1. Oxidation of 1,4-dioxane by a combination of hydrogen peroxide and ferrous iron.

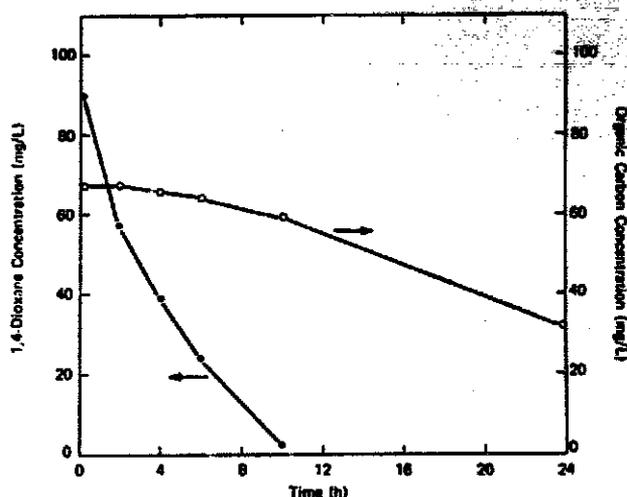


Fig. 2. Removal of 1,4-dioxane and organic carbon during hydrogen peroxide oxidation.

To determine whether 1,4-dioxane was completely oxidized during the reaction, samples of the test solution containing 12 moles H_2O_2 per mole compound were periodically analyzed for the concentration of organic carbon remaining in solution. As shown in Fig. 2, the rate of organic carbon removal was considerably slower than the disappearance of 1,4-dioxane from solution. After 10 h of incubation, removal efficiencies were 97% and 10.5% for 1,4-dioxane and organic carbon, respectively. Following 24 h of incubation, the organic carbon concentration of the reaction mixture was decreased by 48%.

The stoichiometry calculated for the oxidation of 1,4-dioxane,



suggests that 10 mol hydrogen peroxide are required for the complete degradation of 1 mol 1,4-dioxane. While removal of the parent compound occurred rapidly in test solutions containing a 12:1 molar ratio of H_2O_2 to 1,4-dioxane, the oxidation of the residual organic carbon was considerably slower. The incomplete oxidation of organic compounds by a combination of hydrogen peroxide and ferrous iron has been previously described [6], and appears to be due to the formation of low molecular weight organic aldehydes and acids which are resistant to further chemical oxidation. However, such products are known to be readily removed by conventional biological treatment processes.

A series of experiments were also conducted to examine the chlorine oxidation of 1,4-dioxane in aqueous solution. Preliminary studies indicated that the compound was not degraded at 25°C in reaction mixtures prepared at a

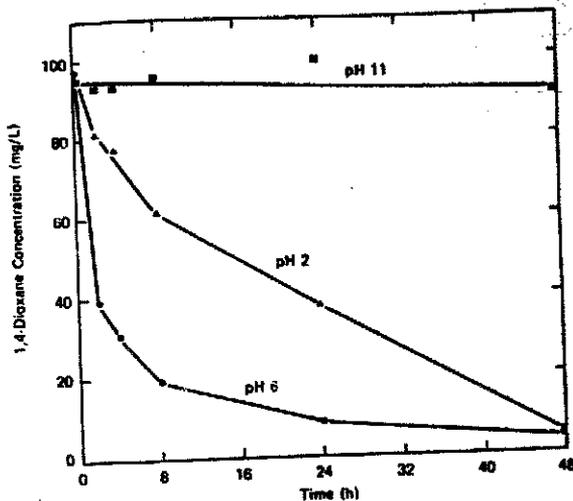


Fig. 3. Chlorine oxidation of 1,4-dioxane in water at 75°C.

pH of 2, 6 or 11. However, when solutions containing 100 mg/L of 1,4-dioxane and 1000 mg/L of NaOCl were adjusted to pH 2 or pH 6 and incubated at 75°C, the compound was rapidly degraded as shown in Fig. 3. The rate of the reaction at pH 6 changed with time. This was presumably due to a decrease in the pH of the solution from pH 6 to pH 2.8 as a result of acid formation during the reaction. The rate of oxidation was negligible in test solutions prepared at pH 11.

The effect of pH on the oxidation of 1,4-dioxane by aqueous chlorine at 75°C was subsequently examined in reaction mixtures prepared using 1.0 M NaH₂PO₄ buffers over the range from pH 5.2 to 6.5. Results of the study are shown in Fig. 4. Destruction of 1,4-dioxane at 75°C proceeded rapidly at pH 5.2, with an initial removal rate of approximately 32.6 mg of 1,4-dioxane consumed per hour. The rate of oxidation decreased as the pH of the reaction mixture was increased, and was negligible at a pH of 6.5 (see Inset, Fig. 4).

To determine whether 1,4-dioxane was completely oxidized during the reaction with chlorine, samples of the reaction mixture prepared at pH 5.2 were periodically analyzed for the concentration of organic carbon remaining in solution. As shown in Fig. 5, the rate of organic carbon removal was somewhat slower than the disappearance of 1,4-dioxane from solution. After 8 h of incubation, removal efficiencies were 97% and 70% for 1,4-dioxane and organic carbon, respectively. Following 24 h, the organic carbon concentration of the reaction mixture was decreased by 85%.

Chlorine oxidation was found to be highly effective for the removal of 1,4-dioxane from water, although the reaction rates were shown to be

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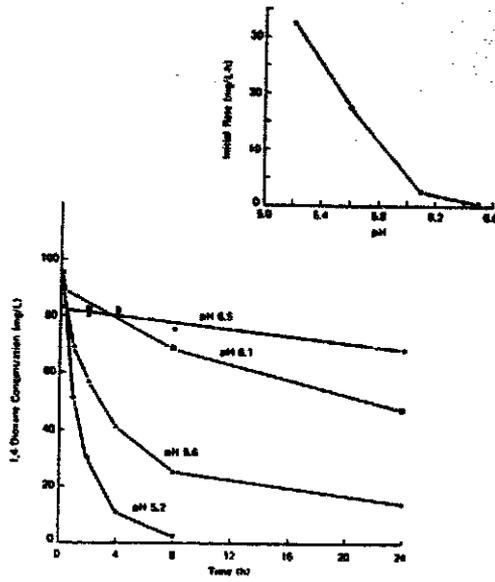


Fig. 4. Effect of pH on the oxidation of 1,4-dioxane by aqueous chlorine in 1.0 M NaH₂PO₄ buffer at 75°C.

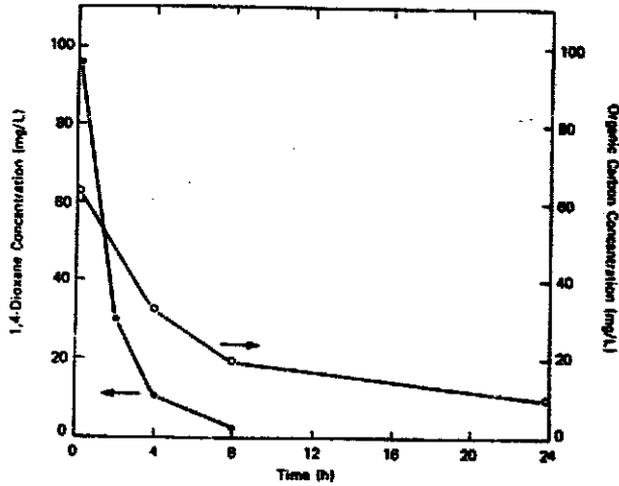


Fig. 5. Removal of 1,4-dioxane and organic carbon during chlorine oxidation chlorination at pH 5.2 at 75°C.