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THE ENVIRONMENTAL FATE AND MECHANISM OF FORMATION OF 2-ETHYL-5,5'-DIMETHYL-1,3-DIOXANE (2EDD) – A MALODOROUS CONTAMINANT IN DRINKING WATER

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ABSTRACT

A malodorous chemical, 2-ethyl-5,5'-dimethyl-1,3-dioxane (2EDD) created a drinking water taste and odor episode in Pennsylvania (USA) during 1992. The odor episode occurred as the result of a reaction between propionaldehyde and neopentyl glycol in the waste tank of a resin manufacturer. Samples of this waste water were extracted and analyzed. An *in situ* aqueous preparation of 2EDD was completed to demonstrate that 2EDD could have formed under the conditions found in the waste water. The stability (fate) of 2EDD was studied at different aqueous pHs (pH3, 5, 7, and 9). Some hydrolysis of 2EDD was found at pHs<7 after one week, but 2EDD appeared to be stable at pH 9. The odor characteristics and odor threshold of 2EDD were determined by the method of flavor profile analysis. The odor threshold concentration of 2EDD was found to be between 5 and 10 ng/l and was described as having a sweet, tutti fruitti odor (near the odor threshold concentration) and a burnt, sickening sweet odor at higher concentrations. This study also discovered that slight antagonism in chloraminated drinking water may occur at or near the threshold odor level of 2EDD.

KEYWORDS

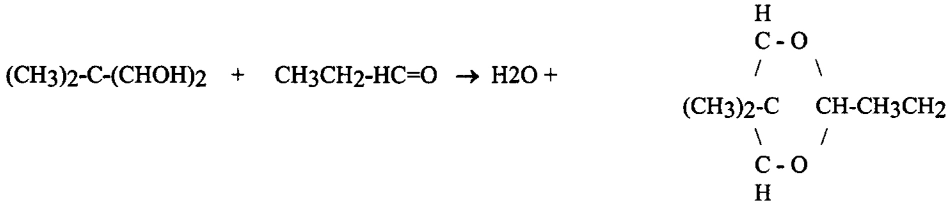
Dioxane; 2EDD; drinking water; flavor profile analysis; odor threshold; stability; taste and odor.

INTRODUCTION

A taste and odor incident in Pennsylvania occurred in the drinking water supplied by the Philadelphia Suburban Water Company (PSWC) during the month of February 1992 (Preti *et al.*, 1993; Staudte *et al.*, 1993). Odorous chemical discharges into the PSWC drinking water source, Neshaminy Creek (a tributary to the Delaware) were apparently coming from an industrial waste treatment facility in Hatfield, PA. The odor was described as "sweet chemical odor" (Preti *et al.*, 1993). The effluent from the waste treatment facility included waste from a resin manufacturer. Apparently, at least some of the odorous chemical in the finished drinking water survived both the wastewater and drinking water treatment processes. Substituted 1,3-dioxanes were the suspected culprit. Particularly, 2-ethyl, 5,5'-dimethyl-1,3-dioxane (2EDD) was believed to be responsible for the odor problem at the Neshaminy Creek Drinking Water Treatment Plant of the PSWC

(Preti *et al.*, 1993; Staudte *et al.*, 1993). The odor threshold for this compound was believed to be on the order of 10 ng/l (Preti *et al.*, 1993), although this was not determined by an odor panel.

Dioxanes are cyclic acetals. Cyclic acetals and ketals have been used as chemical protecting groups in organic synthesis and are prepared from ketones/aldehydes and diols (Sanderson *et al.*, 1988; Fife and Natarajan, 1986; Dauben *et al.*, 1954). The reactions can occur spontaneously in aqueous solutions. The chemical 2EDD is formed from the reaction of neopentyl glycol and propanal. Figure 1 shows the reaction where water is released as the other primary reaction product. The wastewater from the resin manufacturer contained 2EDD at 950 ppb (Staudte *et al.*, 1993; Preti *et al.*, 1993).



$$(CH_3)_2\text{-C-}(CHOH)_2 + CH_3CH_2\text{-HC=O} \rightarrow H_2O +$$

2-EDD

Figure 1. Formation of 2-ethyl-5,5'-dimethyl-1,3-dioxane.

The first objective of this study was to investigate the mechanism of formation of 2EDD under the actual high concentrations and low pH (pH 4.2-6.1) in which the starting materials existed in the resin wastewater. A second objective was to determine whether 2EDD was stable under natural pH conditions in environmental waters (e.g. Neshaminy Creek) which are greater than pH 7. The final objective was to understand the odor characteristics of 2EDD as determined by an odor panel.

METHODS

Analysis of wastewater

The pH and TOC of the samples were determined by the standard methods (Standard Methods for the Examination of Water and Wastewater, 1992). Samples of wastewater from the resin manufacturer and from the industrial waste treatment facility were extracted and analyzed to confirm the presence of 2EDD and any other related dioxanes or dioxolanes. Separate samples were analyzed for aldehydes which are first derivatized (described below). No "Standard Method" is available for 2EDD. Therefore, a method development and recovery study were completed for the analysis of 2EDD. The method of extraction was an EPA base/neutral procedure (EPA method 3520A), but due to low sample volume, separatory funnels were used to extract by hand instead of using the recommended continuous liquid-liquid extraction method. Samples of 100 ml were extracted with 50 ml methylene chloride with 15 minutes of vigorous shaking. The samples were dried through a column of sodium sulfate and evaporated down to 0.5-1ml with a Kontes tube heater (Vineland, NJ) in Kuderna-Danish tubes facilitated by blowing nitrogen at the surface at a flow rate of 1.25 ml/sec.

After addition of base/neutral internal standards, the samples were analysed by GC/MS using a Finnigan 4000 MS with a splitless injector. The GC was fitted with a 30 m narrow bore (0.25 mm) DB-5 MS fused silica capillary column (J&W Scientific, Folsom, CA). The helium carrier gas flow rate was 40 cm/sec. The initial column temperature was 30°C and held for 4 minutes, programmed at 6°C/min. to 300°C and held at that temperature for 30 min. All mass spectra were NBS library searched. The quality assurance was done using a second fused silica capillary column with DB-5 phase stationary phase (J&W Scientific, Folsom, CA).

For the analysis of aldehydes in the wastewater samples, a modified Method 6252 Ozonation By-Product: Aldehydes (Standard Methods for the Examination of Water and Wastewater, 1992) was used. This method involves derivatization of the aldehydes with o-2,3,4,5,6-pentafluorobenzylhydroxylamine (PFBHA). After derivatization, the samples were extracted as described above. The quantitative analysis of aldehydes was performed on a Perkin Elmer Model 8500 GC equipped with an electron capture detector (ECD) with a DB-5 fused silica capillary column, 60 m bore (0.25 mm ID) (J&W Scientific, Folsom, CA) with a splitless injector. The injector and detector temperatures were 250°C and 350°C, respectively. The helium carrier gas flow rate was 35 ml/sec. The initial column temperature was 50°C and held for 1 minute, programmed at 5°C/min. to 90°C, then 4°/min. to 250°C and held for 2 minutes. The makeup gas for the ECD was zero-grade nitrogen at a flow rate of 40 ml/min.

Chemical mechanism study

An experiment was completed to determine if a mixture of the reactive chemicals which were present in the resin manufacturer's waste could form the compound 2EDD at pH 4.2-6.1, the apparent cause of the taste and odor incident (Preti *et al.*, 1993; Staudte *et al.*, 1993). Neopentyl glycol and propionaldehyde (Aldrich Chemical Co., Milwaukee WI, Cat. # 12,658-6 and # P5,145-1, 97% pure, respectively) were mixed in distilled water at the concentrations (2,500 ppm and 6,500 ppm, respectively) and pH as in the waste tank. The chemicals were mixed in the dark on a shaker at low speed for two weeks at room temperature. This was completed in triplicate. The one-liter samples were extracted into 500 ml of methylene chloride, (Pesticide Grade, EM Science, Gibstown, NJ) by continuous liquid-liquid extraction (Corning Pyrex One-Step$_{TM}$ Continuous Extractor/Concentrator (Corning Corp., NY) for 10 hours (Fowler, 1991). The extracts were individually evaporated to 5 ml in the concentrator. The extracts were analyzed by GC/MS as described above.

Stability of 2EDD

A study was completed to determine the general stability of 2EDD at different aqueous pHs because 2EDD was formed at low pH (pH 4.2-6.1) and was present in the environment at a pH of greater than 7.5. Two one-liter samples of 500 ppb 2EDD in buffered water were prepared at the following pHs: pH 3, 5, 7, and 9. To achieve these aqueous pHs, combinations of potassium phosphate, sodium phosphate, and phosphoric acid were added to develop an ionic strength of 0.2 M. The 2EDD solutions were placed in the dark at room temperature on automatic shakers and were shaken for two weeks. Periodically, the shaking was briefly interrupted and 100 ml aliquots were removed for the analysis of kinetics of degradation. For analysis, the 100 ml aqueous aliquots were hand extracted in separatory funnels with 50 ml methylene chloride. EPA Base-Neutral Recovery Standards were added before extraction as a quality assurance measure. The extracts were dried through Pasteur pipette columns of sodium sulfate. The extracts were concentrated to a volume of 0.5 ml as described above with a Kontes tube heater in 10 ml Kuderna-Danish tubes facilitated by blowing nitrogen at the surface at a flow rate of 1.25 cc/sec. The samples of pH 3 and 9 were analyzed at days 3, 7, and 14. The samples at pH 5 and 7 were only analyzed at days 7 and 14. All extracts were analyzed by GC/MS.

Synthesis and purification of 2EDD for FPA

For taste and odor analysis, a pure sample of 2EDD was synthesized under optimum conditions. The starting materials, neopentyl glycol and propionaldehyde were first purified to minimize any byproducts. Neopentyl glycol was crystallized from 100% acetonitrile. The neopentyl glycol was dried by blowing GC grade pre-purified nitrogen over it, then stored in a dessicator. Three grams were used in the subsequent reaction. Propionaldehyde (20 ml) was doubly distilled under nitrogen just before synthesis. The middle fraction of the first distillation was saved for the second distillation. The middle fraction of the second distillation consisted of a total of 4 ml of which 1.9 ml was used in the subsequent reaction. The boiling point of this fraction was 47-50°C. The boiling point listed in the Merck Index for propionaldehyde is 46-50°C. The method of McGorrin *et al.* (1987) as described by Staudte *et al.* (1993) was used for the synthesis. The final product 2EDD was separated from the reaction matrix immediately by distillation.

The GC/MS was completed on a Hewlet Packard 5890 GC equipped with an MS detector. The programmed temp. GC conditions were 40°C for 10 minutes, 4°C /minute to 150°C, then 30°C/minute to 250°C. A sniff port on a parallel capillary DB-5 column was used to smell the peaks (sensory GC). Quality assurance was completed using a fused silica capillary column with DB-5 phase stationary phase (J&W Scientific, Folsom, CA). All mass spectra were NBS library searched. The maximum spectral match as well as mass spectra interpretation and retention time of a peak was used to identify a compound.

Flavor profile analysis

The pure compound 2EDD was diluted in distilled Milli-Q water to concentrations of 0.001 to 100 µg/l. A trained taste and odor panel evaluated the response of odor intensity versus the concentration of the 2EDD by the flavor profile analysis method (Standard Methods for the Examination of Water and Wastewater, 1992) and assessed the odor threshold concentration by a ranking test (Chapter 9, Jellinek, 1985). The purified 2EDD in water, was prepared at the concentration observed at the effluent of the water treatment plant to determine if the FPA panel could smell the chemical. This was completed in the presence and absence of appropriate chloramine residual disinfectant.

RESULTS AND DISCUSSION

Chemical analysis of the wastewater of the resin manufacturer

Table 1 shows the pH and DOC of the samples of the original waste water from the resin manufacturer, analyzed three years after refrigerated storage. Table 2 shows that 2EDD apparently formed between pH 4.2-6.1 and was stable under refrigeration. Also, the 2EDD was present in the bioreactor at the industrial waste treatment facility at pH 7.7, located upstream from the Neshaminy River plant.

Table 1. Determination of pH and DOC of the samples

	Date Collected	pH	DOC (mg/l)
1. Resin Manufacturer Raw Waste Water	2/22/92	6.1	32,555
2. Resin Manufacturer Process Wash Water	2/13/92	5.9	27,714
3. Resin Manufacturer Composite Tank Wagon	1/20/92	4.2	14,878
4. Wastewater Treatment Bioreactor	2/92	7.7	352
5. Blank 1	3/6/95	5.7	0.3
6. Blank 2	3/6/95	5.7	0.3

The waste samples had to be diluted 400 times with Milli-Q water (blank water - see below) to get an accurate DOC measurement. Above values are the final (actual) DOC after dilution taken into account.

Table 2. Determination of 2EDD in the water samples

Sample	Sample Date	pH	2EDD (mg/l)
1. Resin Manufacturer Process Waste Water	2/13/92	5.9	49
2. Resin Manufacturer Composite Tank Wagon	1/20/92	4.2	22
3. Wastewater Treatment Bioreactor	2/92 no quantified	7.7	present -
4. Blank 1	3/6/95	5.7	< DL
5. Blank 2	3/6/95	5.7	< DL

< DL means less than detection limit.

Table 2 also shows that less than detectable levels were present in the blank Milli-Q water samples which were passed through an extra glass column of activated carbon with an empty-bed contact time of 5 minutes with the addition of 50 ppb Base-Neutral Spiking Solution (Supelco, Bellefonte, PA; catalog # 4-8869) to serve as recovery standard.

The GC/MS analysis of the Resin Manufacturer Process Wash Water identified several aldehydes, glycols, 2EDD and another related chemical, 2-ethyl-4-methyl-1,3-dioxolane. The concentration of 2EDD as shown in Table 2 is 49 mg/l. The 2-ethyl-4-methyl-1,3-dioxolane isomers total concentration is 3.6 mg/l . 2EDD was also confirmed to be present in the Resin Manufacturer Composite Tank Wagon sample at a concentration of 22 mg/l. The two isomers of 2-ethyl-4-methyl-1,3-dioxolane are not present in this sample. This work confirmed that the original source of the 2EDD was not from the industrial waste facility, but from the resin manufacturer. The question remains what is the stability of 2EDD at the pH of formation (pH 4.2-6.1).

The concentration of 2EDD in the bioreactor of the industrial waste facility (at pH 7.7) was not quantified, but its presence was confirmed by the GC/MS. In 1992, the concentration of 2EDD in the waste of PSWC was estimated to be 950 ppb (Staudte *et al.*, 1993). When the bioreactor effluent in 1992 was analyzed, it contained 4 ppb 2EDD (Staudte *et al.*, 1993). Since our analysis was completed two years after sample collection, it is likely that the 2EDD concentrations decreased by hydrolysis. Samples had been stored under refrigeration which would not completely prevent such degradation. If significant biological degradation had occurred, it would be expected that aldehydes, which are easily biodegraded both aerobically and anaerobically, would have been lost from the samples. However, aldehydes were found (16.3 ppb of propanal alone) in the bioreactor sample indicating that the 2EDD was not significantly biodegrading.

Mechanism study

The GC/MS analysis of the aqueous reaction mixture of neopentyl glycol and propionaldehyde after 2 weeks of shaking at room temperature confirmed the presence of 2EDD. This means that 2EDD could have formed in the waste from the resin manufacturer when the chemicals neopentyl glycol and propionaldehyde were present in the waste (at room temperature).

Stability study

The hydrolysis study was completed to determine if the mixture of the reactive chemicals which were present in the resin manufacturer's wastes could form the compound 2EDD and continue to be present under the conditions in which they were collected as presented in Table 1 (at pH 4.2-7.7) and if 2EDD could maintain its stability in natural waters at a pH > 7.0. The hydrolysis studies were forensic in nature and were not completed to determine rate constants. Figure 2 shows a graphic presentation of the stability of 2EDD at different aqueous pHs after shaking for a two week period in the dark. Since the method of hand extraction does not have very good precision (variation > 10%), a difference of 10 on the relative response scale probably is not significant. Therefore, the relative response at pH 9 is thought to be the same throughout the study meaning that 2EDD is stable at pH 9. After three days, the concentration of 2EDD had decreased (probably from hydrolysis) at pH 3. There are no data at day 3 for pHs 5 and 7, but the relative responses after one week appear to be within ten percent for pHs 3, 5, and 7. Assuming the hydrolysis fits an inverse exponential pattern, and the "leveling-off" of the curve begins after a few days at pH≤7, more data points are needed at the beginning to get a better understanding of the kinetics. Measurements should have been taken at intervals of hours instead of days for the lower pHs. Note that this solution was 0.5 ppm of 2EDD and the Resin Manufacturer samples were higher and losses from poor extraction recovery are not considered. The recoveries of EPA Base-Neutral Standards (20-53% mean recoveries, all standards) were mostly at the low end of the EPA recovery range of acceptability (e.g. 26-127% for pyrene). Although the Resin Manufacturer Composite Tank Wagon sample had a low pH (pH 4.2), the concentration was high to begin with and therefore 2EDD was still present. The presence of 2EDD in the Resin Manufacturer Composite Tank Wagon sample indicates that the solution was at equilibrium with the aldehydes and neopentyl glycol present at this high concentration.

Figure 2 shows that in the environment at pH > 7 and in the industrial waste treatment bioreactor, the 2EDD is stable and would not significantly hydrolyze in the natural water environment. This confirms the forensic data of Staudte *et al.* (1993).

Odor characterization

A GC/MS analysis of the purified 2EDD showed only one peak on the total ion chromatogram and it was identified as 2EDD. A sniff port on a parallel capillary DB-5 column of the HP GC/MS was used to smell the peaks. The one peak in distillate fraction 2 at 20.6 minutes of the total ion current mass chromatogram, identified as 2EDD, was given a sensory GC descriptor of "tutti frutti", near the odor threshold concentration present at the GC sniff port. An FPA panel described the odor as burnt, sickly sweet at higher concentrations. This assessment is not completely in agreement with Cocheo *et al.* (1991) and Preti (1993). Different descriptors appear to be cultural. A consensus should be made for a less biased descriptor. Consumer complaints from all reported taste and odor events indicate that, even at low concentrations, 2EDD was interpreted to have an unpleasant smell in natural waters. However, panelists in this study found the odor of 2EDD in its purified form in deionized water to be pleasant at low concentrations. The descriptor of burnt, sickening sweet odor at higher concentrations did agree with previous studies.

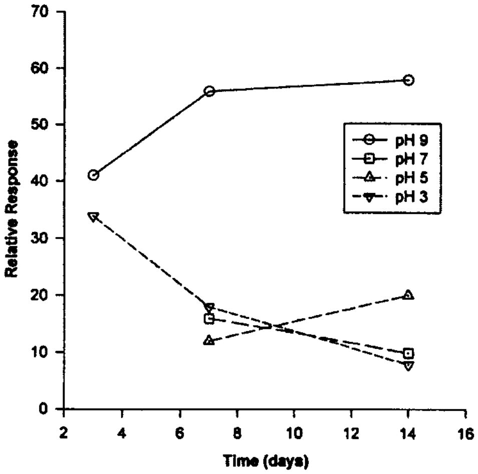


Figure 2. Stability of 2EDD at different pHs over time.

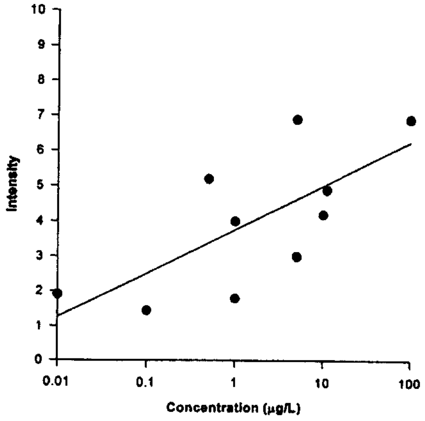


Figure 3. Weber-Fechner curve of 2EDD (odor intensity vs log concentration) of two panel sessions combined.

The flavor profile analysis panel on four different days evaluated different concentrations of 2EDD in distilled water (pH 5-6). Figure 3 shows the day 1 and day 2 results plotted as Weber-Fechner Curves (Odor Intensity vs Log Concentration of 2EDD). The panelists used descriptors such as: fruity, apple, menthol and sweet or burnt sweet, solvent sweet, and sickening sweet to describe different concentrations of the 2EDD. The sensory panel response on day 1 and day 2 showed that the odor threshold was less than 10 ng/l . A ranking test was completed by two panelists after the second day of the FPA panel. The two panelists correctly ranked the solutions and each sample had a detectable sweet-type odor at the 10-100 ng/l levels. The odor at low concentrations was described as sweet (tutti frutti). Both sets of data were combined on Figure 3.

A second ranking test on day 3 with 2 panelists was completed with concentrations of 1 to 100 ng/l and odor free water. The two panelists ranked the 10-100 ng/l samples in the correct order. The two panelists ranked the 2.5, 5, and 10 ng/l samples as equivalent. This assessment indicates that the odor threshold concentration is between 5 and 10 ng/l. This odor threshold concentration is at the threshold concentration level of the common earthy odorous chemicals found in drinking water, e.g. geosmin.

A final check on the odor threshold concentration was performed on day 4 of the panel studies. Concentration levels tested were 2.5 to 100 ng/l. The panel ranked the 100 concentration as the highest followed by 10 or 50 and then ranked the concentration of 5 and 2.5 ng/l threshold or odor free. This confirms the previous results that the odor threshold concentration is between 5-10 ng/l (5-10 parts per trillion).

An FPA panel on day 3 studied 10 µg/l and 100 ng/l 2EDD in the presence of chloramine since chloramination is practiced at the Philadelphia Suburban Water Company. Chloraminated water from the Metropolitan Water District of Southern California (pH > 7) was used for this study. The FPA panel showed that the chloramine interfered with the identification of the 2EDD sweet-type odor at the 10 ng/l concentration level of 2EDD. The 100 ng/l concentration of 2EDD was not affected by the chloraminated sample. This study indicates slight antagonism in chloraminated drinking water only near the threshold odor level.

CONCLUSIONS

This study further confirmed that 2EDD was the source of the taste and odor episode which occurred in Pennsylvania during 1992. 2EDD was found in the waste water of a resin manufacturer and could have formed during storage of a glycol and aldehyde waste under acidic aqueous conditions and was found to be stable at pH 7.7 in a treated waste water. Hydrolysis of 2EDD occurs at pH < 7. However, due to the high concentrations of neopentyl glycol and propionaldehyde in the waste water, 2EDD was confirmed by GC/MS to be present even at pH 4-6. The odor threshold for 2EDD is in the part per trillion range even in the presence of chloramines (≤ 100 ng/l).

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