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1,4 dioxane removal from groundwater using point-of-entry water treatment techniques

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1,4 DIOXANE REMOVAL FROM GROUNDWATER USING POINT-OF-ENTRY WATER TREATMENT TECHNIQUES

BY

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B.S. in Civil Engineering, University of New Hampshire,
2009

THESIS

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DEDICATION

I wish to express my gratefulness to my parents who have shown unwavering support throughout my academic and personal endeavors.

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First and foremost I would like to thank my advisor Dr. Nancy Kinner for the contagious passion she shows not only in her work, but in her students. I am lucky to have had you in my life as a professor, an advisor, and now a longtime friend.

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ABSTRACT

1,4 DIOXANE REMOVAL FROM GROUNDWATER USING POINT-OF-ENTRY WATER TREATMENT TECHNIQUES

by

Michael A. Curry

University of New Hampshire, September, 2012

This feasibility study investigated the removal of an emerging organic contaminant, 1,4 dioxane, from groundwater using point-of-entry (POE) treatment techniques in response to its discovery in some small New Hampshire groundwater-based private drinking water systems. The New Hampshire Department of Environmental Services (NHDES) is evaluating future treatment options for dioxane contamination of these small, groundwater-based private systems. Treatment technologies assessed for dioxane removal included: air stripping, carbon adsorption, direct UV photolysis, and UV-peroxide (H_2O_2) oxidation. Criteria used to assess the suitability of these technologies for POE application included: dioxane removal efficiency, capital and operations and maintenance (O & M) cost, ease of use, and safety. Initial tests indicated that air stripping and direct photolysis were not feasible treatment options for a maximum contaminant level (MCL) of 3 μg/L dioxane. Carbon adsorption and UV-Peroxide oxidation were both found to treat dioxane to ≤ 3 μg/L (96% and 82% removal, respectively). This study determined that carbon adsorption using a coconut-based carbon is the most feasible dioxane treatment option for a POE system based on cost evaluations and treatment experience.

Chapter 1 - INTRODUCTION

Use and Occurrence of 1,4 Dioxane

1,4 dioxane, hereafter refereed to simply as “dioxane” (Figure 1), is a synthetic industrial chemical which found its key role in the past as a stabilizer for chlorinated solvents, particularly of 1,1,1 trichloroethane (TCA, methyl chloroform). Prior to 1957, TCA was not commonly used because a good stabilizer was not available. Then, the United States (U.S.) patent office received its first request to use dioxane as a stabilizer for TCA (Dow, 1954). The development of this dioxane patent formula helped TCA earn widespread acceptance within the degreasing industry (Doherty, 2000). Used in the electronics, metal finishing and fabric cleaning industries, dioxane reduces the degradation of important properties of solvents (Mohr, 2001). With the 1990 enactment of the Montreal Protocol, the use of TCA has been significantly reduced because of its ozone depleting properties. TCA production was eventually eliminated as of January 1996, thereby decreasing this direct use of dioxane (USEPA, 2010). However, dioxane is resistant to degradation, so it continues to be present in the environment.

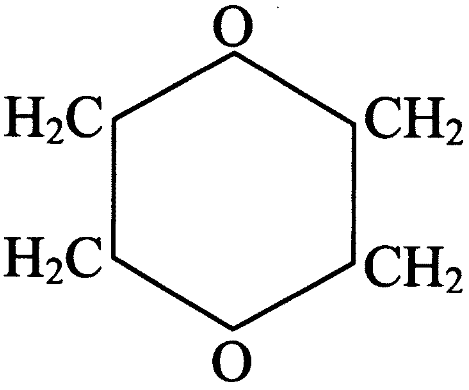


Figure 1: 1,4 Dioxane Structure

Ethoxylation is another major source of dioxane where ethylene oxide (C_2H_4O) is added to alcohols in order to make them more soluble in water (e.g., sodium dodcyl sulfate forms sodium lauryl sulfate (SLS)). Ethoxylation is a process used in manufacturing some surfactants used in personal care products (PCPs) (Esso Research and Engineering, 1967). During this process, ethylene oxide can dimerize (Figure 2) into dioxane (Black et al., 2001).

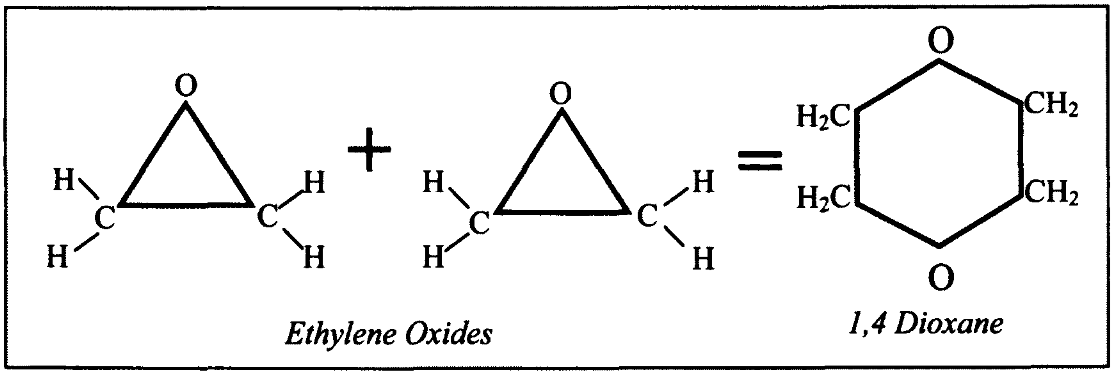


Figure 2: Ethylene Oxide Dimerization

In 1988, approximately 400 million pounds of ethoxylates were used in the manufacturing of common shampoos, detergents, and dish washing soaps (Mohr, 2010)(Table 1).

Table 1: Occurrence of 1,4 Dioxane in Cleaning Finished Products

Year	**No. of Products Tested**	**No. of Products Containing 1,4 Dioxane**	**1,4 Dioxane Range (ppm)**	**1,4 Dioxane Average (ppm)**
1992	34	31	5-141	41
1993	12	7	50-112	79
1994	27	6	20-107	45
1995	6	3	42-90	74
1996	10	7	6-34	14
1997	10	6	6-34	19

Source: (Black et al., 2001)

Along with its association with solvents and surfactants, dioxane has also been an ingredient in the production of cellulose acetate membranes, liquid scintillation cocktails, tissue preservatives, printing inks, paint production, adhesives, and is found in aircraft deicing fluids (Mohr, 2010).

Occurrence of dioxane in groundwater has been reported throughout the U.S. and in countries such as Canada. In Japan, dioxane was found in 87% of a survey of surface and groundwater samples at levels up to 95 μg/L (Abe, 1998). In December 2010, the New Hampshire Department of Environmental Services (NHDES) found 67 locations, including landfill and Superfund sites, at which dioxane was detected in groundwater at an average of 243 μg/L. A majority of the sites where dioxane is found are linked to industrial areas or hazardous waste landfills. There is concern that dioxane impurities in PCPs will not be degraded in municipal wastewater treatment facilities, subsequently contaminating natural waters. Contamination of natural waters may lead to future problems for drinking water facilities that use these sources. Current conventional water treatment practices (e.g., sedimentation, filtration, biological treatment) have proven to be relatively ineffective at removing dioxane from source water (Mohr T. K., 2010). Dioxane is also linked to groundwater impacted by waste sites where chemical solvents (e.g., TCA) were disposed. Many NH groundwater aquifers which are contaminated serve as potable water supplies for rural areas, where surface water sources are not available. In these cases, point-of-entry (POE) treatment systems to remove dioxane for private residences and other small users may be required to meet NH drinking water recommendations ($\mathrm{MCL}_{1,4\ \mathrm{Dioxane}} = 3\ \mu\mathrm{g/L}$).

Properties of 1,4 Dioxane

Once released into the environment, the physical and chemical properties (Table 2) of dioxane make it not only persistent, but difficult to treat with a POE system. Dioxane, a heterocyclic ether, is resistant to biodegradation without tetrahydrofuran (THF) present as a co-metabolite (Shangraw & Plaehn, 2006);(Zenker, 2004);(Parales et al., 1994). Its low Henry's Law Constant (K_H) indicates it will not readily volatilize out of water. Additionally, the unfavorable octanol-water partition coefficient (K_{ow}) and organic carbon partition coefficient (K_{oc}) imply that dioxane is hydrophilic and will not adsorb to sediment, but will transport well in groundwater. As a result, dioxane is moderately resistant to traditional treatment methods (e.g., air stripping, activated carbon adsorption) for the volatile organic carbons (VOCs) with which it often co-exists (Zenker et al., 2003). Consequently, it remains a contaminant of concern (COC), even at sites where chlorinated solvents such as TCA have been remediated.

Table 2: 1,4 Dioxane Properties

Property	**1,4 Dioxane**	**Source**
Boiling Point (°C at 760 mm Hg)	101.32	(Riddick et al., 1986)
Density (g/mL at 20°)	1.0336	(Riddick et al., 1986)
Water Solubility (mg/L at 20°C)	Miscible	(Riddick et al., 1986)
Octanol-Water Partition Coefficient log(K_{ow})	-0.27	(Howard, 1990)
Sorption Partition Coefficient log(K_{oc})	1.23	(Lyman & Rosenblatt, 1982)
Henry's Law Constant (K_H dimensionless)	1.96×10^{-4}	(Howard, 1990)
Maximum Rate of Microbial Utilization (k_c mg of dioxane/mg total suspended solids per day)	0.45 ± 0.03	(Zenker et al., 2004)

Health Effects and Regulations of 1,4 Dioxane

Concern about dioxane contamination in groundwater has steadily increased in recent years, due in part to advances in analytical techniques that now allow detection at low concentrations. Human exposure pathways include inhalation of contaminated air, dermal contact with contaminated products (e.g., shampoos, detergents), and ingestion of contaminated water (ATSDR, 2007).

Citing toxicology studies, the USEPA (2009) listed dioxane as a probable human carcinogen. The National Cancer Institute (NCI, 1978) conducted a study on the toxicity of dioxane ingested by rats and mice and found that it had significant carcinogenic effects. More recent studies with rats and mice show an increase in cancer occurrence, particularly of the nasal cavity and liver when exposed to drinking water spiked with dioxane (Kano et al., 2009).

USEPA (2011) established a health advisory concentration of 35 µg/L in drinking water based on a 10^{-4} increased cancer risk. Currently, no federal drinking water standards or maximum contaminant levels (MCL) exist for dioxane, leaving regulation to individual states. Only Colorado has adopted a water quality standard (6.1 µg/L). However, many other states are adopting regulatory guidelines, action levels, and remediation targets (Table 3).

Table 3: Regulatory Guidelines for 1,4 Dioxane in Water

State	**Type of Guideline**	**Concentration (µg/L)**
California	Advisory Level	3
Colorado	Drinking Water Standard	3.2
Connecticut	Comparison Value for Risk Assessments	20
Maine	Maximum Exposure Guideline	32
Massachusetts	Guideline	3
New Hampshire	Proposed Risk-Based Remediation Value	3
New York	Dept. of Health Drinking Water Standard	600
South Carolina	Drinking Water Health Advisory	70

Source: (Mohr, 2010)

Research Objectives

In 2009, concern was raised over dioxane contamination of groundwater-based drinking water in NH (guideline = 3 μg/L). The NH guideline is based on a more cautious decrease in cancer risk (10^{-5}) than the EPA health advisory concentration. However, future regulations may see a standard as low as 0.35 μg/L based on a cancer risk of 10^{-6} (2011). NHDES is particularly concerned about rural, private groundwater well contamination with dioxane due to the vulnerability of these systems. As of 2004, 62% of the NH population relied on groundwater for its drinking water needs. More than half of the population (~460,000) use private drinking water wells which do not require water quality monitoring (NHDES, 2008). A preliminary investigation by NHDES confirmed dioxane contamination in at least 67 sites around New Hampshire. Contamination ranged from 1-11,000 μg/L with an average concentration of 243 μg/L. Of these 67 contaminated sites, six are public or private water supplies while the majority of the others are associated with landfill or Superfund sites.

Because many of the water sources contaminated with dioxane are small and private, POE treatment systems are required. Treatment of dioxane with conventional water technologies used at larger facilities (e.g,, coagulation and flocculation, membrane filtration) is often impractical for private POE applications and most often ineffective for dioxane removal. Advanced oxidation processes (AOP) are known to achieve substantial removal rates of dioxane (Zenker et al., 2003), but are usually considered too complex for POE treatment application.

Design considerations for POE systems are more restrictive than for large facilities. Large water treatment facilities can use advanced technologies because they have an experienced staff, and large volumes of water to be treated. Important factors for POE systems are:

- Ease of use
- Simple monitoring requirements

- Minimal and relatively non-hazardous chemical requirements
- Low capital and operation and maintenance (O & M) costs
- Minimal energy consumption
- Small space requirements
- Minimal noise and odor production

The objective of my research, funded by the NHDES and the University of New Hampshire (UNH) Environmental Research Group (ERG), was to evaluate possible POE treatment technologies to remove dioxane from private groundwater systems. Technologies assessed included: air stripping, carbon adsorption, direct UV photolysis, and UV-Peroxide (H_2O_2) advanced oxidation. Criteria used to assess the suitability of these technologies for POE application included: dioxane removal efficiency, capital and O & M cost, ease of use, and safety.

Chapter 2 – METHODS AND MATERIALS

Objectives

The objective of my research, funded by the NHDES and the University of New Hampshire (UNH) Environmental Research Group (ERG), was to evaluate possible POE treatment technologies to remove dioxane from private groundwater systems. Technologies assessed at the bench scale level included: air stripping, carbon adsorption, direct UV photolysis, and UV-Peroxide (H_2O_2) oxidation. Criteria used to assess the suitability of these technologies for POE application included: dioxane removal efficiency, capital and O & M cost, ease of use, and safety.

Standard Preparation

The dioxane used in this research was reagent grade (99+ % extra pure) supplied by Acros Organics (Waltham, MA). Groundwater was pumped from a pristine bedrock well located on the northeast side of Gregg Hall at UNH (Durham, NH).

Air Stripping

Air stripping is a common desorption process for removing chlorinated VOCs (e.g, TCA) associated with dioxane in groundwater. This process (Figure 3) is governed by gas (mass) transfer theory of the contaminant through the bulk water phase, air-water interface, and bulk air phase (Weber, 1972).

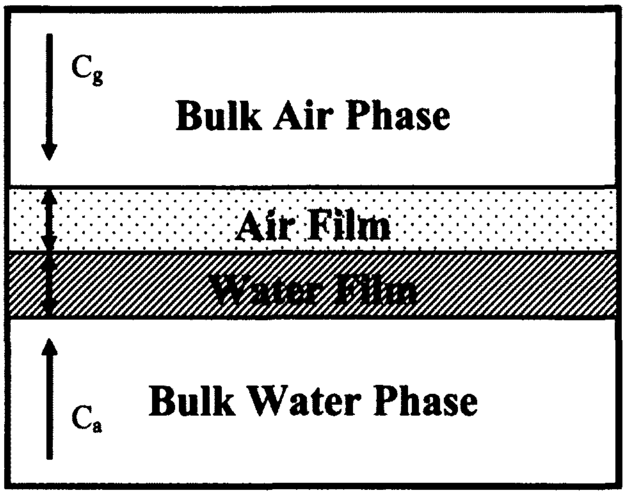


Figure 3: Schematic Representation of Gas Transfer Theory-Two Film Theory

The tendency of a chemical to transfer between the aqueous (bulk water) and gas (bulk air) phase is represented by the dimensionless Henry's Law constant (K_H). This constant describes the equilibrium concentration of a compound in the aqueous (C_a) and gas (C_g) phases at a fixed temperature.

$$K_H = \frac{C_{\text{air}}}{C_{\text{liquid}}}$$

Chemicals which have a higher Henry's law constant (e.g., VOCs), generally have a greater potential for volatilization from the aqeous phase (Mohr, 2010). However, dioxane's low dimensionless Henry's law constant (1.96×10^{-4}) and high solubility in water indicate that its propensity to transfer from the aqueous phase to the gas phase will be low.

The air stripping studies used two Whisper 60 aquarium air pumps (Tetra® Holdings; Cincinnati, OH) in conjunction with 3/16 in. Elite silicone airline tubing (Hagen Inc.; Castleford, UK) and 1 in. ceramic air stones to provide aeration. U201 Flowmeters (Matheson Tri-Gas®; Basking Ridge, NJ) were used to measure the air flowrate supplied to each sample (Figure 3).

Dioxane solutions were prepared within 30 minutes of the start of the experiment to minimize volatilization losses. The temperature and pH of each sample were measured before and after the experiment to ensure stable water chemistry and that no other reactions were occurring (e.g., photo-oxidation).

Figure 4: Air Stripping Experimental Setup

Initial Air Stripping Experiment

Groundwater spiked with ~120 μg/L of dioxane was aerated in 6 separate beakers over 25 hours to determine the effectiveness of air stripping (Table 4). The purpose of the initial test was to determine if aeration could reduce the dioxane concentration in groundwater. The air flowrate was monitored at 500 standard cm^3/min (sccm) per beaker. At a fixed sample volume of 150 mL, air to water (A:W) ratios over the experimental run ranged from 0-5,000:1. Samples were aerated in a dark room to protect against external ultraviolet (UV) sources causing unwanted direct photolysis of dioxane. Samples were analyzed according to USEPA Method 8260B by the NHDES Laboratory (Concord, NH). Samples had a 14 day hold time before analysis. Reported concentrations do not have confidence intervals because deuterated dioxane was used as a surrogate for percent recovery.

Table 4: Preliminary Sampling Regime for Initial Air Stripping Experiment

[redacted]	Sample Time (hours)					
	0	1	4	12	8	25
[redacted]	✓				✓	✓
[redacted]	✓	✓	✓	✓		✓
[redacted]	✓					✓

Detailed Air Stripping Experiment

The initial aeration test indicated that as much as 61% of the 104 µg/L dioxane was removed from the groundwater by air stripping . Packed tower air strippers generally have air-to-water ratios which range from 5-300 (Lagrega at al., 2001) as opposed to the 5000:1 ratio used in the initial test. POE units used for radon removal (Kinner et al., 1990) used an air-to-water ratio ranging from 119-156:1 dictated by pump parameters. Therefore, sampling times and air flowrates were lowered to simulate ratios more commonly used in water treatment (A:W ≤ 240:1). Lower A:W ratios resulted in shorter sampling times and decreased air flowrates (Table 5). Mixing rates among the samples were not quantified. However, mixing was not believed to be a limiting factor due to the small sample volume (150 mL) and the air stone aeration area. The concentration of dioxane spiked into the samples was reduced to ~50 µg/L, as this is a more representative based on the results of NHDES survey of the state's groundwater wells. The air flowrate was sustained at 100 sccm in a dark room to protect against external ultraviolet (UV) sources. The temperature and pH of each sample were measured before and after the experiment to ensure stable water chemistry and that no other reactions were occurring (e.g., photo-oxidation).

Table 5: Sampling Regime for Detailed Air Stripping Experiment

[redacted]	Sample Time (hours)					
	0	0.5	1	2	4	6
[redacted]	✓			✓		✓
[redacted]	✓	✓	✓	✓	✓	✓
[redacted]	✓					✓

Activated Carbon Adsorption

Adsorption is a mass transfer process in which compounds present in the liquid phase (adsorbate) accumulate on a solid phase (adsorbent) and are thus removed from the liquid. In drinking water treatment, this process has been used for the removal of taste and odor causing compounds, organic and inorganic constituents and synthetic organic compounds (e.g., dioxane). During adsorption, dissolved species diffuse into the porous carbon granules and are then adsorbed (physically or chemically) onto the inside surface of the adsorbent. Granular activated carbon (GAC) is known to have a wide range of pore sizes enabling it to accommodate different types of adsorbates (Montgomery Watson Harza, 2005).

Activated carbon samples were supplied by Norit Americas Inc. (Marshall, TX), Calgon Carbon Corp. (Pittsburgh, PA), and TIGG Corp. (Oakdale, PA). These GAC samples were readily available and represent a variety of manufacturers and raw material bases (Table 6). A variety of samples were chosen because GAC has different physical surface adsorption characteristics depending on the raw material (e.g., wood, coconut, coal) and manufacturing process used.

Table 6: Activated Carbon Samples for Adsorption Studies

Carbon	Manufacturer	Raw Base Material
GAC 830	Norit Activated Carbon	Coal
GCA 830	Norit Activated Carbon	Coconut
F200	Calgon Carbon Corp.	Coal
OLC	Calgon Carbon Corp.	Coconut
5DC 830	TIGG Corp.	Coconut
5D 1240	TIGG Corp.	Coal
5DW 0830	TIGG Corp.	Wood

The numerical portion of the carbon title represents the size of the carbon based on standard US sieve sizes (e.g., "830" indicates granular sizes that are > 8 mesh and <30 mesh). For all adsorption experiments, the GAC was hand crushed with a mortar and pestle in a chemical hood. The GAC was passed through a #200 sieve, and heated in a muffle furnace to 550°C for 90 minutes to remove organic interferences.

F200 Isotherm Studies: Initial Sorption Evaluation

During this initial isotherm study, Calgon F200 carbon was used to determine the potential capacity of dioxane sorption. The capacity of GAC for dioxane sorption is described as microgram (μg) of dioxane sorbed per gram (g) of GAC. F200 coal-based carbon was chosen due to its widespread use in drinking water treatment (e.g., taste and odors, chlorinated solvents). The purpose of this study was to determine: (a) the extent to which dioxane sorption occurred (capacity) and (b) the detectability of dioxane concentrations in the sorption experiments. A measurable quantity of dioxane must be present in the samples at the end of an isotherm experiment to determine the GAC adsorption capacity (mass of dioxane sorbed/mass of carbon present). The analytical reliable detection limit (RDL) for dioxane is 2 μg/L (NHDES, 2009).

Dioxane solutions with initial targets of low, medium and high initial dioxane concentrations (C_o, Table 7) were prepared 48 hours in advance of the isotherm experiments and refrigerated. The standard solutions were covered with aluminum foil. Results (Appendix B) showed that these standard concentrations were lower than expected after storage.

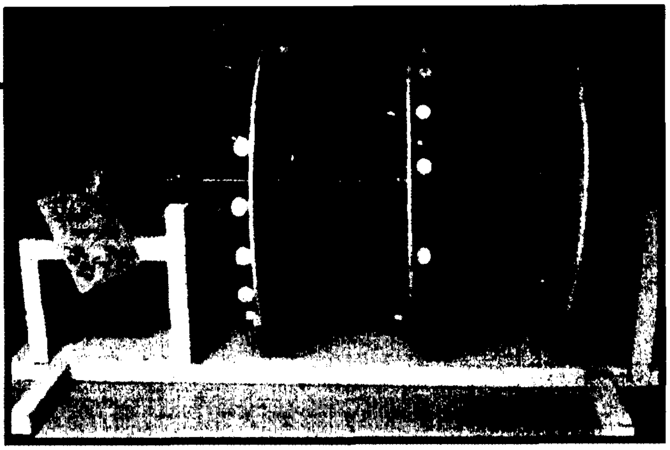
Table 7: 1,4 Dioxane Standard Concentrations (C_0) After 24 Hour Storage

Standard	**Expected Conc. (µg/L) at t = 0**	**Actual Conc. (µg/L) at t = 0**
Low	15	20
Medium	60	21
High	120	29

The lower initial concentrations indicated standard preparation errors. Dioxane loss during sample hold time was not considered likely because VOA sample vials were used. To combat these errors, dioxane standards were prepared immediately beforehand for the experiments.

Calgon F200 was crushed and 0.5 ± 0.0002 g were then added to 60 mL VOA vials which were pre-cleaned in a muffle furnace at 550°C for 90 min. Teflon-lined plastic caps for the vials were washed with 0.5 M chromic acid to oxidize trace organics. Low, medium, and high concentrations were added to the vials along with the sieved F200 carbon. Identical dioxane solutions were added to sample vials which did not contain any F200 (controls).

Sample vials were placed in an end-over-end rotary mixer (Figure 5) for 96 hours (20 rpm) which was an adequate time to reach equilibrium (Kinner & Malley, 2007). Solution control samples containing no GAC were also placed on the rotary mixer to determine whether dioxane was lost through other means (e.g., improper seals, sorption to glass). Each individual sample consisted of triplicate 60 mL vials decanted into a glass beaker to form a composite sample. The composite sample contained excess sample volume to account for any losses which could have occurred during the mixing process (e.g., leaking samples, broken vials). Duplicate 40 mL samples were taken from each composite beaker by filtering the sample to remove GAC using 60 mL BD Luer-Lok™ disposable syringes and 1.2 µm glass fiber filters (Whatman; Florham Park, NJ) mounted in Swinnex™ (Millipore; Billerica, MA) syringe filter holders. Samples were taken at t = 0 hours and t = 96 hours and analyzed according to USEPA Method 8260B by the NHDES Laboratory (Concord, NH). Samples had a 14 day hold time before analysis. Reported concentrations do not have confidence intervals because deuterated dioxane was used as a surrogate for percent recovery (Appendix T).



22 in. diameter mixer operating at 20 rpm

Figure 5: End-Over-End Rotary Mixer

F200 Isotherm Studies: Revised Sorption Evaluation

F200 isotherm methods and materials for this study were identical to those of the initial sorption study except for adjustments made to dioxane solution preparation. Revised from the initial experiment, dioxane standards were prepared immediately before the test (instead of 48 hours in advance) to obtain initial concentrations (C_o) closer to desired values (15-120 µg/L). The change in procedure yielded improved results (Appendix C) for actual initial concentrations (Table 8).

Table 8: 1,4 Dioxane Standard Concentrations for Revised Sorption Evaluation

Standard	**Expected Conc. (µg/L) at t = 0**	**Actual Conc. (µg/L) at t = 0**
Low	15	12
Medium	60	44
High	120	84

The 0.5 ± 0.0002 g of sieved F200 was added to the 60 mL VOA vials. During the experiment, the end-over-end rotary mixer stopped for an unknown amount of time between 24-72 hours. Consequently, these results may not be comparable to similar studies with a known contact time. The background groundwater samples contained dioxane contamination ≤ 4.7 µg/L. Blank groundwater contamination indicated that laboratory technique was most likely causing contamination.

F200 Isotherm Studies: Final Sorption Evaluation

The methods and materials for this study were identical to the previous ones, except revisions were made to the dioxane solution preparation procedure to minimize laboratory contamination. The first adjustment was to fill and seal *all* blank groundwater samples before any dioxane solutions were prepared. The second adjustment was to check the calibration of the Eppendorf Reference© micropipetter (Hauppauge, NY) using laboratory water (reverse osmosis water) and a laboratory scale before every solution preparation, adjusting the volume as needed. 0.5 ± 0.0006 g of sieved F200 was added to 60 mL VOA vials and mixed end-over-end for 96 hours These two adjustments yielded initial dioxane concentrations (C_o) closer to desired values and produced blank groundwater samples without detectable dioxane (RDL = 2 µg/L). Revisions in procedure were used in all subsequent GAC studies.

Table 9: 1,4 Dioxane Standard Concentrations for Final Sorption Evaluation

Standard	**Expected Conc. (µg/L) at t = 0**	**Actual Conc. (µg/L) at t = 0**
Low	15	16
Medium	60	66
High	120	139

GAC Comparison Isotherm Study

Seven different types of GAC (Table 6) were crushed using a mortar and pestle and sieved using an ASTM #200 sieve. 0.5 ± 0.0010 g of this GAC was added to 60 mL VOA vials pre-cleaned in a muffle furnace at 550°C for 90 min. Teflon-lined plastic caps for the vials were washed with chromic acid to oxidize trace organics. Dioxane solutions of low and high concentrations were added to the vials along with the sieved GAC. Similar dioxane concentrations were added to sample vials which did not contain any GAC to serve as controls.

Sample vials were then set in an end-over-end rotary mixer for 96 hours. Each individual sample consisted of triplicate 60 mL vials decanted into a glass beaker to form a single composite sample. Duplicate 40 mL samples were taken from each composite beaker by filtering the contents using a 60 mL BD Luer-Lok™ disposable syringe and 1.2 µ glass fiber filters (Whatman; Florham Park, NJ) mounted in a Swinnex™ (Millipore; Billerica, MA) syringe filter holder. Samples were taken at t = 0 hours and t = 96 hours and analyzed by NHDES according to USEPA Method 8260B. Samples had a 14 day hold time before analysis.

GAC Isotherm Experiments

Three GAC types with high percent dioxane removal from the initial GAC comparison study continued through isotherm testing. These included F200 (Calgon Corp.), OLC (Calgon Corp.), and GCA 830 (Norit Activated Carbon). The isotherm study evaluated the capacity of each carbon for dioxane. Using results from the previous GAC experiments in this research, capacities (q_e, Table 10) were estimated for each carbon type using the Equation 1:

$$q_e = \frac{V \times (C_0 - C_e)}{M} \qquad \text{(eq. 1)}$$

q_e = Carbon specific capacity ($\frac{\mu g \text{ of dioxane}}{g \text{ of dry carbon}}$)
V = Vial volume (L)
M = Mass of dry carbon in vial (g)
C_0 = Initial dioxane concentration ($\frac{\mu g}{L}$)
C_e = Final dioxane concentration ($\frac{\mu g}{L}$)

Table 10: Estimated GAC Capacities

Carbon	**Manufacturer**	**Base**	**Estimated Capacity (q_e) µg 1,4 dioxane/ g carbon**
GCA 830	Norit Activated Carbon	Coconut	14.5
F200	Calgon Carbon Corp.	Coal	14.2
OLC	Calgon Carbon Corp.	Coconut	14.6

Estimated capacities were calculated (Appendix F) using Eq.1 using initial dioxane concentrations (C_0) and carbon dosages (*M*) based on the initial sorption experiments. The final dioxane concentrations (C_e) required at the end of the 96 hour mixing period could be estimated by rearranging the equation to:

$$C_e = C_o - \frac{M \times q_e}{V} \qquad \text{(eq.2)}$$

Final dioxane concentrations (C_e) of ~15 µg/L were desired, so the initial carbon dosages could be calculated for F200 as shown in Table 11. 15 µg/L was chosen as it is significantly greater than the RDL of 2.0 µg/L. The carbon dosage requirements for the other two GAC types are shown in Appendix G.

Table 11: Carbon Dosage Requirements for F200

C_0 (µg/L)	Mass of GAC (g)	Volume of Mixing Vials (L)	C_e (µg/L)
100	0.4	0.067	15.2
80	0.3	0.067	16.4
60	0.2	0.067	17.6
40	0.1	0.067	18.8
20	0.025	0.067	14.7

Sieved GAC was added to 60 mL VOA vials pre-cleaned in a muffle furnace at 550°C for 90 minutes. Teflon-lined plastic caps for the vials were washed with chromic acid to remove trace organics. Dioxane solutions of 20, 40, 60, 80, and 100 µg/L were added to the vials along with the sorted GAC. Replicate samples for the 20 and 100 µg/L samples were prepared to test for experimental variability. Identical dioxane solutions were added to sample vials which did not contain any GAC to serve as controls.

Sample vials were placed in an end-over-end rotary mixer for 96 hours. Each individual sample consisted of duplicate 60 mL vials decanted into a glass beaker to form a single composite sample. Duplicate 40 mL samples were taken from each composite beaker by filtering the contents using 60 mL BD Luer-Lok™ disposable syringes and 1.2 µm glass fiber filters mounted in Swinnex™ the syringe filter holders. Samples were taken at t = 0 hours and t = 96 hours and analyzed by the NHDES according to the USEPA Method 8260B.

Results from the 96 hour mixing study were used to calculate capacities (q_e) at each concentration. These capacities and concentrations were applied to the Freundlich equation which is commonly applied to powdered carbons used for water treatment (Weber, 1972):

$$q_e = K_F C^{\frac{1}{n}} \qquad \text{(Eq. 3)}$$

q_e = carbon specific capacity ($\frac{\mu g \text{ of dioxane}}{g \text{ of dry carbon}}$)
K_F = constant ($\frac{\mu g \text{ of dioxane}}{g \text{ of dry carbon}}$)($\frac{L}{\mu g \text{ of dioxane}}$)$^{1/n}$
$\frac{1}{n}$ = constant (unitless)
C_e = effluent dioxane concentration ($\frac{\mu g}{L}$)

Rearranging Eq. 3 indicates units for K_F as $\frac{\mu g \text{ of dioxane}/g \text{ of dry carbon}}{(\mu g \text{ of dioxane}/L)^{\frac{1}{n}}}$. To simplify the units of K_F and $\frac{1}{n}$ in this study, they were constants. As long as the effluent dioxane concentrations were calculated in $\frac{\mu g}{L}$, then the capacity (q_e) can be reported in $\frac{\mu g \text{ of dioxane}}{g \text{ of dry carbon}}$. Data used with the Freundlich equation are generally fitted to the logarithmic form which yields a straight line with a slope of $\frac{1}{n}$ and an intercept equal to log K_F.

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad \text{(Eq. 4)}$$

Using the logarithmic Freundlich equation and a linear regression from isotherm plots, the Freundlich constants were calculated for each carbon type. With these constants, new Freundlich capacities were calculated at specific initial dioxane concentrations to compare potential GAC exhaustion time, effluent quality and cost of the GAC for POE application. In following the procedure used by Kinner and Malley (2007), the calculated capacity of the carbon was not corrected for the use of crushed carbon, also known as powdered activated carbon (PAC). Comparison of PAC to GAC dosage based on the value of $1/n$ indicates that GAC capacities in this study may be slightly underestimated.

Direct UV Photolysis

Ultraviolet (UV) photolysis is the process by which energy from UV light (photons) is absorbed by molecules causing a photochemical change (degradation). This process is largely controlled by three factors including: (a) how well the target molecule (dioxane) absorbs UV light of a specific wavelength (molar absorption), (b) how much UV light the target molecule requires for photochemical degradation (quantum yield), and (c) how well the water matrix transmits light (UV absorbance). Both molar absorption (ε) and quantum yield (Φ) are chemically dependent on molecular structure (Linden & Rosenfeldt, 2010). Research has shown that dioxane has a relatively low molar absorptivity coefficient (ε) indicating that it is not likely to undergo significant photochemical reactions (Martijn et al., 2010; Stefan & Bolton, 1998). The third factor, UV absorbance (A), can be affected by various dissolved or suspended constituents in the water matrix (e.g., natural organic matter, metals, turbidity, nitrate) (Linden & Rosenfeldt, 2010).

Methods for UV photolytic research were described and standardized by Bolton & Linden (2003). UV direct photolysis (and UV-peroxide) experiments used a collimated beam apparatus (Figure 6) with a low pressure high output (LPHO) mercury lamp (Ondeo Infilco Degrémont Inc.; LPHO; Richmond; VA).

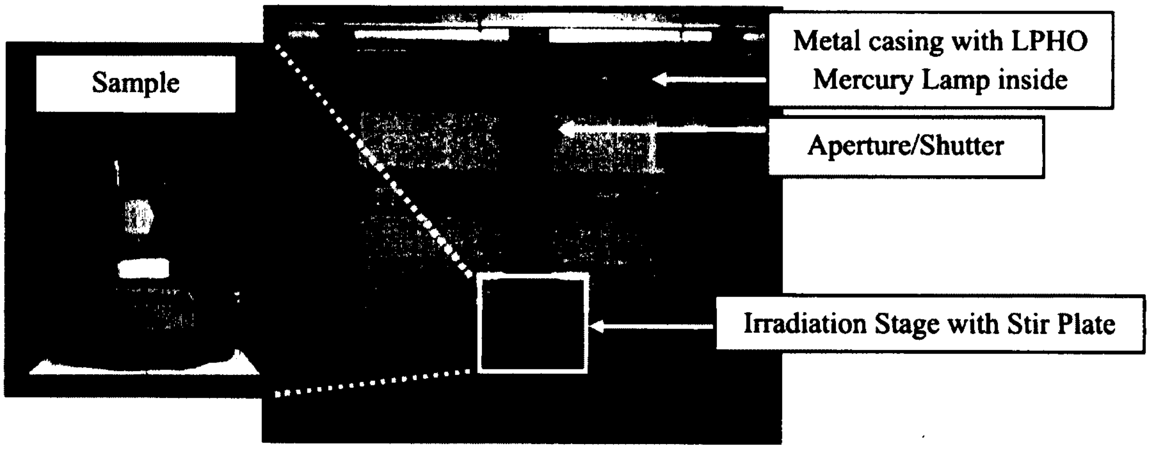


Figure 6: Collimated Beam Apparatus

LPHO lamps emit 85% of their UV light at a wavelength of 254 nm (Linden & Rosenfeldt, 2010). Appropriate UV dose or fluence (mJ/cm^2) was calculated as the product of the average irradiance (mW/cm^2) and exposure time using an Excel spreadsheet provided by Bolton Photosciences Inc. (2004)(Appendix H). UV irradiance of the collimated beam was measured over the exposure surface area of the sample using a radiometer (International Light Technologies; IL1700; Peabody; MA) known to be within calibrated specifications of ± 5% (Malley, 2011). Sample absorption coefficients were measured using a spectrophotometer (Hitachi High Technologies Corp.; U-2000; Tokyo, Japan). The spreadsheet computed the average irradiance (E'_{avg}) using inputs including UV irradiance readings, sample volume (mL), sample diameter, distance from UV lamp to top of water surface, and sample absorption coefficient (cm^{-1}) at 254 nm. These inputs in the IUVA-Bolton Photosciences spreadsheet combine to help calculate the petri factor, reflection factor, water factor, and divergence factor of the sample in order to correct the UV dose for the experimental setup and sample conditions. Once all inputs to the IUVA-Bolton Photosciences spreadsheet are made, the user enters the desired UV dosages and is provided with required irradiation times for a particular sample.

Initial UV Bench Scale Study

Initial UV experiments compared water samples which were irradiated with UV light (collimated beam apparatus, Figure 6) to those samples which were not. UV irradiance readings, sample volume (mL), sample diameter, distance from UV lamp to top of water surface, and the sample absorption coefficient (cm^{-1}) at 254 nm were entered into the IUVA-Bolton Photosciences spreadsheet to determine the time required for a sample to receive a specific UV dose (mJ/cm^2)(Appendix G). The initial UV dose used was 10,000 mJ/ cm^2, equivalent to an exposure time of 25.5 hours. A high UV dose was chosen to verify if direct photolysis had the ability to degrade dioxane.

A groundwater solution containing ~130 µg/L of dioxane was prepared. 150 mL of this standard were placed into two 250 mL chromic acid (0.5 M) washed beakers with stir bars. One sample beaker was positioned on the irradiation stage under the collimated beam apparatus, while the other sample beaker was placed in a dark room to prevent stray UV exposure. Both beakers were stirred for the duration of the experiment. Duplicate 40 mL samples of each were taken at t = 0 hours and t = 25.5 hours and analyzed by NHDES using USEPA Method 8260B.

UV Bench Scale Study with Additional Monitoring

This study was designed to determine the cause of significant dioxane reductions observed in both the irradiated and non-irradiated samples during the initial UV bench scale study. The procedure used was the same as the initial UV bench scale study except for the addition of two samples: (1) a beaker that was neither irradiated nor stirred, and (2) another beaker which was sampled and sealed immediately. To further prevent stray UV exposure, a black cloth covered the collimated beam apparatus during the experiment. Samples were also monitored for temperature and pH changes before and after the experiment.

A groundwater solution containing ~20 µg/L of dioxane was prepared. 150 mL of this standard were placed into four 250 mL acid-washed beakers, two of which contained stir bars. One beaker (stirred) was positioned under the collimated beam apparatus, while the other two beakers (only one stirred) were placed in a dark environment to avoid external UV exposure. The fourth beaker was sampled immediately and sealed. Duplicate 40 mL samples were taken at t = 0 hours and t = 25.5 hours and analyzed according to EPA Method 8260B.

UV Batch Study with SPV-8 UV Reactor

Although direct photolysis bench scale studies yielded only marginal dioxane removals, a final batch scale study was conducted using a small LPHO UV reactor. A Sterilight Platinum SPV-8 series reactor was used with an ICE Controller (Trojan Technologies; London, ON) capable of supplying a UV dose of 40 mJ/cm^2 at a flow of ~30 Lpm (8 gpm). This reactor was turned on 30 minutes before use to allow proper warm-up. A 18.9 liter (5 gal.) low-density polyethylene carboy (Thermo Fisher Scientific Nalgene®; Waltham, MA) and I/P Masterflex® Standard BDC Drive peristaltic pump (Cole-Palmer Instrument Co.; Vernon Hills, IL) were used in the batch system (Figure 7). The pump used an Easy Load Masterflex® I/P Drive Head and Masterflex® Tygon Long Flex Life #73 tubing. The system was constructed with PVC sampling ports, before (inlet) and after (outlet) the UV reactor. All fittings and sealing tape used were either Teflon or PVC.

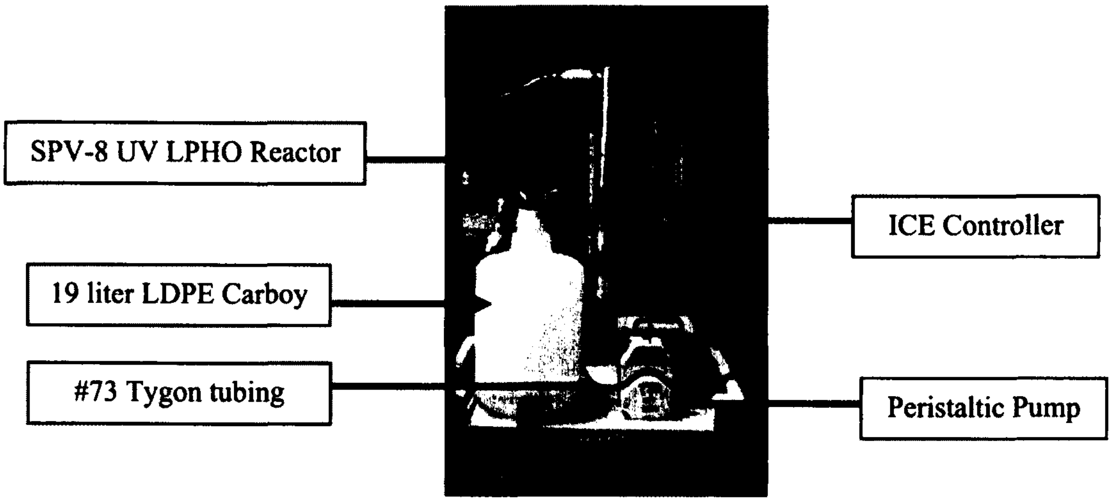


Figure 7: UV Batch Scale Laboratory Setup

A common table salt tracer was used to find the time required for complete mixing within the system. The UV reactor remained off during the tracer experiment. The reservoir was filled with 17.9 L of reverse osmosis water and the pump operated at ~3.8 Lpm (1 gpm). A conductivity meter (Oakton® Instruments; Vernon Hills, IL) was lowered into the reservoir and the conductivity (μS) recorded. A 1 L solution of R.O. water and a salt concentration of 2,000 mg/L was spiked into the reservoir and the conductivity was measured until equilibrium was reached at 2.5 minutes. Dioxane was added in the batch scale study in the same 1 L spike method.

The first control (no dioxane) study used 18.9 L (5 gal.) of reverse osmosis water pumped through the system at ~3.8 Lpm. After 5 hours of exposure (UV dose = 19,200 mJ/cm^2), duplicate samples were taken from the outlet sampling point to test for dioxane. The sample had a dioxane concentration of <2.0 μg/L (RDL). The UV reduction equivalent of this reactor is a function of flow and UV transmittance of the water using biodosimetry with MS-2 and *Bacillus pumilus* (Malley, 2011).

For the second control study, the reservoir was filled with 17.9 L of groundwater and the pump turned on (~3.8 Lpm). A 1 L dioxane spike was slowly introduced to the top of the reservoir to create an overall concentration of ~130 μg/L. The UV reactor remained off for this test. Duplicate 40 mL samples were taken from the inlet and outlet ports (t = 2.5 min. and 1, 2, 3, 4, 5 hours). Changes in dioxane concentration occurred, but by other means (e.g, aeration) not be attributed to UV direct photolysis.

For the UV irradiation study, the reservoir was filled with 17.9 L of groundwater and the pump turned on (~3.8 Lpm). With the UV reactor on, a 1 L dioxane spike was slowly introduced to the top of the reservoir to create an overall concentration of ~130 μg/L. Duplicate 40 mL samples were taken from the inlet and outlet ports (t = 2.5 min. and 1, 2, 3, 4, 5 hours).

All samples were analyzed according to EPA Method 8260B by the NHDES Laboratory.

UV-Peroxide Oxidation

UV-peroxide oxidation is an advanced oxidation process (AOP) by which hydrogen peroxide (~2-10 mg/L), in the presence of UV light, disassociates to form two hydroxyl radicals (OH·).

$$H_2O_2 + UV \rightarrow 2\ OH\cdot$$

Hydroxyl radicals are some of the strongest chemical oxidants known and are effective for destruction of many organic contaminants in water (Linden & Rosenfeldt, 2010). Similar to direct UV photolysis, the disassociation process is limited by the quantum yield (Φ) and molar absorption (ε) of the target molecule (hydrogen peroxide). Although hydrogen peroxide has a high hydroxyl radical quantum yield, hydrogen peroxide is a very good absorber of UV light (Stefan & Bolton, 1998) thereby limiting the creation of hydroxyl radicals in the UV-peroxide process. Just as with direct photolysis, the UV absorbance (A) of the water matrix by various dissolved or suspended constituents (e.g., natural organic matter, metals, turbidity, nitrate) can also affect the efficiency of hydroxyl radical production (Linden & Rosenfeldt, 2010).

In addition to UV absorption limitations in the UV-peroxide process, there are also problems associated with hydroxyl radical scavenging. Hydroxyl radicals are non-selective oxidants and may be scavenged by carbonate species (alkalinity), natural organic matter, reduced metal ions (e.g., Fe^{2+}), and sulfide (Montgomery Watson Harza, 2005).

Bench scale studies for UV-Peroxide oxidation were similar to those for direct UV photolysis (Bolton & Linden, 2003) with a few supplemental steps including the addition of monitoring for hydrogen peroxide and alkalinity to assess hydroxyl scavenging effects. UV-peroxide experiments used the collimated beam apparatus (Figure 5) with a low pressure high output (LPHO) mercury lamp. The desired UV dosage (mJ/cm^2) was determined using the same method and spreadsheet (Bolton Photosciences, 2004) as for direct UV photolysis. Hydrogen peroxide for this study was 3.3% w/w (Acros Organics; Waltham, MA) and measured using self-filling reagent ampoules (CHEMetrics, Inc.; Calverton, VA). The pH of each sample was measured with an Accumet Excel XL 50 meter kit and ATC probe (Fisher Scientific; Waltham, MA) before and after the experiments. Alkalinity (mg/L as $CaCO_3$) was monitored for hydroxyl scavenging capability in each sample before and after the experiment using the HACH® Digital Tritrator Method 8203.

Initial UV-Peroxide Experiment

The initial experiment compared water samples at hydrogen peroxide concentrations of 0, 3, and 6 mg/L irradiated at a UV dose of 600 mJ/ cm^2 (1.5 hour exposure). These values were selected based on existing water reuse facilities with UV-peroxide systems for micropollutant destruction (Martijn et al., 2010).

A groundwater solution containing ~20 µg/L of dioxane was prepared. This study consisted of three phases, one for each peroxide concentration. For Phase I: 150 mL of the 20 µg/L dioxane standard was added to two muffled (550°C) and cooled 250 mL beakers with stir bars. One sample beaker was positioned under the collimated beam apparatus, while the other beaker was placed in a darkened room to avoid external UV exposure. No hydrogen peroxide was added to either sample. The beakers were stirred for 1.5 hours (UV dose = 600 mJ/ cm^2) and duplicate 40 mL samples taken. For Phase II: 500 mL of the standard was spiked with 3 mg/L H_20_2. 150 mL of this solution was then measured into two acid-washed 250 mL beakers with stir bars. One sample beaker was positioned under the collimated beam apparatus, while the other was placed in a darkened room to avoid external UV exposure. Both beakers were stirred for 1.5 hours and duplicate 40 mL samples taken. The beaker which contained hydrogen peroxide was measured after irradiation for residual concentrations. For Phase III: this phase was identical to Phase II, except that 6 mg/L H_20_2 was added to the solution instead of 3 mg/L.

All samples were analyzed according to EPA Method 8260B by the NHDES Laboratory.

UV-Peroxide Experiment for Scavenging Effects

Marginal dioxane reduction results from UV-peroxide Phase II and III indicated the possibility of hydroxyl radical scavenging by naturally occurring alkalinity. This study was designed to: 1) determine if hydroxyl scavenging was occurring, and 2) determine if a higher dose of UV and H_20_2 would be more effective.

Phase I: To determine if hydroxyl scavenging was occurring, R.O. water was substituted for groundwater due to its lack of interferences. An R.O. solution containing ~15 µg/L of dioxane was prepared and spiked with a hydrogen peroxide to provide a dose of 3 mg/L in the sample. 150 mL of this solution was added into a muffled 250 mL beaker with a stir bar. The beaker was stirred and irradiated for 1.5 hours (UV dose = 600 mJ/ cm^2) and duplicate 40 mL samples taken. $H_20_2$was measured for initial and residual concentrations.

For Phase 2: A groundwater solution containing ~15 µg/L of dioxane was prepared and spiked with a hydrogen peroxide dose of 12 mg/L. 150 mL of this solution was then added to two acid-washed 250 mL beakers with stir bars. One sample beaker was positioned under the collimated beam apparatus, while the other beaker was placed in a closed room to avoid external UV exposure. Both beakers were stirred for 3.2 hours (UV dose = 1200 mJ/ cm^2, 2× the exposure time and UV dose) and duplicate 40 mL samples taken. $H_20_2$was measured for initial and residual concentrations.

Analytical Methods

All 1,4 dioxane studies used pre-cleaned vials for sampling and were analyzed by the NHDES according to EPA Method 8260B for volatile organic compounds by gas chromatography/mass spectrometry (GC/MS). The preparation technique used was a heated purge and trap for aqueous samples, EPA Method 5030. The reliable detection limit (RDL) of dioxane for this method was 2.0 μg/L for samples received between September 9th, 2009 and October 25th, 2010 and 1.0 μg/L for dioxane samples received after. Dioxane concentrations were reported corrected for the percent recovery (%R) of a surrogate standard used, 1,4 dioxane-d8, or deuterated 1,4dioxane (Appendix T). Major interferences for this method include the presence of VOCs and large amounts of suspended solids.

The pH of samples was measured with an Accumet Excel XL 50 meter kit and ATC probe (Fisher Scientific; Waltham, MA) following the electrometric method, Standard Method 4500B. The pH meter was calibrated weekly at minimum on a 3 point calibration curve.

Alkalinity (mg/L as $CaCO_3$) was monitored for hydroxyl scavenging capability using the HACH® Digital Titrator Method 8203 (Standard Method 2320B). This method has a range of 10-4000 mg/L as $CaCO_3$.

Hydrogen peroxide measurements in the UV-peroxide study were done with self-filling reagent ampoules using the Ferric Thiocyanate Method (Boltz & Howell, 1978). The detection range was from 0-1 and 1-10 mg/L H_20_2 with a MDL of 0.05 mg/L.

Chapter 3 – RESULTS AND DISCUSSION

This laboratory study was designed to determine the effectiveness of four potential POE water treatment systems (e.g., air stripping, activated carbon adsorption, UV direct photolysis, and UV-peroxide oxidation) to cost effectively remove dioxane from groundwater and meet NHDES maximum contaminant level guidelines (NH MCL) of ≤ 3 μg/L. Important selection factors considered for POE water treatment units include: ability to meet the NHDES MCL, ease of use, monitoring and chemical requirements, noise and odor production, energy consumption, footprint, and capital and O & M costs.

Air Stripping

Preliminary Air Stripping Test

The initial air stripping study was designed to investigate the unidentified dioxane losses in direct photolysis experiments. Not initially considered viable as a treatment option, further literature research (Appendix A) showed a 30% reduction in high dioxane concentrations (610 μg/L) was possible using high A:W ratios (Bowman, 2001). Our preliminary study compared two groundwater samples spiked with dioxane (~100 μg/L), one aerated at 500 sccm for 25 hours and one not. Results showed 61% and 22% reductions in the aerated and non-aerated samples, respectively (Figure 8). The difference between the two samples (39%) indicated that air stripping had a significant effect on the dioxane concentration. A definitive cause for the 22% dioxane reduction in the control samples is unknown; however, likely causes include volatilization and/or analytical variability. While these results (Appendix J) compared favorably with dioxane reductions of 30% reported by Bowman (2001), such high dioxane removal rates

(61%) could be attributed to the initial high dioxane concentration (C_o~100 μg/L) and the high volume of air supplied (A:W = 5000:1) in this study.

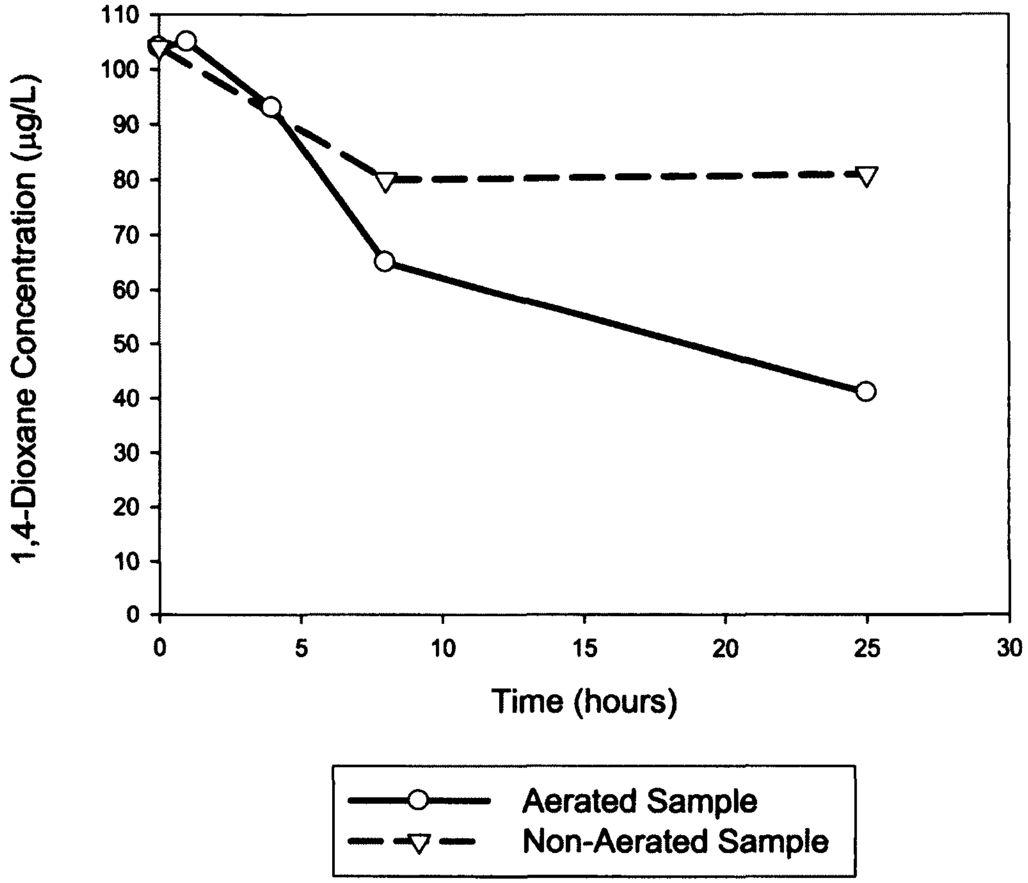


Figure 8: Preliminary Air Stripping Test

<u>Air Stripping Test Using Typical POE A:W Ratios</u>

Following the preliminary experiment, revisions were made to determine if air stripping could be successfully applied at typical POE A:W ratios as described by Kinner et al., (1990). They found that homeowners disliked the noise caused by the POE aeration units and would unplug them. Therefore, experimental conditions were revised to include lower A:W ratios (1-240:1) as well as lower influent dioxane concentrations (~30 μg/L) to better mimic a typical POE application. Lower A:W ratios were achieved by decreasing the airflow rate and sampling time to

100 sccm and 6 hours, respectively. Small reductions in concentration of only 16% and 13% were observed in the aerated and non-aerated samples, respectively (Figure 9). As with the preliminary experiment, control sample results may be due to volatilization and/or analytical variability.

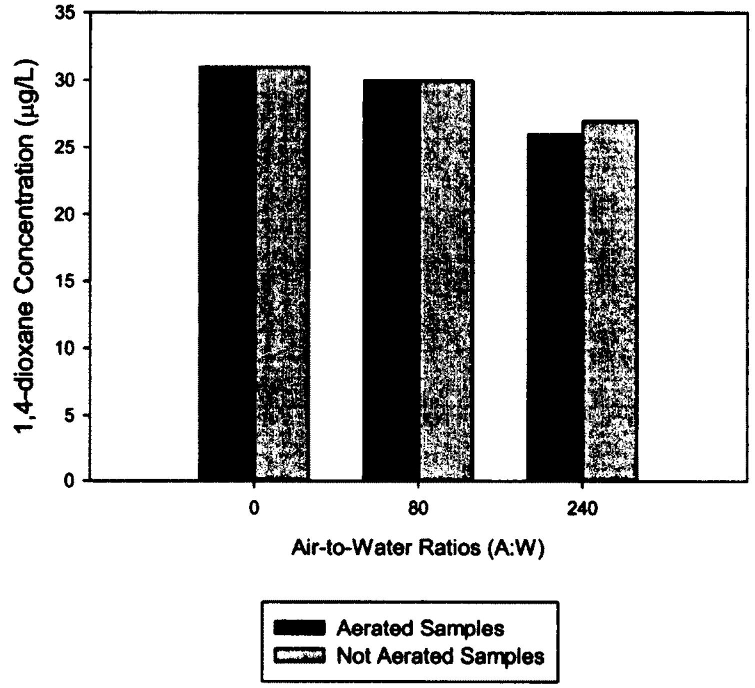


Figure 9: Air Stripping Test Using Typical POE A:W Ratios

The mass transfer efficiency appeared to decrease when the dioxane concentrations and A:W ratios were lower, suggesting that air stripping cannot treat dioxane in groundwater to levels at or below the MCL goal of 3 µg/L when initial concentrations are ~30 µg/L (Appendix K). Air stripping studies conducted by Earth Tech Inc. (2004) resulted in similar conclusions when initial dioxane concentrations were 7.6-11.1 µg/L. Using 40 ft. tall packed tower air strippers, dioxane reduction reached a maximum of 10% using similar A:W ratios (183-291:1).

A comparison of air stripping results between Figures 8 and 9 exhibit the effects of Fick's Law on mass transfer efficiency. Fick's Law relates the flux (driving force) of a solute across the air-to-water interface as a function of the concentration gradient between the phases. Because the concentration gradients in Figure 9 were lower than that in Figure 8, the overall transfer rates decreased. The limitations presented in Fick's Law make air stripping difficult at low concentration commonly associated with dioxane contamination. Steps to overcome mass transfer limitations (e.g., increasing the mass transfer interface, increasing air flow) could potentially result in further dioxane reduction; however, results obtained in the air stripping experiments as well as results found in the literature indicate that air stripping is not a viable treatment option to treat dioxane to levels required by New Hampshire.

Activated Carbon Adsorption

Limited carbon isotherm data is available for dioxane from manufacturers because the K_{ow} suggests adsorption is not an effective treatment method. Despite this, the Beede waste oil Superfund site (Plaistow, NH) obtains 90% dioxane reduction in their effluent using GAC filters in place for chlorinated solvent removal. These results created interest in generating carbon adsorption isotherms for dioxane. The purpose of the isotherm studies was to determine if commercially available GAC could cost effectively treat dioxane to ≤ 3 µg/L.

F200 Isotherm Study

Initial isotherm studies used Calgon's F200 coal based carbon (GAC) because of established track record for many contaminants as well as its common use in NH POE systems (e.g., MtBE). F200 is used in POE units installed in NH homes for treatment of MTBE contamination in drinking water (Kinner and Malley, 2007).

During this experiment, dioxane concentrations of 16-134 µg/L in the presence of a consistent mass of carbon (0.5 ± 0.0006 g) were mixed for 96 hours. The proximity of final concentrations in the results (despite differences in initial concentrations) indicated equilibrium between the GAC and aqueous phase dioxane was reached within the 96 hour mixing period (Figure 10). All subsequent isotherm experiments would use 96 hours as a mixing time to ensure equilibrium was reached. Controls which lacked GAC were monitored to determine whether dioxane was lost from solution by means other than carbon adsorption (e.g., improper seals, sorption to glass). The control samples contained an average of 2.29 ± 2.00% more dioxane at the end of 96 hours, most likely due to issues with analytical precision.

Results of this experiment (Appendix D) indicated dioxane reductions of 72%, 94%, and 96% in the low, medium, and high standards, respectively (Figure 10). Successful sorption results in this study encouraged further research on the capacities of dioxane sorption by GAC.

The similarity of final dioxane concentrations (C_e = 4.5, 3.9 and 4.9 µg/L) regardless of varying initial dioxane concentrations (C_0 = 16, 64, and 134 µg/L, respectively) suggested a final dioxane concentration of ~4-5 µg/L in the aqueous phase. This limit could be due to a limit in dioxane transport kinetics (e.g., bulk solution transport, film transport, intraparticle transport), dioxane adsorption limitations (e..g, adsorption mechanism, available sorption sites, GAC particles size), or competitive adsorption from other solutes found in the groundwater (e.g., iron, NOM). This limit may possibly be overcome by increasing the contact time, mixing energy, or changing the adsorbent type, size, or dose. Subsequent GAC experiments further evaluated the concentration limits of dioxane sorption.

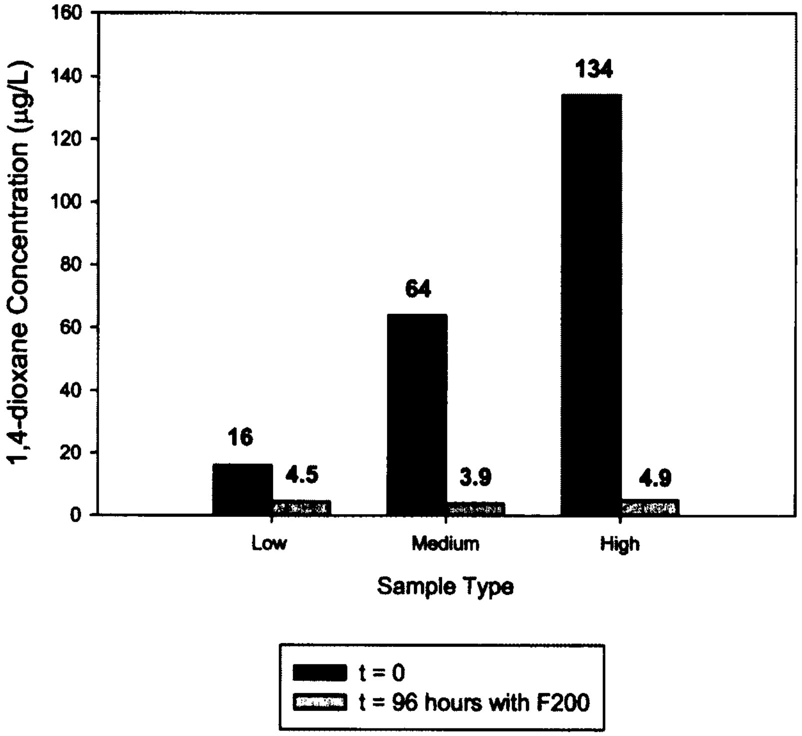


Figure 10: F200 Isotherm Study: Final Sorption Evaluation

GAC Comparison Isotherm Study

The purpose of this experiment was to determine the three most effective commercially available carbons for dioxane sorption for use in further isotherm studies. Seven different types of GAC were tested representing different manufacturers (Calgon Carbon Corp., Norit Activated Carbon, TIGG Corp.) and raw base materials (coal, coconut, wood)(Table 12).

Table 12: GAC Type for Comparison Study

Carbon	Manufacturer	Base Material	Apparent Density (g/cc)
GAC 830	Norit Activated Carbon	Coal	0.50
GCA 830	Norit Activated Carbon	Coconut	0.47
F200	Calgon Carbon Corp.	Coal	0.59
OLC	Calgon Carbon Corp.	Coconut	0.48
5DC 830	TIGG Corp.	Coconut	-
5D 1240	TIGG Corp.	Coal	0.43-0.48
5DW 0830	TIGG Corp.	Wood	0.24-0.30

Low (13 μg/L) and high (112 μg/L) dioxane concentrations were placed in VOA bottles with a consistent mass of carbon (0.5 ± 0.0010 g) and mixed for 96 hours. Controls, which lacked GAC, were monitored to determine whether dioxane was lost from solution due to other means. The high dioxane control samples attained a 16% reduction in dioxane over the course of 96 hours (Table 13). The likely cause of a significant reduction in the control sample may be volatilization that occurred during the the post-experiment filtration of the samples to remove residual GAC. Due to this loss, the initial concentration of the high sample was assumed to be an average (112 μg/L) of t = 0 and t = 96 hours rather than 102 μg/L or 122 μg/L. The lack of change seen in the low control sample supports the hypothesis that losses could be attributed to volatilization, and was seen more dramatically at high concentrations as expected by Fick's Law.

Table 13: Dioxane Concentrations in Controls Lacking GAC

Sample	1,4 dioxane (µg/L) t=0	1,4 dioxane (µg/L) t=96 hours
Low	13	13
High	122	102

At the low concentration (13 µg/L), all GAC types, except the wood based carbon (5DW 0830), reduced dioxane concentrations to below the RDL (2.0 µg/L). The wood based carbon had a low apparent density compared to other GAC types which may have affected the sorption efficiency. At the high concentration (112 µg/L), dioxane samples showed reductions ranging from 75-97% (Table 14). GCA 830, F200, and OLC were chosen for continued isotherm testing. F200 was chosen over the GAC 830 and 5D 1240 (all coal based carbons) because it is commonly used in NH POE applications for a range of groundwater contaminants.

Table 14: Low and High Concentration for 1,4 Dioxane Removal Results

Activated Carbon Type	1,4 dioxane (µg/L) t=0	1,4 dioxane (µg/L) t=96 hours	Percent Reduction
Norit GAC 830 (Coal)	13	< 2	>85%
	112	3.6	96.8%
Norit GCA 830 (Coconut)	13	< 2	>85
	112	3.8	96.6%
Calgon F200 (Coal)	13	< 2	>85%
	112	6.0	94.6%
Calgon OLC (Coconut)	13	< 2	>85%
	112	2.8	97.5%
TIGG 5DC 830 (Coconut)	13	< 2	>85%
	112	9.5	91.5%
TIGG 5D 1240 (Coal)	13	< 2	>85%
	112	8.7	92.2%
TIGG 5DW 0830 (Wood)	13	3.5	>85%
	112	27	75.9%

*Graphical representation in Appendix G, percent recovery for each sample in Appendix E

GAC Isotherm Experiments

GAC isotherms were created across the range of dioxane concentrations (0-100 μg/L) typically experienced by POE systems in NH. Preliminary capacities (q_e) were calculated (Table 15) for the three types of GAC using Eq. 1. Based on a sample vial size of 67 mL and a carbon dosage of 0.5 g,

$$q_e = \frac{0.067\ \mathrm{L} \times (112\ \frac{\mu\mathrm{g\ dioxane}}{\mathrm{L}} - 6.0\frac{\mu\mathrm{g}}{\mathrm{L}})}{0.5\ g\ \mathrm{F200}}$$

$$= 14.2\ \mu\mathrm{g\ of\ dioxane/g\ of\ F200\ carbon}$$

Table 15: Initial GAC Capacities for Dioxane

GAC Type	Capacity, q_e (μg of dioxane/g of carbon)
Norit GCA 830 (Coconut)	14.5
Calgon F200 (Coal)	14.2
Calgon OLC (Coconut)	14.6

Capacities calculated were lower than values found in the literature. Johns et al. (2007) reported capacities for Filtrasorb 200 (Calgon F200) of ~3,500 μg dioxane/g of activated carbon. The higher capacity could be due to higher initial dioxane concentration used in their experiment (800 μg/L vs. 112 μg/L). Differences in experimental design including equalization times, solution characteristics (e.g., additional contaminants, pH, temperature), and GAC characteristics (e.g., activation procedure, surface area, density) could also account for dissimilar GAC capacities. It is important to note that in following the isotherm procedure used by Kinner and Malley (2007), the calculated capacity of the carbon was not corrected for the use of crushed carbon, also known as powdered activated carbon (PAC).

Using the estimated capacities (Table 15) and rearranging Eq. 1, values were chosen for initial concentrations (C_0) and carbon dosages (M) to provide estimated effluent concentrations (C_e) ≈15 μg/L (RDL = 2.0 μg/L), so dioxane could be detected at the end of each isotherm (Appendix H).

For F200, using Eq. 2, C_0 of 100 μg/L will yield a C_e ≈15 μg/L.

$$C_e = 100\ \mu g/L - \frac{0.4\ g \times 14.20\ \frac{\mu g}{L}}{0.067\ L}$$

$$= 15.2\ \mu g/L$$

Samples for the three select carbon types were filled with calculated initial concentrations and carbon dosages (Appendix H). These vials were mixed for 96 hours and sampled. Controls which lacked GAC were monitored to determine whether dioxane was lost from solution due to other means. Isotherm results (Appendix I) from the 96 hour mixing study were then applied to the logarithmic Freundlich equation, plotted (Figures 11-13) with a linear regression, and Freundlich constants calculated (Table 16).

$$\text{Logarithmic Freundlich Equation: } \log q_e = \frac{1}{n}\log C_e + \log K_F$$

Table 16: Freundlich Isotherm Constants for Three GAC Types

GAC Type	K_F (95% Confidence Interval)	$\frac{1}{n}$ (95% Confidence Interval)
Norit GCA 830 (Coconut)	9.0 ± 3.2	0.30 ± 0.17
Calgon F200 (Coal)	10.1± 3.3	0.22 ± 0.19
Calgon OLC (Coconut)	7.8 ± 2.9	0.53 ± 0.10

Because GAC adsorption is not the treatment method of choice for dioxane, published Freundlich constants are not available for comparison. The coefficient of determination, also known as the

R^2 value, for Figures 11-13 indicate that the linear regressions do not have a strong fit to the data for two out of three isotherms. However, due to limited number samples (7) for each isotherm it was decided that all data points should be included in the regression to avoid altering the conclusions of the study. To account for the error involved in linear regression, confidence intervals provide ranges for data associated with the regression analysis.

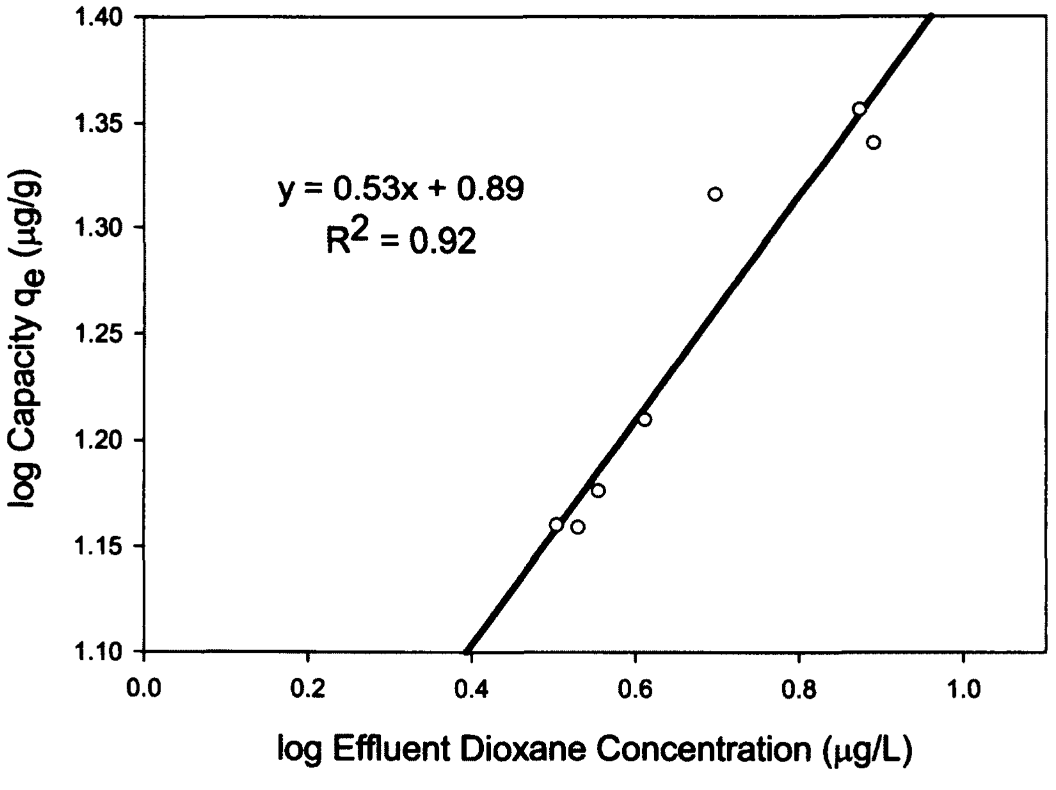


Figure 11: Freundlich Isotherm for OLC

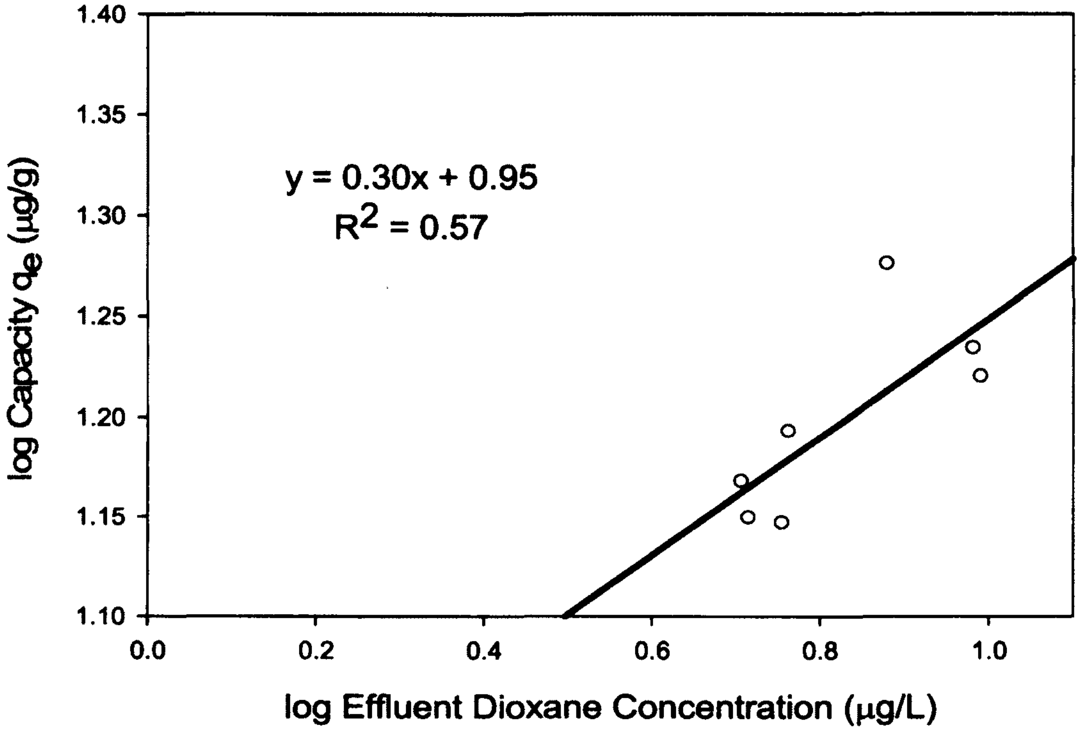


Figure 12: Freundlich Isotherm GCA 830

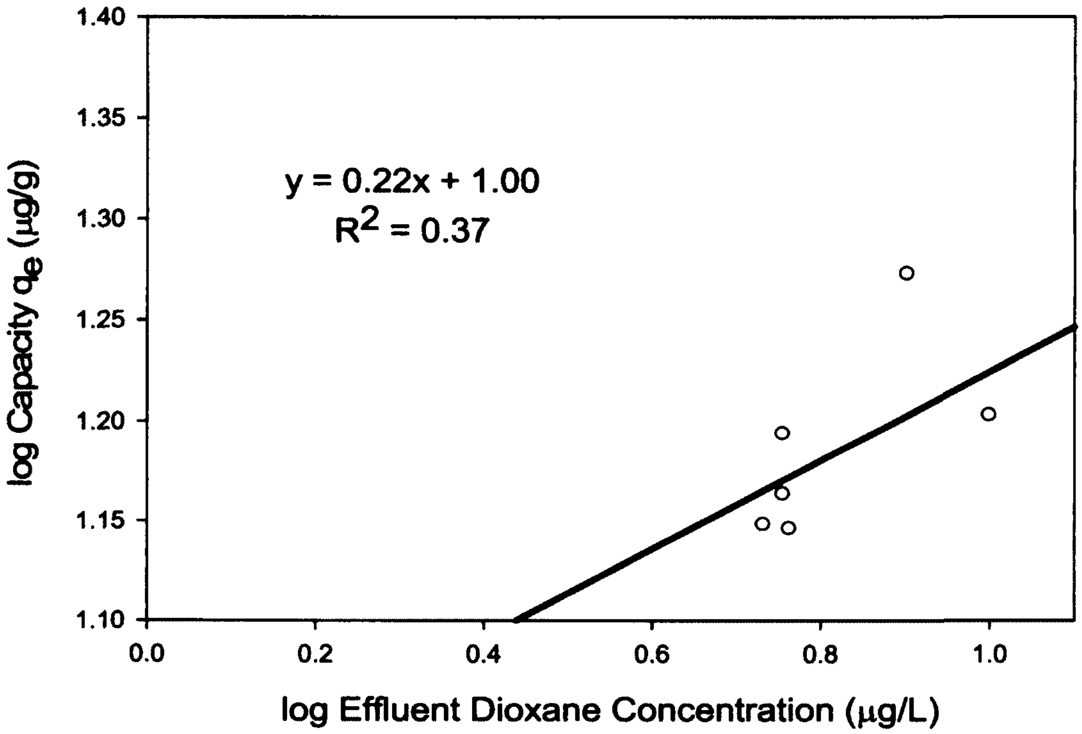


Figure 13: Freundlich Isotherm for F200

Using the linear regression analysis from each of the isotherm plots, carbon capacities were calculated using an initial concentration of 20 µg/L. With each new carbon capacity, a 95% prediction interval was found to determine the range of predicted values at the specific initial dioxane concentration of 20 µg/L. Applying Freundlich capacities to POE design assumptions provides projected values for daily carbon usage, exhaustion time, and annual carbon cost for a single POE unit (Table 17).

Table 17: GAC Comparison for POE Unit

Carbon	Capacity at C_0= 20 (µg/g)	Carbon Use per day (g)	Exhaustion Time for a 2ft³ POE Reactor (days)	Cost per lbs (2010 pricing)	Annual Carbon Cost
GCA 830	23 ± 9	500-1092	26-57	$1.64	$650-1,400
F200	21 ± 9	537-1263	26-62	$2.12	$900-2,150
OLC	40 ± 12	309-579	47-88	$1.63	$400-750

* For GAC comparison, point-of-entry design assumptions included: C_0 = 20 µg/L,C_F = 3 µg/L, Q = 250 gpd, POE Reactor volume = 2 ft^3, 95% Prediction intervals.

Carbon cost per pound does not include shipping charges which would vary depending on quantity purchased. It is important to note that this annual cost does not include the capital or installation cost of the GAC units. Service, GAC re-bedding, and spent GAC disposal for carbon used for MtBE removal currently costs approximately $275 per unit service visit (McGarry, 2011). For cost estimation purposes, this service value was assumed to be comparable to that of what dioxane would be. Table 18 outlines estimated drinking water costs including POE unit service, re-bedding, and GAC disposal based on contracts provided by the NHDES. As expected for POE systems, the average cost per 1000 gallons treated is significantly higher than the national average due to the labor costs associated with re-bedding and the large amount of carbon required for adequate dioxane removal. From the three GAC types compared, OLC (coconut base, Calgon Carbon Corp.) had the best projected capacity, exhaustion time, and annual cost of $1,800-3,000 or $20-32 per 1,000 gal treated (Table 18). Drinking water costs were estimated using preliminary GAC isotherm research. For more reliable cost estimation and kinetics purposes, laboratory column tests (e.g., rapid small-scale column tests (RSSCT)) are considered more accurate for estimating system performance.

Table 18: Drinking Water Cost

GAC Type	Number of Service [illegible] per Year	Annual Estimated Cost [illegible]	Cost per 1,000 gal. treated
Norit GCA 830 (Coconut)	7-15	$2,500-5,500	$28-61
Calgon F200 (Coal)	6-14	$2,500-6,000	$28-66
Calgon OLC (Coconut)	5-8	$1,800-3,000	$20-32

*National drinking water average = $2 per 1,000 gal. treated

(USEPA, Water On Tap: what you need to know, 2009)

UV Direct Photolysis

The purpose of the UV studies was to determine if direct photolysis could efficiently degrade dioxane in groundwater to acceptable guidelines of <3 µg/L. Stefan & Bolton (1998) reported dioxane as a weak absorber of UV light which indicates direct photolysis would not be successful. Corresponding results were observed by Martijn et al. (2010) finding no significant degradation of dioxane (C_0=200 µg/L) at a UV dosage of 1200 mJ/cm^2. However, studies have shown in natural water systems that UV irradiation can form small amounts of hydrogen peroxide, a precursor to the hydroxyl radical which has the ability to degrade dioxane (Scully at al., 1996). For all of the experiments the background UV absorbance of the groundwater samples was between 0.01-0.03 cm^{-1}.

Initial UV Bench Scale Experiment

The initial UV bench scale study compared two groundwater samples spiked with ~130 µg/L of dioxane over a 25 hour period. One sample was irradiated with a high dosage of UV light (10,000 mJ/cm^2), while a control sample was in an environment receiving minimal UV light. Both samples were stirred during the experiment.

65% and 43% dioxane removals were attained in the irradiated and control samples respectively (Figure 14). The irradiated sample final concentration was 44 µg/L compared to 75 µg/L in the control sample. The difference between sample removal rates (+22% for the irradiated sample) was attributed to direct photolysis. Successful direct photolysis contradicts Stefan & Bolton (1998) and Martijn et al. (2010), however, those experiments did not irradiate samples at such a high UV dose (1,000 mJ/cm^2 vs. 10,000 mJ/cm^2). High removal rates in the control sample indicated dioxane losses through volatilization as observed in the air stripping study to greater degree (43% vs. 22%). The difference in control sample losses between the studies may be caused by the difference in mixing mechanisms used in the two experiments: bubble aeration vs. magnetic stir bar. Control sample results due to volatilization compare similarly to the ~30% volatilization results found by Bowman et al. (2001) and are logical given that the sample had to be stirred for 25 hours.

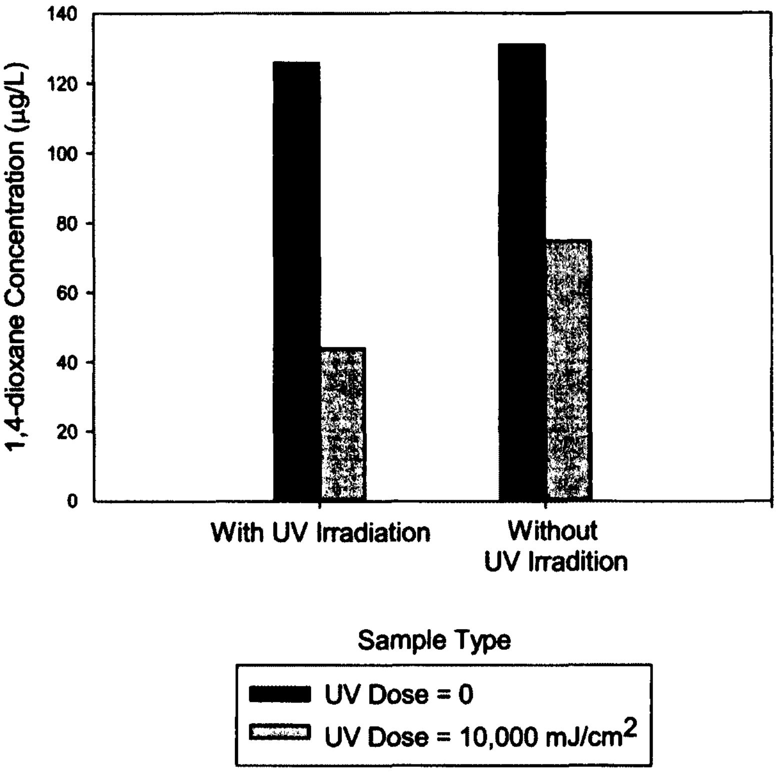


Figure 14: Initial UV Bench Scale Experiment

UV Bench Scale Study with Additional Monitoring

A high removal rate in the control sample from the initial experiment indicated some additional removal mechanism, most likely volatilization from sample agitation. To further understand removal mechanisms, the experiment was repeated with the addition of a sample which was neither stirred nor irradiated. Temperature and pH were also measured before and after the study to ensure that the water chemistry was stable and no other reactions were occurring. Groundwater samples spiked with ~120 µg/L dioxane were tested over a 25 hour period. The difference between control samples helped determine if dioxane was volatilizing without agitation from stirring.

47% dioxane removals were attained in the irradiated and stirred control samples (Figure 15). The similarity of the removal rates of the irradiated and controlled stirred samples indicated little to no effect from direct photolysis as found by Martijn et al. (2010). The sample that was not stirred or irradiated showed minimal removal (9%) compared to the control sample which was stirred (47 %). The losses in the control sample compare favorably to those obtained in the initial UV experiment (43% vs. 47%). These losses indicated that a majority of the dioxane removal could be attributed to volatilization from the samples being continuously stirred over the course of the study. Temperature and pH remained relatively consistent between the beginning and the end of the study (Appendix N).

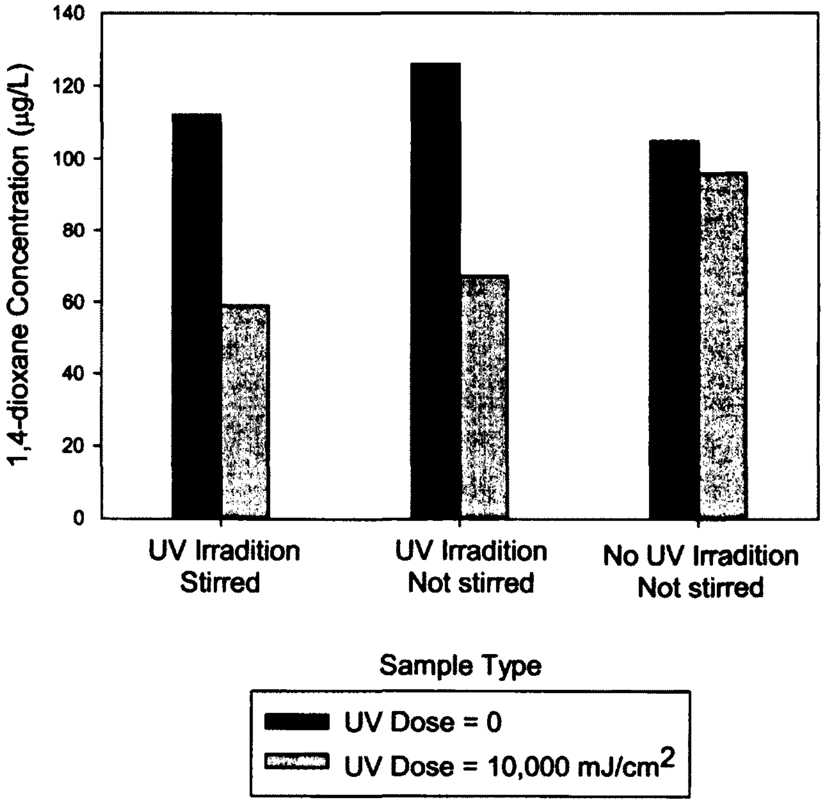


Figure 15: UV Bench Scale with Additional Monitoring

UV Batch Reactor Study

A 5 gallon batch reactor study was used for final consideration of photolysis. A POE-sized UV reactor (SPV-8 Unit, Trojan Technologies; London, ON) supplied a high UV dose of 19,200 mJ/cm^2 over the course of 5 hours at a water flow of 3.78 lpm (1 gpm). A control study was completed without the UV source on to help determine dioxane losses not attributed to irradiation.

Without irradiation there was little removed of the 134 μg/L dioxane present with only a slight variability (5%) over 5 hours (Figure 16). This indicated that there was little to no dioxane loss from aeration, agitation, or sorption from the closed loop batch reactor. The small variations in concentration observed may have resulted from incomplete mixing of the dioxane spike or precision of the analytical method. UV irradiation showed high removal rates at high UV dosages. A clear dioxane reduction (30%) from an initial averaged concentration of 127.5 μg/L to a final concentration of 88 μg/L (Figure 16) was observed. However, with high initial dioxane concentrations and UV dose, the 30% reduction in dioxane from direct photolysis was not considered viable as a POE technology because of the lack of efficiency. The dioxane reduction attributed to photolysis at low UV dosages (1,200 mJ/cm^2) is similar to results reported by Martijn et al. (2010).

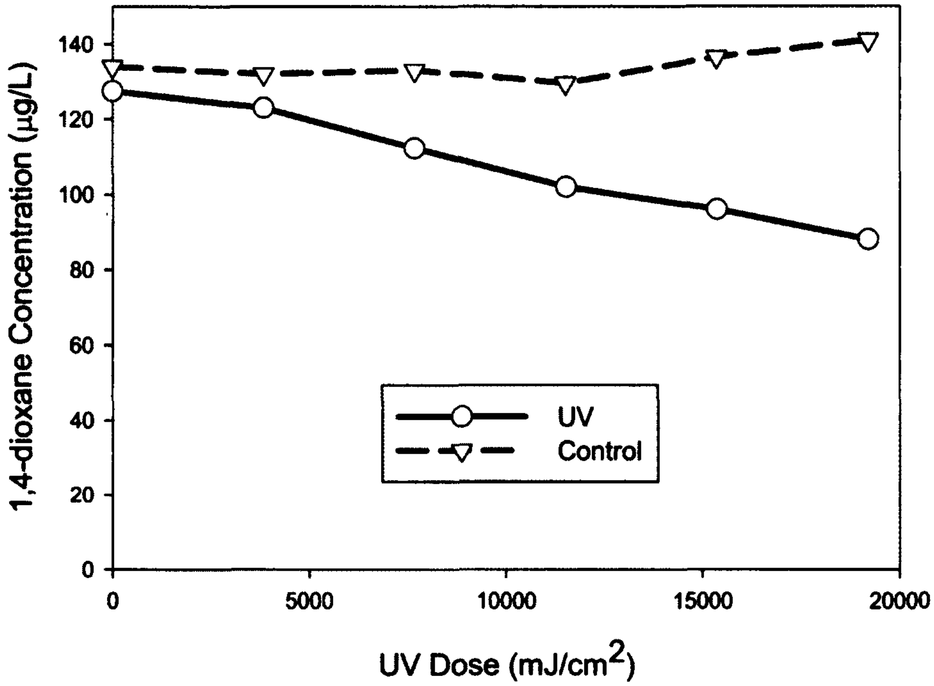


Figure 16: UV Batch Reactor Study with SPV-8 UV Unit

At high UV doses, the possibility of forming of hydroxyl radicals in natural waters increases due to an increase in the sample's UV exposure. The generation of hydroxyl radicals in natural waters can be attributed to several different mechanisms including the photolysis of hydrogen peroxide, ozone, nitrate, nitrite, dissolved organic matter (DOM), and metal ions (Brezonik & Fulkerson-Brekken, 1998). Vione et al. (2006) found that DOM was the main source (and sink) for hydroxyl radicals in a surface water sample while nitrate was the main source in a groundwater sample. Evaluation of these naturally occuring parameters in NH groundwater as well a their effects on hydroxyl radical production would be required for further consideration of direct photolysis.

UV-Peroxide Oxidation

After minimal success with dioxane destruction through direct UV photolysis, hydrogen peroxide (H_2O_2) was included in the bench scale studies in an effort to improve removal. Known for removal of difficult to treat contaminants, UV-peroxide oxidation is an effective AOP able to treat dioxane levels to < 5 μg/L from an initial dioxane concentration of 367 μg/L (Wojcicka & Cavalcante, 2004). Dioxane has a favorable second order rate constant for destruction with hydroxyl radicals at 2.8×10^9 liters/mole•sec (MWH, 2005). However, chemical use (hydrogen peroxide) and treatment complexities present significant obstacles for application in a POE system.

Initial UV-Peroxide Experiment

Preliminary testing compared three different groundwater samples spiked with dioxane to a concentration of 18 μg/L. Samples were spiked with 0, 3, and 6 mg/L H_20_2. The pH and alkalinity of each sample were monitored before and after the experiment to provide an estimation of the groundwater hydroxyl scavenging ability. Initial groundwater alkalinity was measured at 112 ± 2 mg/L as $CaCO_3$. All samples were stirred and irradiated at a UV dose of 600 mJ/cm^2, a median dosage applied at existing water treatment facilities (Martijn et al., 2010). Although the UV dose administered in a POE system has the possiblity to be higher than that applied at existing water treatment facilities, this initial experiment was conducted to determine the effectiveness of UV-peroxide using groundwater vs. to pre-treated surface water.

11%, 28%, and 51% reductions in dioxane concentration were observed for the groundwater samples spiked with 0, 3, and 6 mg/L of hydrogen peroxide, respectively (Figure 17). Dioxane reduction did not meet expectations based on the low initial concentration and high

UV-peroxide dosages. Martijn et al. (2010) reported 55% and 57% reduction rates at higher initial dioxane concentrations (200 µg/L) using similar UV and hydrogen peroxide dosages. The lack of dioxane destruction was attributed to interferences in the groundwater, specifically alkalinity (112 ± 2 mg/L as $CaCO_3$) which can act as a scavenger for hydroxyl radicals. Final dioxane concentrations did not approach the treatment goal of ≤ 3 µg/L in either sample spiked with hydrogen peroxide.

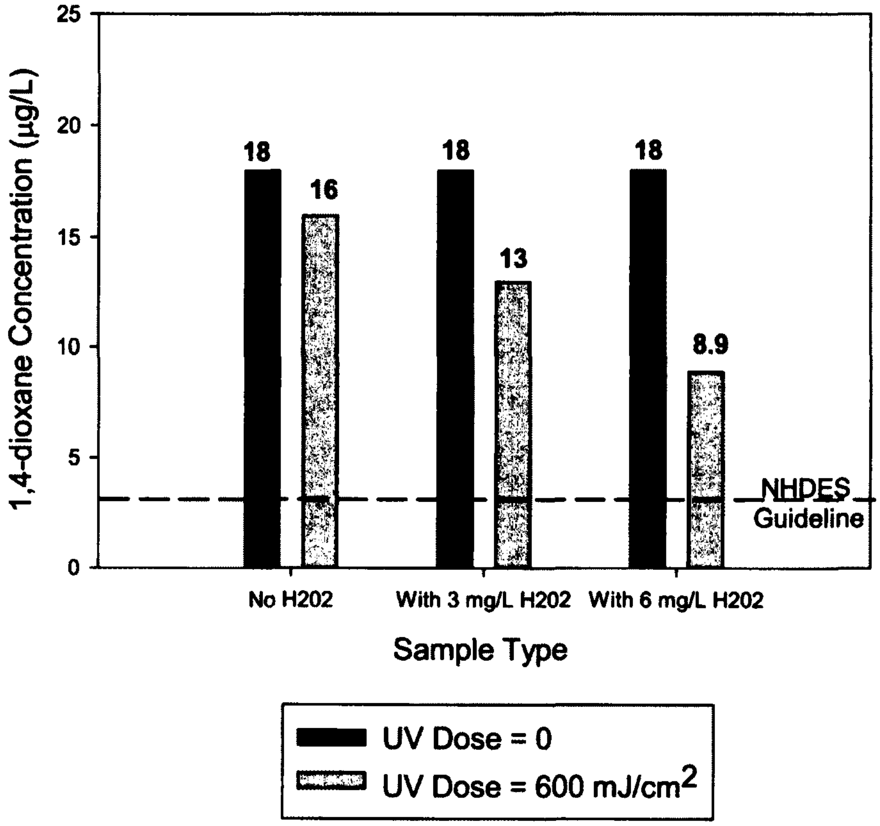


Figure 17: Initial UV-Peroxide Experiment

above bar = 1,4-dioxane concentration in µg/L

UV-Peroxide Experiment for Scavenging Effects

The second UV-peroxide study was designed to determine: a) if the groundwater was causing hydroxyl interference, and b) if an increased UV and hydrogen peroxide dosage would result in greater dioxane removal. A reverse osmosis (R.O.) water sample (minimal interferences, alkalinity < 10 mg/L as $CaCO_3$) spiked to a final dioxane concentration of 13 μg/L was dosed to 3 mg/L hydrogen peroxide and irradiated with a UV dose of 600 mJ/cm^2. Groundwater with 13 μg/L of dioxane was spiked with 10 mg/L hydrogen peroxide and irradiated with a UV dose of 1200 mJ/cm^2. This treatment represented the high range of dosing for UV-peroxide treatment.

The R.O. water showed > 92% reduction in dioxane concentrations to below an analytical RDL of 1 μg/L (Figure 18). Martijn et al. (2010) reported similar results (98% removal) when using Milli-Q water for the sample. These results confirmed that interferences in the groundwater were inhibiting dioxane degradation. Interferences in dioxane degradation can be caused by the presence of UV-absorbing compounds or by hydroxyl radical scavengers. Compounds that absorb UV-light and prevent the formation of hydroxyl radicals include nitrate, organic matter, and suspended material. Compounds that scavenge hydroxyl radicals and thereby inhibiting target degradation include carbonate, bicarbonate, reduced metal ions, DOM, and nitrite. The natural buffering capacity of water (alkalinity) in the form of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) species is of particular concern in natural waters because their concentrations are often three orders of magnitude higher than the target contaminant. Crittenden et al. reported that even low alkalinities of 50 mg/L (compared to ~112 mg/L $CaCO_3$) reduced the rate of TCE destruction by a factor of 10 at a pH of 7 (MWH, 2005).

An 82% reduction in dioxane to a final concentration of 2.3 μg/L (Figure 18) was observed when UV and hydrogen peroxide dosages were increased to 1200 mJ/cm^2 and 10 mg/L, respectively. It is important to note the low initial dioxane concentration (13 μg/L) of dioxane in the samples. Martijn et al. (2010) reported corresponding results (82% removal) at similar UV and hydrogen peroxide dosages and an initial dioxane concentration of 200 µg/L.

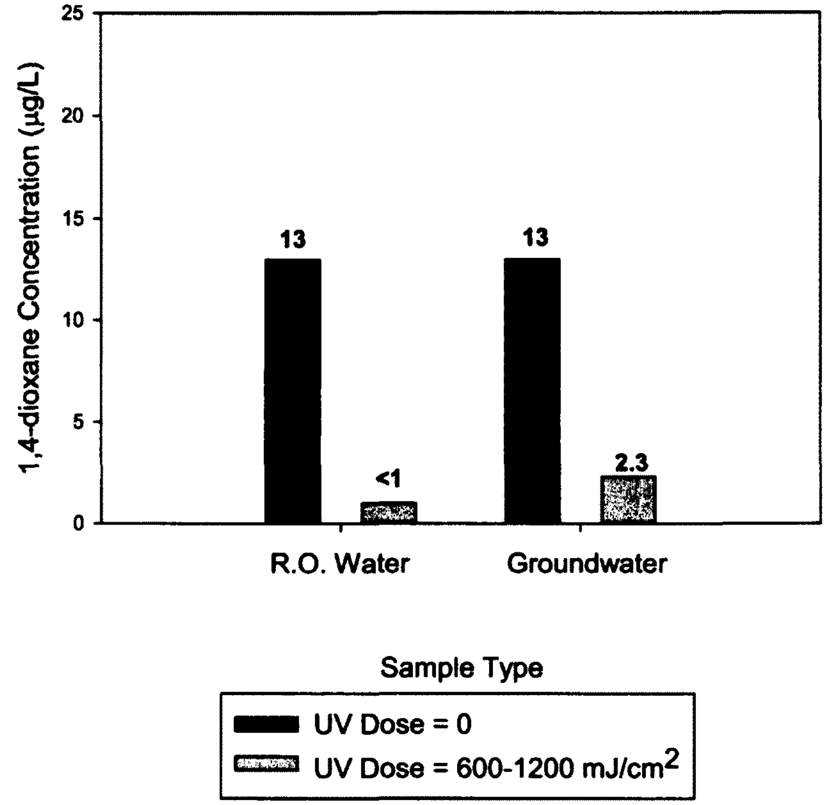


Figure 18: UV-Peroxide Experiment for Scavenging Effects

Although UV-Peroxide was able to degrade dioxane to below the NH MCL, there are concerns regarding its chemical hazard, chemical supply, and lack of record in POE systems. Hydrogen peroxide at high concentrations used for water treatment (30% w/w) is known to be corrosive as well as an irritant when in contact with the skin. It also bears an explosion hazard when in the presence of sparks, heat, acids, metals, or organic materials. At lower concentrations, the hydrogen peroxide volume required for projected treatment of 250 gpd of water to the NH MCL exceeds 100 liters annually (Table 19). In addition to concerns of chemical use, hydrogen peroxide for drinking water treatment requires a post quenching step (e.g. GAC adsorption) for peroxide removal. Hydrogen peroxide is a strong oxidant and irritant making residual removal a mandatory step for drinking water. This ancillary treatment step would add to an already complex POE UV-peroxide treatment system.

Table 19: Annual Hydrogen Peroxide Use in Liters

[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	3 mg/L	31	10	3
	6 mg/L	63	21	7
	12 mg/L	105	35	12

*See Appendix R for calculations

The most significant concern with applying UV-Peroxide treatment to a POE unit is that the process is entirely unproven. The design process would require significant bench, pilot, and full scale studies before reaching an acceptable safety levels for the public. Although not recommended for POE use, continued research on UV-peroxide treatment should involve quantification of hydrogen peroxide doses required for acceptable dioxane concentrations in groundwater. Variables that could affect hydrogen peroxide dosage include alkalinity, pH, hydrogen sulfide, metal ions, nitrite, and nitrate.

The use of vacuum UV (VUV) technology has been shown to create hydroxyl radicals directly from the photolysis of water. Xenon lamps with an emission wavelength of 172 nm have been shown to enable the oxidation and mineralization of dissolved organic substrates in water without the addition of chemicals (Oppenlander et al., 2005). More recent studies have indicated that VUV may be more efficient at generating hydroxyl radicals than other AOPs (Wanget al., 2010). Although research by Oppenlander & Gliese (2000) has shown that VUV can successfully mineralize organic micropollutants (e.g., alcohols and phenols), there has been little to no work done with respect to dioxane. Concerns with VUV include capital cost of the UV source, UV interferences at low wavelengths (~172 nm), oxidation intermediates, as well as byproduct formation. Further investigation into VUV would be required before its consideration as a possible dioxane treatment technology.

Chapter 5 – APPLICATIONS FOR RESIDENTIAL TREATMENT

Reductions of dioxane concentrations in groundwater occurred in three out of the four treatment techniques examined (air stripping, GAC adsorption, UV-peroxide). However, treatment capabilities and process efficiency limit which techniques may be applied in residential settings. This section is intended as a guide to choosing the appropriate POE technology based on water characteristics (e.g., dioxane concentration, alkalinity). Research completed on these techniques was preliminary, focusing on the feasibility of each process instead of optimization. As a result, pilot-scale testing is recommended for all technologies before residential application.

Air Stripping

Air stripping through diffused bubble aeration was not effective at removing dioxane (≤ 3 µg/L) from groundwater at low initial concentrations (20-30 µg/L), indicating that this technology should not be used exclusively for POE treatment. However, preliminary stripping experiments with high dioxane concentrations (> 100 µg/L) and high A:W ratios (5000:1) reduced dioxane concentrations by as much as 39%. Further research into the overall feasibility and economics of air stripping is necessary to validate and reinforce these findings. In addition, other types of aeration not tested (e.g., fine bubble, pressurized in-line aeration, spray aeration) may prove to be more effective at removing dioxane than the methods applied in this research.

If stripping is applied in a POE unit, strict emissions control is necessary. Care must be taken to ensure that dioxane emissions do not accumulate where the unit is installed (e.g., cellar) or where the off-gas pipe is located (e.g., roof), as dioxane vapors can be harmful to the user. In addition to emissions control, clogging and fouling issues should be investigated before installation. Groundwater characteristics such as iron (Fe^{+2}, Fe^{+3}), manganese (Mn^{+2}), nutrients, and hardness should be measured. Groundwater concentrations of ferrous iron are particularly of concern in NH groundwater, as this compound can precipitate when oxidized (Sutherland & Adams, 2004). Clogging of groundwater aeration units (diffused bubble) has been observed with the likely culprit being iron precipitates (Kinner, Malley Jr., & Clement, 1990). Increased levels of nutrients (e.g., nitrate) can cause biofouling problems in the stripping system.

Many of the clogging and fouling issues associated with air stripping can be minimized with proper maintenance and monitoring practices. Pretreatment practices (e.g., ion exchange, GAC) may be applied to reduce the effects of iron, manganese, and hardness. However, the investigation of radionuclides must be completed for GAC adsorption pretreatment processes to ensure there is no danger of long term accumulation (gamma emissions) (Kinner, Malley Jr., & Clement, 1990).

GAC Adsorption

Adsorption using GAC was effective at removing dioxane from groundwater below the NH MCLG of 3μg/L. All GACs, which were of a coal or coconut base, were able to treat dioxane to <3 μg/L. From the carbons tested (Table 12), OLC (coconut base, Calgon Carbon Corp.) provided the highest capacity at 38 μg of dioxane/g of OLC carbon. Filtrasorb 200 (coal, Calgon Carbon Corp.), commonly used in NH POE applications, provided a capacity of 20 μg of dioxane/g of F200 carbon. GAC capacities were based on an influent concentration of 20 μg/L. This research indicated that a coconut based carbon may yield better dioxane sorption results in GAC units than coal based carbons, although costly ($20-32 per 1,000 gal. treated, Table 18). Assuming a common GAC POE reactor volume of 2ft^3, dioxane breakthrough would occur in as short of a time as 1.5 months, requiring re-bedding. The safe practice would be to install a second POE unit in series with the first to guard against drinking water contamination from any unit failure. Breakthrough times could also be increased through the expansion of the typical GAC POE reactor volume which is commonly $2ft^3$,

Because GAC indiscriminately adsorbs many solutes, design must take into account other species present in the groundwater (e.g., natural organic matter (NOM), hydrogen sulfide, and other radionuclides). These compounds, along with other organic and inorganic pollutants, may compete for adsorption sites on the GAC or clog the bed. If present, further investigation of radon and radionuclides must be completed in to ensure there is no danger of long term accumulation (gamma emissions) on the GAC (Kinner, Malley Jr., & Clement, 1990).

Similar to air stripping, GAC performance may be hindered by iron hydroxide and manganese oxide precipitation, calcium carbonate scaling ($CaCO_3$), and biofouling. Evaluation of iron (Fe^{+2}, Fe^{+3}), manganese (Mg^{+2}), hardness (Ca^{+2}, Mg^{+2}), and pH would be required for pretreatment considerations. Ion exchange pretreatment may help alleviate issues associated with manganese, iron, and calcium carbonate. However, the investigation of radionuclides must be completed in ion exchange pretreatment processes to ensure there is no danger of long term accumulation (gamma emissions). Past studies on MtBE removal using POE GAC systems in New Hampshire indicate that these issues are not likely sources of serious concern for 1,4 dioxane treatment because the shorter exhaustion rate (< 6 months vs. 1 year). However, these parameters still need to be addressed before a POE system is implemented.

UV Direct Photolysis

Direct photolysis was not proven to reduce dioxane concentrations in groundwater and therefore should not be considered as a treatment option.

UV-Peroxide

UV-peroxide advanced oxidation was not found to be efficient at reducing dioxane concentrations in groundwater. The NH MCLG (3 µg/L) was only accomplished with low (13 µg/L) initial dioxane concentrations and a high dose of UV (1200 mJ/cm^2) and hydrogen peroxide (10 mg/L). Efficient dioxane destruction was not observed likely due to interferences in the groundwater (e.g., hydroxyl radical scavenging, UV absorbance). Groundwater characteristics such as alkalinity, NOM, metal ions (Fe^{+2}, Mg^{+2}), and hydrogen sulfide (H_2S) determine if hydroxyl radicals produced will likely be scavenged (MWH, 2005). Of these characteristics, alkalinity is likely to be one of the most common obstacles for UV-peroxide treatment. The natural buffering capacity of water (alkalinity) in the form of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) species is of particular concern in natural waters because their concentrations are often three orders of magnitude higher than the target contaminant. Crittenden et al. reported that even low alkalinities of 50 mg/L (compared to ~112 mg/L) reduced the rate of TCE destruction by a factor of 10 at a pH of 7 (MWH, 2005).

Chemical doses coupled with a required hydrogen peroxide post-quenching step make UV-peroxide a complicated application in a POE residential treatment system. However, the most significant concern with applying UV-Peroxide treatment to a POE unit is that the process is entirely unproven. The design process would require significant bench, pilot, and full scale studies before being accepted for use in a residential POE system.

Chapter 6 – CONCLUSIONS

Air Stripping

- Contrary to what the dimensionless Henry's Law Constant of 1.96×10^{-6} (Howard, 1990) indicates, dioxane exhibits some degree of volatilization from water. Air stripping was proven to significantly reduce dioxane concentrations in groundwater (39%) when initial concentrations were high (> 100 μg/L). However, high reduction rates required high A:W ratios (5000:1) and were not proven to reach levels below 26 μg/L.
- Air stripping was not found to be effective at removing dioxane from groundwater when 1) initial dioxane concentrations were closer to values which POE systems would experience (20-30 μg/L), 2) the required final concentrations were low (≤ 3 μg/L), and 3) when A:W ratios were realistic (240:1).

GAC Adsorption

- GAC adsorption studies indicate that 6 out of the 7 carbons tested were able to treat dioxane to < 2.0 μg/L in groundwater. Dioxane adsorption was most successful in coconut and coal based carbons. Only the wood based carbon (5DW 0830) was not able to treat to this level.
- Isotherm studies for OLC, F200, and GCA carbons indicated short exhaustion times between 26 and 88 days for a 2 ft^3 POE unit with 250 gpd flow and an influent dioxane concentration of 20 μg/L.
- OLC was the most efficient carbon tested, resulting in a single POE unit exhaustion time of between 47-88 days at an annual carbon cost of $550.
- Further evaluation (pilot scale) of coconut based carbon (e.g., OLC) is recommended based on the isotherm results which compare coal and coconut capacities.

UV Direct Photolysis

- UV direct photolysis was found to be ineffective at degrading dioxane in groundwater at high doses of UV light (10,000 mJ/cm^2). In both *Bench Scale Study A* and *Study B*, a majority (42.7- 46.8%) of the total dioxane reduction (47.3-65.1%) could be attributed to volatilization from the samples being stirred. This conclusion compares favorably with the air stripping results.
- The *UV Batch Reactor Study* confirmed the ineffectiveness of direct photolysis showing only 31.0% dioxane reduction using a UV dose (19,200 mJ/cm^2) at a high initial dioxane concentration (127.5 μg/L). Assuming this removal rate, the influent dioxane concentration to a POE unit would need to be ≤ 9.7 μg/L to reach the NH MCLG of 3 μg/L.

UV-Peroxide Oxidation

- UV-Peroxide was not found to effectively degrade low concentrations (< 20 μg/L) of dioxane in groundwater at typical and high dosages of hydrogen peroxide (3-10 mg/L) and UV irradiation (600-1200 mJ/cm^2). Control samples in the UV-Peroxide studies indicate that groundwater interferences such as alkalinity (117 mg/L as $CaCO_3$) greatly inhibit dioxane degradation by scavenging hydroxyl radicals.
- Compounds that scavenge hydroxyl radicals and thereby inhibiting target degradation include carbonate, bicarbonate, reduced metal ions, DOM, and nitrite.

Chapter 7 –Recommendations

Air Stripping

- Further research on air stripping is not recommended when initial dioxane concentrations are low (20-30µg/L), as seen in many New Hampshire aquifers.
- Air stripping may be a viable pre-treatment option in cases where the initial dioxane concentration is high (> 100 µg/L). In these cases, air stripping could be a cost effective pre-treatment option to decrease the operating costs of the primary treatment technology (e.g., carbon adsorption).

GAC Adsorption

- Further evaluation of coconut based carbon is recommended based on the isotherm results. Laboratory column tests (e.g., rapid small-scale column tests (RSSCT)) could provide a more accurate prediction of GAC performance in a POE system.

UV Direct Photolysis

- UV direct photolysis is ineffective at degrading dioxane in groundwater. Further research is not recommended.

UV-Peroxide Oxidation

- UV-Peroxide is not a viable POE option for the treatment of dioxane in groundwater because the technology is unproven in this application. Significant testing would need to be completed to validate UV-Peroxide as an acceptable POE treatment system for dioxane.

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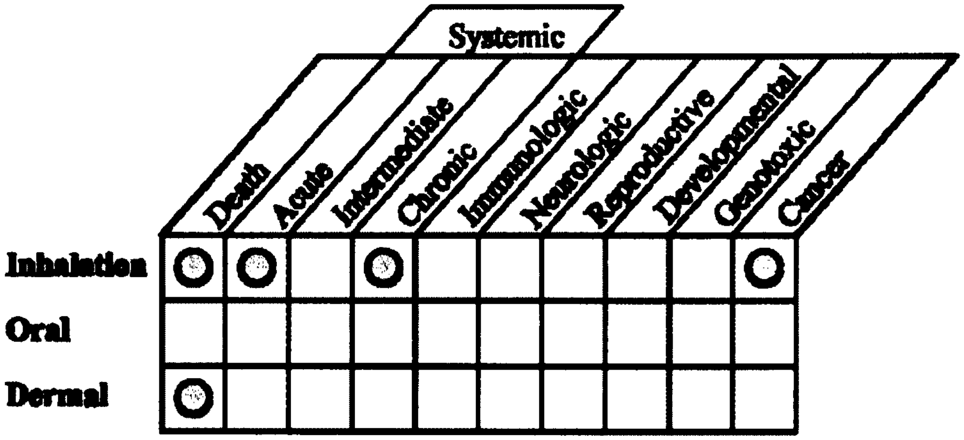
Appendix A: Literature Review

The objective of this research, set by the NHDES, was to evaluate possible POE treatment technologies for the reduction of dioxane in private groundwater systems. This appendix reviews the literature available on different processes used to remove dioxane (dioxane) from water along with their potential applicability to POE systems. The review covers the public health and regulatory aspects of dioxane, as well as specific treatment processes including air stripping, activated carbon adsorption, bioremediation, and oxidation. It should be noted that much of literature involves large scale processes (>1,000 gpd) which may not be applicable for a POE (<250 gpd) system (McGarry, 2009). The applicability of a process to POE treatment will be discussed along with its dioxane removal efficiency and the test conditions under which they were achieved. Many of the publications evaluated several processes. Therefore, the same reference will be listed in several sections.

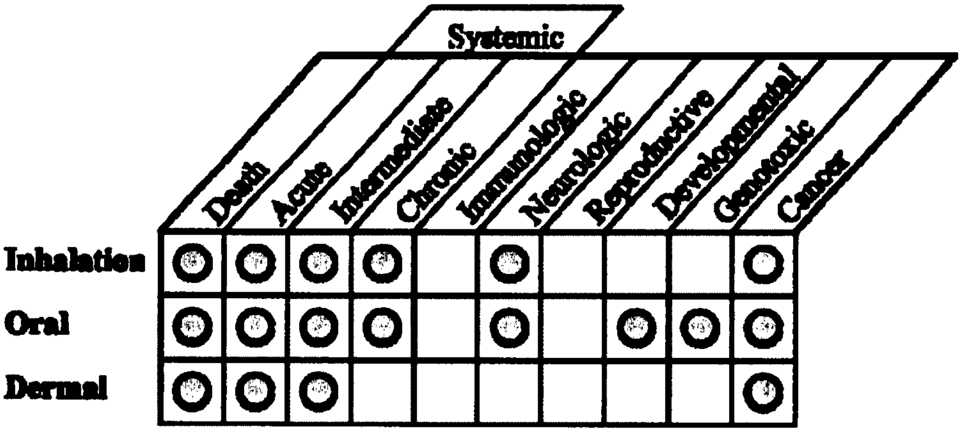
Public Health Effects

In 2007, the Agency for Toxic Substances and Disease Registry (ATSDR) completed a toxicological profile of dioxane noting exposure can occur from inhalation of contaminated air, ingestion of contaminated drinking water or food, and dermal contact (ATSDR, 2007). Limited information is available on dioxane's direct health effects on humans. However, extensive research on animals (e.g., rats, mice, guinea pigs) provides sufficient evidence that the liver and kidneys are the target organs for toxicity (Kano et al., 2009).



		Systemic							
	Death	Acute	Intermediate	Chronic	Immunologic	Neurologic	Reproductive	Developmental	Genotoxic	Cancer
Inhalation	○	○		○						○
Oral										
Dermal	○									

Human



		Systemic								
	Death	Acute	Intermediate	Chronic	Immunologic	Neurologic	Reproductive	Developmental	Genotoxic	Cancer
Inhalation	○	○	○	○		○				○
Oral	○	○	○	○		○		○	○	○
Dermal	○	○	○							○

Animal

○ Existing Studies

Figure 19: Available1,4 Dioxane Health Effect Studies (ATSDR, 2007)

A Minimum Risk Level (MRL) is defined as an estimate of daily human exposure to a substance that is likely to be without an appreciable risk of adverse non-carcinogenic effects over a specified duration of time (Table 20).

Table 20: Minimum Risk Levels for Humans as a Result of Exposure to 1,4 Dioxane (Adapted from ATSDR)

Exposure Type	**Duration**	**Minimum Risk Level (MRL)**	**MRL in Drinking Water***
Inhalation	Acute	2 ppm	-
	Chronic	1 ppm	-
[redacted]	[redacted]	[redacted]	[redacted]

Acute: <14 days *Intermediate: 14-365 days* *Chronic: >365 days*

**Assuming 2L of water per day and an average body weight of 70 kg (Appendix S)*

Most groundwater sites are contaminated at relatively low concentrations (μg/L) compared to concentrations used in toxicity studies (mg/L). Chronic (low concentration, long duration) exposure risk may be more appropriate than acute (high concentration, short duration), especially with respect to drinking water. Chronic two year exposure to dioxane in drinking water was linked to liver cancer in rats and mice (Kano et al, 2009).

Air Stripping

Preliminary research on dioxane's properties reveals a low Henry's Law constant (K_H) of 4.88×10^{-6} atm m^3/mole coupled with high solubility. The key property controlling the transport of dioxane is its solubility. The high solubility of dioxane (Figure 20) can be attributed to the two oxygen atoms (in red) which are available for interaction with water molecules (Mzurkiewicz & Tomasik, 2005).

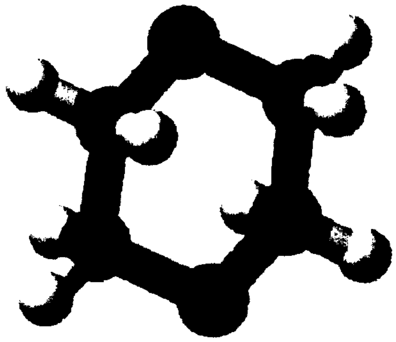


Figure 20: 1,4-Dioxane Model

(Oxygen = Red   Carbon = Black   Hydrogen = White)

The combination of a high solubility with a low Henry's law constant makes air stripping ineffective at removing dioxane from water (Mohr, 2001). However, some case studies have shown limited success in dioxane stripping from water. Air stripping may not be viable to use as a sole method to reduce dioxane to regulatory limits, but it could be effective in combination with other processes.

Bowman et al. (2001) investigated the effectiveness of an air stripper as pre-treatment for an AOP to remove chlorinated solvents in Industry, CA. The air stripper was run at 10 gpm, pH range of 7.2-8.6. The average removal efficiency for dioxane was 29.5% with influent and effluent concentrations of 610 and 430 µg/L, respectively.

A case study at U.S. Air Force Plant 44 (Tucson, AZ) to determine if existing large-scale air strippers, designed to remove chlorinated solvents, could be adjusted to remove dioxane. Influent dioxane concentrations were 10-15 µg/L with a target effluent concentration of 6 µg/L. The treatment system consisted of three parallel trains of two stage air stripping towers (primary and secondary) with a design flow of 5,000 gpm. When the primary and secondary towers were operated at air to water ratios of 7:1 and 25:1, respectively, no dioxane was removed. When air to water ratio were increased to 69-291:1 a maximum dioxane removal rate of ~10% was achieved. (Earth Tech, Inc., 2004)

The limited studies done on dioxane removal as well as the variable results for air stripping indicate that while this technology may be applied to POE units, attaining low effluent concentrations (≤ 3 µg/L) may be difficult.

Activated Carbon Adsorption

The octanol-water partition coefficient (K_{ow}) for dioxane suggests that carbon adsorption techniques will not be effective. However, granular activated carbon (GAC) systems designed to remove volatile organic compounds (VOCs) at the Beede waste oil site (Plaistow, NH) have shown as recently as August 2009, a 90% reduction in dioxane concentrations (35 µg/L to 3.4 µg/L) (Pea09). GAC manufacturers do not have isotherm data for dioxane, making it difficult to predict the characteristics of a POE activated carbon system.

The dioxane removal efficiencies of GAC produced from agricultural by-products (e.g., rice straw, soybean hull, peanut, pecan, walnut shells) were compared to that of commercial carbon (e.g., Filtrasorb 200 and Centaur 20 × 50; Calgon Carbon Corporation; Pittsburgh, PA) (Johns et al., 1997). A mixed suite of six organic compounds was employed testing (benzene, toluene, dioxane, acetonitrile, acetone, methanol). In the study, 0.1 g of carbon are added to a 10 mL organic solution containing 800 µg/L of each compound. Carbon adsorption was the lowest for dioxane. It also had the greatest variability in removal rates. Estimations made from the organics adsorption graph (Figure 1 in the paper) showed carbon capacities for Filtrasorb 200 (F200) and Filtrasorb 400 (F400) of ~3,500 µg dioxane/g carbon. However, only the GAC produced from walnut and pecan shells exceeded 50% dioxane removal. Commercial grade GAC showed removal rates in the 40% range. The reduced affinity for dioxane compared to the other compounds was attributed to competition with the other adsorbates (e.g., benzene, toluene, acetonitrile, acetone, methanol. Fortunately, at residential sites where dioxane is a concern, it is the sole organic contaminant present.

At a groundwater contamination site in South El Monte, CA, the local water authority conducted monitoring on a GAC system which consisted of two 20,000 lb carbon reactors. The groundwater was contaminated with a variety of chlorinated solvents as well as dioxane. The system was run at 9.7 gpm to help reduce 1,1-DCA contamination (Bowman, 2001). It failed to significantly reduce the dioxane concentrations which averaged 20 μg/L.

Local success at the Beede Waste Oil site (Plaistow, NH) shows GAC is capable of treating dioxane to below regulatory limits (≤ 3 μg/L). The low water demand of a household POE system (≤ 250 gpd) meant a multi-pass low flow GAC system could treat dioxane to required regulatory levels. Such POE adsorption units are common in the home water treatment industry. A GAC system could also be used in series with another process technology (e.g., air stripping) to attain better dioxane removal. Future application of GAC for dioxane removal from groundwater depends on carbon exhaustion rates. Research needed includes the development of isotherms in order to determine GAC POE re-bedding frequency and cost.

Bioremediation

Dioxane is widely thought to be recalcitrant to microbial activity under normal environmental conditions, but some studies have found success. Bioremediation studies involving dioxane as the sole substrate as well as by co-metabolism (i.e., primary substrate = tetrahydrofuran (THF), propane) have been reported (Shangraw & Plaehn, 2006). Co-metabolic studies have shown greater success than when dioxane was the sole substrate.

THF (Figure 21), an industrial solvent, is the most common primary substrate used with dioxane due to similarity in structure. However, THF is not usually a co-contaminant with dioxane in residential situations, so it would need to be added to stimulate biodegradation. However, THF addition for co-metabolism is not practical in POE applications.

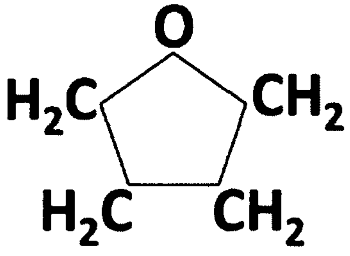


Figure 21: Tetrahydrofuran

1,4 Dioxane as Sole Substrate

In 1993, Parales et al. reported a bacterium (*Actinomycete* CB1190) capable of aerobically growing on dioxane as its sole carbon and energy source after being gradually weaned from a THF enrichment. Direct enrichments on dioxane were unsuccessful; CB1190 preferentially degraded THF in a pure culture. The bacteria were initially isolated from an industrial waste sludge produced at a dioxane-contaminated site in Darlington, SC. At 30°C, the pure culture had a specific activity of 0.33 mg of dioxane per min per mg of microbial protein and mineralized ~50% of the dioxane to CO_2. No other organic intermediates were found in the samples after dioxane degradation. Successful biodegradation of dioxane in this study was only found with gradual, long term enrichments. THF still was definitely the preferred substrate of the isolated CB1190 culture.

Confirmation of Parales' results on the CB1190 strain came in 2005 (Mahendra & Alvarez-Cohen). Using the same pure culture that was isolated from the dioxane-contaminated industrial sludge and supplied by Parales, growth was achieved using dioxane as the sole substrate in aerobic conditions. Growth continued for up to 28 days at an optimal temperature of 30°C.

In 2004, Kim and Engesser isolated 20 strains from sewage sludge (Stuttgart, Germany) which were known to degrade ethers as a sole carbon and energy source, including 18 *Rhodococcus* strains and two *Sphingomonas* strains. Strains were aerobically incubated at 30°C. None of the 20 isolates were able to grow on dioxane or THF.

These studies indicate that bioremediation using dioxane as a sole carbon source is a difficult process to maintain making it unlikely to be applied successfully to a POE unit.

1.4 Dioxane as a Co-Metabolite

A complete, fullscale study of dioxane and THF biodegradation in groundwater was performed at the Lowry Landfill Superfund site (Denver, CO). THF is an obligate co-metabolite in dioxane biodegradation. Promising bench-scale reductions in dioxane (73%) and THF (88%) concentrations led to a pilot study with parallel 300 gal., fixed film, moving bed bio-reactors to study the effects of temperature (25° and 15°C). The full scale system was designed with three aerobic, fixed film, moving bed bio-reactors able to reduce dioxane concentrations (C_0=25,000 µg/L) to $\leq$ 1 µg/L using indigenous bacteria (Flow rate = 6 gpm, Temperature = 23°C) (Shangraw & Plaehn, 2006). In this study, oxygen was the electron acceptor and dioxane (or THF) the electron donor.

Zenker et al. (2004) designed a laboratory scale trickling filter to biodegrade cyclic ethers including dioxane and THF at concentrations encountered in contaminated groundwater. Using oxygen as the electron acceptor and dioxane (or THF) as the electron donor, the filter was operated for 1 year at low (200 μg/L) and medium (1,000 μg/L) influent dioxane loading. The average air flow rate through the filter was 0.17 L/min with a hydraulic residence time of 14.4 minutes. At low loading levels with THF present, the filter was capable of consistent dioxane biodegradation to ~2-10 μg/L. However, the system was more effective at removing THF due the bacteria's greater affinity for it as compared to dioxane. The biodegradation of dioxane was inhibited with the presence of THF in the system until the primary substrate (THF) reached relatively low levels. This competitive inhibition is commonly observed in co-metabolic processes where two substrates (dioxane and THF) are competing for the same enzyme.

In a study funded by the U.S. Department of Defense, Steffan (2007) used two aquifers to show that dioxane was recalcitrant when a primary substrate (propane or THF) was not present. It did not matter whether aerobic, nitrate, iron, or sulfate reducing or methanogenic conditions existed. dioxane was not degraded in any of the anaerobic microcosms over >400 days. Biodegradation of dioxane was observed after >100 days in microcosms of strain ENV478 which had been stimulated with propane and THF. This and previous studies demonstrate that biological treatment and natural attenuation are unlikely to be successful remedial choices for sites contaminated with dioxane, unless a suitable primary substrate is present.

Phytoremediation

In 2000, Aitchison et al. successfully showed that hybrid poplar trees (*Populus deltoids*, DN34-Imperial California) effectively removed dioxane from soil and water. The poplar trees were able to remove 54.0 ± 19.0% of a 23,000 μg/L solution of dioxane after 9 days of exposure through uptake and translocation. The hybrid cuttings also remediated contaminated soil (10 mg/kg) leaving only 18.8 ± 7.9% of the original dioxane in the soil after a 15 day exposure. In both experiments, a majority of the dioxane assimilated by the poplars was transpired through the leaves into the air where it was photo degraded. It is important to note that this experiment only involved short-term results on relatively young poplar plants (8-12 weeks). Although a promising soil remediation solution, phytoremediation would be difficult to apply to a drinking water application.

Advanced Oxidation Processes

Advanced oxidation of dioxane is the most common process employed in industrial waste situations, however, the use of hazardous chemicals make it difficult to apply to a POE system Common AOPs for dioxane make use of ultraviolet irradiation (UV), hydrogen peroxide (H_2O_2), ozone (O_3), titanium dioxide (TiO_2) in different combinations to mineralize dioxane. Listed below in Table 19 in are common AOPs used for dioxane:

Table 21: Advanced Oxidation Processes for 1,4 Dioxane Removal In Water

Advance Oxidation Process	**Acronym**	**Pilot Study Manufacturer**
Hydrogen Peroxide with Ultraviolet Irradiation	H_2O_2 + UV	Trojan Technologies, Inc (London, Ontario, Canada)
Ozone with Hydrogen Peroxide	O_3+ H_2O_2	HiPOx®, Applied Process Tech. (Long Beach, CA)
Titanium Dioxide with Ultra-Violet Irradiation	TiO_2 + UV	Purifics ES Inc. (London, Ontario, Canada)

Advanced Oxidation Processes (AOPs) work by creating hydroxyl radicals, highly reactive species, through the combination of different chemicals and catalysts. These processes require careful monitoring, expensive equipment, and the use of costly chemicals which make them undesirable for use in a POE system. Developed AOP technologies can treat dioxane concentrations to drinking water standards (< 3µg/L) at sites where there is a need for a large scale treatment system (Table 20).

Table 22: Advanced Oxidation Processes for 1,4 Dioxane Treatment

Advanced Oxidation Process	Contaminant conc. (µg/L)	Treated conc. (µg/L)	Source
$O_3 + H_2O_2$	470	<2	(Bowman, 2001)
$UV + H_2O_2$	>70	7	(Stefan & Bolton, 1998)
$UV + TiO_2$	3,000	8	(Wojcicka & Cavalcante, 2004)

In 2004, Wojcicka & Cavalante completed a comprehensive study comparing the ability of these three AOPs ($O_3 + H_2O_2$, $UV + H_2O_2$, $UV + TiO_2$) to be added to a groundwater treatment plant and treat dioxane in groundwater. The parameters monitored during the study included hydroxyl radical scavenging potential, general water characteristics, and by-product formation (i.e., bromate from bromide in ozone treatment). The results from the initial bench-scale study concluded that the scavenging potential was the most important water characteristic to evaluate due to its effect on AOP efficiency. The pilot-scale study used systems supplied and optimized by manufacturers in the water treatment industry. All three AOP systems were evaluated in parallel after the water was pre-chlorinated (to oxidize metals and rejuvenate filter media) and filtered just as at the water treatment plant. dioxane was reduced in all three systems from 47-151 µg/L to a targeted concentration of < 10 µg/L when the systems were optimized (number of UV lamps on, flow rates, chemical dosing).

Stefan and Bolton (1998) conducted experiments which were able to define the degradation routes for dioxane when treated with a dilute aqueous H_20_2 solution (30%) and ultraviolet (UV) light as the catalyst for hydroxyl radical generation (UV + H_2O_2). After 5 min. irradiation with UV light, 90% removal was achieved. They noted pH adjustments may be required because the pH was 4.2 after treatment. The reactor volume used was 28 L recirculated at 110 L/min.. Difficulties with applying this process to a POE system lie in the chemical requirements of hydrogen peroxide, a strong oxidant which must be handled with care. However, if only low dosages of H_2O_2 are required, this may be feasible and effective. Further bench scale research regarding source water characteristics (dioxane concentration, scavenging abilities) are needed to determine UV + H_2O_2 viability in a POE unit.

In 2001, Bowman completed an O_3 + H_2O_2 pilot study with support from the San Gabriel Basin Water Quality Authority using a HiPOx® system from Applied Process Technology, Inc. (Long Beach, CA). The pilot test was performed in South El Monte, CA at a site contaminated with chlorinated solvents and dioxane (20.2 μg/L). The pilot unit was run at 10 gpm with H_2O_2 and O_3 influent concentrations of 6.90 mg/L and 3.12 mg/L, respectively. The optimized H_2O_2 and O_3 dosages resulted in an effluent dioxane concentration of < 2 μg/L. This case study also cited two other groundwater contamination sites where the implementation of an ozone and hydrogen peroxide system were able to reduce the dioxane concentration to < 3 μg/L. The on-site generation of O_3 in this pilot study means it cannot be applied to a POE system for cost and safety concerns.

A photocatalytic oxidation evaluation was completed in 2005 using a Photo-Cat® treatment system supplied by Purifics ES, Inc. (London, Ontario, Canada). This new system uses UV light to activate titanium dioxide (TiO_2) beads which act as a catalyst to produce hydroxyl radicals. The Photo-Cat® was capable of treating dioxane concentrations of ~150 μg/L to below detection limit of 1.9 μg/L , a near 99% reduction. The results also showed that by-product production (i.e., bromate) is not of concern when using this treatment technology. High costs make photocatalytic presently undesirable for POE treatment. Laboratory systems capable of treating 250 gpd were quoted at $70,000, with an operation cost of ~$1.00 per day (Powell, 2010).

Appendix B: F200 Isotherm Studies-Initial Sorption Evaluation Data

Table 23: F200 Initial Sorption Concentration Results

Sample	1,4 Dioxane Concentration (μg/L)			
	t = 0 hrs. No GAC	t = 96 hrs. No GAC	t = 96 hrs. With GAC	% Removal
Groundwater Blank	**6.3** (110%)	**5.8** (113%)	< **2.0** (115%)	-
Low Conc. - 15 μg/L	**20**[1] (113%)	**18** (111%)	**2.1** (111%)	90
Med. Conc. - 60 μg/L	**21** (119%)	**20** (118%)	< **2.0** (108%)	> 90
High Conc. - 120 μg/L	**29** (114%)	**27** (112%)	**2.7** (107%)	91

[1] Sample spike = 54 μg/L (112%)

Table 24: Mass of F200 for Initial Sorption

0.5000
0.5000
0.5006
0.5002
0.4999
0.5002
0.5002
0.5004
0.4999
0.5002
0.4999
0.5000
0.4998
0.5004
0.5005
0.5005
0.5000

Average (g)	0.5002
Std. Dev. (g)	0.00025

Appendix C: F200 Isotherm Studies-Revised Sorption Evaluation Data

Table 25: F200 Revised Sorption Concentration Results

Sample	1,4 Dioxane Concentration (µg/L)			
	t = 0 hrs, No GAC	t = 96 hrs, No GAC	t = 96 hrs, With GAC	% Removal
Groundwater Blank	**3.8** (108%)	**4.7** (106%)	< **2.0** (102%)	-
Low Conc. 15 µg/L	**12**[1] (95%)	**11** (109%)	**2.3** (108%)	81
Med. Conc. 60 µg/L	**44** (103%)	**42** (108%)	**2.3** (103%)	95
High Conc. 120 µg/L	**84** (107%	**83** (106%)	**5.2** (105%)	94

[1]Sample spike = 37 µg/L (102%)

Table 26: Mass of F200 for Revised Sorption

[illegible]
0.4990
0.5000
0.4990
0.5000
0.5000
0.5002
0.5004
0.5000
0.5000
0.5003
0.5000
0.5002
0.5002
0.5005
0.5000
0.5002
0.5000

Average (g)	0.5000
Std. Dev. (g)	0.00041

Appendix D: F200 Isotherm Studies: Final Sorption Evaluation Data

Table 27: F200 Final Sorption Concentration Results

Sample	1,4 Dioxane Concentration (µg/L)			
	t = 0 hrs, No GAC	**t = 96 hrs, No GAC**	**t = 96 hrs, With GAC**	**% Removal**
Groundwater Blank	**<2.0** (112%)	**<2.0** (112%)	**<2.0** (108%)	-
Low Conc. - 15 µg/L	**16** (110%)	**16** (109%)	**4.5** (111%)	72
Med. Conc. - 60 µg/L	**64** (119%)	**66** (118%)	**3.9** (112%)	94
High Conc. - 120 µg/L	**134** (121%)	**139** (113%)	**4.9** (118%)	96

Table 28: Mass of F200 for Final Sorption

[illegible]
0.5020
0.5000
0.5010
0.5000
0.5000
0.5000
0.5010
0.5000
0.5010
0.5000
0.5010
0.5000
0.5010
0.5010
0.5000
0.5001
0.5000

Average (g)	0.5005
Std. Dev. (g)	0.0006

Appendix E: GAC Comparison Isotherm Study Data

Table 29: Standard Concentrations for GAC Isotherm Study

	t = 0 hrs	**t = 96 hours**	**Average**
High Conc. Standard-µg/L	**122** (131%)	**102** (112%)	112
Low Conc. Standard-µg/L	**13** (117%)	**13** (117%)	13

Table 30: GAC Comparison Results After 96 Hour Mixing

Types of Activated Carbon	1,4 Dioxane Concentration		
	Groundwater Blank with GAC	**Low Conc.-µg/L (13 µg/L at t = 0)**	**High Conc. -µg/L (122 µg/L at t = 0)**
GAC 830	**<2.0** (125%)	**<2.0** (128%)	**3.6** (109%)
GCA 830	**<2.0** (116%)	**<2.0** (127%)	**3.8** (124%)
F200	**<2.0** (105%)	**<2.0** (128%)	**6.0** (107%)
OLC	**<2.0** (122%)	**<2.0** (136%)	**2.8** (148%)
SDC 830	**<2.0** (135%)	**<2.0** (124%)	**9.5** (112%)
SD 1240	**<2.0** (124%)	**<2.0** (119%)	**8.7** (121%)
SDW 0830	**<2.0** (113%)	**3.5** (116%)	**27** (117%)

Appendix F: Initial Carbon Capacity Estimations

Using the High 96 hour concentration data from the initial GAC comparison isotherm study, estimated capacities (q_e) were calculated using Equation 1 for the three most promising carbon types:

Table 31: Dioxane Concentrations for Initial GAC Comparison Study

	96 Hour Mixing Test: Carbon Types						
Concentration	**F200**	**5D 1240**	**GAC 830**	**5DC**	**OLC**	**GCA 830**	**5DW**
Blank	-	-	-	-	-	-	-
Low	<2	<2	<2	<2	<2	<2	3.5
High	6.0	8.7	3.6	9.5	2.8	3.8	27
Carbon Base	Coal			Coconut			Wood

*Yellow indicates that the GAC was chosen for further testing, GCA 803 (coconut base) was chosen over GAC 830 (coal base) for continued testing because F200 showed comparable results and was considered the industrial standard for coal based carbon in water treatment.

Example for F200:

$$\text{Equation 1: } q_e = \frac{V \times (\mathrm{C_o} - \mathrm{C_e})}{M}$$

$$q_e = \frac{0.067\ L \times (112 - 6.0\ \frac{\mu\mathrm{g}}{\mathrm{L}})}{0.5\ g\ of\ F200}$$

$$q_e = 14.20\ \frac{\mu g\ of\ dioxane}{g\ of\ F200\ carbon}$$

Appendix G: GAC Comparison for Dioxane Sorption

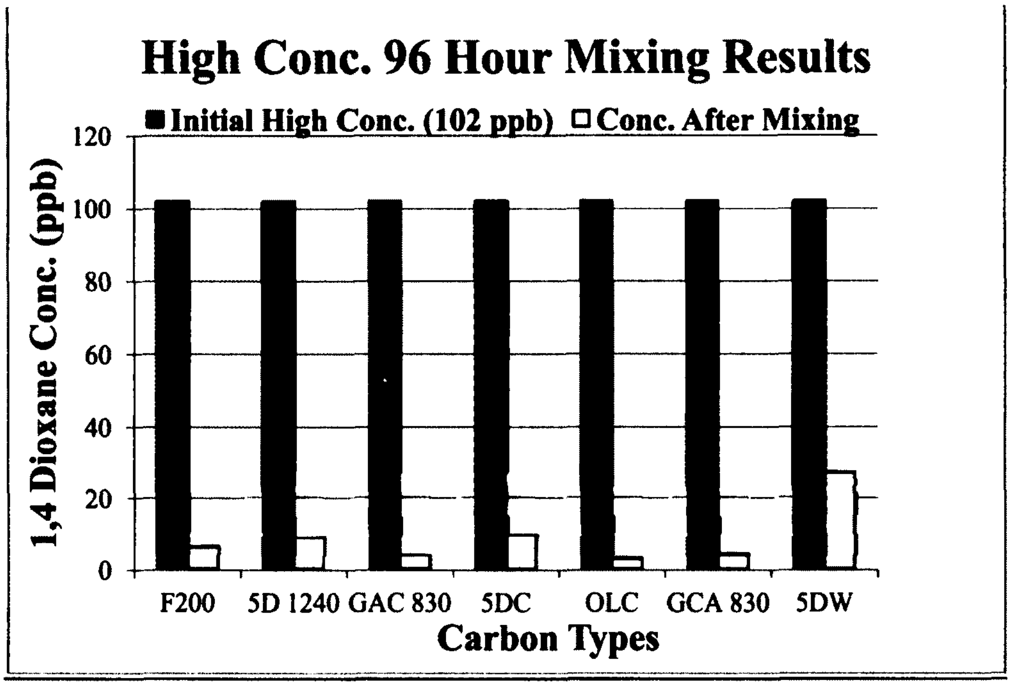


Figure 22: High Initial Concentration GAC Comparison Graph

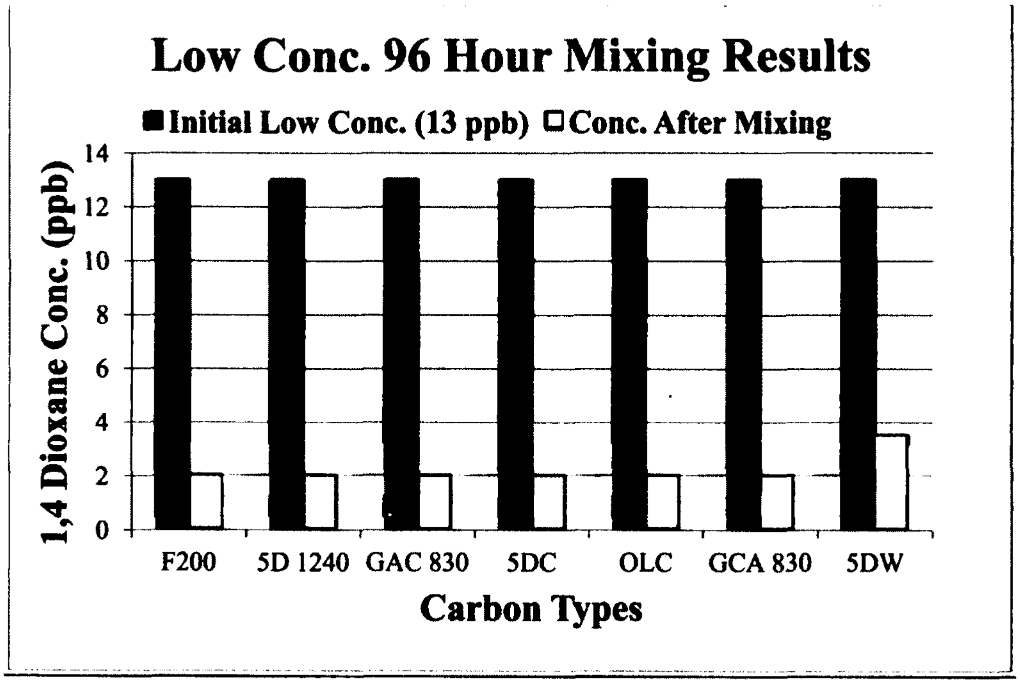


Figure 23: Low Initial Concentration GAC Comparison Graph

Appendix H: Carbon Dosage Requirements Calculations

Table 32: F200 Carbon Dose Requirements

For F200		**where** q_e(µg/g)=	14.20
C_0 (µg/L)	M (g)	Volume (L)	C_e (µg/L)
100	0.4	0.067	15.2
80	0.3	0.067	16.4
60	0.2	0.067	17.6
40	0.1	0.067	18.8
20	0.025	0.067	14.7

Table 33: OLC Carbon Dose Requirements

For OLC		**where** q_e(µg/g)=	14.63
C_0 (µg/L)	M (g)	Volume (L)	C_e (µg/L)
100	0.4	0.067	12.64
80	0.3	0.067	14.48
60	0.2	0.067	16.32
40	0.1	0.067	18.16
20	0.025	0.067	14.54

Table 34: GCA 830 Carbon Dose Requirements

For GCA 830		**where** q_e(µg/g)=	14.50
C_0 (µg/L)	M (g)	Volume (L)	C_e (µg/L)
100	0.4	0.067	13.44
80	0.3	0.067	15.08
60	0.2	0.067	16.72
40	0.1	0.067	18.36
20	0.025	0.067	14.59

Appendix I: GAC Isotherm Experimental Data

Table 35: Concentration of Dioxane Standards

Standard (µg/L)	Time (hours)	Conc. - µg/L (Percent Recovery)	Averaged Conc. µg/L
100	t = 0	**89** (118%)	89.5
	t = 96	**90** (122%)	
80	t = 0	**68** (128%)	71.0
	t = 96	**74** (121%)	
60	t = 0	**53** (123%)	52.5
	t = 96	**52** (116%)	
40	t = 0	**39** (118%)	36.0
	t = 96	**33** (110%)	
20	t = 0	**16** (120%)	16.0
	t = 96	**16** (119%)	
Groundwater Blank	t = 96	**<1.0** (114%)	-

Table 36: Dioxane Isotherm Results for OLC

OLC	C_0 (µg/L)	Carbon (g)	C_e (µg/L)	Capacity (µg dioxane/g carbon)
OLC Blank	-	0.50000	<2.0 (117%)	-
OLC 20	16.0	0.02510	7.8 (122%)	21.9
OLC 20 Replicate	16.0	0.02510	7.5 (119%)	22.7
OLC 40	36.0	0.10053	5.0 (121%)	20.7
OLC 60	52.5	0.20030	4.1 (122%)	16.2
OLC 80	71.0	0.30127	3.6 (122%)	15.0
OLC 100	89.5	0.40028	3.4 (121%)	14.4
OLC 100 Replicate	89.5	0.40028	3.2 (115%)	14.5

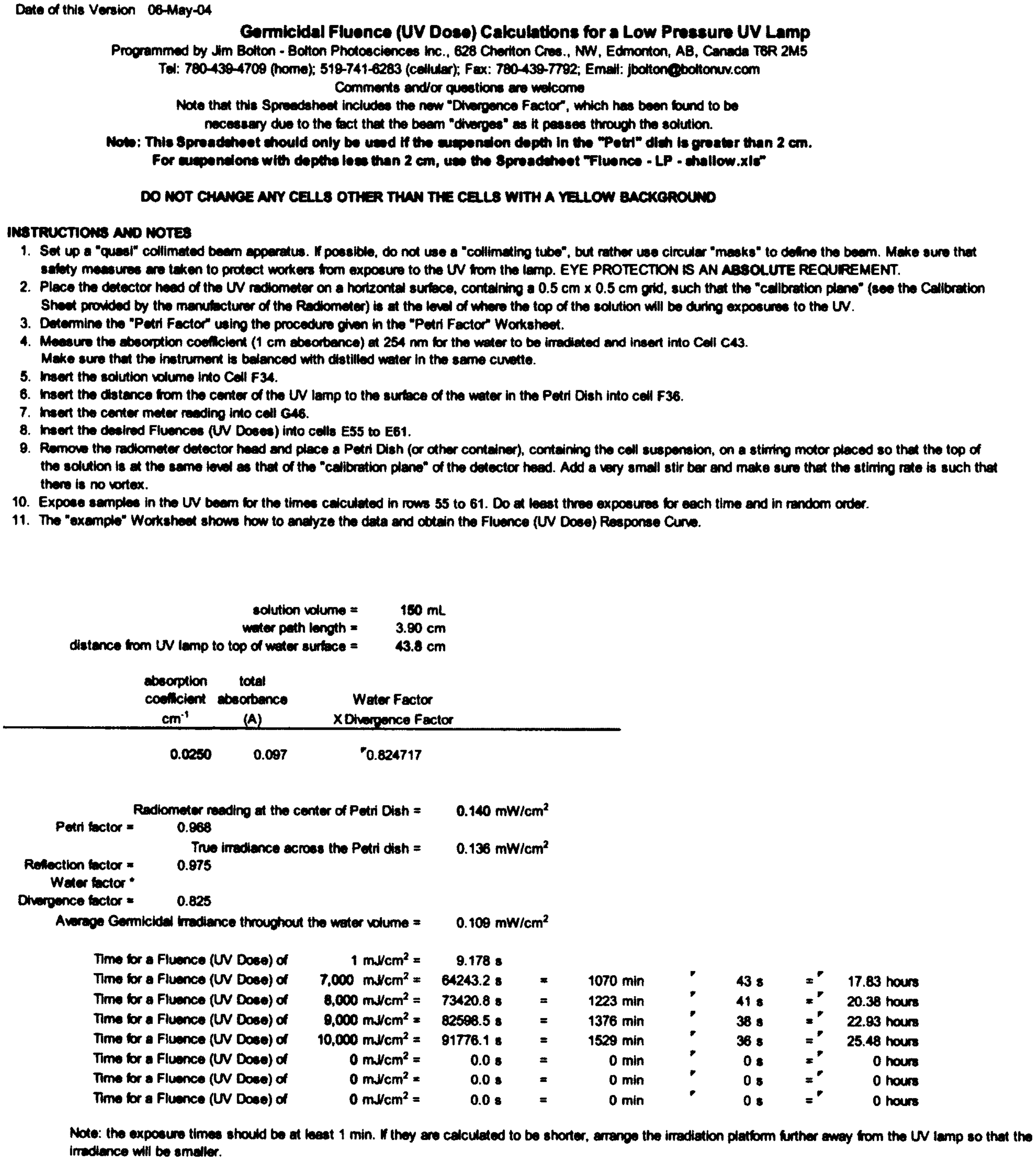
Table 37: Dioxane Isotherm Results for GCA

GCA	C_0 (μg/L)	Carbon (g)	C_e (μg/L)	Capacity (μg dioxane/g carbon)
GCA Blank	-	0.50000	<2.0 (119%)	-
GCA 20	16.0	0.02502	9.6 (120%)	17.1
GCA 20 Replicate	16.0	0.02502	9.8 (121%)	16.6
GCA 40	36.0	0.10083	7.6 (112%)	18.9
GCA 60	52.5	0.20077	5.8 (117%)	15.6
GCA 80	71.0	0.30033	5.1 (118%)	14.7
GCA 100	89.5	0.40063	5.7 (118%)	14.0
GCA 100 Replicate	89.5	0.40063	5.2 (118%)	14.1

Table 38: Dioxane Isotherm Results for F200

F200	C_0 (μg/L)	Carbon (g)	C_e (μg/L)	Capacity (μg dioxane/g carbon)
F200 Blank	-	0.50000	<2.0 (100%)	-
F200 20	16.0	0.02520	10 (116%)	16.0
F200 20 Replicate	16.0	0.02520	10 (115%)	16.0
F200 40	36.0	0.10013	8.0 (119%)	18.7
F200 60	52.5	0.20077	5.7 (116%)	15.6
F200 80	71.0	0.30050	5.7 (114%)	14.6
F200 100	89.5	0.40075	5.8 (111%)	14.0
F200 100 Replicate	89.5	0.40075	5.4 (120%)	14.0

Appendix J: IUVA-Bolton Photosciences Spreadsheet (Low Pressure-Deep Sample)



Date of this Version 06-May-04

Germicidal Fluence (UV Dose) Calculations for a Low Pressure UV Lamp

Programmed by Jim Bolton - Bolton Photosciences Inc., 628 Cheriton Cres., NW, Edmonton, AB, Canada T6R 2M5
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Comments and/or questions are welcome
Note that this Spreadsheet includes the new "Divergence Factor", which has been found to be
necessary due to the fact that the beam "diverges" as it passes through the solution.
Note: This Spreadsheet should only be used if the suspension depth in the "Petri" dish is greater than 2 cm.
For suspensions with depths less than 2 cm, use the Spreadsheet "Fluence - LP - shallow.xls"

DO NOT CHANGE ANY CELLS OTHER THAN THE CELLS WITH A YELLOW BACKGROUND

INSTRUCTIONS AND NOTES

1. Set up a "quasi" collimated beam apparatus. If possible, do not use a "collimating tube", but rather use circular "masks" to define the beam. Make sure that safety measures are taken to protect workers from exposure to the UV from the lamp. EYE PROTECTION IS AN ABSOLUTE REQUIREMENT.
2. Place the detector head of the UV radiometer on a horizontal surface, containing a 0.5 cm x 0.5 cm grid, such that the "calibration plane" (see the Calibration Sheet provided by the manufacturer of the Radiometer) is at the level of where the top of the solution will be during exposures to the UV.
3. Determine the "Petri Factor" using the procedure given in the "Petri Factor" Worksheet.
4. Measure the absorption coefficient (1 cm absorbance) at 254 nm for the water to be irradiated and insert into Cell C43.
   Make sure that the instrument is balanced with distilled water in the same cuvette.
5. Insert the solution volume into Cell F34.
6. Insert the distance from the center of the UV lamp to the surface of the water in the Petri Dish into cell F36.
7. Insert the center meter reading into cell G46.
8. Insert the desired Fluences (UV Doses) into cells E55 to E61.
9. Remove the radiometer detector head and place a Petri Dish (or other container), containing the cell suspension, on a stirring motor placed so that the top of the solution is at the same level as that of the "calibration plane" of the detector head. Add a very small stir bar and make sure that the stirring rate is such that there is no vortex.
10. Expose samples in the UV beam for the times calculated in rows 55 to 61. Do at least three exposures for each time and in random order.
11. The "example" Worksheet shows how to analyze the data and obtain the Fluence (UV Dose) Response Curve.

solution volume = 150 mL
water path length = 3.90 cm
distance from UV lamp to top of water surface = 43.8 cm

absorption coefficient cm^{-1}	total absorbance (A)	Water Factor X Divergence Factor
0.0250	0.097	0.824717

Radiometer reading at the center of Petri Dish = 0.140 mW/cm^2
Petri factor = 0.968
True irradiance across the Petri dish = 0.136 mW/cm^2
Reflection factor = 0.975
Water factor * Divergence factor = 0.825
Average Germicidal Irradiance throughout the water volume = 0.109 mW/cm^2

Time for a Fluence (UV Dose) of	1 mJ/cm^2 =	9.178 s					
Time for a Fluence (UV Dose) of	7,000 mJ/cm^2 =	64243.2 s	=	1070 min	43 s	=	17.83 hours
Time for a Fluence (UV Dose) of	8,000 mJ/cm^2 =	73420.8 s	=	1223 min	41 s	=	20.38 hours
Time for a Fluence (UV Dose) of	9,000 mJ/cm^2 =	82598.5 s	=	1376 min	38 s	=	22.93 hours
Time for a Fluence (UV Dose) of	10,000 mJ/cm^2 =	91776.1 s	=	1529 min	36 s	=	25.48 hours
Time for a Fluence (UV Dose) of	0 mJ/cm^2 =	0.0 s	=	0 min	0 s	=	0 hours
Time for a Fluence (UV Dose) of	0 mJ/cm^2 =	0.0 s	=	0 min	0 s	=	0 hours
Time for a Fluence (UV Dose) of	0 mJ/cm^2 =	0.0 s	=	0 min	0 s	=	0 hours

Note: the exposure times should be at least 1 min. If they are calculated to be shorter, arrange the irradiation platform further away from the UV lamp so that the irradiance will be smaller.

Figure 24: Bolton Photosciences Excel Spreadsheet

Appendix K: Preliminary Air Stripping Test Data

Table 39: Preliminary Air Stripping Results

Sample Type	**1,4 Dioxane Concentration (µg/L)**					
	Sample Time (hrs)					
	0	**1**	**4**	**8**	**12**	**25**
Non-Aerated (Controls)	**104** (104%)	-	-	**80** (105%)	-	**81** (104%)
Aerated	**104** (104%)	**105** (106%)	**93** (109%)	-	**65** (111%)	**41** (106%)
Aerated Groundwater Blank	**5.5** (107%)	-	-	-	-	**<2.0** (112%)

Table 40: Air:Water Ratios for 150 mL Sample at 500 sccm

Time (hrs)	**Time (min.)**	**Total Air Supplied in scc's (@ Q=500 sccm*)**	**A:W Ratios for a 150 mL Sample**
0	0	0	0
1	60	30,000	200
4	240	120,000	800
8	480	240,000	1600
12	720	360,000	2400
25	1500	750,000	5000

*Standard cubic centimeters per minute

Appendix L: Primary Air Stripping Test Data Using Typical A:W Ratios

- Determination of sampling times at a flowrate within the range (0-500 sccm) of the U201 Matheson flowmeter

Table 41: Primary Air Stripping Results at Typical A:W Ratios

Sample Type	**1,4 Dioxane Concentration (µg/L)**					
	Sample Time (hrs)					
	0	**0.5**	**1**	**2**	**4**	**6**
Non-Aerated (Controls)	**31** (125%)	-	-	**30** (113%)	-	**27** (117%)
Aerated	**31** (125%)	**29** (113%)	**28** (124%)	**30** (111%)	**28** (119%)	**26** (114%)
Aerated Groundwater Blank	**<2.0** (113%)	-	-	-	-	**<2.0** (117%)

Table 42: Air:Water Ratios for 150 mL Sample at 100 sccm

Time (hrs)	**Time (min.)**	**Total Air Supplied in scc's (@ Q=100 sccm*)**	**A:W Ratios for a 150 mL Sample**
0	0	0	0
0.5	30	3,000	20
1	60	6,000	40
2	120	12,000	80
4	240	24,000	160
6	360	36,000	240

*Standard cubic centimeters per minute

Appendix M: Initial UV Bench Scale Study Data

Table 43: Initial UV Bench Scale Results (Percent Recovery)

	Time (hours)		
Sample Type	**0**	**25.5**	**% Removal**
Irradiated and Stirred-µg/L	**126** (102%)*	**44** (100%)	65.1
Not Irradiated and Stirred-µg/L	**131** (97%)	**75** (93%)	42.7
R.O. Blank- µg/L	**5.2** (100%)	-	

*Estimated concentration because the sample exceeded the calibration curve upper limit

Appendix N: UV Bench Scale Study with Additional Monitoring

Table 44: UV Bench Scale Study Results with Additional Monitoring

	Time (hours)		
Sample Type	0	24	**% Removal**
Not Irradiated or Stirred - μg/L	**105** (140%)	**96** (105%)	8.6
Not Irradiated, Stirred- μg/L	**126** (122%)	**67** (113%)	46.8
Irradiated and Stirred- μg/L	**112** (116%)	**59** (131%)	47.3
Not Irradiated, Sealed- μg/L	**112** (121%)	**113** (105%)	-0.9

Table 45: pH and Temperature Data for UV Bench Scale Study with Additional Monitoring

	Not Irradiated, Not Stirred	**Not Irradiated, Stirred**	**Irradiated, Stirred**	**Not Irradiated, Sealed**
Temp. Before Experiment (°C)	18	18	18	18
Temp. After Experiment(°C)	19.5	19.5	20	19.5
pH Before Experiment	7.8	7.9	7.9	7.9
pH After Experiment	8.1	8.3	8.2	7.9

Appendix O: UV Batch Reactor Study Data

Table 46: Batch Control Study Results

Time (hrs)	Inlet Conc. -µg/L	Outlet Conc. -µg/L	% Difference	Inlet and Outlet Avg. Conc. -µg/L
0	**133** (123%)	**135** (119%)	1.5%	134
1	**134** (121%)	**130** (124%)	-3.1%	132
2	**133** (135%)	**133** (122%)	0.0%	133
3	**131** (116%)	**128** (121%)	-2.3%	128
4	**139** (112%)	**134** (124%)	-3.7%	137
5	**138** (121%)	**144** (106%)	4.2%	141

*UV Batch Blank < 2.0 µg/L

Table 47: UV Batch Reactor Study Results

Time (hrs)	Inlet Conc. µg/L	Outlet Cond. µg/L	Avg. Conc. µg/L	% Difference	UV Dosage[1] (mJ/cm^2)
0	**133** (131%)	**122** (124%)	127.5	-9.0%	0
1	**124** (125%)	**122** (118%)	123	-1.6%	3,840
2	**113** (130%)	**111** (127%)	112.25	-2.3%	7,680
3	**102** (119%)	**102** (116%)	102	0.0%	11,520
4	**95** (112%)	**97** (116%)	96	2.1%	15,360
5	**88** (115%)	**88** (113%)	88	0.0%	19,200

*Groundwater Blank < 2.0 µg/L

[1] Output from Bolton Spreadsheet (LP-Deep)

Appendix P: Initial UV-Peroxide Experiment Data

Table 48: Initial UV-Peroxide Results

UV Dosage (mJ/cm^2)	1,4 Dioxane Concentration (µg/L)		
	No H_20_2	With 3 mg/L H_20_2	With 6 mg/L H_20_2
0	**18** (113%)	**18** (116%)	**18** (113%)
600	**16** (123%)	**13** (117%)	**8.9** (123%)

Table 49: Alkalinity for Initial UV-Peroxide Experiment

UV Dosage (mJ/cm^2)	Alkalinity (mg/L as $CaCO_3$)		
	No H_20_2	With 3 mg/L H_20_2	With 6 mg/L H_20_2
0	110	112	110
600	112	115	110

Table 50: pH for Initial UV-Peroxide Experiment

UV Dosage (mJ/cm^2)	No H_20_2	With 3 mg/L H_20_2	With 6 mg/L H_20_2
0	8.1	8.2	8.1
600	8.4	8.4	8.4

Table 51: Hydrogen Peroxide Concentration for Initial UV-Peroxide Experiment

UV Dosage (mJ/cm^2)	Hydrogen Peroxide Conc. (mg/L)		
	No H_20_2	With 3 mg/L H_20_2	With 6 mg/L H_20_2
0	-	3	6
600	-	3	5.5

Appendix Q: UV-Peroxide Experiment Data for Scavenging Effects

Table 52: UV-Peroxide Results for Scavenging Effects (Percent Recovery)

	1,4 Dioxane Concentration (µg/L)			
	R.O. Water		**Groundwater**	
UV Dosage (mJ/cm^2)	**No UV or H_2O_2**	**With 3 mg/L H_2O_2**	**No UV or H_2O_2**	**With 10 mg/L H_2O_2**
0	**13** (118%)	**13** (118%)	**13** (123%)	**13** (123%)
600-1200	**13** (121%)	**<1.0** (112%)	**14** (111%)	**2.3** (119%)

Table 53: Alkalinity Results for UV-Peroxide Experiments for Scavenging Effects

	Alkalinity (mg/L as $CaCO_3$)			
	R.O. Water		**Groundwater**	
UV Dosage (mJ/cm^2)	**No UV or H_2O_2**	**With 3 mg/L H_2O_2**	**No UV or H_2O_2**	**With 10 mg/L H_2O_2**
0	0	-	116	116
600-1200	0	0	112	120

Table 54: pH Results for UV-Peroxide Experiment for Scavenging Effects

	R.O. Water		**Groundwater**	
UV Dosage (mJ/cm^2)	**No UV or H_2O_2**	**With 3 mg/L H_2O_2**	**No UV or H_2O_2**	**With 10 mg/L H_2O_2**
0	4.9	-	7.6	-
600-1200	5.3	5.4	8.5	8.6

Table 55: Hydrogen Peroxide Results for UV-Peroxide Experiment for Scavenging Effects

	R.O. Water		**Groundwater**	
UV Dosage (mJ/cm^2)	**No UV or H_2O_2**	**With 3 mg/L H_2O_2**	**No UV or H_2O_2**	**With 10 mg/L H_2O_2**
0	-	3	-	>10
600-1200	-	3	-	>10

Appendix R: Hydrogen Peroxide Dosing Calculations

Example:

Using 3.3% hydrogen peroxide for a dose of 3 mg/L:

$$365\ days \times 946\ \frac{L}{Day} \times 3\ \frac{mg}{L}\ H_2O_2\ Dose\ \div 33{,}000\ \frac{mg}{L} H_2O_2\ strength = 31\ L$$

Hydrogen Peroxide Dose (mg/L)	**3**	31	10	3
	6	63	21	7
	12	126	41	14

Appendix S: MRLs for Humans Converted to Drinking Water Levels

Assumptions: 2 L of drinking water/day

Average adult = 70 kg

Oral Exposure (Acute)

$$\text{MRL} = 0.4\ \frac{mg\ of\ dioxane}{kg\ of\ body\ weight \times day}$$

$$0.4\ \frac{mg}{kg \times day} \times 70\ \frac{kg}{1\ adult} = 28\ \frac{mg}{day}$$

$$28\ \frac{mg}{day} \times \frac{1\ day}{2\ Liters} = 14\ \frac{mg}{day \times Liter}$$

Appendix S: Laboratory Percent Recovery Correction Calculation

High recovery rates of the surrogate standards triggered the NHDES laboratory to begin reporting 1,4 dioxane concentration as adjusted concentrations. Dioxane concentrations were corrected based on the percent recovery of a surrogate standard, in our case, deuterated-1,4dioxane with the following equations:

$$Percent\ Recovery\ (\%R) = \frac{Experimental\ Concentration\ of\ Surrogate}{True\ Concentration\ of\ Surrogate} \times 100\%$$

$$Reported\ Value = Experimental\ Concentration\ of\ dioxane\ \times \frac{100\%}{\%R}$$