Published in final edited form as:

Water Res. 2008 December ; 42(20): 4949–4954. doi:10.1016/j.watres.2008.09.020.

Photooxidation and subsequent biodegradability of recalcitrant tri-alkyl phosphates TCEP and TBP in water

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Abstract

Biodegradable organic carbon (BDOC) from OH radical oxidation (UV/H₂O₂) of the recalcitrant industrial anti-foaming agents and flame retardants, tri-n-butyl phosphate (TBP) and tris(2-chloroethyl) phosphate (TCEP), was quantified with respect to the fraction of the TBP or TCEP photooxidized. For 50–96% contaminant oxidation via •OH, BDOC was similar in solutions of either compound, and ranged from 0.25 to 0.5 mg L⁻¹ (TBP₀ and TCEP₀ = 5 mg L⁻¹). In addition, for this contaminant oxidation range, complete dehalogenation of TCEP was observed, along with a significant change in pH. Oxidation of TCEP results in both H⁺ and Cl⁻ release, while the TBP mineralization pathway results in CO₂, H₂O, H⁺, and PO₄³⁻. For low µg/L levels of TCEP contamination in treated surface waters, UV/H₂O₂ oxidation of TCEP or TBP would not be expected to impact pH or chloride concentrations, however, a portion of the TCEP or TBP oxidation products, likely in non-halogenated aldehyde form, would become an available carbon source for bacterial growth in storage, distribution, or during further physical treatment.

Keywords

Biodegradable organic carbon; UV; Hydrogen peroxide; Hydroxyl radical; tris(2-chloroethyl) phosphate; tri-n-butyl phosphate

Introduction

Tris (2-chloroethyl) phosphate (TCEP, CAS No. 115-96-8) is a halogenated, biorecalcitrant organic compound that is commonly listed among a class of emerging contaminants associated with wastewater pollution of our freshwater resources, Andresen et al. (2004), Haggard et al. (2006), Kolpin et al. (2002), Lee and Rasmussen (2006), Stackelberg et al. (2007). This anthropogenic organic compound's resistance to conventional potable water and wastewater treatments is well documented, Meyer and Bester (2004), Reemtsma et al. (2006), Stackelberg et al. (2007), Westerhoff et al. (2005). Furthermore, when wastewaters

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are used for groundwater recharge, the risk of groundwater contamination with TCEP is high. In analysis of wastewater effluents used for this purpose, little TCEP attenuation (<33% reduction in TCEP₀) was observed in wastewaters passed through soil columns for a duration of 1 month, Cordy et al. (2004).

Biodegradable organic carbon assays (BDOC) are often used to assess water quality post-engineered-oxidation. Powerful oxidants like ozone are known to react with natural organic matter in water to produce smaller, readily-biodegradable compounds such as aldehydes, Graham (1999). Applications of ozone or UV, in combination with H₂O₂, to produce •OH in a treated water are also known to enhance conversion of TOC to BDOC for certain energy inputs, Gerald E. Speitel et al. (2000), Volk et al. (1993). When this free radical chemistry precedes biological activated carbon filtration, enhanced disinfection-by-product reduction and DOC removal can be observed, Gerald E. Speitel et al. (2000), Toor and Mohseni (2007).

When significant fractions of aqueous organic matter are biorecalcitrant and biological filtration is employed for finishing treated water, pre-oxidation can be utilized to convert sufficient levels of organic carbon from non-biodegradable to biodegradable. Treating secondary wastewater effluents with the photo-oxidation/reduction process, UV-TiO₂-O₃, was observed to increase the biodegradable fraction of DOC; sequential UV-TiO₂-O₃-BAC (biologically-active carbon filtration) removed >40% of the secondary effluent DOC, Li et al. (2005). A sequential application of photo-Fenton and sequencing batch biofilter reactors has been used to treat a model wastewater rich in the halogenated, non-biodegradable organic compound, 4-chlorophenol; the ratio of BOD₅ to COD in the wastewater was observed to increase with increasing •OH production, Bacardit et al. (2007).

Since TCEP is not affected by conventional aerobic biological treatment processes, the conversion of TCEP from non-biodegradable to biodegradable via photosensitized •OH oxidation (UV-H₂O₂) was studied as a possible remediation strategy. pH, Cl⁻ concentration, TCEP concentration, and BDOC in the test water were evaluated across a range of UV fluences in the presence of H₂O₂ as a means to track the decay progress of TCEP.

Replicate UV-H₂O₂ exposures were also conducted with solutions of a non-halogenated, yet similarly-structured, organophosphate plasticizer, tri-n-butyl phosphate (TBP, CAS No. 126-73-8) as illustrated in Figure 1. Structural relationships between •OH oxidation of the studied organophosphates and BDOC formation were assessed. The potential for biological attenuation of TCEP-intermediates post-UV-H₂O₂ treatment of TCEP-contaminated wastewaters is evaluated.

Methods

UV Irradiations

The bench-scale quasi-collimated beam apparatus contained 4 low-pressure-Hg UV lamps (General Electric #G15T8) emitting primarily at a wavelength of 254 nm. Average UV fluence applied to the entire solution volume was calculated by multiplying the incident irradiance by factors accounting for the divergence of the collimated beam, reflection at the water surface, variation in the irradiance over the surface of the solution, and photon absorption with depth in the water column, Bolton and Linden (2003). A radiometer (IL 1700, SED 240/W, International Light, Peabody, MA), with a UV detector calibrated to 254 nm, was used to measure the incident irradiance.

Solutions of carbonate buffer (pH 7) spiked with 5 mg L⁻¹ of either TCEP (ACROS, 97%) or TBP (ACROS, 99%), and 50 mg L⁻¹ H₂O₂ (30% solution; EMD) were irradiated while

continuously mixed. The total solution volume for each exposure was 150 mL. Solution temperature was not regulated; previous measures of temperature with increasing low-pressure UV lamp exposure did not indicate that the imparted energy would significantly raise or lower ambient temperatures (exposure time < 1 hr). The carbonate buffer contained the major inorganic constituents of a soft lake water, Esthwaite Water (UK), and was prepared according to a previously published recipe, Smith et al. (2002). Anions in solution: HCO_3^- (23.5 mg L⁻¹), Cl^- (9.93 mg L⁻¹), SO_4^{2-} (11 mg L⁻¹), and NO_3^- (1.86 mg L⁻¹). Cations in solution: Ca^{2+} (10.6 mg L⁻¹), Mg^{2+} (1.46 mg L⁻¹), and Na^+ (5.75 mg L⁻¹). Controls included UV irradiated solutions without H_2O_2 , and untreated TCEP solutions. Residual H_2O_2 was removed by enzymatic action before analyses; UV treated solutions were spiked to 0.2 mg L⁻¹ bovine liver catalase (Aldrich) and mixed for a period of 1.5 hours to ensure complete degradation of H_2O_2 -residuals.

BDOC Assay

The UV irradiated solution (150 mL) was transferred to a carbon-free Erlenmeyer flask (250 mL). A portion (25 mL) of the treated solution was preserved (acidified with H_3PO_4 to pH<3; stored at 4.5 °C) for later TOC analysis. To the 125 mL aliquot of treated solution, 1 mL of MLSS (mixed-liquor suspended solids) was added. The MLSS was sampled from an aeration basin at the North Durham Water Reclamation Facility (Durham, NC, USA) and stored at 4.5 °C. The inoculum was aerated for 1–2 hours prior to use. The Erlenmeyer flask was capped with aluminum foil and the solution was continuously agitated on an orbital shaker (100 rpm) at 20 °C for 5 days. Khan *et al.* found complete mineralization in standard solutions of known BDOC (2.5 – 12.28 mg L⁻¹ as C) inoculated with MLSS, after 5 days of incubation at room temperature. Non-purgeable organic carbon (NPOC) was determined for the “day 0” and “day 5” samples by first acidifying to pH<3 with H_3PO_4 (6 N) and then sparging with air. A Shimadzu TOC-5050A TOC analyzer was used to measure the NPOC in a 26 µL injection. The difference in measured NPOC from day 0 to day 5 was equated to the BDOC of the treated sample.

Chromatography

Residual TCEP was extracted from 1 mL of UV- H_2O_2 treated solution with 1 mL of chloroform via rapidly-mixed liquid-liquid extraction. An aliquot of chloroform, containing TCEP and hexachlorobenzene (HCB; Alfa Aesar, >99%) as an internal standard, was collected for GC-MS (Shimadzu GC-2010 & GCMS-QP2010) analysis. Prior to sample injection, the injector port was warmed to 300 °C, the ion source temperature was set to 240 °C, and the interface heated to 275 °C. After injection, the column oven temperature was increased from 50 to 325 °C over 21 min. The quadrupole-MS detector was programmed to quantify the response to ‘m/z’ specific to both analyte and internal standard, using single-ion-monitoring. Inorganic anions were measured in 1mL samples of UV- H_2O_2 treated TCEP solutions using ion chromatography (Dionex DX-120). The IC utilized a self-regenerating suppressor (Dionex ASRS Ultra II 4mm), a 4 × 250 mm anion column (Dionex AS14A), and a carbonate buffer mobile-phase.

Results and Discussion

Observed Oxidation

To dilute solutions of TCEP or TBP (5 mg L⁻¹) in carbonate buffer 50 mg L⁻¹ H_2O_2 was added prior to UV irradiation. Photolysis of H_2O_2 was the predominant mode of $\bullet\text{OH}$ formation. An examination of the UV absorbance properties of TCEP and TBP found that both compounds are poor light-absorbers in the UV-C range ($\epsilon_{\lambda=200-300\text{nm}} < 5 \text{ M}^{-1}\text{cm}^{-1}$). Therefore, at an initial concentration of 50 mg L⁻¹, was the only significant photon absorber

($\lambda=254$ nm) in irradiated solutions. As no direct photolysis of TCEP was observed, Figure 2 depicts the indirect photolysis via $\bullet\text{OH}$ of TCEP in model surface water (pH 7).

To achieve TCEP oxidation levels greater than 95%, up to $6000 \text{ mJ}\cdot\text{cm}^{-2}$ was applied to $50 \text{ mg}\cdot\text{L}^{-1} \text{ H}_2\text{O}_2$ solutions. A total of 22 solutions, with or without H_2O_2 , were exposed to UV_{254} . Figure 3 presents the observed photooxidation of TBP in solution at pH 7. Like TCEP, no TBP photodegradation was observed in solutions without H_2O_2 .

A total of 15 TBP solutions, with or without H_2O_2 , were exposed to UV_{254} . For both compounds, between 90 and 100% oxidation was achieved. However, for TCEP, a 10-times-greater UV fluence was needed to achieve the same level of removal as TBP. This agrees with previously observed $\bullet\text{OH}$ -oxidation kinetics for TCEP and TBP, which reported a 2nd-order reaction rate with $\bullet\text{OH}$ for TBP ($6.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) that is an order of magnitude faster than for TCEP ($7.4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$), Watts and Linden (2008).

BDOC With Oxidation

All UV irradiated solutions were inoculated with sampled MLSS at a dilution ratio of 1:125 mL. To assess the accuracy of the BDOC assay, standard organic carbon solutions of sodium acetate (14 mg L^{-1}) in prepared lake water (pH 7) were inoculated with MLSS (N=4). Figure 4 plots the measured BDOC in acetate solutions, and untreated TCEP and TBP solutions after 5 days of incubation at ambient temperature (20 C).

In acetate solutions, the bacterial consortium achieved the expected level of carbon consumption. In agreement with previous research on the bio-recalcitrance of TCEP in treated waters, none of the organic carbon present as TCEP was available for metabolic processes. However, the presence of TCEP in solution did not hinder the biodegradation of acetate when both compounds were present. Dissolved carbon in the form of TBP was also not readily biodegradable; thus identifying the tri-alkyl phosphate structure as a significant molecular component for bio-recalcitrance rather than, or in addition to the presence of Cl hetero-atoms. The presence of TBP in an acetate solution did not impede the mineralization of acetate.

For solutions with measurable oxidation of TCEP, BDOC concentrations were a function of the degree of TCEP photooxidation. Figure 5 plots measured BDOC with the fraction of TCEP_0 oxidized.

For a 5 mg L^{-1} TCEP solution, the organic carbon content is equivalent to 2.5 mg L^{-1} as C. The biodegradable portion of the total organic carbon in solution remains negligible until half of the initial TCEP is photooxidized. For all BDOC measurements in solutions with less than 50% TCEP remaining, the mean BDOC is 0.155 mg L^{-1} as C. However, applying Student's t-test, the p-value for this group mean is 0.1448 indicating that the true mean could be 0 mg L^{-1} BDOC. Conversely, the mean BDOC in solutions with more than 50% TCEP degradation is 0.40 mg L^{-1} , with a p-value of 0.00018; evidence that for this level of TCEP oxidation some conversion from non-biodegradable to biodegradable organic carbon has occurred.

When less than 5% of the initial TCEP remains in solution, only 1/5 of the initial DOC is bio-available. It is apparent that that a significant fraction of the TCEP oxidation intermediates retain the recalcitrant properties of the parent compound. However, for this level of TCEP oxidation, another 1/5 of the initial DOC has been mineralized to CO_2 .

Despite the lack of Cl atoms on its alkyl chains, •OH-oxidation intermediates of TBP also retained a significant degree of biorecalcitrance. Figure 6 plots BDOC with increasing TBP photooxidation.

In solutions where up to 96% TBP photooxidation was achieved, levels of BDOC were similar to oxidized-TCEP solutions. For all BDOC measurements in solutions with greater than 50% of the initial TBP remaining, the mean BDOC is 0.053 mg L⁻¹ as C. Applying Student's t-test, the p-value for this group mean is 0.1848. The mean BDOC in solutions with greater than 50% TBP oxidation is 0.30 mg L⁻¹, with a p-value of 0.004. Mean BDOC in solutions where greater than 50% of either TBP or TCEP was photooxidized were not significantly different.

Oxidizing TBP to such an extent that all DOC is present as a TBP-oxidation-intermediate led to increased levels of BDOC. Previous research into the reaction rates of tri-alkyl phosphates with •OH has highlighted the H-abstraction mechanism of •OH attack at the first carbon on the alkyl chain, Khaikin (1998). The two end products of aqueous radical decomposition of tri-butyl phosphate have been identified as butyraldehyde (see Figure 7) and a dibutyl phosphate, Clay and Witort (1974), Khaikin (1998).

If it is assumed that butyraldehyde (C₄H₈O) is the sole constituent of BDOC from TBP, and 1 mol of C₄H₈O is formed from 1 mol of TBP, Khaikin (1998), then the maximum BDOC from TBP photooxidation (TBP₀ = 5 mg L⁻¹) would be 0.9 mg L⁻¹ as C. This assumption appears to be validated by the observed BDOC in Figure 6. Between an applied UV fluence of 1045 and 1500 mJ/cm², BDOC increases slowly from 0.79 to 0.89 mg L⁻¹, while from 500 mJ/cm² to 1045 mJ/cm², BDOC increases rapidly from 0.36 to 0.79 mg L⁻¹. However, additional advanced analytical chemistry techniques would be required to further clarify the significance of butyraldehyde formation from photooxidation of TBP, and the carbonyl's subsequent consumption by aerobic heterotrophic microorganisms in MLSS.

Chloride from TCEP

A significant unknown regarding •OH-oxidation of TCEP is the impact of aqueous radical attack on molecular structure, and subsequent C-Cl cleavage on the alkyl chain. Figure 8 plots the measured Cl⁻ concentration in solutions of TCEP and H₂O₂ irradiated with UV.

No additional Cl⁻ (initial Cl⁻ concentration in the pH 7 buffer was 10 mg L⁻¹) was observed until at least 25% of TCEP was photooxidized. In solutions where observed TCEP oxidation was between 50 and 96%, Cl⁻ increased rapidly until the stoichiometric limit of Cl⁻ (1.8 mg L⁻¹ Cl⁻) from 5 mg L⁻¹ of TCEP was reached. In its parent form, TCEP is considered a potentially carcinogenic organic contaminant, CAEPA (2006). Of interest for future investigations would be the impact of •OH dehalogenation of TCEP on mutagenicity or toxicity of TCEP-contaminated waters.

pH With Oxidation

The simplified oxidation pathway for TCEP in the presence of molecular oxygen can be described as follows:

As a fraction of the initial DOC (0.5 mg L⁻¹) from 5 mg L⁻¹ TCEP was oxidized to CO₂ at the highest UV fluence and significant dehalogenation was observed from •OH attack, it was of interest to quantify the release of another mineralization product, H⁺. Figure 9 highlights

the change in pH for the weak carbonate buffer as the oxidized fraction of TCEP or TBP is increased.

In UV/H₂O₂ treated solutions of TCEP, a significant fraction of TCEP was oxidized (>60%) before the buffer capacity was exhausted. For 95% TCEP oxidation, the solution pH dropped to 4.25. Assuming carbonate species are the predominant acids and bases in solution, to lower the pH from 7 to 4.25 required abstraction of 37% of the available H⁺ from TCEP. TBP mineralization can also be expressed with H⁺ as an end-product (see Equation 2). However, a significant pH change was not observed in solutions of oxidized TBP. This is indicative of the insignificant concentration of acidic oxidation products from TBP relative to the buffer capacity of the irradiated solution.

Conclusions

UV/H₂O₂ is an advanced treatment that can be applied to degrade recalcitrant and, in the case of TCEP, potentially carcinogenic tri-alkyl phosphates in water. Greater than 95% removal of TCEP was observed in model lake water for an initial H₂O₂ concentration of 50 mg L⁻¹ and a monochromatic-UV_{254nm} fluence of 6000 mJ/cm². The same level of oxidation of the non-halogenated tri-alkyl phosphate, TBP, required an order of magnitude lower UV fluence (600 mJ/cm²). With either TBP or TCEP and bicarbonate as the only •OH-scavengers, significantly greater UV fluences would be expected to achieve similar oxidation levels in waters with other forms of DOC. In addition, in waters of higher pH (>7), the carbonate anion would scavenge a larger fraction of available OH than its conjugate acid in an equimolar buffer solution at lower pH.

For advanced water treatments that structurally-alter organic compounds *in situ*, chemical conversion of contaminants into readily-assimilated products can be an important consideration of design and operation. In parent form, both TBP and TCEP remained unchanged in dilute solutions of MLSS for the given incubation conditions. Elevated levels of BDOC (mean values: 0.25 – 0.5 mg L⁻¹ as C) were observed in solutions where >50% of TCEP had been photooxidized. While a fraction of the total organic carbon, measured BDOC was significantly non-zero in these solutions, unlike comparable solutions with lesser levels of TCEP oxidation. Similar BDOC was observed in TBP solutions with increasing •OH-oxidation. However, increasing the applied UV fluence, such that TBP was no longer measurable, led to still higher BDOC measurements; albeit at a slower rate of BDOC formation per mJ/cm² (from 500 to 1050 mJ/cm²: 0.43 mg L⁻¹ increase in BDOC; from 1050 to 1500 mJ/cm²: 0.10 mg L⁻¹ increase in BDOC). At 1500 mJ/cm², the measured BDOC (0.89 mg L⁻¹) was similar to the expected concentration, from previously reported •OH-oxidation pathways for TBP, of a lighter-weight oxidation product, butyraldehyde.

Coinciding with BDOC formation, Cl⁻ and H⁺ concentrations in TCEP solutions increased with increasing •OH-oxidation. Though it remains unclear whether or not their separation from TCEP enhanced the bio-availability of DOC from TCEP; similar levels of BDOC were observed from oxidation of the studied tri-alkyl phosphates, with or without Cl. For 96% oxidation of TCEP (5 mg L⁻¹ initially), 100% release of Cl⁻, 20% mineralization of TOC, and 20% of TOC as BDOC was observed. For low mg L⁻¹ levels of TCEP contamination in treated waters, UV/H₂O₂ oxidation of TCEP/TBP would not be expected to impact pH or chloride concentrations, however, a portion of the TCEP/TBP oxidation products, likely in

non-halogenated aldehyde form, would become an available carbon source for bacterial growth in storage, distribution, or during further physical treatment.

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Figure 1.
tri-n-butyl phosphate (left) and tris(2-chloroethyl) phosphate (right).

Figure 2.

The fraction of TCEP remaining in pH 7 buffer containing 0 or 50 mg·L⁻¹ H₂O₂ with increasing UV fluence (0 – 6000 mJ·cm⁻²). Each point represents the final TCEP concentration in a 150 mL UV-irradiated solution. The solid line depicts the best fit for a first-order, exponential decay function to the observed data. Dashed-lines depict the confidence interval for the model fit (α=0.05)

Figure 3.

The fraction of TBP remaining in pH 7 buffer containing 0 or 50 mg·L⁻¹ H₂O₂ with increasing UV fluence (0 – 600 mJ·cm⁻²). Each point represents the final TBP concentration in a 150 mL UV-irradiated solution. The solid line depicts the best fit for a first-order, exponential decay function to the observed data. Dashed-lines depict the confidence interval for the model fit ($\alpha = 0.05$)

Figure 4. BDOC concentrations in standard solutions of acetate (14 mg·L⁻¹), TCEP, TBP, and co-solutions of TCEP or TBP and acetate.

Figure 5.

BDOC concentrations in UV-irradiated TCEP solutions (5 mg L⁻¹) containing H₂O₂ (50 mg L⁻¹) as a function of the fraction of TCEP₀ oxidized. Solid line depicts nonlinear best-fit for observed BDOC with dashed-lines representing the 95% confidence interval.

Figure 6.

BDOC concentrations in UV-irradiated TBP solutions (5 mg L^{-1}) containing H_2O_2 (50 mg L^{-1}) as a function of the fraction of TBP_0 oxidized, and, for solutions where TBP was no longer detected ("TBP<DL"), as a function of UV fluence. Solid line depicts non-linear best-fit for observed BDOC with dashed-lines representing the 95% confidence interval.

Figure 7.
Butyraldehyde

Figure 8.

Cl^- concentrations in solutions of TCEP (5 mg L^{-1}) and H_2O_2 (50 mg L^{-1}) irradiated with UV as a function of the fraction of TCEP oxidized.

Figure 9.
pH in solutions of photooxidized TCEP and TBP