



## Application of a novel plasma-based advanced oxidation process for efficient and cost-effective destruction of refractory organics in tertiary effluents and contaminated groundwater

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Received 29 June 2009; Accepted 12 August 2009

### ABSTRACT

Corona discharge is emerging as a promising advanced oxidation process (AOP) for the treatment of a variety of organic contaminants, including compounds that are not effectively destroyed by more common AOPs. This paper presents laboratory and field results describing the destruction of regulated and Contaminant Candidate List (CCL) compounds in tertiary-treated wastewater effluent and contaminated groundwater during the operation of a novel Hydro-Non-Thermal-Plasma (HNTP) AOP system. The system generates a plasma discharge above the target water matrix, which emits an “electron wind”, ultraviolet (UV) irradiation,  $O_{3(g)}$  and hydroxyl radicals ( $\bullet OH$ ) into a relatively thin water layer. The synergism between these oxidizing agents results in efficient degradation of refractory organics (typically >95%) rendering further chemical dosage unnecessary. Batch experiments revealed the dominating kinetics to be first order for MTBE ( $k = 7.5 \times 10^{-4} s^{-1}$ ) and TCE ( $k = 4.8 \times 10^{-4} s^{-1}$ ). This study is the first report of pilot-scale HNTP destruction of (mainly) TCE, 1,4-dioxane and NDMA from a contaminated water source (groundwater in California). The pilot-scale HNTP reactor showed high removal efficiencies of 95.3%, 91.7% and 95.3%, for these three contaminants, along with energy efficiency ( $E_{EO}$ ) values comparable to other AOP systems.

**Keywords:** AOP; Non-Thermal Plasma; MTBE; TCE; NDMA

### 1. Introduction

Deteriorating source water quality and increasingly stringent drinking water and wastewater regulations are leading to the development of new, innovative treatment technologies. Advanced oxidation processes (AOPs) have been implemented particularly for the destruction of refractory organic compounds, such as trichloroethylene (TCE; Jung et al., 2003), methyl tert-butyl ether (MTBE; Baus et al., 2005; Alnaizy and Ibrahim, in press),

N-nitrosodimethylamine (NDMA; Lee et al., 2007), pharmaceuticals and personal care products (PPCPs) and potential endocrine disrupting compounds (EDCs) (Snyder et al., 2006), emanating from industrial applications. Conventional water treatment is often ineffective in removing or destroying such micropollutants due to their very low concentrations and physical and chemical characteristics. In contrast, AOPs produce highly reactive oxygen species (ROS), particularly hydroxyl radicals ( $\bullet OH$ ), with the potential to degrade and mineralize these refractory contaminants. The most common AOPs combine either UV radiation or ozone ( $O_{3(aq)}$ ) with hydrogen peroxide ( $H_2O_2$ ). Commercial AOPs are typically

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employed in wastewater reuse (e.g., Orange County Groundwater Replenishment System, CA, USA; or Bach et al., 2009) and groundwater remediation applications, but they are gaining popularity in drinking water treatment as well (e.g., Prairie Waters Project, CO, USA).

When selecting an AOP for a particular application, utilities must consider a variety of technical, operational, and budgetary issues. For example, the UV and ozone AOPs require significant chemical addition and quenching of residual  $H_2O_2$ . UV AOPs are also inefficient in waters with high turbidity and/or UV absorbance due to reduced UV transmission. With respect to the ozone AOP, the process may require handling and storage of compressed oxygen, and ozone residuals are rapidly depleted after reacting with  $H_2O_2$ , which eliminates potential disinfection credits. However, the primary limitation with AOPs is their energy intensive nature and high operation and maintenance (O&M) costs, particularly when compounded by chemical feeds. Despite these concerns, AOPs are becoming more prevalent in water and wastewater treatment due to the increasing awareness and concern for emerging contaminants in water supplies. Therefore, there is high demand for the development of robust, energy-efficient AOPs with the ability to handle a variety of water qualities without chemical addition.

Corona discharge is emerging as a promising AOP for the treatment of a variety of organic contaminants, including species that are not effectively destroyed by more conventional AOPs (Johnson et al., 2003). Several studies on corona-based water treatment systems have recently been published (Grymonpre et al. 1999; Sugiarto et al. 2002; Johnson et al., 2003; Wang et al., 2006; Locke et al., 2006; Grabowski et al., 2006; Zhang et al., 2007). The corona systems described in these studies vary considerably in size, power supply and technical characteristics. In general, current corona discharge systems can be divided into three categories: systems in which the corona is formed above the water surface (Johnson et al., 2003; Grabowski et al., 2006; Locke et al., 2006), formed inside the water volume (Zhang et al., 2007, Lukes et al., 2008) and discharged in an aerosol (Pokryvailo et al., 2003). Thus far, no strong evidence exists to indicate which of the methods is superior. Moreover, most of the work in this field is still conducted at bench scale, and most, if not all, of the investigated systems have not yet been tested in the field for a prolonged period of time. Furthermore, to the best of our knowledge, none of the corona-based technologies have been demonstrated at the pilot or commercial scale.

This paper evaluates the performance of a novel AOP system developed in Israel by Aquapure Ltd. The investigated technology is based on the concept of Hydro-Non-Thermal-Plasma (HNTP) treatment with an "electrode to plate" configuration (Locke et al., 2006).

In order to produce corona discharge, a powerful electric field needs to be applied (usually  $>10^6$  V/cm). Such an electric field, which is inversely proportional to the corona electrode area, can be achieved by sharpening the edges of a carbon fiber electrode.

Corona discharge can either be positive or negative depending on the polarity of the applied voltage, and it can be realized in either DC or pulse mode. In the latter case, using short-duration (nanosecond time scale), high-voltage and high-current pulses an intense corona discharge can be achieved. The pulse mode produces a corona discharge that is several orders of magnitude more powerful than that produced by the DC alternative. The short pulse duration and large amplitude of the corona discharge prevents short-circuiting between the corona electrodes. In addition, the corona discharge is accompanied by efficient generation of  $\bullet OH$ , ultraviolet (UV) light and ozone.

This study presents results from laboratory- and pilot-scale experiments. In the laboratory, batch experiments were conducted to determine the dominating kinetic expressions that describe the destruction of two selected contaminants: TCE and MTBE. In the field, a pilot-scale HNTP reactor was evaluated based on its ability to destroy TCE, 1,4-dioxane, NDMA and other organic contaminants in a contaminated California groundwater well.

## 2. Materials and methods

### 2.1. Description of the system

The components of Aquapure's plasma-based AOP are shown schematically in Fig. 1. The system consists of three main parts: (1) a high-voltage generator, (2) an oxidation reactor that contains the corona-generating, carbon-fiber electrode and ground electrode and (3) an ozone injection unit. The water flows in a thin layer on the ground electrode, which constitutes the chamber floor, and  $\sim 10$  mm below the tips of a second carbon-fiber electrode. High-voltage (up to 40 kV) pulses are applied to the electrodes by a nanosecond-pulse generator operating at frequencies of 500 to 1,000 Hz. Pulse parameters are as follows: (1) output voltage amplitude up to 40 kV; (2) rise time of 18 ns; (3) pulse duration at full width and half of the maximum voltage  $\sim 40$  ns; and (4) maximum pulse energy of 1 J. The high-voltage pulses form an intense corona discharge originating at the carbon fiber, where the maximum electric field is obtained, and terminating at the water surface. This results in ionization of ambient air within the reactor and the simultaneous formation of strong oxidizing agents, including  $\bullet OH$ , ozone and UV radiation. The power dissipated in this corona discharge amounts to several tens of megawatts,

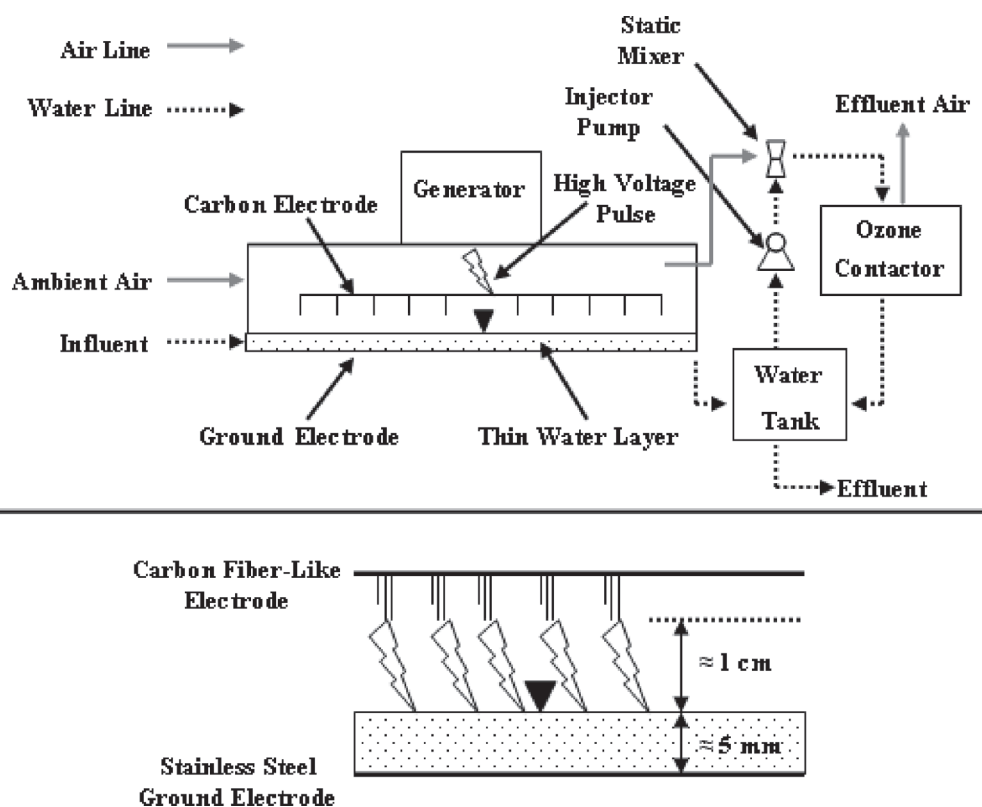


Fig. 1. Schematic of the tested plasma-based AOP.

thereby making the system, to the best of our knowledge, one of the most powerful corona discharges tested in the laboratory.

The use of carbon fiber electrodes allows for extremely strong electric fields and long life spans due to their large quantities and micron-size dimensions. The formation of dense non-thermal plasma has been shown to produce intense UV radiation and to the formation of ozone, OH radicals and  $\text{H}_2\text{O}_2$  in the vicinity of the carbon fiber (Locke et al., 2006).

After flowing through the reactor, the water is collected in a water storage tank and is eventually pumped through an injector to a static mixer where it mixes with ozone-enriched air ( $\approx 0.1\text{--}0.2\%$  by weight). Ozone-enriched air is drawn by the venturi-type injector from the reactor headspace, and some of the gas is dissolved into the water using the static mixer. The subsequent ozone contactor provides additional exposure of the target contaminants to dissolved ozone and increases the efficiency of the process. The ozone injection system serves two purposes: (1) it draws fresh air from the surrounding area into the reactor, which was found to increase process efficiency, and (2) re-injects ozone-enriched air from within the reactor back into the water. Operation of the injector is optional, depending on the ozone sensitivity of the target contaminants. In

the experiments described in this paper, the injector was activated.

## 2.2. Description of batch experiments

The MTBE experiments were conducted in 200 L at  $25^\circ\text{C}$ . Additional water quality characteristics were as follows: alkalinity of  $175\text{ mg/L}$  as  $\text{CaCO}_3$ , pH of 7.6, and turbidity of 2 NTU. The system was operated at a water recirculation rate of  $480\text{ L/h}$ , ambient air flow rate of  $1,100\text{ L/h}$ , and pulse power frequency of 500 Hz. TOC and  $\text{NO}_3\text{-N}$  concentrations in this water are negligible. The TCE experiment was conducted in 150 L of tertiary-treated wastewater at  $25^\circ\text{C}$ . Additional water quality characteristics are as follows: alkalinity of  $126\text{ mg/L}$  as  $\text{CaCO}_3$ , pH of 7.0, total organic carbon (TOC) of  $6.9\text{ mg/L}$ ,  $\text{NO}_3\text{-N}$  of  $17\text{ mg/L}$  and turbidity  $< 1\text{ NTU}$ . The system was operated at a water recirculation rate of  $480\text{ L/h}$ , ambient air flow rate of  $1,100\text{ L/h}$ , and pulse power frequency 500 Hz.

## 2.3. Description of continuous field experiments with contaminated groundwater in California, USA

The system was continuously operated with water from a contaminated groundwater site in California. The

Table 1  
Concentrations of the major micropollutants in the treated groundwater versus current US Federal regulations.

Pollutant	Average concentration in groundwater ( $\mu\text{g/L}$ )	US EPA Maximum Contaminant Level (MCL) ( $\mu\text{g/L}$ )
N-Nitrosodimethylamine (NDMA)	87	N/A <sup>a</sup>
Trichloroethylene (TCE)	30	5.0
1,4-dioxane	18	N/A <sup>b</sup>
Chloroform	0.75	80 <sup>c</sup>
1,2-Dichloroethane	1.0	5.0
1,1-Dichloroethane	7.4	7.0

<sup>a</sup>EPA & California action level for 1,4-dioxane is 3  $\mu\text{g/L}$  (Also listed on EPA CCL 3).

<sup>b</sup>California NDMA notification level is 0.01  $\mu\text{g/L}$  and action level 0.3  $\mu\text{g/L}$  (Also listed on EPA CCL 3).

<sup>c</sup>Chloroform is regulated as one of the total trihalomethanes (TTHMs) for which the MCL is 80  $\mu\text{g/L}$ .

wells in this site are contaminated by a wide range of pollutants, including NDMA, 1,4-dioxane and a variety of chloro-organic solvents, the most prevalent being TCE. Relevant water quality parameters and contaminant concentrations are given in Table 1. Continuous, single-pass experiments performed in multiple phases using either a single reactor or two reactors operating in series. Varying operational parameters included two frequencies (500 and 1,000 Hz) and two water flow rates (0.56 and 0.94  $\text{m}^3/\text{h}$ ) corresponding to hydraulic residence times (HRTs) of 50 and 84 s, respectively. In this case, the HRT is defined as the time the water is exposed to the corona discharge.

#### 2.4. Analyses

MTBE samples from the laboratory-scale experiments were analyzed by an external lab according to Standard Method 6200B with a reporting limit of 1.3  $\mu\text{g/L}$ . TCE samples from the laboratory-scale experiments were performed by the Southern Nevada Water Authority according to EPA Method 524.2 with a reporting limit of 0.5  $\mu\text{g/L}$ . During the pilot-scale experiments, pH, temperature, turbidity, conductivity, and total organic carbon (TOC) were recorded in all experiments. Temperature and pH were recorded in the field by portable instruments. Other parameters were analyzed by Curtis and Tompkins Ltd. (Berkeley, California) (Table 1). TCE samples were analyzed according to EPA method 8260 with a reporting limit 0.5  $\mu\text{g/L}$ , and NDMA samples were analyzed according to EPA method 1625 with a reporting limit of 2  $\text{ng/L}$ . Ozone gas concentrations inside the reactor were obtained via an ozone monitor (InUSA, model IN-2000-L2-LC). Dissolved ozone concentrations were measured by either the indigo colorimetric method (Standard Methods, analysis 4500) or by an ozone colorimetric test kit, purchased from Merck (cat. no. 1187550001).

For gas-phase sampling and analyses, air samples were taken from the reactor headspace during the continuous pilot-scale experiments. Samples were collected from the air line exiting the pilot unit prior to entering the ozone destruction unit. VOC analysis was carried out by Air Toxics Ltd (Folsom, California) using EPA method TO-15.

### 3. Results and discussion

The results are divided into two sections: (1) the batch kinetic experiments, in which MTBE and TCE were used as representative contaminants, and (2) the continuous pilot-scale experiments at a contaminated groundwater site, during which TCE, 1,4-dioxane, NDMA and other organic contaminants were monitored.

#### 3.1. Laboratory-scale kinetic experiments

Batch experiments were conducted to study the oxidation kinetics of two important organic micropollutants: TCE and MTBE. TCE was studied because it is regulated under the US Safe Drinking Water Act and is present in many US groundwaters. MTBE was chosen because of its ubiquity (especially in the vicinity of petrol stations), high solubility and very low affinity for common adsorbents (Keller et al., 1998; Baus et al., 2005; Zang et al., 2005). MTBE is also listed on the US EPA's Contaminant Candidate List (CCL) 3. Figs. 2 and 3 show the results attained in the batch experiments of MTBE and TCE, respectively. Both regression curves followed first-order kinetics.

The observed first-order kinetics is presumably the result of the oxidation being predominantly controlled by steady-state concentrations of short-lived, non-selective  $\bullet\text{OH}$ . Thus, the reaction proceeds rapidly with high contaminant concentrations as there is a greater chance of

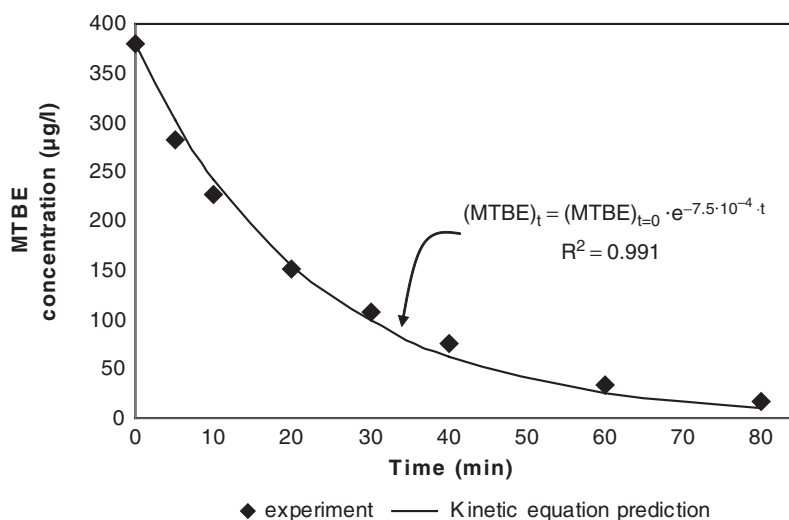


Fig. 2. Measured and predicted MTBE concentrations versus time. The data were best fitted with the first-order kinetic expression shown on the plot ( $k = 7.5 \times 10^{-4} \text{ s}^{-1}$ ).

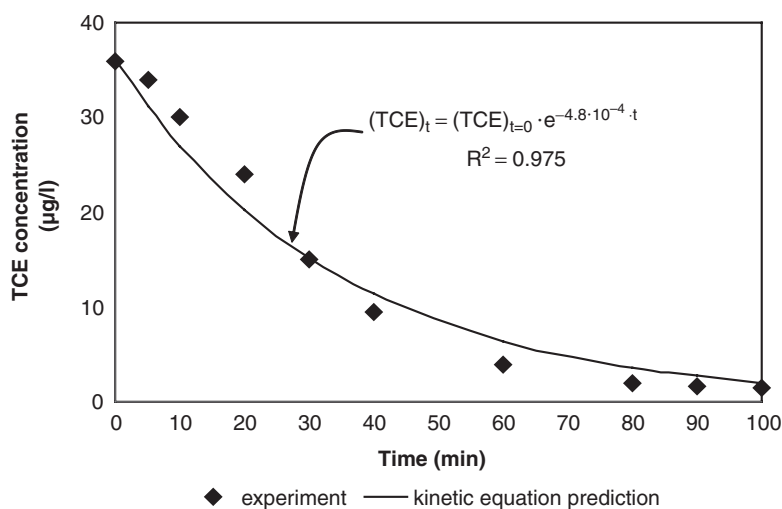


Fig. 3. Measured and predicted TCE concentrations versus time. The data were best fitted with the first-order kinetic expression shown on the plot ( $k = 4.8 \times 10^{-4} \text{ s}^{-1}$ ).

interaction between the  $\bullet\text{OH}$  and the target compounds. A similar trend was reported by Johnson et al. (2003), Grymonpre' et al. (2003), Karpel Vel Leitner et al. (2005), Grabowski et al. (2005) and Sano et al. (2005).

Note that the characteristics of the water matrices were different in the two experiments, particularly with regard to known  $\bullet\text{OH}$  radical scavengers such as background TOC, carbonate species ( $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ ) and nitrate. Therefore, the significant finding that is reported is the nature of the kinetic equation (i.e., first order) rather than the value of the kinetics constants which are specific to the experimental conditions. Note also that despite the fact that MTBE and TCE are completely dif-

ferent compounds, both compounds were degraded at comparable rates and to a similar extent (>95%) over the duration of the test, indicating the efficiency and indiscriminative nature of  $\bullet\text{OH}$  oxidation. It is emphasized that the target molecule (TCE) was successfully and rapidly degraded in the presence of a relatively high TOC concentration (TOC on the order of several mg/L), demonstrating the potential of the system as a polishing unit for tertiary wastewater effluents. The ozone concentration measured in the gas phase of the reactor during the batch experiments was approximately 1,400 ppm. This gas concentration corresponds to an equilibrium aqueous phase concentration of  $\sim 0.5 \text{ mgO}_3/\text{L}$ . The average

ozone concentrations measured in the aqueous phase were approximately 0.1 mgO<sub>3</sub>/L, which is much lower than those applied in ozone-based advanced oxidation systems.

### 3.2. Pilot-scale experiments

Table 1 shows the concentrations of organic micropollutants at the California groundwater site along with their corresponding maximum contaminant levels (MCLs). In addition to the regulated contaminants, NDMA and 1,4-dioxane are listed on the EPA CCL 3 and have been targeted for priority research. Based on initial concentrations, NDMA and TCE are the primary contaminants and are present at approximately 87 µg/L and 30 µg/L, respectively. However, the water is also contaminated with a variety of other micropollutants at concentrations lower than 20 µg/L (the most dominant being 1,4-dioxane at a concentration of 18 µg/L). The groundwater was further characterized by a temperature of ~22°C, pH 6.7, turbidity 0.27 NTU, and TOC <0.5 mg/L.

Table 2 lists the results attained in three field experiments in which the system was fed with the groundwater characterized in Table 1. The experiments differed from each other by two operational parameters: the influent water flow rate (0.56 and 0.94 m<sup>3</sup>/h) and the electrical

frequency (500 and 1,000 Hz) applied. Changes in these operational parameters also affected the normalized pulse-power generator energy consumption for each scenario (i.e., Experiment #1 = 2.14 kWh/m<sup>3</sup> for the two reactors operating in series, Experiment #2 = 0.64 kWh/m<sup>3</sup> and Experiment #3 = 1.86 kWh/m<sup>3</sup>). Other operational parameters, such as the air flow rate through the injector and the gap between electrode and water, were held constant. The results presented in Table 2 are average values from two replicate experiments. Note that in Experiment #1 two identical reactors were operated in series (i.e., the effluent of the first reactor served as the influent to the second reactor), and in Experiments #2 and #3 only one reactor was operated.

High treatment efficiencies were attained in Experiment #1 (two reactors operated in series) for TCE, NDMA, and 1,4-dioxane. For each contaminant, destruction exceeded 90% with a flux on the order of 10 mg/L-h. Less dominant pollutants in the groundwater, such as 1,1-dichloroethylene, 1,2-dichloroethane and chloroform were oxidized either to non-detectable concentrations or to extremely low concentrations (results not shown).

Using only a single reactor, Experiments #2 and #3 evaluated the effects of two major operational parameters (water flow rate and frequency) on the oxidation efficiency. In Experiment #2, the water flow rate was increased by 67% relative to Experiment #1. For TCE and

Table 2  
Results of pilot scale experiments (water temperature 22°C).

	TCE (µg/L)	NDMA (µg/L)	1,4-Dioxane (µg/L)
Experiment #1: Operating frequency 500 Hz, water flow rate 0.56 m <sup>3</sup> /h, two reactors in series			
Influent	30	87	18
Reactor 1 effluent	6.7	5.1	5.4
Reactor 2 effluent	1.4	4.1	1.5
Overall treatment efficiency (%)	95	95	92
Flux (mg/h)	14	39	79
Compliance with US EPA MCL	Yes	N/A <sup>a</sup>	N/A <sup>a</sup>
Experiment #2: Operating frequency 500 Hz, water flow rate 0.94 m <sup>3</sup> /h			
Influent	30	87	18
Reactor 1 effluent	14	4.7	8.8
Treatment efficiency (%)	53	95	51
Flux (mg/h)	15	79	8.9
Experiment #3: Operating frequency 1,000 Hz, water flow rate 0.56 m <sup>3</sup> /h			
Influent	30	87	18
Reactor 1 effluent	5.2	4.9	3.8
Treatment efficiency (%)	83	80	94
Flux (mg/h)	12	6.8	39

<sup>a</sup>Currently an unregulated contaminant.

1,4-dioxane, this change resulted in higher treatment fluxes but lower efficiencies. For NDMA, the higher flow rate resulted in similar treatment efficiency and thus a much higher flux, thereby indicating rapid kinetics and a very high efficiency for NDMA oxidation by the plasma system. This finding is noteworthy because NDMA, a potent carcinogen, constitutes a challenge for ozone-based oxidation processes (Mitch et al., 2003). Previously, cost-effective treatment for NDMA had only been achieved by UV-based technologies (Mitch et al., 2003; Patel, 2007; Lee et al., 2007), but this technology is also limited in many cases for NDMA removal (Mezyk et al., 2004).

In Experiment #3, the water flow rate was identical to that applied in Experiment #1, but the electrical frequency was increased from 500 Hz to 1,000 Hz. As a result, the pulse generator power increased from 0.60 kW to 1.04 kW. As shown in Table 2, the higher frequency resulted in a somewhat higher destruction rate, but this improvement did not seem to increase treatment efficiency or justify the large increase in energy demand, as represented by the  $E_{EO}$  energy efficiency index (Table 3):

$$E_{EO} = \frac{P}{(F \cdot \log(C_i/C_f))} \quad (1)$$

where  $P$  = power of plasma machine (kW);  $F$  = water flow rate ( $m^3/h$ );  $C_i$ ,  $C_f$  = initial and final concentrations of the assessed contaminant

It is emphasized that in all three experiments, no significant toxic byproducts (such as chlorinated halo-organics) could be detected in the liquid effluent. In the gas phase, very low concentrations of certain VOCs, particularly acetone, were detected. However, acetone is not

a significant contaminant with respect to human health at these low concentrations.

### 3.3. Energy efficiency

Table 3 shows the energy required for oxidation as calculated by the common energy efficiency index,  $E_{EO}$ , for all the major pollutants in the treated groundwater.  $E_{EO}$  is defined as the energy (in units of kWh/ $m^3$ ) consumed during treatment in order to achieve an order of magnitude reduction of a given contaminant (Bolton et al., 1996). Table 3 also shows  $E_{EO}$  values pertaining to a commercial UV/ $H_2O_2$  AOP system located at the same site and treating the same groundwater and also  $E_{EO}$  values quoted in the literature (Lobo et al., 2007; Calgon Carbon, 2009) for other AOP systems.  $E_{EO}$  results from the investigated system are average values of two replicate experiments. For Experiment #1, the first  $E_{EO}$  value relates to the results of the first reactor and the second value relates to the second reactor, which was connected in series. It can be seen that the  $E_{EO}$  values remain more or less similar in both reactors, except for NDMA oxidation.

The performance of the plasma AOP at the tested site was directly compared to a pilot-scale UV/ $H_2O_2$  AOP. The UV/ $H_2O_2$  efficiencies are based on an internal report by Carollo Engineers (2008). According to this report, the  $E_{EO}$  of the plasma reactor (frequency of 500 Hz and flow rate of 0.56  $m^3/h$ ) was nearly identical to that of the UV/ $H_2O_2$  system with respect to TCE. The plasma reactor was more efficient for NDMA destruction in all three experiments (except for the second reactor in Experiment #1). There was no basis for comparison between the plasma and UV/ $H_2O_2$  reactors

Table 3

$E_{EO}$  values calculated for pilot experiments for the three major contaminants in the treated groundwater, as compared with  $E_{EO}$  values of a commercial UV/ $H_2O_2$  system and  $E_{EO}$  values reported in the literature.

Exp. #	Water flow rate and frequency	TCE $E_{EO}$ [kWh/ $m^3$ ]/ Order of magnitude of reduction	NDMA $E_{EO}$ [kWh/ $m^3$ ]/ Order of magnitude of reduction	1,4-Dioxane $E_{EO}$ [kWh/ $m^3$ ]/ Order of magnitude of reduction
1	0.56 $m^3/h$	1.65	0.87	2.05
	500 Hz	1.58	11.3	1.93
2	0.94 $m^3/h$	1.93	0.50	2.05
	500 Hz			
3	0.56 $m^3/h$	2.44	1.49	2.75
	1000 Hz			
UV/ $H_2O_2$ (Lobo and Ried, 2007)	–	1.7	1.9	–
	–	1–5	0.1–0.3	1–3
(Calgon carbon)	–	–	0.53–1.6	0.53–1.6

Table 4  
Concentrations of contaminants measured in the air flowing out of the plasma reactor.

Compound	Concentration in air leaving the reactor ( $\mu\text{g}/\text{m}^3$ )	Contaminant removal by volatilization (%)
Chloromethane	0.06	–
Chloroethane	0.02	–
Acetone	1.60	–
1,1-Dichloroethane	0.04	1.9
Chloroform	0.04	21
1,2-Dichloroethane	0.02	6
Methylene chloride	0.01	–
Trichloroethylene (TCE)	<0.015	<0.15
1,4-Dioxane	<0.04	<0.8

for 1,4-dioxane. Therefore, it can be concluded that the plasma reactor consumes similar or less energy than the UV/H<sub>2</sub>O<sub>2</sub> system and does not require chemical addition or routine UV lamp cleaning, thereby providing further reductions in O&M costs. Table 3 also shows that the  $E_{\text{EO}}$  values attained in the field experiment fall within the  $E_{\text{EO}}$  range of commercial AOP systems reported in the literature.

#### 3.4. Quality of air leaving the reactor during operation

One of the advantages of AOP processes is the fact that it results in the destruction of target pollutants rather than physical separation from solution, as is the case with filtration, adsorption, and air stripping. However, since the plasma system is open to the atmosphere, evaporation of volatile compounds is possible and thus needs to be quantified and reported. To assess the significance of this phenomenon, air samples were taken from the air discharge in order to quantify the percentage of contaminants (from the overall influx) that was removed through volatilization rather than oxidation.

Table 4 shows an analysis of pollutants in the discharge gas stream. Based on the calculated fluxes of pollutants in the aqueous and gas phases, it was concluded that the mass of pollutants that volatilized rather than oxidized was negligible, and that in most cases, the contaminants were completely oxidized. Acetone, whose concentration in the gas phase was found to be relatively high, is a well known oxidation byproduct. Acetone is highly volatile and thus tends to be stripped to the gas phase, but it is not considered to be a health risk at the concentrations shown in Table 4 (<http://www.acgih.org>). From the original pollutants, only dichloroethane (1,1 and 1,2) and chloroform could be detected but at extremely low concentrations. Chloromethane is most likely an oxidation byproduct but is not considered a

health risk at these concentrations. Other compounds listed in Table 4 are from unknown sources and do not seem to be connected to the oxidation pathway.

#### 4. Conclusions

This paper presented laboratory and field results describing the destruction of regulated and CCL compounds by a plasma AOP. The results of this study indicate that plasma AOPs are viable alternatives to more conventional processes such as UV/H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and warrant further research into their effectiveness and efficiency in destroying other emerging contaminants. Specific conclusions from this study are as follows:

- Batch laboratory experiments indicated the kinetic equations for TCE and MTBE to approximately conform to first-order kinetics with respect to the oxidized compounds. Despite the very different backgrounds (tap water vs. treated municipal effluents) the system was shown to be capable of reducing both compounds to very low concentrations, conforming to the most stringent regulations. O<sub>3</sub> concentration in the reactor aqueous phase were very low (~0.1 mg/L), a fact which distinguishes the reported system from conventional ozone based treatment methods.
- The system was operated in the field and tested for the destruction of a variety of pollutants in contaminated groundwater in California. The system demonstrated high levels of destruction (>90%) for TCE, NDMA, 1,4-dioxane and several other pollutants present at lower concentrations. The plasma AOP also achieved the EPA MCL for TCE.
- Based on  $E_{\text{EO}}$  values for the various contaminants, the plasma AOP was similar or more efficient than the pilot-scale UV/H<sub>2</sub>O<sub>2</sub> AOP, and the plasma system achieved similar  $E_{\text{EO}}$  levels to those reported in the

literature for other AOPs. Further testing to document performance down to low ng/L levels is planned in the near future.

- Generation of oxidation byproducts was found to be insignificant.
- Gas phase tests revealed that the percentage of pollutants that were volatilized rather than oxidized was negligible.

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