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OZONATION OF SEDIMENTS FROM AN URBAN LAKE: AN EXPLORATORY INVESTIGATION

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Abstract - An exploratory investigation was conducted on the effects of application of ozone on the removal of organic and inorganic contaminants and the reduction of settleable solids in urban lake sediments. Homogenized sediment samples were treated in a batch reactor with an external recirculation loop and ozone feed from a Venturi injector. The ozone generating system was fed with ambient air with small footprint and operational simplicity. Ozone mass application (g/h) and contact time (min) were varied over wide ranges during testing. The effects of the ozone mass applied per unit time and the contact time on contaminant removal efficiencies were analyzed and a trade-off between the costs of ozonation and of solids treatment and disposal was proposed. The minimum ozone mass application required for total contaminant removal apparently depended on the type of organic contaminant present. An apparent influence of inorganic contaminant speciation on the removal efficiency was found and discussed.

Keywords: Urban lake sediment; Ozone application; Removal of organic contaminants and heavy metals; Settleable solids reduction.

INTRODUCTION

Overview

Urban lakes usually receive pollutants from both point and non-point sources. Lake sediments represent the accumulation of organic loads from natural and anthropogenic sources and of metal complexes in the aquatic environment (McDonald *et al*., 1999). The degree of mobility of sediments can influence pollution control in lakes. Sumpter (2005) and Sedlak and Pinkston (2011) covered all uncertainties related to the presence and the dangerous effects of organics on aquatic ecosystems. Regarding inorganic compounds, Cotta *et al*. (2006) stated that the presence of heavy metals in aquatic systems is of great concern since they are not degradable, are toxic and are persistent. Furthermore, sediments that contain metals are not only a “reservoir” where chemical species are deposited but also an active compartment with a fundamental role in the redistribution of metal species to the aquatic biota. Thus, the presence of metals in sediments is a serious threat to the aquatic environment. Loizeau *et al*. (2004) evaluated the impact of a sewage treatment plant effluent on sediment quality in a small bay in Lake Geneva and concluded that the quantity of heavy metals deposited in the bay was considerable and, because of sediment instability, was a potential hazard for the biota.

According to Hunt (1998), “there is a real need to assess the level of metal contamination in sediments, in order to develop sediment quality criteria. Further, within sediments the total metal concentration does not help predict what is bio-available”.

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Ozone Application and Environmental Benefits

Ozonation is an attractive alternative treatment process for removal of chemical and biological pollutants. Ozone can readily oxidize contaminants in the solid, liquid and gas phases; furthermore, ozone generates free radicals and decomposes at the same time, generating oxygen (Langlais *et al*., 1991; Beltran, 2004). Ozone alone has been shown by several studies to be effective in the treatment of slurries, sediments and sludges (Imaoka and Osumi, 1997; Cassidy *et al*., 2002; Zeng *et al*., 2000 and 2002; Hong *et al*., 2008). The importance of the removal of trace organics from aquatic environments was emphasized by Sumpter and Johnson (2005), who stated that natural degradation of synthetic organics in aquatic environments can generate degradation products that are potentially harmful. One of the most important groups of organic pollutants is the Polycyclic Aromatic Hydrocarbons (PAHs), which are hydrophobic, persistent and toxic in the environment, mostly through accumulation in sediments and the fatty tissue of fish. Their hydrophobic character leads to rapid association with particulate matter and partitioning to either sediments or tissue. Imaoka and Osumi (1997) treated marine sediments of a cove in Japan in an ozonation column and found that total organic carbon, nitrogen and sulphur concentrations in the sediments decreased upon ozonation; however, they increased in the treated supernatant. Zeng *et al*. (2000, 2002) found that ozonation for 2 hours removed 50 to 100% of various PAHs in the solid and liquid phases of the sediments. Cassidy *et al*. (2002) applied ozone oxidation followed by biodegradation to treat Poly-Chlorinated Biphenyls (PCBs) and PAHs in sediments. The oxidation products were more soluble and biodegradable than the parent compounds and PAH ring cleavage was observed.

Carrére *et al*. (2005) noted that low ozone doses (up to 1.5 mg O_3/L) efficiently removed the PAHs naturally present in sewage sludge and that higher ozone doses were consumed mainly to solubilize and mineralize the tested sludge. Hong *et al*. (2008) treated sediment samples with ozone introduced into the headspace of a small reactor that incorporated rapid, successive cycles of pressurization (690 kPa) and depressurization. They claimed that this technique enabled more effective treatment than conventional ozonation. Standard ozonation reached 40 to 60% removal of PAHs from river sediments in one hour of contact time, whereas the pressure-assisted technique removed 96% in one hour of contact time. The treatment costs were reported to be attractive; however, they are site-specific. Enhancement of the ozone treatment by the pressure-depressurize cycles was attributed to soil aggregate fracturing by the pressure cycles, which exposed the contaminants. However, they stated that their technique seemed to be suited for *ex situ* treatment of excavated soil or dredged sediment on land, not for lake sediments. Ozonation was also reported to be a possible technology to reduce the amount of biological sludge by reacting with solid particles and increasing the biodegradability (Ahn *et al*., 2002; Deleris *et al*., 2002). Thus, sludge handling costs could decrease significantly. Park *et al*. (2003) observed that sludge ozonation led to significant improvements in sludge settleability and dewaterability, thus improving treatment efficacy and associated costs. Beltran (2004) covered the effects of ozonation on sludge production and settling and observed an improvement in the sedimentation rate for preozonated samples.

Study Area Characterization

The tested sediment samples were collected from Lake 1 in Ibirapuera Park, a 1.0 km^2 green area for sports and recreation in the southern region of the city of São Paulo, Brazil. Lake 1 receives a point source pollution load (mainly domestic sewage) from small creeks and also receives treated effluent from a small flotation-based sewage treatment plant located at the confluence of Sapateiro creek and Lake 1. Regarding non-point pollution sources, according to the State Water Authority SABESP (2001), rainfalls bring down particles and chemicals from the atmosphere and also wash the land surrounding the lakes, carrying solids, dust, oil residues, etc. into the Park´s lakes.

Organic sediments have been accumulating for many years at the bottom of the lake as a rather thin and mobile layer. Sediments travel from the channel-shaped Lake 1 to the round-shaped Lake 2. Indeed the shape of Lake 1 indicates a high potential for sediment mobility, which is favored by its small average depth. Bathymetric data from Lakes 1 and 2 (SABESP, 2007) indicated average thicknesses of about 0.15 m close to the lakes´ margins and about 0.30 m in the central, deepest (about 10 m deep) portion of Lake 2. Another report (SABESP, 2001) informed that Lakes 1 and 2 have surface areas of approximately 14,000 and 50,000 m^2, respectively, and average depths of 1.5 and 4.2 m, respectively, and that the average hydraulic residence time in Lake 1 is about 0.8 days.

Relevance of This Work

The available technical literature on sediment treatment to remove PAHs covers inland soil remediation by ozone and ozonation of marine sediments and slurries. Additionally, the ozone application equipments utilized for soils and marine sediments had a degree of sophistication (see later in this article) and, in some cases, they could not handle large amounts of sediments and/or be utilized *in situ*. Also found was a work that assesses contamination of sediments from alpine (oligotrophic) lakes, but not urban tropical lakes. There are many works on metal contamination of oligotrophic lake sediments and many works on lake sediment characterization and mobility, but no work on both organic and inorganic contaminants in tropical lake sediments; Brazilian references on urban lake sediment characterization containing discussion of pollution sources (and nothing else) were found, but no reference on urban, tropical lake sediment remediation by ozone and its effects on the removal of both organic (chlorinated compounds, steroids, PAHs, etc.) and inorganic contaminants was found in our search. Furthermore, this work investigated settleable solids reduction by ozonation, which has very important consequences for the cost and logistics of handling large quantities of sediments during and after remediation procedures. This work provides experimental results to cover the previously mentioned areas in need of data not provided by the available literature on lake sediment remediation with ozone.

MATERIALS AND METHODS

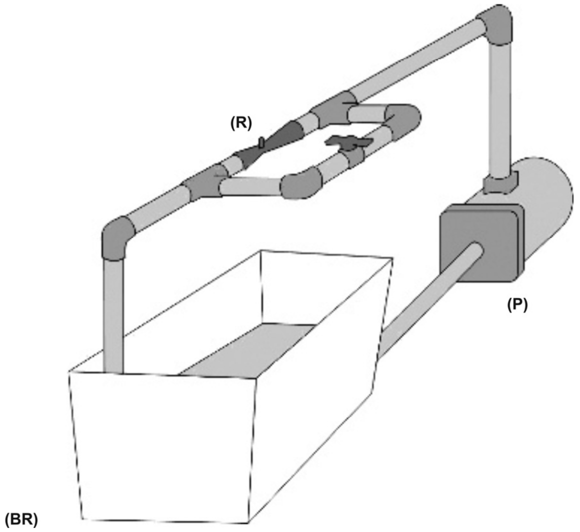
Sediment Collection and Homogenization

Sediments from Lake 1 were collected once a week over two months by a field worker from SABESP wearing impermeable overalls and boots, who entered Lake 1 (water at low waist level) holding a suction hose connected to a pump at the other end. The hose was positioned and held underwater at the sediment layer, always at the same location, half the distance from the entrance to Lake 1to the entrance of Lake 2. Sample collection was conducted for about 10 minutes on each collection day by pumping sediments into high density, inert polyethylene containers. The containers were deemed to be non-toxic and without risk of contaminating the sediment samples by the water authority SABESP. The filled containers were then placed in the dark, inside the cargo compartment of a van and taken immediately to the test laboratory (half an hour trip), where the contents of all containers were slowly mixed in a homogenization tank with a plastic paddle for about two minutes. Aliquots from the homogenized sediments were used to fill lab grade containers that were directed to laboratories for physicochemical, chemical and microbiological characterization analyses, as well as for metal and organics analyses.

Ozonation Treatments

A very compact ozonation system fed with ambient air was utilized. The ozone generating system employed did not require pressurized oxygen tanks and their associated housing; its operation was easy, with low operational costs. The ozone generation system utilized in the tests was modular. This means that we could add modules in parallel to reach the desired ozone mass (g O_3/h) to be applied to the samples. The amount of ozone to be generated per hour *per module* could be adjusted by means of a rotating knob installed on each module. The knob controlled the energy input. For instance, a dosage of 20 g O_3/h was generated by operating two modules with the control knob turned at the maximum (360 degree turn) and a third module operated with the knob turned by about 180 degrees.

The homogenized sediments were subjected to ozonation treatments: 25 L for each batch treatment conducted under certain conditions with regard to contact time and ozone dosage. The treatments were carried out with a 25 L capacity, open batch reactor coupled with a recirculation loop (see Figure 1). The ozone feeding line from the outlet of the ozone generating system was connected to a Venturi injector in the recirculation loop. The loop worked as follows: during ozone application, a pump transported the sediments out of the batch reactor and into the recirculation loop at a flow rate of 5 m^3/h for all the ozone treatments, so that a 25 L volume was recirculated approximately each 18 seconds. A gas mixture of ozone and oxygen (ozone/oxygen mass ratio estimated at 2.4%) fed the loop through the Venturi injector. The gas flow rate from the ozone generator was 5 L/min and the gas mixture reached the Venturi injector via a silicon tube connected from its mid-portion top to the outlet of the ozone generator. The tube material resists ozone well and does not allow diffusion through it. Ozone production (g/h) was checked during each test. Gas and liquid flow rates were measured throughout testing by means of rotameters. Ozone production was not measured in local conditions. The ozone dosages were predicted based on manufacturer's data. The dosages considered are applied dosages, not consumed ozone.



BR = Batch Reactor;
P = recirculation Pump;
R = Recirculation loop with Venturi injector. A point on top of the Venturi injector is where a tubing conveying the ozone/oxygen mixture from the ozone generator was connected.

Figure 1: Scheme of batch reactor and recirculation loop with Venturi injector

Langlais *et al*. (1991) reported that a gas/liquid flow ratio lower than 0.067 ft^3 per min/gallon per min (about 0.50 L/L) is necessary to optimize ozone transfer to water by means of a Venturi injector. Our investigation dealt with very dilute sediments; thus, the referred ratio was not taken at face value. For our reactor, the gas/liquid flow ratio was about 0.06 L/L, much lower than the recommended upper limit for ozone dissolution in water. The injected gas mixture was transferred with high efficiency (reported as above 90% by the injector's manufacturer) into the liquid phase of the sediments going through the loop. The ozone generator had a nominal generating capacity of 8 g O_3/h. The feed air was dehumidified and particulate materials were removed before it entered the electric discharge gap in the generator to generate ozone. Ozone dosages of 10, 20 and 30 g O_3/h and contact times (Tc) of 5, 10, 20 and 60 min were tested, the latter value only with regard to physicochemical/microbiological characterization. Immediately after each treatment, aliquots of ozonated sediments were drawn out of the reactor and used to fill flasks to be directed to the analytical laboratories.

Analytical Methods

Physical-Chemical and Microbiological Characterization of Sediments

Aliquots of the homogenized sediments collected in one liter amber flasks were capped and directed to analysis. The characterization work was done based on APHA/AWWA/WEF (2005): total fixed and volatile solids (sections 2540B and 2540D), chemical oxygen demand (section 5220B, open reflux method), coliforms (section 9223B, enzyme substrate test) and settleable solids (section 2540F).

Organics Analyses

Aliquots of the homogenized sediments were collected in 500 mL Schott flasks with contamination-free screw caps, totally wrapped in aluminum foil to protect against light and placed in Styrofoam containers filled with ice, which were directed to analysis. The sediment samples were subjected to solid phase extraction, followed by cleanup as per APHA/AWWA/WEF (2005) procedures 3540C, 3630C and 8100C. An exploratory analysis of the samples was conducted using gas chromatography (GC) with flame ionization detector (FID) and chromatographic profiles of ozone-treated and non-treated samples were compared. Volatile and semi-volatile organic compounds were identified with a gas chromatograph (GC) coupled to a mass spectrometer (MS) and a mass spectral data library (methodology detailed in Carvalho *et al*., 2005). Sixteen priority PAHs (USEPA, 2008) in sediment samples were targeted and determined by GC-FID according to APHA/AWWA/WEF (2005) Sections 3540C and 3630C. According to the laboratory, the detection limits of PAHs ranged from 0.09 to 0.58 μg/mL and quantification limits from 0.18 to 1.75 μg/mL. The lower limits are considered to be rather high. Given the somewhat wide variation of these lower limits depending on the specific PAH, the non-detection of certain PAHs after ozone treatment was a possibility.

Metal Analyses

Aliquots of the homogenized sediments were collected in plastic flasks with preserver (drops of nitric acid solution) and directed to analysis. The procedure for heavy metals followed APHA/AWWA/WEF (2005) part 3000, Section 3120B - metal analysis by emission spectroscopy based on the inductively coupled plasma. For determination of total metals (ionic plus metallic species) in the liquid phase, samples received nitric acid and hydrochloric acid to release the metals from the samples. For the determination of dissolved metals (ionic species), samples were heated, filtered and the filtrate was rinsed with warm deionized water. For determination of total metals in the solid phase, samples were dried and exposed to nitric acid, hydrochloric acid and hydrogen peroxide. Yttrium was used as the reference for sample recovery.

RESULTS AND DISCUSSION

Characterization of Sediment Samples

Table 1 presents the characterization results for homogenized sediment samples. The raw sediment sample (without ozone application) is denoted as (0;0), meaning (zero g O_3/h; zero min contact time).

Table 1 shows that the COD results tended to decrease slightly and the TFS and TVS results tended to increase slightly with application of 10 g O_3/h; however, both values decreased with the application of 20 g O_3/h. The observed behavior of the TFS and TVS values must be related to the finding reported by Jekel (1994) that ozone at relatively low dosages can act as a flocculant, incorporating colloidal matter onto particulate matter, thus increasing slightly the total solids content. Gottschalk *et al.* (2010) stated that the micro-flocculation effects of ozone can lead to dissolved solids being adsorbed onto suspended solids, thus normally increasing the amount of suspended solids and also the COD value. Beltran (2004) commented that ozonation changes the nature of natural organic matter, thus influencing COD values; the author also stated that the DOC (Dissolved Organic Carbon) content in turn affects the overall ozone decomposition rate constant. Variations in DOC speciation between samples occur normally, so that slight variations in ozone effectiveness between the homogenized samples were bound to happen. Thus, if the ozone dosage (the applied ozone mass per unit time) is increased above the amount of ozone consumed by micro-flocculation and general oxidation and an adequate contact time is selected, then both the TS content and the COD should drop significantly.

Table 1 shows that increasing ozone dosages and contact times led to decreasing values of settleable solids. Moussani *et al.* (2008) reported significant reductions of volume and mass of waste activated sludge with ozonation; ozone dosages between 0.125 and 2 mg O_3/mg of Total Solids reduced Total Solids, Total Suspended Solids and Volatile Solids from 15% to 80%, 8% to 48% and 6% to 46%, respectively. The reduction in settleable solids could mean significant savings in disposal costs in the future if lake sediments are dredged out and processed towards a final disposal. The sharp drop in the value of settleable solids (from 26 down to 3.5 mL/L) when the ozone dosage was increased from 10 to 20 g O_3/h (see Table 1) indicates that the ozone dosage apparently exerted a bigger effect on the reduction of settleable solids than contact time.

Table 1: Physicochemical and microbiological characterization of the sediments

Treatment, (g O_3/ h; Tc in min.)	Unit	(0; 0)	(10; 20)	(10; 60)	(20; 60)
Chemical Oxygen Demand (COD)	mg O_2/L	583	550	554	529
Total Solids (TS)	mg/L	1230	1270	1290	1140
Total Fixed Solids (TFS)	mg/L	870	890	903	804
Total Volatile Solids (TVS)	mg/L	360	380	387	336
Settleable Solids (SS)	mL/L	41	32	26	3.5
Total Coliforms	MPN/100 mL	9.0×10^5	1.0×10^5	7.0×10^4	5.8×10^3
Tot. Coliform Removal Efficiency	(%)	-	88.9	92.2	99.4
Fecal Coliforms	MPN/100 mL	6.0×10^4	5.5×10^4	4.8×10^4	1.0×10^2
Fecal Coliform Removal Efficiency	(%)	-	8.3	20.0	99.8

MPN = Most Probable Number.
Tc = Contact Time of ozone.

The total coliform inactivation results did not bear a clear relationship to the relative importance of the dissolved ozone concentration and the contact time. However the fecal coliform inactivation results in Table 1 suggest that the dissolved ozone concentration was more important than contact time. In fact, increasing the ozone dosage from 10 to 20 g/h while keeping a long contact time (60 min) caused the fecal coliform inactivation efficiency to go up from 20.0 to 99.8%.

Suspended solids can protect microbes from disinfectants; in fact, effective fecal coliform inactivation took place only when a significant decrease in settleable solids (about 90% reduction) was achieved through ozonation. Another factor that accounts for the low coliform removal efficiency at the low end of ozone dosages (applied ozone mass per unit time) was noted by Assirati (2005), who stated that ozone oxidation of compounds that confer color to pond effluents (dissolved organic matter) had priority over ozone consumption for coliform inactivation; the author also claimed that total coliform reduction efficiencies were not influenced by the ozone contact time. Similarly, our results for total coliform inactivation suggest that the contact time did not have a significant influence on total coliform inactivation, in comparison to ozone dosage.

Organics Analyses

The pioneering work of Thomey, Bratberg and Kalisz (1989) concluded that the Gas Chromatographic (GC) technique with flame ionization detection (FID) "provided a more adequate representation of the degree of hydrocarbon contamination in soil". In fact, the GC-FID technique is considered to be suitable for analysis of volatile hydrocarbons in water and soil, according to the Atlantic RBCA (2010). An exploratory analysis was conducted in which chromatographic profiles, obtained by GC-FID of raw and ozone-treated samples, were compared with regard to the intensity and the number of peaks. Figure 2 presents the chromatograms of the corresponding raw and ozone-treated samples. The ozone treatment was arbitrarily chosen to be 20 g O_3/h and 5 min of contact time. The chromatogram of the ozone-treated sample shows significantly smaller peak intensities and a lower peak number than the chromatogram of the raw sample. The exploratory analysis from a single ozone treatment was followed by systematic tests of several ozone treatments applied to homogenized sediment samples. The focus was on the removal of certain classes of organics and metals. The results for organics are shown in Tables 2 and 3 and the results for metals in Tables 4 and 5.

The Gas Chromatography–Mass Spectrometer (GC-MS) technique is the first choice for the detection and quantification of volatile and semi-volatile hydrocarbons (Hubschmann, 2009). Table 2 presents the organic compounds detected by GC-MS in treated and non-treated samples. The procedure executed by the lab was presence/absence, which does not need analytical standards (unavailable at that time) but cannot quantify the identified compounds. For such a simplified procedure, detection limits for the identified compounds cannot be provided. The treated samples are identified by labels showing the applied ozone mass, g O_3/h and the contact time Tc in minutes. Twenty four organic compounds were detected in the raw sediment sample and were separated into the chemical groups shown in Table 2. The ozone treatments (20;5), (20;10), (20;20), (30;5) and (30;10) (g O_3/h; Tc in min) led to the detection of seven, three, zero, one and zero organic compounds, respectively, as shown in Table 2.

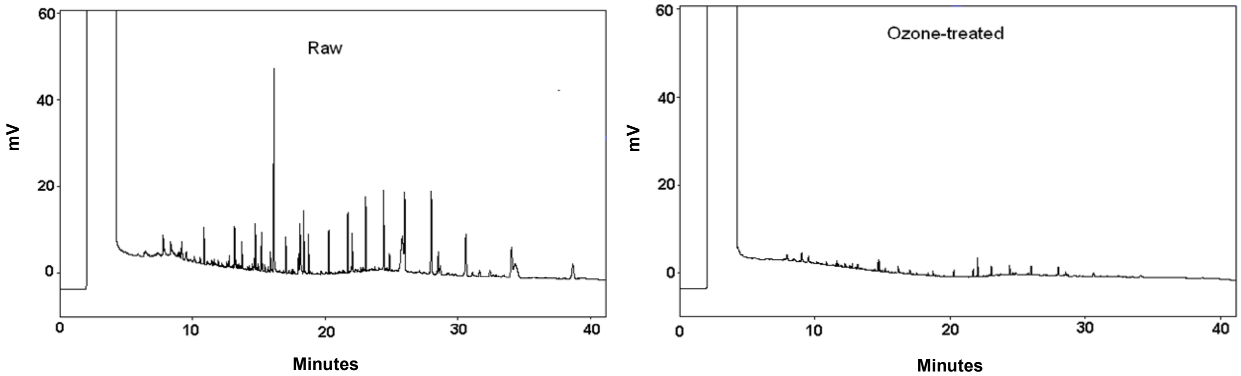


Figure 2: GC-FID Chromatograms of raw and ozone-treated samples Ozone treatment: 20 g O_3/h; 5 min of contact time.

Table 2: GC-MS detected compounds per sample treatment

Treatment (g O_3/h; Tc in min)	**(0;0)**	**(20;5)**	**(20;10)**	**(20;20)**	**(30;5)**	**(30;10)**
Chlorinated compounds						
Phenyl, 3 chloro	+	-	-	-	-	-
Heptachlor	+	-	-	-	-	-
Chlordane	+	-	-	-	-	-
2H, 1,4 – benzodiazepine – 2 – 1,7 chloro – 1,3 - dihydro – 5 – phenyl – 1- (TMS)	+	-	-	-	-	-
2 – butene, 1 – chloro – 4 – ethoxy	+	-	-	-	-	-
Phenyl, 4 chloro – 5 - azlocillin	+	-	-	-	-	-
1,4 cyclohexadiene, 1,4 dichloro	+	-	-	-	-	-
Nonane, 1 chloro – 5 - methylene	+	-	-	-	-	-
Aromatics						
2- isopropyl – 5 – methyl – 4,6 – dinitrophenyl acetate	+	-	-	-	-	-
Phenol, nonyl -	+	-	-	-	-	-
Benzo [a] antracene	+	+	-	-	-	-
Benzophenone	+	-	-	-	-	-
Benzophenone, 4 - methyl	+	+	-	-	-	-
9- Phenyl – 5H - benzocycloheptene	+	+	-	-	-	-
Steroids						
17 β – hydroxy – 5α - Androstan – 3 – one (DHT)	+	-	-	-	+	-
5 α - Pregnane – 3, 20 – dione (5α-DHP)	+	+	-	-	-	-
Phthalates						
N – Butyl - isobutylphthalate	+	-	-	-	-	-
Isobutylphthalate	+	+	-	-	-	-
Di – isobutylphthalate	+	+	-	-	-	-
Di – isopentylphthalate	+	-	-	-	-	-
Dioctylphthalate	+	-	+	-	-	-
Siloxanes						
Pentasiloxane, dodecamethyl	+	+	-	-	-	-
Cyclotetrasiloxane	+	-	+	-	-	-
Pentasiloxane, dodecanethyl	+	-	+	-	-	-
(+) = detected, (-) = non-detected.						

Regarding the identified chemical groups, the chlorinated compounds probably originated from herbicide and biocide residues that ended up in lake water and also from chlorination of treated effluent released into Lake 1 from an existing sewage treatment plant (STP). Aromatic and polycyclic aromatic hydrocarbons are ubiquitous, persistent (semi- or non-volatile) pollutants usually arising from combustion of fossil fuels and vehicular emissions, as well as from industrial operations and agrotoxic applications. With regard to the identified steroids, possible sources were the STP effluent and untreated wastewater discharged into small creeks that flow into Lakes 1 and 2.

According to Sumpter (2005), the consequences of the presence of endocrine-disrupting chemicals (EDCs) such as steroids, pesticides and phthalates for the aquatic organisms and wildlife in the surrounding areas “are unknown and largely uninvestigated”. The author also mentioned “important unresolved issues such as the impact of EDCs at the population level”. Steroids and other endocrine disrupting substances such as phthalates and pharmaceuticals are normally not removed by conventional physico-chemical treatment (practiced at the STP). Sedlak and Pinkston (2011) stated that our ability to deal with the presence of pharmaceuticals in receiving waters is seriously limited by a lack of understanding of the attenuation mechanisms of pharmaceuticals in aquatic environments. The identified phthalates might have originated from plastic residues, since they are commonly employed as additives to plastic materials in order to confer upon them certain properties such as elasticity and malleability. With time, phthalates from plastics tend to be released into the liquid phase. Sumpter and Johnson (2005) analyzed several issues associated with trace chemicals in aquatic environments and stated that the natural breakdown of synthetic organic compounds “such as pharmaceutical products and pesticides in the aquatic environment can generate degradation products that are potentially harmful”.

Siloxanes are from a class of compounds varying from liquids to hard resins whose molecules are composed of chains of alternate silicon and oxygen atoms (Webster’s, 2002). They probably originated from soil associated with the sediments.

Table 2 indicates that all chlorinated compounds were removed with an ozone dosage of at least

20 g/h at the lowest contact time of 5 min. The removal of all detected aromatic compounds was also achieved with the same dosage, but with a longer contact time (10 min). One steroid (DHT) was detected in the raw sample and also in the (30;5) treatment sample, but was not detected in the (20;5), (20;10) and (20;20) treatment samples. One possible explanation would be the occurrence of variations in compound concentration and/or speciation among samples, regardless of the sample homogenization procedure.

All identified phthalates and siloxanes were removed with the application of 20 g/h at a contact time of 20 min.

Next we consider the relative importance of ozone dosage and contact time in light of the PAH removal results from Table 3, which lists PAHs detected from a Priority Contaminant List (USEPA, 2008) and their total concentrations per ozone treatment. Regarding the treatments with 20 g O_3/h, varying the contact time from 5 to 20 min did not lead to any significant change in the total PAH removal efficiency. With application of 30 g O_3/h, increasing the contact time from 5 to 10 min led to an increase in the total PAH removal efficiency from 68.1 to 82.1%. Thus, the relative importance of ozone dosage and contact time on the removal of total PAHs is not clear.

Some unexpected results surfaced: for the same contact time (5 min), increasing ozone application from 20 to 30 g O_3/h led to a reduction of the total PAH removal efficiency from 82.1% down to 75.1%. Furthermore, Table 3 shows several cases of PAHs that went undetected after application of 20 g O_3/h but were detected after application of 30 g O_3/h. Explanations for the apparent discrepancies are as follows:

The sample homogenization procedure does not imply a homogeneous PAH content (either in species, or in concentration) for all the samples. Actually, the concentrations of individual PAHs varied significantly from sample to sample (individual values not shown in Table 3). Furthermore, the homogenization procedure could have changed to some extent the size distribution of solids in the sediments, thus influencing PAH concentration and speciation. In addition, changes in the size distribution of particles influence ozone consumption; for instance, a smaller particle size means larger surface area per unit volume, meaning a larger particle-associated ozone demand.

Previous works provide evidence for several other factors at work during ozone treatment of PAH-contaminated sediments that could explain those unexpected results, as follows: According to Moore and Ramamoorthy (1984), PAHs entering the aquatic environment exhibit high affinity for suspended particulates in the water column due to their hydrophobic nature. It is common knowledge that an increased suspended solids concentration of a sample implies an increased ozone consumption by the sample, all other factors being constant. Chemical factors also play a role in PAH removal: the chemical structure of PAHs in terms of number of rings and carbon atoms and also their vapor pressure dictate the degree of volatilization (Moore and Ramamoorthy, 1984) and thus the removal of PAHs by such a mechanism. According to Carrére *et al.* (2005), the lower the PAH molecular weight, the higher the solubility and an increasing PAH solubility in water and a decreasing number of 5-carbon rings lead to increasing PAH removal by ozonation. There is also a complicating factor reported by O´Mahony *et al.* (2006). They treated PAH-contaminated soil with ozone and reported that increasing moisture content was found to have an adverse effect on ozone treatment, since PAHs in soil become less accessible to ozone when water occupies pore spaces. The authors obtained a reduction above 50% in phenanthrene concentrations in all soils after application of 20 mg O_3/L during six hours, i.e., a far higher ozone dosage and a far longer contact time than used in this work. Masten and Davies (1997) also tested ozone as a PAH oxidizing agent in soils and reported percent removals of phenanthrene and pyrene of 95% and 91% respectively, “while chrysene was reduced by 50% only, due to its more hydrophobic nature”. Still according to the authors, “a number of identified byproducts were simultaneously discovered which were more polar than the parent compounds, thus having better biodegradability and aqueous solubility”.

Hence, several factors play roles in PAH immobilization in sediments as well as in PAH removal by ozonation. Clear-cut conclusions regarding the effects of ozone dosage and contact time on total PAH removal cannot be established. It seems that, of all the classes of organic compounds found in the lake sediments, PAHs are the ones that would require the largest amount of applied ozone mass per unit time for effective removal.

Metal Analysis

To evaluate metal removal by ozone, a sediment sample was treated with 20 g O_3/h during 20 minutes. This treatment was chosen based on the characterization results (Table 1) that indicated this ozone dose as promising; a contact time of 20 min was picked as a realistic value in real scale operations, where 60 min would be too long and most probably unfeasible economically. Table 4 shows the results for the liquid phase of sediments.

Table 4 shows that for all targeted metals, the concentrations of dissolved species were much lower than their corresponding metallic/bound metal species concentrations. Considering only positive removals, the calculated average removal efficiencies for dissolved and total metals in the liquid phase were (84 ± 17)% and (84 ± 7)%, respectively. Some removal efficiency values of dissolved species and total metals were negative (dissolved Mn, Cu and Zn; total Sn). Possible explanations regarding the dissolved species: the ozone oxidation of metal complexes probably released some ionic species, thus increasing their concentration in solution and the sample homogenization procedure would not insure a homogeneous metal content in all samples. As for the negative removal efficiency value for total Sn, the latter explanation applies. Table 5 shows the results obtained for the solid phase of sediments.

Table 3: PAHs and total concentration per sample treatment

Treatment (g O_3/h; Tc in min)	**(0;0)**	**(20;5)**	**(20;10)**	**(20;20)**	**(30;5)**	**(30;10)**	**Detection limit (μg/mL)**
Naphthalene	+	-	-	+	+	-	0.43
Acenaphthylene	+	+	-	+	+	-	0.08
Acenaphtene	+	+	-	+	+	-	0.06
Fluorene	+	+	-	+	+	+	0.24
Phenanthrene	+	+	+	+	+	+	0.48
Anthracene	+	+	-	+	+	+	0.18
Fluorantene	+	+	+	+	+	+	0.27
Pyrene	+	-	+	+	+	-	0.30
Benzo [b] anthracene	+	+	-	+	+	+	0.32
Crysene	+	+	-	+	+	+	0.12
Benzo [b] fluorantene	+	+	+	+	-	+	0.07
Benzo [k] fluorantene	+	+	+	+	+	+	0.13
Benzo [a] pyrene	+	+	+	+	+	+	0.27
Dibenzo [a,h] flurantene	+	+	+	+	+	+	0.19
Benzo [g,h,i] perylene	+	+	-	+	+	-	0.06
Indene [1,2,3,cd] pyrene	+	+	-	-	+	+	0.58
Total concentration (μg/mL)	229	57	53	59	73	41	---
Total removal efficiency (%)	---	75.1	76.9	74.2	68.1	82.1	---

(+) = detected; (-) = non-detected

Table 4: Metal removal results from the liquid phase of sediments Ozone Treatment: 20 g O_3/h; 20 min contact time.

Metals (dissolved, total)	**Untreated sample (mg/L)**	**Treated sample (mg/L)**	**Removal Efficiency (%)**
diss Fe	2.30	0.82	64.3
diss Mn	0.04	0.05	***
diss Cr	< LOD	< LOD	----
diss Cu	0.01	0.02	***
diss Zn	1.10	1.30	***
diss V	0.14	0.01	92.9
diss Pb	< LOD	< LOD	----
diss Sn	< LOD	< LOD	----
diss Ni	0.02	0.001	95.0
diss Hg	< LOD	< LOD	----
tot Fe	283.00	57.00	79.9
tot Mn	1.90	0.47	75.3
tot Cr	0.70	0.11	84.3
tot Cu	1.80	0.31	82.8
tot Zn	11.00	1.80	83.6
tot V	0.99	0.16	83.8
tot Pb	0.84	0.14	83.3
tot Sn	0.34	0.40	***
tot Ni	0.17	0.001	99.4
tot Hg	< LOD	< LOD	----

LOD = Limit of Detection, range 2.0 to 15.0 μg/L depending on the metal. (***) No removal.

Table 5: Metal removal results from the solid phase of sediments Ozone Treatment: 20 g O_3/h; 20 min contact time.

Total Metals	Untreated sample (mg/kg)	Treated sample (mg/kg)	Removal Efficiency (%)
Fe	5660	1200	79
Mn	38	9.4	75
Cr	14	2.4	83
Cu	36	6.2	83
Zn	378	220	42
V	19.8	3,2	84
Pb	16.8	2.8	83
Sn	6.8	8,0	-18 (***)
Ni	3.4	1.0	71
Hg	< LOD	< LOD	----

LOD = Limit of Detection, range 2.0 to 15.0 μg/L depending on the metal.
(***) No removal.

The removal efficiencies in Table 5 were in the 71-84% range, except for Zn (42% removal efficiency) and Sn (no removal). Zinc (Zn) was the second most abundant metal (iron was first) in the solid phase of sediments. Coincidentally or not, there was also no removal of total Sn in the liquid phase of the sediments (see Table 4). It is interesting to point out that, in their classification of metal ions, Stumm and Morgan (1996) include both Zn^{+2} and Sn^{+2} and also Pb^{+2} in the group of metal cations with low electronegativity, defined as the ability to attract electrons, especially in a chemical bond. By this rationale only, oxidation or the removal of electrons of these cations would be less difficult than for other cations; however, the opposite situation is observed for them.

Regarding the actual removals, the average removal efficiency of metals in the solid phase calculated from the positive values in Table 5 was (75 ± 14)%. Thus, the average metal removal efficiencies for dissolved and total metals in the liquid phase of sediments (both 84%) were superior to the average total metal removal efficiency obtained for the solid phase. Particles, because of their relatively large surface areas, are scavengers for metal ions and are often reactive elements in their transport from land to rivers and lakes (Stumm and Morgan, 1996) and they obviously exert an ozone demand. Thus, it is believed that oxidation of solid-associated metals exerts a higher ozone demand than oxidation of metals in the liquid phase and this fact alone may explain the higher average removal efficiency values obtained for the liquid phase as opposed to the solid phase of sediments.

The metal removal results for metallic and ionized metal species indicated removal of metals from both the solid and liquid phases at the same time. For metal mass conservation, the removed metals must have gone somewhere. The explanation is as follows: Immediately after each ozone treatment had been completed, samples from the reactor were withdrawn and placed into flasks sent to the lab for analysis. Metal species (ionic and metallic) from both phases that reacted with ozone in the presence of water must have formed metallic species (in the case of ions) and compounds (e.g. hydroxide and oxides, in the case of metallic species) that stayed at the bottom and on the walls of the reactor as an undetected thin film after sample collection. An important detail was that the walls and bottom of the reactor were of opaque orange color, which certainly acted to obscure the precipitated metals from view. Thus, these reactive species were not accounted for in the total and dissolved metal analyses.

NOTE ON AN *IN SITU* TEST

Months after the end of the experimental work in this text, a pilot scale test was conducted *in situ* at Lake 1 during an entire afternoon. The treatment setup was: sediment collection by a pump followed by ozonation in a reactor with a recirculation loop, followed by sediment thickening in a geotextile press bag. Both the ozone reactor and the press bag and their command panels were on the back of a truck. The extracted water was returned to Lake 1. The thickened sediments, with greatly reduced settleable solids content and toxicity level, were transported to a suitable disposal site nearby. This pilot test showed that treatment of Lake 1 sediments was feasible and could be accomplished in a matter of months.

CONCLUSIONS

Effects of Ozone Mass Application on Removal Efficiencies

a) Regarding the application of 20 g O_3/h:

At short contact times (5, 10 min), chlorinated and aromatic compounds were totally removed, whereas phthalates and siloxanes were removed only at longer contact times (20 min). Total and fecal coliform removals above 99% were obtained only after a long contact time (60 min). For this contact time, settleable solids reduction above 90% was achieved.

- The results for settleable solids reduction indicate there is a trade-off between ozonation costs (which increase with contact time) and solids treatment and disposal costs (which decrease with settleable solids reduction).
- For our experimental conditions and a long contact time (60 min), the costs related to ozone application to sediments for purposes of both disinfection and settleable solids reduction could be significantly higher than costs for ozone application for removal of organic contaminants. Thus, treatment objectives should be clearly defined in order to assess treatment costs.
- For a 20 min contact time, the average removal efficiency for both dissolved and total metals in the liquid phase of sediments was 84%, and the average removal efficiency for total metals in the solid phase was lower, 74%. This can be explained by the fact that solid-bound metals exert a higher ozone demand than dissolved metals.

b) Regarding the application of 30 g O_3/h:

- There were reasonable removal efficiencies (range 68-82%) for PAHs at short contact times (5, 10 min), the total removal of phthalates and siloxanes at 5 min contact time and total removal of steroids at 10 min contact time.

Contaminant Type and Speciation Effects on Removal

- Results strongly suggest that, for the target contaminant groups in the sediments, the order of removal from the easiest to the hardest group was: chlorinated and aromatic compounds, phthalates and siloxanes, steroids and PAHs.
- In terms of ozone mass application per unit time, the experimental results suggest that, regarding the target chemical groups, the organic compounds that were the hardest to remove effectively from the lake sediments were the PAHs.
- With regard to metals in the liquid and solid phases of sediments, apparently neither scarcity nor abundance of any particular metal had any effect on its removal efficiency. Average removal efficiencies for total metals in the liquid phase of sediments were better than for their counterparts in the solid phase of sediments. This can be explained by a higher ozone demand for metal oxidation in the solid phase than in the liquid phase.

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