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Perchlorate behavior in the context of black carbon and metal cogeneration following fireworks emission at Oak Lake, Lincoln, Nebraska, USA

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Abstract

The imprints of fireworks displays on the adjacent water body were investigated from the perspective of cogeneration of black carbon, metals and perchlorate (ClO_4^-). In particular, the mixing and dissipation of ClO_4^- were studied at Oak Lake, Lincoln, Nebraska, following fireworks displays in 2015 and 2016. Following the display, ClO_4^- concentration in the water increased up to 4.3 $\mu\text{g/L}$ and 4.0 $\mu\text{g/L}$ in 2015 and 2016, respectively. A first-order model generally provided a good fit to the measured

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perchlorate concentrations from which the rate of dissipation was estimated as 0.07 d^{-1} in 2015 and 0.43 d^{-1} in 2016. SEM images show imprints of soot and metal particles in aerosol samples. EDS analysis of the lake sediment confirmed the presence of Si, K, Ca, Zn and Ba, most of which are components of fireworks. The $\delta^{13}\text{C}$ range of -7.55‰ to -9.19‰ in the lake water system closely resembles fire-generated carbon. Cogeneration of black carbon and metal with perchlorate was established, indicating that ClO_4^- is an excellent marker of fireworks or a burning event over all other analyzed parameters. Future microcosmic, aggregation and column-based transport studies on black carbon in the presence of perchlorate and metals under different environmental conditions will help in developing transport and fate models for perchlorate and black carbon particles.

Keywords: Black carbon, Perchlorate, Cogeneration, Metal, Fireworks, Lake water system

1. Introduction

The occurrence of perchlorate (ClO_4^-) in aquatic environments is attributed to natural and anthropogenic sources (Lee et al., 2015; Rajagopalan et al., 2006; Ye et al., 2013). Anthropogenic sources include perchlorate salts of potassium and ammonium used in rocket fuel and fireworks/explosives, respectively (Srinivasan and Viraraghavan, 2009). Naturally formed perchlorate occurs in nitrate deposits found in arid regions, minerals, and in the atmosphere (USEPA, 1998). Perchlorate ingestion may pose adverse health risks, especially to pregnant women, newborns and young children (Dasgupta et al., 2006; Kirk et al., 2005), because it interferes with the shuttle of iodine to the thyroid gland, inhibiting production of thyroid hormones required for normal metabolism, growth and development (Wolff, 1998). Elevated perchlorate concentrations may also pose risks to fish and other aquatic life (Motzer, 2001). Perchlorate has been reported in retail milk, breast milk and dairy beverages, leading to a USEPA maximum daily intake ceiling of $0.7 \mu\text{g}$ per kg body weight per day (Parker et al., 2008). Aside from its potential to harm endocrine and reproductive systems, perchlorate is considered a "likely human carcinogen" (USEPA, 1998). The potential impact of perchlorate on humans and ecosystems is directly related to its transport and decomposition with time (Greer et al., 2002; Motzer, 2001).

Black carbon (BC), also known as soot particles, is generally used to designate products of incomplete combustion of biomass (Schmidt and Noack, 2000). China and India generate nearly 35% of global BC emission. Atmospheric deposition, surface runoff, and soil erosion are responsible for BC accumulation and distribution in soils, freshwater, and the ocean (Graetz and Skjemstad, 2003; Kuhlbusch and Crutzen, 1996; Preston and Discussions,

2006; Schmidt et al., 2006; Schmidt and Noack, 2000; Ye et al., 2013). The health effects of BC depend on particle size and the chemical substances absorbed and/or adsorbed within the matrix and onto surfaces (Knicker et al., 2007). Smaller particles can be more detrimental than larger ones (Bair, 1989; Lipmann and Albert, 1969; Taylor, 1996). Inhalation of black carbon causes respiratory and cardiovascular diseases, and has been implicated in cancer and birth defects. It can also change patterns of rain and cloud formation, potentially leading to climate change (USEPA, 1998). Soot particles are typically associated with a complex mixture of organic compounds, some of which are carcinogens, viz. certain metals, polycyclic aromatic hydrocarbon (PAHs) and dioxins (Lighty et al., 2000). Wet deposition generally limits the atmospheric lifetime of BC aerosols to a few days. Hence, surface and subsequently subsurface waters are the most likely pathways of long-range BC transport.

Fireworks release various water and air pollutants, including perchlorate, soot particles, gaseous pollutants such as SO_2 , NO_2 and O_3 , organics, and fine metal particles. Detection of perchlorate in ground and surface water has led to evaluations of sources, distribution and biogeochemical processes influencing perchlorate behavior and fate in aquatic environments (Lee et al., 2015; Park, 2003). Investigation and remedial measures for perchlorate and black carbon are needed as these pollutants pose serious health hazards to both humans and ecosystems (Li et al., 2013; Schmidt and Noack, 2000; Shrestha et al., 2010). Though fireworks are a major contributor of perchlorate, there is a knowledge gap concerning the relationship between fireworks and the environmental occurrence of perchlorate (Shi et al., 2011).

BC is much more stable ($\sim 10,000$ years in soil) than other soil organic matter forms (Nguyen et al., 2009; Swift, 2001). Perchlorate salts, however, are highly soluble in water but perchlorate readily adheres to geologic and organic surfaces, leading to negligible abiotic attenuation. BC can readily adsorb natural organic matter (NOM) and colloids (Accardi-Dey and Gschwend, 2002). Both BC and perchlorate are dissipated to varying extents through microbial degradation and abiotic oxidation. Attenuation of perchlorate is primarily mediated by microaerophilic or anaerobic microorganisms using a $\text{ClO}_4^- \rightarrow \text{ClO}_3^- \rightarrow \text{ClO}_2^- \rightarrow \text{Cl}^- + \text{O}_2$ pathway. Many health and environmental concerns related to the dispersion of BC particles in natural waters have been raised, although it is conventionally believed that BC is quickly deposited in sediments upon entering water bodies (Kirk et al., 2005).

Little attention has been given to the worldwide problem of perchlorate and black carbon co-generation. Transport of BC and perchlorate dissipation likely depend on the water quality matrix and environmental factors such as rainfall, temperature and the microbiological community. There is a great need to understand the cogeneration, transport, retention and fate of black

carbon and perchlorate in the aquatic environment. Our objectives were to: (1) characterize the signature of fireworks in air, water and sediment in the vicinity of Oak Lake, Lincoln, Nebraska, USA, with emphasis on cogeneration of perchlorate, black carbon and metals through chemical and microscopic analyses and (2) evaluate the dissipation signature of perchlorate in the surface water system following fireworks display events in 2015 and 2016.

2. Materials and methods

2.1. Study location, sample collection and water quality analyses Samples were collected at Oak Lake, a 2.37 km engineered lake in Lincoln, Nebraska, USA (Latitude 40.806862N, Longitude 96.681679E, 354.22m elevation). As per the Public Health and Education Department (PHED), Oak Lake has an overall average depth of approximately 2 m, including 0.6m of mud and silt on the bottom and 0.6m of clear water on top. The annual Independence Day celebration held at the lake ends with a half-hour fireworks display consisting of approximately 1,450 shells of various sizes (7.5–15 cm in diameter). Wind and other climate data for the location can be retrieved through the NCEI Local Climatological Data tool available at <https://www.ncdc.noaa.gov/cdo-web/datatools/lcd> by clicking on Nebraska (and Lancaster County) and selecting data for the Lincoln Airport.

Figure 1 shows the location of the site, fireworks display site, and sampling locations at the lake and creek. Aerosol sampling for particulates was conducted on the eve of the 2016 Independence Day celebration (3 July, 6–7 p.m.) using Whatman glass microfiber filter (GF/A) of 0.8 μm pore size and an air pump (Agilent Technologies, CA, USA). Water samples were collected from five locations: Oak Lake East and West (OL#E and W); Oak Lake Island (OL#Is); and Oak Creek upstream and downstream (OC# US and DS) from pre-event (2 July to the fifth day after the event (8 July 2016) ($n = 21$). To obtain a background perchlorate concentration, a sample was collected on 20 October 2016. Lake bed sediment samples were dried overnight at room temperature, homogenized and passed through a 2-mm nylon sieve, and stored at 4 °C in acid-washed plastic containers until analysis. Monitoring began one day before and continued until five days after the event. OL#E and OL#W were also sampled for perchlorate on 2, 3 to 6 and 8 July 2015. The 2015 data were obtained from the Lincoln Public Health Department in response to an inquiry about the potential impacts of the fireworks display on water quality.

In-situ measurements of pH, electrical conductivity (EC), dissolved oxygen (DO), temperature, turbidity, and redox potential (ORP) were obtained with a Hanna Multiprobe electrode (HI 9828). Major anion analyses were completed

Figure 1. Site location: (A) Satellite image of Oak Lake in Lincoln, Nebraska, USA; (B) Oak Lake with sampling locations. Green box indicates sampling site of Oak Lake in west, east and island designated by OL#W, OL#E and OL#IS respectively; red circle shows fireworks event site; and the two white triangles show Oak Creek upstream (OC#US) and downstream (OC#DS) sampling location.

using a Dionex ICS-90 Ion Chromatograph equipped with an AS14 ion exchange column (APHA, 2017). Major cations were measured using a Perkin Elmer AAnalyst 400 spectrophotometer. Total Organic Carbon (TOC) was determined by persulfate oxidation (APHA, 2017) using an OI Model 1010 organic carbon analyzer. Dissolved metals were measured on a GVI Platform XS collision cell inductively coupled plasma mass spectrometer (ICP-MS). Detection limits were determined by repeated analysis of a low-level spiked matrix sample (USEPA, 1998). No quantitative BC analysis was conducted.

2.2. Perchlorate analysis

A liquid chromatography tandem mass spectrometry (LC/MS/MS) method based on EPA Method 331.0 was adopted for perchlorate analyses (Wendelken et al., 2005, 2006). A Waters Corporation (Milford, MA, USA) Quattro Micro triple quadrupole mass spectrometer, operated in electrospray ionization mode, was used for multiple reaction monitoring (MRM) quantification of perchlorate and chlorate. Oxygen isotope labelled sodium perchlorate ($^{18}\text{O}_4$ -perchlorate, 1,000 $\mu\text{g/L}$ in water), obtained from ThermoFisher Scientific (St. Louis, MO, USA), was used as the internal standard. Reference standards for sodium perchlorate and sodium chlorate were prepared from reagent grade NaClO_4 and NaClO_3 (Sigma Aldrich, St. Louis, MO, USA). Stock solutions (1,000 $\mu\text{g/L}$) were prepared in purified ASTM Type I organic-free reagent water. Calibration solutions were prepared by dilution in purified water at 1–225 $\mu\text{g/L}$, with a 100 $\mu\text{g/L}$ internal standard. Chromatographic separation was achieved isocratically using a Dionex IonPac AS16 (2 $\times$ 250 mm) analytical column with a mobile phase of 100 mM ammonium acetate in 1:1 (v/v) acetonitrile/water at a flow rate of 0.3 mL/min. Run time was 9 min per sample. The instrument on-column detection limit for perchlorate was 7.2 pg determined from the standard deviation of eight replicate injections of 50 μL of a 1 pg/ μL calibration standard ($S_{\text{rel}} = \pm 5\%$). Within 28 days of collection, refrigerated (4 °C) surface water samples were passed through a 0.45 μm pore size syringe filter directly into an autosampler vial and spiked with internal standard prior to LC-MS/MS analysis. Reactant and product ions for each compound are listed in Supplementary Table 1, together with cone voltage, collision energy and retention times. Laboratory duplicates of field samples with measurable perchlorate concentrations were within $\pm 5\%$.

2.3. $\delta^{13}\text{C}$ analysis

Carbon isotope analysis of dissolved organic carbon used heated (105 °C) oxidation of a filter sample (Lang et al., 2012) with persulfate followed by

trapping of evolved carbon dioxide on a Multiprep sample introduction system interfaced with an Isoprime stable isotope mass spectrometer (GV Instruments, Manchester, UK). Working water-soluble carbon isotope standards calibrated against benzoic acid (IAEA 601, $\delta^{13}\text{C} = -28.81\text{‰}$) and sucrose (NIST 8542, $\delta^{13}\text{C} = -10.45\text{‰}$) were used to convert measured values to VPDB.

2.4. SEM/EDS analysis

Scanning Electron Microscopy (SEM) was used to view the topography of the particles reflecting differences in their composition. Energy Dispersive X-ray Spectroscopy (EDS) was used to identify elements and their relative proportions in an area of interest at a very high resolution. For SEM/EDS analysis, the specimen on filter fiber and lake sediment was placed within the vacuum chamber at the bottom of the SEM column and the area was inspected for soot and metal particles at high magnification.

2.5. Dissipation kinetics

Pseudo-first-order and second-order equations were fitted to the perchlorate data to model dissipation kinetics in the aqueous phase (Bagheri et al., 2017; Wilkin et al., 2007). The pseudo-first-order and second-order equations are expressed as:

$$dC/dt = -k_{obs} C \quad (1)$$

$$dC/dt = -k_{2obs} C^2 \quad (2)$$

where C , k_{obs} , k_{2obs} and t denote perchlorate concentration in the aqueous phase ($\mu\text{g/L}$), the observed first-order (d^{-1}) and second order rate constants ($\mu\text{g}^{-1} \text{L}^{-1} \text{d}^{-1}$), and time (d), respectively.

2.6. Multivariate analysis

The statistical package SPSS 21 was used to carry out Principal Component Analysis (PCA) and cluster analysis after normalization by obtaining a Z score for each parameter, i.e., subtracting the mean of the parameter from the individual value and dividing by the standard deviation. A Varimax orthogonal rotation was used to generate non-related principal components. The Ward method of rotation was used for cluster analyses.

3. Results and discussion

3.1. Perchlorate generation and dissipation

Figure 2 shows temporal changes in perchlorate levels before and after the fireworks display. ClO_4^- concentration in the water increased after the event from $<0.14 \mu\text{g/L}$ in the days prior to $4.3 \mu\text{g/L}$ in 2015 and from <0.14 to $4.0 \mu\text{g/L}$ in 2016. Chlorate (ClO_3^-), a common biodegradation product of perchlorate, was not detected in any of the samples. In both years the maximum ClO_4^- concentration was observed within 48 h near the location of the fireworks display (west side of the lake, OL#W), while the concentration reached its peak much later at the east side (OL#E). The maximum concentration at the east location was lower than that of OL#W throughout the monitoring period following the event. These observations suggest maximum generation of ClO_4^- in the vicinity of the fireworks display, followed by spreading through wind and mixing of the lakewater (Munster et al., 2009). Confined dispersion of perchlorate is evident from the below detectable concentration throughout the observation period in nearby Oak Creek. Overall perchlorate concentrations were slightly higher in 2015 than in 2016.

Perchlorate dissipation was slow in both years, suggesting a need for long-term monitoring and comparison of field data with laboratory experiments. In 2016, ClO_4^- concentration on the eastward site (OL#E) was below detection until the fireworks event, and then increased at 24 h after the event, whereas for the westward site (OL#W), it increased during the event. This suggests that the transport of perchlorate from west to east was slow, likely due to low wind speed and water movement. In 2015, perchlorate was detected in the water prior to the studied fireworks event, which suggests either unknown anthropogenic sources in the vicinity of Oak Lake or dry/wet deposition of perchlorate generated from a series of fireworks events (community and individual scale) in the surrounding area as part of the Independence Day celebration. Similar observations were reported by Wilkin et al. (2007), including a large variation in ClO_4^- concentration in two consecutive years (minimum of $\sim 11 \mu\text{g/L}$ in 2005 and $44.2 \mu\text{g/L}$ in 2006) following a fireworks display at a lake in Ada, OK, USA. This may be attributed to atmospheric conditions at the time of the event, viz. wind velocity and direction, atmospheric stability, and inversion layers that will regulate the fallout of perchlorate-enriched particles and the distance of dispersion. The quantity of fireworks and duration of the event will obviously affect ClO_4^- generation, as reported for November and July 2005 events in Ada, OK (Wilkin et al., 2007).

In our study, due to state regulations and other factors, the quantity of fireworks and duration were similar in the consecutive years (City of Lincoln

Figure 2. Perchlorate concentrations at Oak Lake 2015 (OL#E and OL#W) and 2016 (OL#E and OL#W) water sampling locations (a and b) before, during and after July 3rd fireworks and c) rainfall events in 2015 and 2016.

Public Works and Utilities Department, personal communication). The difference in the peak ClO_4^- concentration observed between the two years is likely due to a difference in amount of fireworks used (20–22 min), firecrackers used in the surrounding neighborhood, and differences in wind speed and oxygenation, which regulates the amount of ClO_4^- generated and aerial dispersion. The background ClO_4^- concentration on 20 October 2016 was below the detection limit. While there was relatively little difference in the peak ClO_4^- concentration measured in the two years of our study, dissipation was slower in 2015 than in 2016.

The first-order model generally provided a good fit to perchlorate dissipation in the surface waters of Oak Lake in 2015 and 2016 (Figure 3), with rate constants of 0.07 and 0.43 d^{-1} . Slow perchlorate dissolution and thus slow diffusion (with variations in lake surface temperature) was reported by Wilkin et al. (2007) and Isobe et al. (2013). Other researchers (Backus et al., 2005; Bagheri et al., 2017) hypothesized enhanced activity of perchlorate reducers after an initial lag phase, with estimated monod kinetic and first-order rate constants of $0.03\text{--}0.30 \text{ d}^{-1}$. A lag of four days in peak concentration was observed in Hamilton Harbor, the location of Canada Day fireworks (July 2004), after which ClO_4^- became undetectable one week after the event (Backus et al., 2005). The present findings also corroborate those of Tan et al. (2004), who estimated natural ClO_4^- attenuation rates of $0.10\text{--}0.45 \text{ d}^{-1}$.

Figure 3. Pseudo-first and second-order modeling of perchlorate dissipation in Oak Lake surface water after the 2015 and 2016 fireworks displays. Dotted straight lines are the fitted linear regressions with corresponding equations and R^2 values; solid lines are the actual curves.

The influence of rainfall events on ClO_4^- concentrations is unclear in either year. A spike in perchlorate concentration was observed on 8 July 2016 after a 7 July rain event capable of producing runoff. This suggests that more perchlorate-bearing particles may have been added to the lake water through surface runoff. That may explain why the increase was more evident at the west bank of the lake. We hypothesize that black carbon and metal particles are carriers of perchlorate; soil particles may also provide transport with runoff water.

3.2. Co-variation of water quality parameters with perchlorate

Major ion and in-situ quality parameters (Table 1) did not show much variation throughout the monitoring period. A comparison was made among the four sampling sites (Figure S1), as 53 organic and inorganic chemicals are used in fireworks as binding, coloring and oxidizing agents (ClO_4^- salts of potassium and ammonium), fuels, and for sound-producing effects (White, 1996). Small increases in pH (Figure S1a) and DO (Figure S1b), decreases in turbidity

Table 1. Water quality parameters in Oak Lake and Creek before and after the 2016 fireworks event at Lincoln, NE, US.

Parameters	Units	Detection Limit	Lake			Creek		
			Before	After	Mean $\pm$ SD	Before	After	Mean $\pm$ SD
pH		–	8.8	9.0	8.9 ± 0.2	8.0	8.0	8.0 ± 0.01
ORP	mV	–	225	171	198 ± 37.6	244.6	216	230 ± 20
Temp	°C	–	22.4	27.7	25.1 ± 3.7	20.6	26.5	23.5 ± 4.2
DO	mg/L	0.10	1.9	5.0	3.4 ± 2.2	2.2	3.4	2.8 ± 0.8
EC	$\mu\text{S}/\text{cm}$	1.0	2767	2776	2773 ± 6.3	1385	1494.4	1439 ± 77
TDS	mg/L	0.10	1383	1387	1385 ± 3.2	693	748.6	721 ± 39
Turbidity	NTU	0.10	54.5	37.5	46 ± 12	84.4	71.3	77.8 ± 9.3
Br	mg/L	0.10	0.1	0.1	0.1 ± 0.0	BDL	BDL	BDL
Cl^-	mg/L	0.10	751	532	642 ± 155	328	90.2	209 ± 168
F	mg/L	0.10	0.8	0.7	0.8 ± 0.1	0.3	0.4	0.3 ± 0.1
NO_3^-	mg/L	0.10	0.4	0.2	0.3 ± 0.1	1.2	1.3	1.2 ± 0.1
Orthophosphate	mg/L	0.10	<0.10	0.1	0.1 ± 0.0	0.3	0.3	0.3 ± 0.1
SO_4^{2-}	mg/L	0.10	106	100	103.3 ± 4.5	66.7	34.1	50.4 ± 23.0
Ca^{2+}	mg/L	0.10	19.0	19.8	19.4 ± 0.5	16.0	46.2	31.1 ± 21.4
K^+	mg/L	0.10	6.6	7.4	7.0 ± 0.6	6.4	7.1	6.8 ± 0.5
Mg^{2+}	mg/L	0.10	21.6	20.7	21.2 ± 0.6	18.5	12.6	15.6 ± 4.2
Na^+	mg/L	0.10	438	417	428 ± 15	169	110	139 ± 42
Cd	$\mu\text{g}/\text{L}$	0.10	0.3	0.3	0.3 ± 0.0	0.2	0.2	0.2 ± 0.01
Co	$\mu\text{g}/\text{L}$	0.05	1.6	3.6	2.6 ± 1.4	3.4	3.6	3.5 ± 0.1
Cu	$\mu\text{g}/\text{L}$	0.05	15.1	9.6	12.4 ± 3.9	11.4	7.0	9.2 ± 3.1
Ni	$\mu\text{g}/\text{L}$	0.10	70.4	15.8	43.1 ± 38.6	33.2	21.5	27.4 ± 8.3
Zn	$\mu\text{g}/\text{L}$	0.10	75.0	38.0	56.5 ± 26.2	48.0	34.0	41.0 ± 9.9
Chlorate	$\mu\text{g}/\text{L}$	0.18	BDL	0.1	0.1 ± 0.1	BDL	BDL	BDL
Perchlorate	$\mu\text{g}/\text{L}$	0.14	BDL	1.9	0.9 ± 1.3	BDL	BDL	BDL
TOC	mg/L	0.05	9.0	9.5	9.2 ± 0.4	3.2	4.5	3.9 ± 0.9

(Figure S1c) and ORP (Figure S1e), and relatively stable EC (Figure S1d) were observed in the Oak Lake water samples. Water quality trends were similar for Oak Creek and Oak Island water samples, although EC was lower and more variable in the OC samples. At the east and west sites, pH was 8.5–9 before the fireworks display and increased after the event. DO levels were similar at all sampling sites before the fireworks display. With the fireworks display, DO increased to a maximum of 8.5 mg L⁻¹ after which it decreased. Before the fireworks event, the redox potential was similar at the four sites, ranging from 220 to 250 mV and decreasing to a minimum of 140mV by four days afterward. Turbidity decreased at the Oak Lake eastward and westward sites preceding the display but changed little thereafter, while it increased then decreased at the Oak Creek sampling sites.

While unreacted ClO₄⁻ salts produce spikes in soluble perchlorate concentrations (Wilkin et al., 2007), detonation of fireworks is expected to lead to conversion of ClO₄⁻ to Cl⁻ (KClO₄ => KCl + 2O₂). Among the major ions, K⁺, Cl⁻ and N-species varied with ClO₄⁻. There were spikes in K⁺ (6.7–8.9 mg L⁻¹), Mg²⁺ (21.7–22.5 mg L⁻¹), Ca²⁺ (19.4–21.9 mg L⁻¹), PO₄³⁻ (0.04–0.08 mg L⁻¹) and Cl⁻ (21.7–22.5 mg L⁻¹) after the fireworks event. Among the metals measured, Cd and Co had the highest concentrations following the event, while there was little variation in other major ions except chlorate.

3.3. Cogeneration of black carbon and metals due to fireworks

SEM/EDS analysis shows the generation and persistence of metal particles due to the fireworks. Figure 4 (a to c) shows SEM images of soot and metal particles on the air filter fibers obtained during aerosol sampling. Imprints of soot/black carbon particles are seen in image 4(b) and metal depositions are seen in image 4(c). EDS analysis of sediment samples showed the relative abundance of various elements (eZAF smart quant results; Figure 4d). Si is the most abundant element in the samples during the fireworks. Other elements generated by the fireworks include O, Ca, Zn, K, Ba and Al. Most are light or intermediate elements except Ba. Lake sediment samples also contained Zn, Ba, K and Ca.

The richness of K, Ba, Al, Ca and Zn suggest strong imprints of fireworks on the aerosol particles as well as lake sediment. Li et al. (2013) also reported K, Ba, Al and Mg in the haze formed after the fireworks event during a Chinese New Year celebration. Sr, Ba, Ca, Na, Cu, Sb, Al and Mg are color-emitters used in pyrotechnical displays (Conkling and Mocella, 2010). In the present study, spikes in Ca, K, Mg and Na were found in lakewater samples. Heavy metals did not show spikes but Cd and Co concentrations were highest after the event. Overall, EDS was more informative than analyses of major ions, TOC, TIC and BC in water samples due to the limited sensitivity of

Figure 4. Scanning Electron Microscope (SEM) images of soot and metal particles in aerosol samples deposited on sampler filter fibers: (A) magnified image of filter fibers; (B) soot particle; (C) magnified image of soot particles; (D) Energy Dispersive Spectrum (eZAF smart Quant results) showing Zn, Ba, K, O and Ca in the Oak Lake bed sediment.

the analytical technique determining concentration. High background concentrations of major ions released from fireworks such as Ca, Na, K, Mg hinders detection of spikes. However, undetectable or very low ClO_4^- concentrations prior to the fireworks event indicates it is a good marker of fireworks or emissions from burning processes. Li et al. (2013) reported two types of nanometal particles, one with abundant S but not Cl, after fireworks, and fresh metal-bearing particles high in Cl but low S. Therefore, perchlorate is a better indicator of direct fireworks effects rather than metals, as previously suggested for urban areas (Shi et al., 2011; Wilkin et al., 2007). We showed BC, metal and perchlorate generation from fireworks by analyzing air, water and sediment samples. TEM and speciation analysis should be conducted for ligand identification and insight into binding of associated metals.

To confirm the origin of black carbon, which was not directly measured in the present study, an isotopic investigation was carried out to understand the type of $\delta^{13}\text{C}$ originating from the fireworks. Figure 5a reports the range

Figure 5. (a) Reported range of $\delta^{13}\text{C}$ of various origins and comparison with the present study. (b) Scatter plot tracing the contribution of organic carbon to perchlorate generation

for $\delta^{13}\text{C}$ of various origins in comparison with the present study range of -7.55‰ to -9.19‰ . This shows the addition of the freshly originated $\delta^{13}\text{C}$ into the lake water system with neither the characteristics of petrol nor biogenic sources and closely resembles fire-generated carbon, i.e. black carbon (Clark and Fritz, 1997; Schidlowski et al., 1984; Ye et al., 2013). The background concentration of $\delta^{13}\text{C}$ measured on 20 October 2016 was the most depleted (-9.19‰) against the most enriched condition of -7.55‰ on 9 July. This is more meaningful in the context of samples collected on 7 and 15 July showing -8.78‰ and -8.19‰ of $\delta^{13}\text{C}$.

Total organic carbon (TOC) was evaluated as an indicator of black carbon cogenesis with perchlorate (Figure 5b). The perchlorate concentration

was below detection before the fireworks but afterward it increased to as high as 4 µg/L. Minimum and maximum TOC concentrations before the fireworks display were 3 mg L⁻¹ and 9 mg L⁻¹, which changed to 5 mg L⁻¹ and 10 mg L⁻¹ after the event. Thus, there was an increase in TOC after the event but it did not correspond to perchlorate generation. This is likely because BC is mainly inorganic at the core and organic molecules become bound or sorbed to it. While not conclusive, a recent study of ¹³C-TOC suggests that a reduction in carbon isotope composition may reflect input from black carbon of pyrogenic origin (Clark and Fritz., 1997; Schidlowski et al., 1984; Kirillova et al., 2014). There is a knowledge gap on the organic carbon composition of black carbon and its variations with different sources.

3.4. Principal component and cluster analyses

Three-dimensional principal component loadings (Figure 6a) show three main characteristics: (i) high component 1 and 2 loadings for perchlorate surrounded by fireworks-cogenerated species like Mg, K, Zn, and Cu along with TOC; (ii) distant component 2 and 3 loadings of pH, DO and temperature; and (iii) a seemingly uncoupled link between fireworks-generated species and that of TDS and EC. The dendrogram obtained from hierarchical clustering (Figure 6b) further substantiates the cogeneration and influence of fireworks by grouping K and perchlorate and connecting with TOC and Co. Metals like Ni, Br, Cu and also NO₃⁻ showed the closest grouping consistent with their cogeneration with the fireworks.

Figure 6. (a) Three-dimensional principal component loadings. (b) Dendrogram from hierarchal cluster analyses showing the distance of *in-situ* parameters, major ions, metals, TOC and perchlorate.

4. Conclusions

Evidence of perchlorate generation due to fireworks and dissipation was observed in both 2015 and 2016. Imprints of black carbon generated by the fireworks event were found in aerosol samples under SEM. Some metal particles were also found on the filter paper and were identified by EDS. The observed increase in perchlorate concentration in Oak Lake after the event was attributed to wet and dry addition of ClO_4^- generated from the fireworks. Dissipation is governed by mixing, dilution and photolysis, and these processes need further investigation. Cogeneration of black carbon and metal with perchlorate was established, indicating that ClO_4^- is an excellent marker of fireworks or a burning event over all of the other analyzed parameters. SEM with EDS provided the best signature of the fireworks. The range of $\delta^{13}\text{C}$ of various origin and comparison with the present study range of -7.55‰ to -9.19‰ confirms that the freshly originated $\delta^{13}\text{C}$ in the lake water system closely resembles fire-generated carbon, i.e. black carbon. Microcosm and column-based transport studies simulating the mobility of black carbon particles in the presence of perchlorate and metals under different environmental conditions are needed to further the development of transport and fate models for perchlorate and black carbon particles.

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Appendix A. Supplementary data — Supplementary data to this article follows the References.

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Supplementary information: Figs. S1a–S1e; Tables S1 & S2.

Supplementary Information

Perchlorate behavior in the context of black carbon and metal cogeneration following fireworks emission at Oak Lake, Lincoln, Nebraska, USA

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Figure S1: Water quality parameters before, during and after July 4, 2015 and 2016 fireworks events: (a) pH; (b) dissolved oxygen; (c) redox potential; (d) turbidity; (e) total dissolved solids; and (f) electrical conductivity.

Table S1. Instrument conditions for LC-MS/MS analysis of perchlorate and chlorate.

Compound	MRM* transition	Cone voltage (V)	Collision voltage (V)	Retention Time (min)
¹⁸ O ₄ Perchlorate (Internal Standard)	107>89	50	30	5.82
Perchlorate	99>83	50	30	5.82
Chlorate	83>67	40	20	5.07

*Multiple Reaction Monitoring

Table S2. Water quality parameters before and after the fireworks display in the Oak Lake and Creek waters.

		Major Ions (mg L ⁻¹)													Chlorine species (µg L ⁻¹)			
		Br	F ⁻	PO ₄ ³⁻	SO ₄ ²⁻	Ca ²⁺	K ⁺	Mg ²⁺	Na ⁺	Cd	Co	Cu	Ni	Zn	Cl ⁻	Chlo	Perchlo	
Before Fireworks Display																		
OL#1E	7/2/16	0.09*	1.09	0.04	105	18.6	6.6	21.3	461	0.3	1.6	15.1	70.4	75	738	BD	BD	9.39
OL#1W		0.09*	0.55	0.04	107	19.4	6.5	21.9	416	Not Measured					765	BD	BD	8.58
OC#1DS		NM	0.28	0.33	66.7	16.0	6.4	18.5	169	0.2	3.4	11.4	33.2	48	328	BD	BD	3.21
After Fireworks Display																		
Sample ID	Date	Br	F	PO ₄ ³⁻	SO ₄ ²⁻	Ca ²⁺	K ⁺	Mg ²⁺	Na ⁺	Cd	Co	Cu	Ni	Zn	Cl ⁻	Chlo	Perchl	TOC
OL#2E	7/4/16	0.08	0.69	*0.08	103.1	20.8	7.8	21.7	432	0.4	3.8	12.2	15.4	46	6.99	BD	1.38	10.1
OL#2W		0.08	NM	0.07	105.1	21.8	7.7	22.5	458	Not Measured					740	0.115	3.98	9.87
OL#5E	7/8/16	NM	NM	0.06	95.8	16.1	8.9	18.6	402	0.2	3.3	7.0	16.2	30	701	BD	1.60	9.09
OL#5W		0.08	NM	NM	96.5	20.5	5.3	20.1	375	Not Measured					680	BD	2.05	8.95
OC#5US		0.04	0.36	0.26	34.1	46.2	7.1	12.6	110	0.2	3.6	7	21.5	34	90.2	BD	BD	4.7

(BD- Below Detection; *-Below Method Detection Limit; NM- Not Measured)