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The Fallout from Fireworks: Perchlorate in Total Deposition

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Abstract Recent studies have shown that natural perchlorate may be an important component to the general population exposure. These studies indicate that natural perchlorate is likely deposited by atmospheric deposition. Perchlorate concentration of total (dry + wet) deposition is relatively unstudied yet these measurements will aid in understanding natural levels in the environment. We sampled total deposition monthly at six sites in Suffolk County, Long Island, NY from November 30, 2005 until July 5, 2007. The mean perchlorate concentration is 0.21±0.04 (standard error) μg L^{-1} with a maximum value of 2.78 μg L^{-1}. Here we show up to an 18-fold increase above the mean concentration in July 2006 and July 2007 samples. It appears that this increase in perchlorate in total deposition is associated with Fourth of July fireworks.

Keywords Fireworks · Groundwater · New York · Perchlorate · Precipitation

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1 Introduction

While perchlorate is known to inhibit iodide uptake of the thyroid gland, whether low microgram levels of perchlorate in drinking water are a health concern is still highly debated (Blount and Valentin-Blasini 2006). The US Environmental Protection Agency has yet to establish a national drinking water standard, while many states have set advisory levels. New York State has implemented advisory levels of 18 μg L^{-1} ClO_4 for the public notification level and 5 μg L^{-1} ClO_4 for the drinking water planning level in groundwater. Advisory levels are as low as 1 μg L^{-1} in Massachusetts, Maryland and New Mexico (EPA 2005). Establishing background concentration of perchlorate in precipitation and groundwater, and determining whether the perchlorate is natural or anthropogenic is a prerequisite for determining drinking water standards.

Since the presence of perchlorate in precipitation has only recently been measured (Dasgupta et al. 2005; Barron et al. 2006), the sources of perchlorate in precipitation are not well known. A major source could be the formation of perchlorate in the atmosphere from chlorine species (Dasgupta et al. 2005). Perchlorate in the atmosphere may also be from sea spray since perchlorate is present in seawater (Martinelango et al. 2006). Perchlorate is present in surface soils of the southwest (Rao et al. 2007), thus it is conceivable that perchlorate in dust is picked up by wind, transported and deposited as dry deposition. An anthropogenic source of perchlorate in the atmosphere may be

fireworks. Atmospheric fallout from fireworks consists of fine particles of burnt black powder, paper debris and residue. Perchlorate in paper debris ranges from 302 to 34,200 μg kg^{-1} (DEP 2006). Two studies (Backus et al. 2005; Wilkin et al. 2007) show direct perchlorate contamination of lake water from fireworks displays.

The Massachusetts Dept. of Environmental Protection has determined that historic fireworks displays are the likely source of perchlorate contamination in two of the nine public water supply systems showing levels above 1 μg L^{-1} (Mass. DEP 2006). Although little information is available on the perchlorate content in fireworks their model predicts that groundwater should be contaminated to the tens of μg ClO_4 L^{-1} within 100 meters of the fireworks display. This assumes 1,000–2,000 aerial shells weighing a total of 1,361 kg, of which 40% is ClO_4 and the contaminated area (fireworks fallout area) is equal to 3,600 m^2.

To establish a perchlorate contribution from the atmosphere we collected monthly samples of total deposition at six sites in Suffolk County, Long Island, NY from November 2005 to July 2007 (Fig. 1). We analyzed samples for ClO_4 and also NO_3, NH_4, Cl, Br, I, SO_4, Na, Mg, K, Ca, Sr and B.

2 Methods

One hundred and eight total (wet plus dry) deposition samples were collected monthly for 20 months between November 30, 2005 and July 5, 2007 at six sites in Suffolk County, NY. Suffolk County is the eastern most county on Long Island, which extends east from Queens and Brooklyn. All sample sites are in or near urban areas (Fig. 1).

Samples were collected using All-Weather Precipitation Gauges purchased from Fisher Scientific. These gauges sample both wet and dry (total) deposition since they are not covered during dry periods. The sampling area of the gauge is 10 cm in diameter. The inner sampling device, used to determine rainfall, is 26 cm in height and 3.2 cm in diameter. Evaporation from these samplers is minimal due to the small opening at the top of the gauge. For example, annual rainfall totals for 2006 at our sites ranged from 110 to 130 cm which are only slightly less than the 137.4 cm value for 2006 reported by The National Weather Service for Islip, NY which is in the center of Long Island (http://www.weather.gov/climate). The variation between our sites and Islip, NY could be due to spatial differences as wet

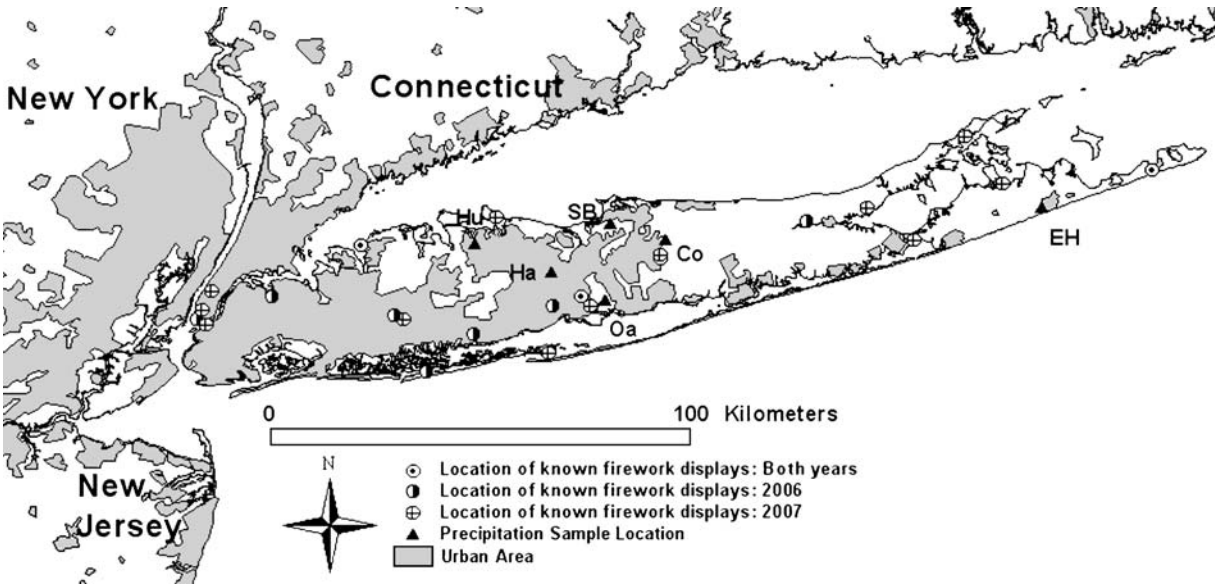

Fig. 1 Location of sample gauges in Suffolk County, Long Island, NY. Site names are abbreviated; *Hu* Huntington, *Ha* Hauppauge, *SB* Stony Brook, *Co* Coram, *Oa* Oakdale, and *EH* East Hampton. *Gray areas* are urban as mapped by the US Geological Survey according to the Digital Chart of the World, revised version of 1998 data. In general, urban areas are a concentration of at least 5,000 persons in continuous collection of houses where the community sense is well developed and the community maintains public utilities, such as, roads, street lighting, water supply, sanitary arrangements etc. Note that two firework display locations overlap near the Coram site. The covered symbol had firework displays both years

precipitation can vary as much as 20 cm (8 in.) across Long Island (Busciolano 2004).

Samples were filtered in the field using a 0.2-μm surfactant-free cellulose acetate (SFCA) filter for perchlorate analysis and 0.45 μm glass fiber filters for all other analysis. Samples were stored in sample rinsed, polypropylene vials untreated for all samples except nitrogen. Vials for nitrogen were acid rinsed with a 10% HCl solution before sample collection. Samples were stored in a cooler while in the field and then at 4°C until analyzed. Samples for nitrogen, once in the laboratory, were frozen until analyzed.

Perchlorate was analyzed using a sequential ion chromatography-mass spectroscopy/mass spectroscopy (IC-MS/MS) technique (Koester et al. 2000) with a method detection limit of 0.005 μg L^{-1}. To account for matrix effects, all samples were spiked with an oxygen-isotope (^{18}O) labeled ClO_4 internal standard. Each sample was measured in duplicate or triplicate and the precision was on average ±5%. B, Br, I, Mg, Na, Ca, K, Sr, Cl, N–NO_3, NH_4 and SO_4, were also analyzed using standard methods.

We used the program Minitab to perform One-way analysis of variance (ANOVA, unstacked) Turkey tests, with a 95% confidence interval. A one-way analysis of variance is a way to test the equality of three or more means at one time by using variances.

The HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model was used to model simple air parcel trajectories from known firework displays for 24 h, in 1 h spacing, from July 4, 2006 and July 4, 2007 at 50 m height (Draxler and Rolph 2003).

3 Results

The mean monthly perchlorate concentration of total deposition samples is 0.21±0.04 (standard error) μg L^{-1}. The maximum monthly value is 2.78 μg L^{-1}. The mean value is similar to that reported from Lubbock, TX, 0.20 μg L^{-1} (Dasgupta et al. 2005), while the maximum is similar to the highest value reported in Ireland, 2.82 μg L^{-1} (Barron et al. 2006). What is striking about our data set is the large peak in perchlorate concentrations in the July samples for both 2006 and 2007 collected after the Fourth of July (Fig. 2). Many communities in and around the Metropolitan New York area, which includes Long Island, have large firework celebrations on the evening

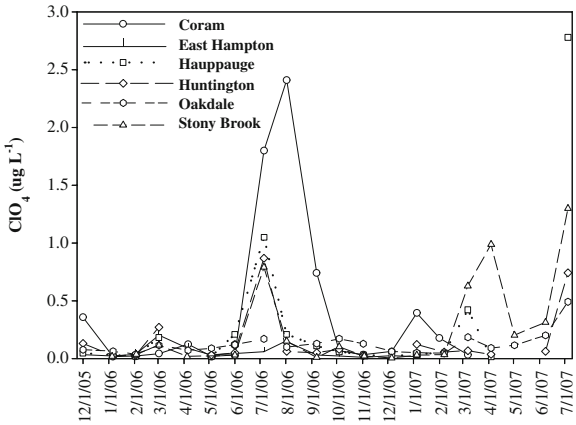

Fig. 2 Monthly perchlorate concentrations for total deposition samples. Collection at Coram was discontinued after March 2007 and discontinued at East Hampton after January 2007

of, and leading up to the Fourth of July. Although fireworks are illegal in New York State, residents also set off fireworks in their neighborhoods. We have located (Fig. 1) known displays during the Fourth of July celebrations reported in Newsday (July 2, 2006 and July 4, 2007), using oral communication with local town clerks, from information on a local fireworks company's website (http://www.grucci.com) and other sources (http://hamptons.plumtv.com; http://www.sagharboryc.com). We have not located all the firework displays, but we believe that we have located the larger ones. Modeled air trajectories, using HYSPLIT, in western Suffolk County, NY, and Atlantic City, NJ, travel in a north to northeast pattern that pass over the rain gauges in Suffolk County. Modeled air trajectories in New York City travel in a similar pattern but do not pass over Suffolk County.

Excluding the samples from July the mean concentration of perchlorate in precipitation is 0.12±0.03 (standard error) μg L^{-1}. Perchlorate concentrations are significantly higher in July compared to all months except August ($p<0.05$). Mean values vary between the six sites, although there was no statistical difference ($p<0.05$). Coram has the highest mean value of 0.40± 0.70 (standard deviation) μg L^{-1}. East Hampton has the lowest mean of 0.06±0.06 μg L^{-1}. Hauppauge has a mean value of 0.27±0.14 μg L^{-1}, Huntington a value of 0.14±0.06 μg L^{-1}, and Stony Brook a mean value of 0.25±0.09 μg L^{-1}. There was no significant correlation (defined as $R^2>0.5$) between ClO_4 and the other ion analyzed.

4 Discussion

In our study area, wet deposition occurred between the Fourth of July and the time of sample collection for both years of this study (http://www.weather.gov/climate). These three storms originated inland and progressed in a west to east direction, moving slightly north during the 2006 events, as noted on NOAA archived radar images (http://www4.ncdc.noaa.gov). The timing of wet deposition combined with modeled air trajectories indicates a high probability that firework fallout is the cause of increased perchlorate concentration in the July samples. The effects of atmospheric pollution from fireworks have been reported by other studies noting increases in SO_2, NO_2, suspended particles and metallic elements (Moreno et al. 2007; Ravindra et al. 2003). Precipitation scavenging can effectively remove pollutants from the atmosphere, with wet deposition being more effective than dry deposition (Loosmore and Cederwall 2004).

Two studies (Backus et al. 2005; Wilkin et al. 2007) which show direct contamination of lake water from firework displays measured perchlorate concentration adjacent to the displays. Our rain gauges are, at the closest, a few km from known displays (Fig. 1). Thus wind properties and storm direction play a role in where the firework fallout eventually settles. Our rain gauges are mostly in areas zoned for business, except for Stony Brook which is on a university campus and Coram, which is in a residential neighborhood. Coram, coincidentally, had the highest concentration in July 2006. Sampling at that site was discontinued after March 2007. Coram is also very near known public firework displays (approximately 1.5 km). Oakdale, which is also near known firework displays, has relatively low concentrations with a value of 0.17 μg L^{-1} on July 6, 2006 and 0.49 μg L^{-1} on July 5, 2007. It is likely that the wind and storm direction did not carry fireworks contamination towards the Oakdale study site in 2006 but that some contamination was received in 2007. Hauppauge measured 2.78 μg L^{-1} on July 5, 2007. There are no known fireworks displays near Hauppauge, yet fireworks fallout from the south is likely influencing Hauppauge rain water. Additionally, there may have been fireworks near Hauppauge that we are unaware of. It is likely that the perchlorate from fireworks in our precipitation samples have traveled some distance in the atmosphere and perchlorate concentrations of precipitation adjacent to large fireworks displays may be much higher than we report.

Our study showed that precipitation concentrations after Fourth of July fireworks displays can be 18 times as much as background levels confirming that, "fireworks constitute a potential source of increasing importance, as fireworks use is rising exponentially with average consumption at 4.5×10^7 kg per year" (Dasgupta et al. 2006). As a result we need to be concerned about the potential impact on our groundwater of increased perchlorate in precipitation associated with fireworks.

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