

Perchlorate and ion chemistry of road runoff

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Environmental context. Recognising that road flares and air bags may contribute perchlorate to road runoff, we analysed perchlorate in runoff from two accident-prone suburban highways during a period of five rain events. This runoff reaches recharge basins where it then infiltrates into the groundwater. The concentrations of perchlorate averaged $\sim 2 \mu\text{g L}^{-1}$, high enough to be of concern if the drinking water standard for perchlorate were in the low μg levels.

Abstract. First flush samples of road runoff were sampled in April 2006 corresponding with five rain events at 12 catch basins and two recharge basins in Suffolk County, NY. Most runoff here is directed into recharge basins or sumps that drain directly into the sole source aquifer. Thus, contaminants from road runoff can contaminate groundwater. In addition to ClO_4 , we present data for Cl, Na, Br, Sr, and nitrogen as nitrate (N-NO_3) as they are the dominant ions in the most probable sources of ClO_4 to road runoff, presumably road flares, road salt, air bags and road-side fertilizers. Correlations between the ions indicate that road salt elevates concentrations of Na, Br and Cl in road runoff. The average ClO_4 value is 2.18 ± 0.66 (standard error of the mean) $\mu\text{g L}^{-1}$ for the catch basins and $2.98 \pm 0.87 \mu\text{g L}^{-1}$ for the two recharge basins. Excess ClO_4 in the present study appears mainly from road flares. On average, only 47% of the ClO_4 in the catch basins and 11% in the recharge basins can be accounted for by bulk precipitation.

Additional keywords: groundwater, New York, non-point source, road flares, road salt.

Introduction

Since perchlorate was added to the USA Environmental Protection Agency (EPA) contaminant candidate list in 1998,^[1] perchlorate has been the focus of much research and debate. Perchlorate inhibits iodide uptake of the thyroid gland,^[2] which is of particular concern for those with iodide deficiencies. This health concern coupled with the mobility of perchlorate poses a threat to groundwater. Suffolk County, Long Island, NY, is particularly sensitive to groundwater contamination as all potable water is derived from the local aquifers. The US EPA has designated the Long Island aquifers as a sole source aquifer (<http://www.epa.gov/region02/water/aquifer/>, accessed 7 December 2008). New York State has implemented advisory levels of $18 \mu\text{g ClO}_4^- \text{L}^{-1}$ for the public notification level and $5 \mu\text{g L}^{-1}$ for the drinking water planning level in groundwater. Advisory levels are as low as $1 \mu\text{g L}^{-1}$ in Massachusetts, Maryland and New Mexico.^[3]

Perchlorate contamination is commonly associated with rocket fuel propellant or Chilean nitrate fertilizer use, yet perchlorate is detected in groundwater samples where these two common sources are not known to be present. In dry regions, atmospheric deposition may account for the unknown perchlorate source.^[4,5] In temperate regions where natural perchlorate does not concentrate, other sources must be considered. In Suffolk County, perchlorate is present in groundwater wells for which there is no known source of perchlorate. By December 2005, Suffolk County Water Authority identified 104 supply wells with ClO_4 concentrations above $0.5 \mu\text{g L}^{-1}$; of these, 21 were above $6 \mu\text{g L}^{-1}$. Although perchlorate can degrade owing to bacterial reduction,^[6,7] groundwater in Suffolk County is

high in oxygen and nitrogen, which would limit the amount of perchlorate degradation (C. Young and G. N. Hanson, Stony Brook University, unpubl. data, 2008).

Road safety flares and car air bags are suggested as possible non-point sources of perchlorate.^[8] Some air bags contain 110–1000 mg of KClO_4 mixed with Zr, Ti and B.^[9] Road safety flares are typically composed of (by weight) 75% $\text{Sr}(\text{NO}_3)_2$, and <10% each of KClO_4 , S, and a binder.^[9] Although some flares do not contain perchlorate, the road flares purchased by Suffolk County Police department have at least ‘some’ perchlorate present (K. Harrison, Orion Safety Products, pers. comm., 2006). Leaching from a road flare manufacturing plant has contaminated groundwater in Santa Clara Valley, CA.^[10] The distribution of perchlorate was generally between 4 and $10 \mu\text{g L}^{-1}$. Prompted by this contamination event, Silva^[11] measured perchlorate content from unburned, partially burned and fully burned road flares. He found that unburned road flares contained 3600 mg of perchlorate per flare, and that fully burned flare residue contained 1.9 mg perchlorate per flare. Based on total flare sales, average cost of a flare, and 3600 mg of perchlorate per flare, researchers have estimated that 140 tons ($\sim 127\,000 \text{ kg}$) of perchlorate is used each year for road flares in the continental United States.^[8] Although road flares have been recognised as a non-point source, there is relatively little research analysing their impact on the environment. Dasgupta et al.^[9] suggested that road flares are not a significant source of contamination based on the small portion of perchlorate used for flare production compared with other uses and on the fact that flares are not commonly disposed of before use. Veeger et al.^[12] regularly found less than the detection limit of $4 \mu\text{g L}^{-1}$ for water

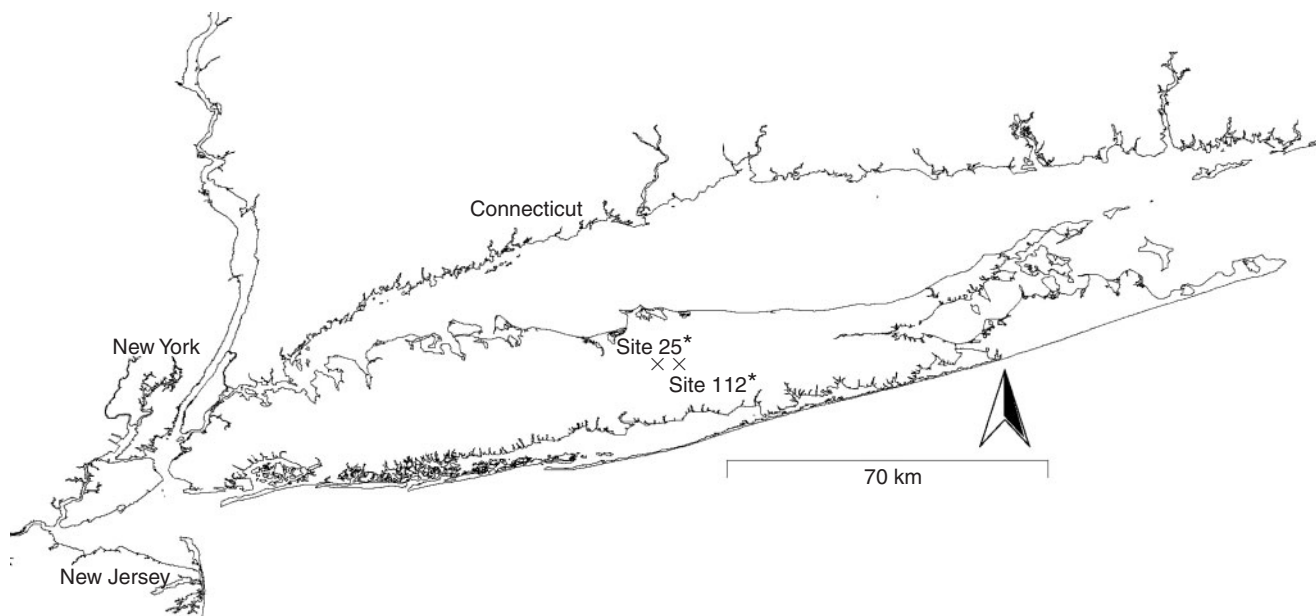


Fig. 1. Map of study sites. *See Fig. 2a, b for site details.

in ditches that collect road runoff where flares had been used in Rhode Island, USA.

Perchlorate concentrations were investigated in road runoff from suburban highways in Suffolk County, Long Island, NY, with a high incidence of traffic accidents, on the assumption that road flares are a possible non-point source of perchlorate contamination to groundwater. Our main purpose was to measure the concentration of ClO_4^- in road runoff. To aid in determining the sources of perchlorate in road runoff, we used Cl, Na, Br, Sr, and nitrogen as nitrate (N-NO_3^-) concentrations measured in the same road runoff samples.

Methods

Site locations

Two locations were chosen in Suffolk County, NY (Fig. 1), to evaluate perchlorate concentrations in road runoff. These locations are on State Highways in suburban areas and, as such, they are adjacent to development such as shopping centres and gas stations. According to Suffolk County Police Department statistics from January 1999 through December 2000, these sites had the highest incidence of traffic accidents in the township of Brookhaven. The Police Department, however, does not keep records as to whether road flares were used at the site of an accident. We have seen that road flares are not only ignited after dusk but are used for accidents that occur during high-traffic periods, independently of the size of the accident. One police officer we spoke with along Site 25 reported that road flares are usually avoided, owing to the mess involved, and high beams on the police cars are the preferred method. Yet persons involved in accidents may ignite road flares even if the police officer on call does not. In addition, the officer stated that road flares are not cleaned up after use.

Site 112 is along State Highway 112 (Fig. 2a) between Horse Block Road and Express Drive North, north of the Long Island Expressway ($40^\circ 49' 39'' - 27'' \text{N}$ and $72^\circ 59' 51'' - 33'' \text{W}$). There were 237 traffic accidents between January 1999 and December 2000. Seven accidents occurred during the sampling period between 1 and 16 April 2006; none of these accidents occurred

after sunset, which was ~ 1930 hours this time of year. One accident, on 6 April, occurred at 1745 hours that was classified as a motor vehicle accident with injuries. An accident with injuries may involve more vehicles and thus warrant the use of flares even though it might be light enough that they are not needed. The study area covers ~ 0.32 km of roadway. Samples were taken at four catch basins at this site. Catch basins are grated at the road surface and capture road runoff into an open pit; some basins direct this runoff through pipes to recharge basins. Sampling locations labelled 1 and 2 are at traffic lights and those labelled 3 and 4 are at shopping centre entrances (Fig. 2a).

Site 25 is along State Highway 25 (Fig. 2b) west of Nicolls Road and east of Oak Street ($40^\circ 51' 39'' - 27'' \text{N}$ and $73^\circ 05' 51'' - 04' 3'' \text{W}$). There were 430 total accidents from January 1999 through December 2000. Site 25 covers a greater length of roadway (3.9 km) and was the location of more accidents than Site 112. At Site 25, 29 accidents occurred during the sampling period. Two after-sunset accidents included injuries. Five accidents that occurred during the day also included injuries. Samples were collected at nine catch basins and two recharge basins. Sample 1 was taken at a traffic light for a fire department station and sample locations 2, 4 and 6 are at intersections with traffic lights. Other samples were located at sidewalk curbs (Fig. 2b).

Sampling

Road runoff samples from catch basins and recharge basins were collected within 24 h after five different rain events during April 2006. Nalgene stormwater samplers (cat. nos. 1100–1000, supplied by Fisher Scientific, <http://www.fishersci.com>, accessed 2 February 2009) were installed in four catch basins at Site 112 and at nine catch basins at Site 25. These samplers allow collection of the 'first flush' of runoff as they fill and seal off after 1 litre is collected. The samplers were hung beneath catch basin grates. Some grates had impeded flow due to sand build-up near the grate. We did our best to remove this sand; however, there was excess sand left on the roads associated with sanding and salting during earlier snowstorms. We found the best method to

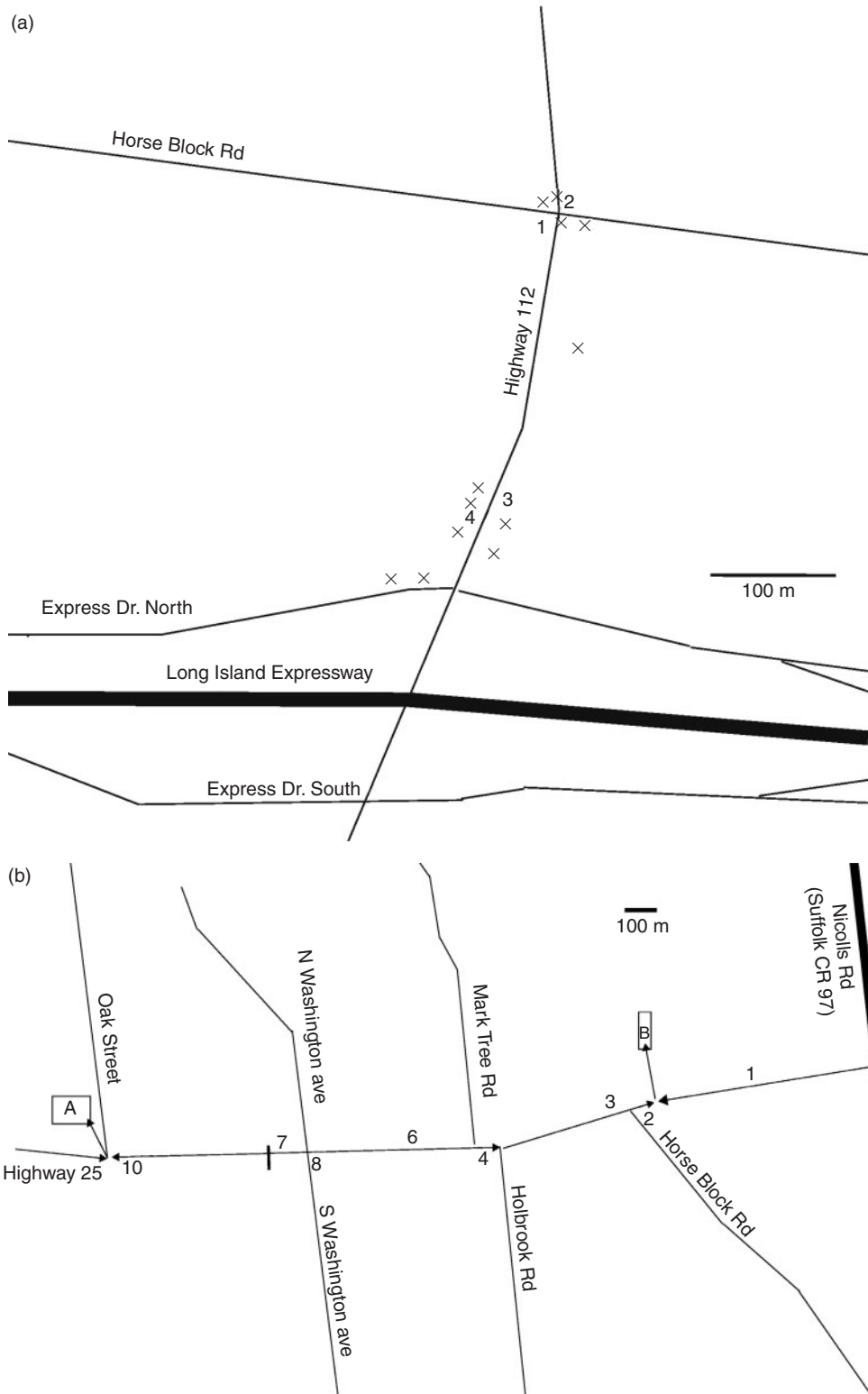


Fig. 2. Details of Site 112: (a) a cross (x) indicates a catch basin that was not sampled. Numbers correspond to sample numbers. Details of Site 25: (b) numbers correspond to sample numbers. A and B are recharge basins. The arrows indicate the direction of the road runoff flow from the catch basins.

determine placement of the samplers was to observe the direction of road runoff flow during a rain event.

Two recharge basins, which recharge the local groundwater and receive water from Highway 25, were also sampled (Fig. 2b). These basins both had standing water at all sampling events.

Residence times of water in recharge basins can vary from a few hours to months, with the average on Long Island being 4 days in wet periods and 20 days with no wet precipitation.^[13] We did not calculate residence time at these basins because we were not able to measure the road runoff inputs or the depth of

Table 1. Average ion concentrations of water in catch basins and recharge basins and bulk precipitation

s.e. is the standard error of the average (Avg.). The number in parentheses next to the sample group is the number of samples collected; not all samples could be analysed for all ions. Samples below detection limits were treated as a zero value and values above the linear range of the analytical method were not included in the calculations. Detailed chemistry of the samples can be found on the web.^[27] N-NO₂, nitrogen as nitrite; N-NH₄, nitrogen as ammonium; N-NO₃, nitrogen as nitrate; nd, not determined

	N-NO ₂ mg L ⁻¹	N-NH ₄ mg L ⁻¹	N-NO ₃ mg L ⁻¹	ClO ₄ μg L ⁻¹	Cl mg L ⁻¹	SO ₄ mg L ⁻¹	Na mg L ⁻¹	Mg mg L ⁻¹	K mg L ⁻¹	Ca mg L ⁻¹	I μg L ⁻¹	Br μg L ⁻¹	Sr μg L ⁻¹	B μg L ⁻¹
Site 112 catch basins (14)														
Avg.	0.41	1.3	2.2	2.5	156	46	101	1.6	4.9	17	11	49	64	231
s.e.	0.22	0.4	0.5	0.9	42	13	24	0.4	1.6	5	2	12	12	101
Site 25 catch basins (19)														
Avg.	0.07	2.0	1.2	2.0	160	38	101	2.5	3.0	25	12	92	60	98
s.e.	0.02	0.5	0.3	0.9	37	8	20	0.7	0.5	10	2	23	13	15
All catch basins (33)														
Avg.	0.21	1.8	1.6	2.2	158	41	101	2.1	3.8	21	11	73	62	153
s.e.	0.09	0.3	0.35	0.7	27	7	15	0.4	0.8	6	1	14	9	44
Both recharge basins at Site 25 (10)														
Avg.	0.02	0.49	0.29	3.0	306	8.3	182	1.4	1.3	8.6	4.6	38	91	54
s.e.	0.00	0.25	0.04	0.9	38	1.2	15	0.1	0.1	0.6	0.2	4	8	6
Bulk precipitation (115)														
Avg.	<0.1	0.16	0.25	0.20	3.6	2.6	2.3	0.28	0.6	0.5	6.7	9.1	3.5	26
s.e.	nd	0.05	0.03	0.04	0.3	0.2	0.2	0.02	0.1	0.1	1.1	0.5	0.3	3

the basin. The surface water near the inflow pipe of the basins was sampled with each collection of the catch basin samples. Sampler 10 drains into recharge basin A and samplers 1–8 drain into recharge basin B (Fig. 2b). Sampler 9 never received water.

The sample bottles were collected within 24 h after each rain event, and taken directly back to the laboratory, where they were filtered with a 0.2-μm surfactant-free cellulose acetate (SFCA) filter for perchlorate analysis and a 0.45-μm glass fibre filter for major ion analysis and stored in sample-rinsed polypropylene sample bottles at 4°C until analysis. Perchlorate was analysed using a sequential ion chromatography–mass spectroscopy/mass spectroscopy (IC-MS/MS) technique^[14] with a method detection limit of 0.1 μg L⁻¹. To account for matrix effects, all samples were spiked with an oxygen isotope (¹⁸O)-labelled ClO₄ internal standard. The precision determined from replicate analysis was ±5%.

The ions B, Br, I, Ca, Mg, Na, K and Sr were analysed by Activations Laboratory (Ancaster, ON, Canada) using inductively coupled plasma mass spectrometry. Detection limits were as follows: B, 1 μg L⁻¹; Br, 3 μg L⁻¹; I, 1 μg L⁻¹; Ca, 700 μg L⁻¹; Mg, 2 μg L⁻¹; Na, 5 μg L⁻¹; K, 30 μg L⁻¹; Sr, 0.04 μg L⁻¹. Most samples above the linear range of this analytical method were reanalysed by direct coupled plasma optical emission spectroscopy in the Department of Geosciences at Stony Brook University. These high-range values were 35 mg L⁻¹ for Na, 20 mg L⁻¹ for Ca and Mg, and 200 μg L⁻¹ for Sr. The ions Cl, nitrogen as nitrite (N-NO₂), N-NO₃, nitrogen as ammonium (N-NH₄), PO₄ and SO₄ were analysed in the Marine Science Research Center at Stony Brook University, using a Lachat's QuickChem 8500 Flow Injection Analysis System (Hach Company, Loveland, CO). Detection limits are 0.1 mg L⁻¹ for N-NO₂, N-NO₃, N-NH₄ and PO₄, and 1 mg L⁻¹ for SO₄ and Cl. The precision for these analyses is 10%.

A total of 115 samples of bulk atmospheric precipitation (including wet precipitation (rain, snow, or fog) or dry precipitation (absorbed gaseous and particulate matter, aerosol particles or dust)) were collected monthly for 20 months between 30 November 2005 and 5 July 2007 at six locations in Suffolk County, NY. These samples were processed with the same protocol as the road runoff samples.

Road salt samples from the Stony Brook University storehouse and from one Suffolk County Highway storehouse were analysed for perchlorate. According to the New York State Procurement Service Group, salt in Suffolk County is purchased from the International Salt Co., which reports that its salt is >98.5% pure NaCl (<http://www.ogs.state.ny.us/purchase/>, accessed 18 January 2009). Approximately 5 g of road salt was dissolved in 50 mL of deionised water, filtered with a 0.2-μm SFCA filter and stored at 4°C until analysis. The Cl content of the Stony Brook University sample was measured with an automated potentiometric titration producing silver chloride (AgCl) using a CMT 10 Chloride titrator (Radiometer, Copenhagen, Denmark) by the Marine Science Research Center at Stony Brook. From this concentration, the concentrations of the other elements could be estimated using ion to chloride mass ratios from the literature.^[15,16] Perchlorate was analysed as mentioned previously.

Results

The average ion concentrations of water in the catch basins and the recharge basins are greater than the average concentrations of bulk precipitation (Table 1) for all ions except N-NO₃. The water

Table 2. Average percentage contribution from bulk precipitation to road runoff

Calculated as the average concentration of bulk precipitation divided by the individual concentrations in the catch basin and recharge basin samples. The average percentage contribution is presented here. N-NO₂, nitrogen as nitrite; N-NH₄, nitrogen as ammonium; N-NO₃, nitrogen as nitrate; nd, not determined

	N-NO ₂	N-NH ₄	N-NO ₃	ClO ₄	Cl	SO ₄	Na	Mg	K	Ca	I	Br	Sr	B
All catch basins	nd	71	93	47	7	17	5	33	33	16	56	38	6	38
Recharge basins	nd	>100	100	11	1	34	1	21	45	15	86	28	4	50

Table 3. Linear correlations (R² values) of the ions with perchlorate for catch basins and recharge basin samples

N-NO₂, nitrogen as nitrite; N-NH₄, nitrogen as ammonium; N-NO₃, nitrogen as nitrate. Values in bold are considered significant ($P < 0.05$)

	All catch basins	Site 112 catch basins	Site 25 catch basins	All recharge basins
N-NO ₂	0.37	0.89	0.47	0.26
N-NH ₄	0.09	0.25	0.08	0.00
N-NO ₃	0.39	0.64	0.28	0.12
Cl	0.14	0.18	0.12	0.65
SO ₄	0.27	0.66	0.10	0.00
Na	0.14	0.34	0.05	0.51
Mg	0.08	0.52	0.03	0.47
K	0.11	0.22	0.06	0.02
Ca	0.08	0.80	0.02	0.38
I	0.22	0.33	0.16	0.55
Br	0.02	0.39	0.00	0.44
Sr	0.50	0.81	0.46	0.61
B	0.30	0.83	0.04	0.04

in the recharge basins has essentially the same concentration of N-NO₃ as bulk precipitation, but the water in the catch basins has higher concentrations than bulk precipitation. Bulk precipitation may account for a large portion of the nitrogen and iodide in the samples and a low portion (<16%) of Cl, Na, Ca and Sr (Table 2). Half of the perchlorate could be attributed to bulk precipitation inputs in the catch basins and 11% in the recharge basins (Table 2). The average ion concentrations of the catch basins between Site 112 and Site 25 do not differ by more than the standard error of the mean for all ions except for B, N-NO₂ and N-NO₃, with Site 112 having higher average values, and for Br, with Site 25 having a higher average value (Table 1). The average values of all catch basins are higher than the recharge basin averages except for Cl, Na and Sr, where the values for the recharge basins are greater.

Perchlorate is not correlated ($R^2 < 0.5$, 95% confidence interval) with any of the ions for water from all catch basins (Table 3). At Site 112, perchlorate concentrations of water in catch basins are positively correlated with N-NO₂, N-NO₃, Ca, Mg, SO₄, Sr and B. Perchlorate concentrations of water collected at the catch basins of Site 25 are correlated with N-NO₂ and Sr. Perchlorate concentrations of water collected from the recharge basins are positively correlated with Cl, Na, Mg, Sr and I. Keep in mind that the linear correlations indicate a correlation of the ions based on one source; ions may not be correlated because multiple sources account for concentrations of the ions.

Major sources of contamination to road runoff are auto exhaust, road de-icers, wear and tear of automobiles and brake-pad wear.^[17] Table 1 in Breault and Granato^[17] details the characteristics of selected elements of potential sources to highway runoff; part of the table is repeated in the following text.

Auto exhaust contains B, Br, Ca, Mg, Na, N, K and Sr. Dust from brake pads contains Mg, Cl and Ca. Bromide is present in fuel. Nitrogen can be present in roadside fertilizers. Road flares contain mostly K, Sr, NO₃ and ClO₄; however, most of the NO₃ and ClO₄ should be consumed during use if they burn completely. De-icers are mostly Cl, Na and Ca; however in Suffolk County, they use only NaCl, with minor amounts of Br, SO₄, B, Mg, N, K and Sr, as well as ClO₄ (as concluded in the present study).

Few studies have characterised the major and minor ion concentrations in auto exhaust and other roadway sources of contamination; instead, most research has been concerned with heavy metal or hydrocarbon contamination. A paper that mentioned mass percentages of Cl, K, Ca, Br, Sr, Mg, Na, Cl, NO₃ and SO₄ of exhaust from automobiles with and without catalytic converters, paved road dust, brake dust and tyre dust^[18] was insufficiently detailed to be able to calculate concentrations of the ions. (Catalytic converters have been required on cars in the United States since 1975; the percentage of cars without catalytic converters in 2006 should be negligible.) However, the mass ratios of the ions aid in determining sources of contamination to road runoff (Figs 3 and 4).

Here we use Cl, Na, Br, Sr and N-NO₃ to evaluate sources as they are the dominant ions in the most probable sources of ClO₄ to road runoff, presumably road flares, road salt and fertilizers. Air bag inflation during a collision is a result of the formation of a mixture of gases and aerosols in which perchlorate is sometimes used as an oxidant.^[19] It is not clear that a significant fraction of perchlorate salts can survive the reaction or that they can escape from the interior of a car.

The Cl to Br mass ratio (mg : mg) of automobile exhaust with catalytic converters is 61, paved road dust and tyre dust are both 30, and brake dust is 38. The auto and road ratios are not similar to those of the catch basin or recharge basin samples (Fig. 3b). Road salt Cl to Br ratios in the literature range from 250 000 to 2000.^[15] Most samples lie within this range (Fig. 3b). The samples at Site 25 show positive linear correlations between Br and Cl concentrations in the catch basins ($R^2 = 0.85$) and in the recharge basins ($R^2 = 0.70$). The Na to Cl mass ratio of exhaust from automobiles is 0.6, paved road dust is 1, tyre dust is 1.1 and brake dust is near zero. Road salt Na to Cl mass ratio for sodium chloride is 0.65.^[15] The Na v. Cl plot suggests that tyre dust and road dust, at low concentrations, and at higher concentrations auto exhaust in addition to road salt are influencing the Na and Cl concentrations (Fig. 3a). All samples show positive linear correlations between Na and Cl with an R^2 of 0.96 in the catch basins at Site 112, an R^2 of 0.88 in the catch basins at Site 25 and an R^2 of 0.80 in the recharge basins.

We found that the salt used by Stony Brook University had 56% Cl, which is in agreement within uncertainty of a value of between 59 and 61% as suggested by the International Salt Co. The road salt collected from campus and the county stockpiles contain 64 and 7.8 $\mu\text{g ClO}_4 \text{ kg}^{-1}$ solid respectively. New

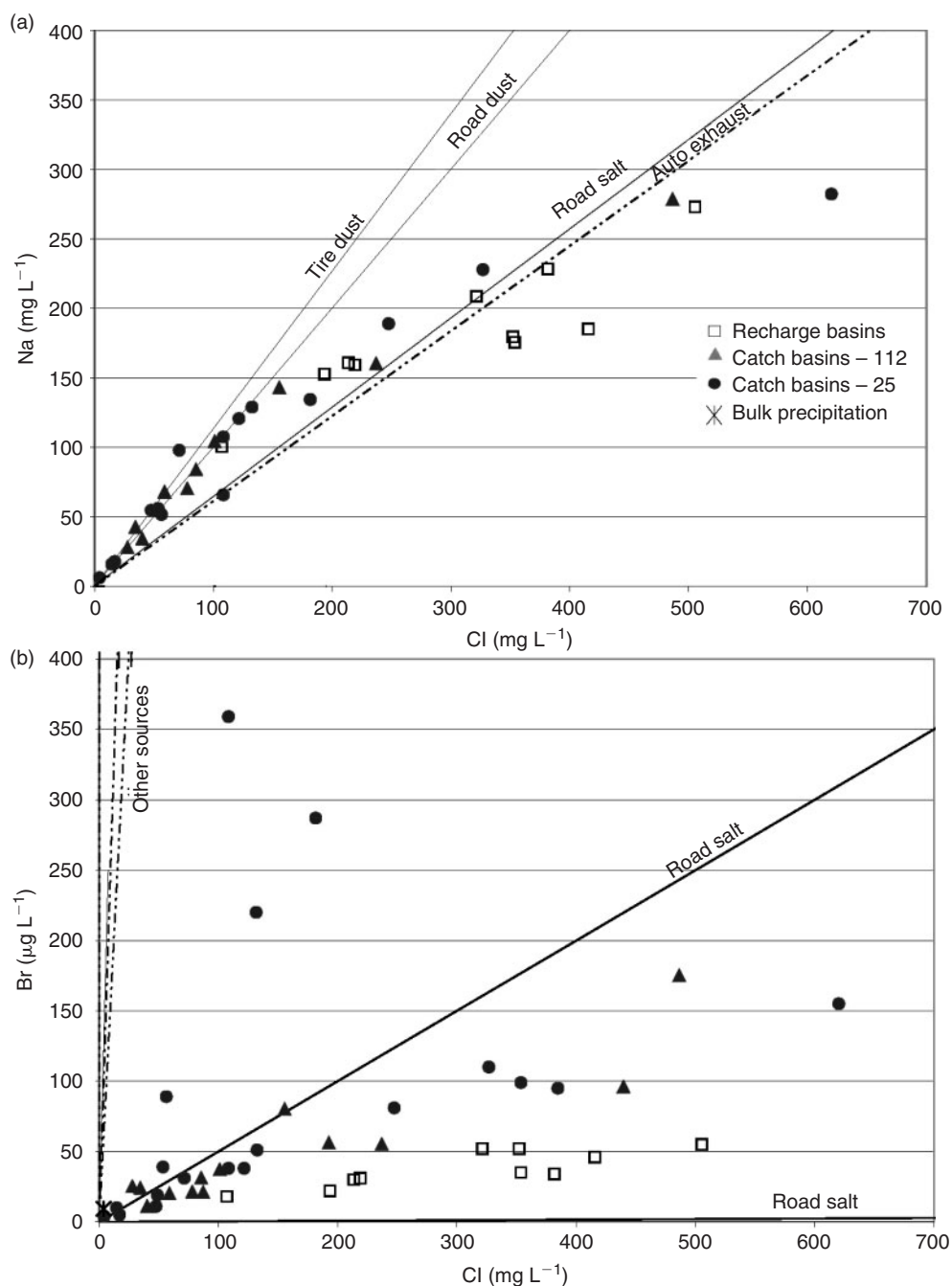


Fig. 3. Chloride concentrations plotted v. Na (a) and Br (b). Bulk precipitation is plotted as an average value and has a very low concentration near 0,0. Mass ratio lines are plotted next to the name of the source.

York State uses an annual average of 10 300 kg road salt per lane-km.^[20] The New York State Department of Transportation requires application of 63–76 kg salt per lane-km per storm. There are four lanes on both Highway 112 and Highway 25, two in each direction. At Site 112, road salting could account for 640–6204 μg ClO₄ per event for the entire study area. Site 25 could receive 7800–75 600 μg ClO₄ per event for the entire study area due to road salting. Assuming the maximum amount of ClO₄ applied and a salting application before each rain event, concentrations of ClO₄ would be diluted to less than 0.5 μg L⁻¹ in road runoff. There was 3.8 inches (9.6 cm) of snow during March 2006, and although snow was not reported during our

study period, salting could have occurred in anticipation of a large storm. Residue, presumably from road salt, was visible on the roadways during sampling. Perchlorate was only measured in two salt samples and therefore we do not have a good estimate of the average concentration, as trace element concentrations are likely variable in salt deposits. Only a few samples fall near the Cl to ClO₄ mass ratio line for road salt (Fig. 4a). Chloride and perchlorate are only linearly correlated in recharge basins but this correlation is not similar in slope to the road salt ratio line (Table 3).

Silva^[11] measured both perchlorate and nitrate concentrations in road flares and the relationship between the two ions

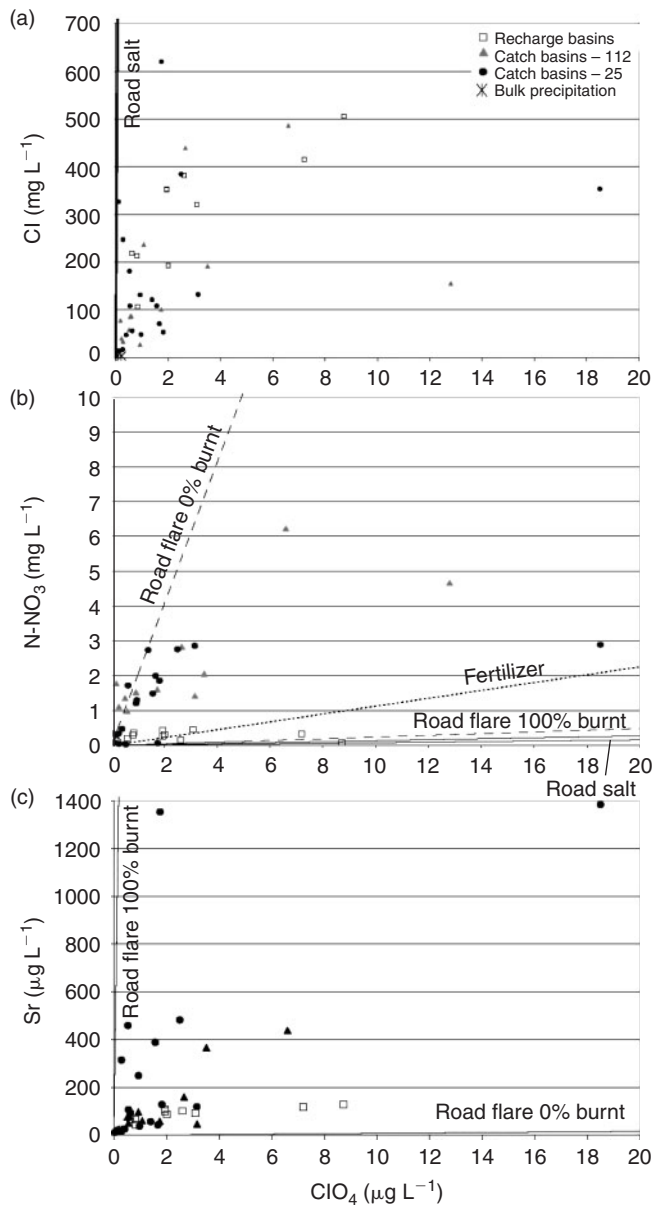


Fig. 4. Perchlorate concentrations plotted v. Cl (a), N-NO_3 (b) and Sr (c). Bulk precipitation is plotted as an average value and has a very low concentration near 0,0. Mass ratio lines are plotted next to the name of the source. Linear correlations of the ions to ClO_4 are in Table 3.

may distinguish road flare use. A fully burnt flare had an N-NO_3 to ClO_4 mass ratio of 24 (mg : mg). An unburned road flare had a mass ratio of 2. The catch basin samples appear to be highly influenced by flares that have not been burnt to completion (Fig. 4b). Perchlorate and nitrate are present in some organic fertilizers. The N-NO_3 to ClO_4 mass ratio for Bulldog Soda, which is sodium nitrate derived solely from mined Chilean caliches, is 113.^[21] This is the main source of perchlorate in organic fertilizers but it is conceivable that this ratio will vary depending on the fertilizer. The road salt mass ratios are 8 and 14 based on the campus road salt sample and the reported Cl to NO_3 ratio in the literature.^[15] Most samples fall above the mass ratio lines of fertilizer, road salt and 100% burnt road flares, with the recharge basins showing the most influence from these sources. Fertilizer may have been used during

the study period because some products recommend an early to late spring fertilizer application (February to June). Nitrate is only correlated with perchlorate in the catch basins at Site 112 (Table 3). Furthermore, the higher concentrations of N-NH_4 in road runoff compared with bulk precipitation could be due to fertilizer use. Any contribution of perchlorate from fertilizer use is likely low as the current use of Chilean nitrate fertilizer is low nationally;^[22,23] however, the Suffolk County Water Authority is promoting organic fertilizer use and one of the fertilizers used by the Water Authority contains Chilean nitrate.^[24,25]

Strontium and perchlorate are highly correlated in all sample locations (Table 3). The road flare Sr to ClO_4 mass ratio for an unburned flare is based on the molar mass of the composition of road flares, a value calculated as 0.82 (Fig. 4c). As perchlorate is used up during the use of the flare, this ratio will increase. It is possible that the catch basin sample concentrations of Sr and ClO_4 are influenced by road flares that were not burnt to completion. It is also possible that if road flares were used, air bags could have been deployed during the accident, possibly increasing perchlorate content in road runoff. The only evidence of air bag use, although anecdotal, is the correlation of perchlorate with boron in the catch basins of Site 112, because boron is a trace element used in air bags.

In summary, the Sr and N-NO_3 v. ClO_4 plots strongly suggest that partially burnt road flares may be an important source of perchlorate. The Na v. Cl plots show that road salt, tyre dust and road dust are important sources of Na and Cl. The Br v. Cl plot suggests that road salt is the main source of Br and Cl. However, the Cl v. perchlorate plot shows that most waters have a much lower Cl to ClO_4 ratio compared with that in the road salt measured in the present study.

Discussion

On average, concentrations of perchlorate in catch basin samples are higher than in bulk precipitation (Tables 1 and 2), suggesting that there are other sources of perchlorate in road runoff. Lower concentrations of some ions in the recharge basins compared with the catch basins may be due to dilution because the samples from the catch basins only receive a first flush of runoff from the highways, which should be expected to be more contaminated than later runoff in intense rain events.^[26] Also, the recharge basins receive runoff from other impervious surfaces besides roads, such as parking lots, which would be expected to have less contaminants, especially from road salt and road flares.

Road salt appears to be an important source of Na and Cl for samples with higher concentrations but not a source of ClO_4 (Figs 3 and 4). The plot of Cl v. ClO_4 (Fig. 4a) clearly shows that road salt is not a major source of ClO_4 , which is consistent with our mass balance calculation suggesting that road salt should add less than $0.5 \mu\text{g L}^{-1}$ if the roads had been salted before each rain event, which is unlikely. The most probable source of most of the perchlorate in road runoff is from road flares as the N-NO_3 v. ClO_4 and Sr v. ClO_4 suggest that the perchlorate is mostly from partially burnt flares (Fig. 4).

We have presented possible sources of perchlorate to road runoff in areas with high incidence of traffic accidents, which include road salt and road flare use and suggest that, partially, road flares are probably the major source of perchlorate. In Suffolk County, NY, as well as other areas that direct road runoff to groundwater recharge basins, the concentrations measured in the current study could be of concern for groundwater quality. Although concentrations of most samples are below the

NY state drinking water planning level of $5 \mu\text{g L}^{-1}$, 10% of the samples are above this level. As ClO_4 is present in groundwater wells in Suffolk County, NY, for which no known source of ClO_4 is present, road runoff may now be considered a possible non-point source of pollution in these wells.

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