

Canopy Interception of Acid Deposition in Southern Ontario

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The impact of tree canopies on acid deposition was examined. Differences in the chemical composition of unintercepted precipitation (dustfall) and canopy intercepted precipitation (throughfall) at 18 southern Ontario forests, collected during the summers of 1995-1996, were chemically analyzed. The methodology of collection and analysis validated using consistency checks for interception loss, maintenance of electrical neutrality and ion correlation. T-test analyses found throughfall fluxes of K^+ , Ca^{2+} , Mg^{2+} , and NO_3^- were significantly higher than dustfall flux ($p < 0.05$), consistent with other studies. Barrie and nearby sites at Orillia and Bracebridge had larger dustfall depositions of base cations and Cl^- suggesting a nearby source of these ions. T-tests revealed large exceedances of pH and sulphate concentration in dustfall over throughfall at the two Scarborough sites; a local point source of sulphates in the Greater Toronto Area was suspected.

Key Words: acid deposition, canopy interception, dustfall, throughfall, Ontario.

Acid rain emerged as an environmental issue after the Industrial Revolution beginning in the 1820s. The term "acid rain" was first used in the 1850s (Howells 1990). More formally the term, acid deposition, today represents material deposited from the atmosphere onto the Earth's surface, with a pH lower than 5.6 (Foster 1993). The main precursors to acid deposition are emissions of sulphur and nitrogen dioxides, as well as chlorinated compounds. These precursors form sulphuric acid, nitric acid and hydrochloric acid. Although natural sources of these precursors exist, the majority are emitted from anthropogenic sources such as smelters, utilities, and vehicles.

Acid deposition, especially in the form of acid rain, has had detrimental effects on aquatic, terrestrial and man-made structures (Ministry of the Environment 1986; Environment Canada 1991). In particular, acid rain can have a deleterious effect on our ecosystems impacting the forest canopy and soils. Poorly buffered soils are robbed of their nutrients leading to poor forest health and the commonly observed crown dieback. In highly acidic conditions, aluminium is leached from soils in a cation exchange. This can have devastating effects on local aquatic populations. Although emission control strategies have reduced precursor emissions of sulphates, these reductions have not been sufficient to mitigate this problem and acid rain monitoring needs to continue (Kumar et al. 2001).

Of particular interest is the impact of acid rain on forest canopies. The chemical composition and volume of incident precipitation change when it passes through a forest canopy. Interception loss of precipitation has been reported in the range of 6 – 43% for deciduous forests (Helvey and Patric 1965). Differences in the chemical composition of dustfall (unintercepted precipitation) and throughfall (forest canopy intercepted precipitation) can be attributed to both wet and dry deposition and the uptake or release of compounds by the leaves (Balestrini et al. 1998; Houle et al. 1999).

Ion exchanges can produce a net change in the concentrations of positive and negative ions dissolved in throughfall. Normally there is a net increase in ion concentration in throughfall (Gaber and Hutchinson 1988a, 1988b; Gjengedal 1996; Prakasa Rao et al. 1995; Houle et al. 1999). The size of positive charge from the net change in cation concentration must equal the size of negative charge from the net change in anion concentration.

Most studies have found enrichment of K^+ , Ca^{2+} , Mg^{2+} , Na^+ , SO_4^{2-} , NO_3^- and Cl^- in throughfall while H^+ and NH_4^+ concentrations are usually reduced (Gaber and Hutchinson 1988b; Gjengedal 1996; Prakasa Rao et al. 1995; Houle et al. 1999). As much as 90% of the H^+ in precipitation passing through a canopy can be absorbed by the leaves (Cappellato et al. 1993). Release of ions from leaves, referred to as foliar leach-

ing, has been observed for K^+ , Ca^{2+} , Mg^{2+} , and other base cations (Lindberg et al. 1985; Houle et al. 1999). Foliar leaching is usually minimal for SO_4^{2-} , Cl^- , and Na^+ (Granat and Hallgren 1992; Cape et al. 1992; Veltkamp and Wyers 1997). NO_3^- can be either absorbed or leached (Neary and Gizyn 1994). Mechanisms for foliar leaching include passive cation exchange for H^+ with the cuticle cell wall (Mecklenberg et al. 1966), the cell interior (Eaton et al. 1973), or the other cells in the interior of the leaf (Burkhardt and Drechsel 1997).

The ecological health implications of acid deposition have prompted much research and monitoring activity, but a recent lack of government funding has slowed both monitoring and research efforts. For two summers, Monitoring Acid Rain Youth Program (MARYP) monitored acid rain and its impacts on local environments in south-central Ontario (Figure 1). The monitoring program included the collection of dustfall and throughfall precipitation and its subsequent chemical analysis. It also included surveys of local tree species, bird populations, frogs, and wildflowers in an ecosystem approach. High school students were hired to collect the precipitation during the months of July and August and to conduct the ecological surveys. Kumar et al. (2001) found the resulting acid rain data to be of high quality when used in a critical load assessment (Arp et al. 1996). Gough et al. (2002) examined the suitability of using a summer-only monitoring program by examining acid rain data collected by Environment Canada in the same region.

In this paper, we expand on the earlier analyses by comparing dustfall and throughfall rain chemistry in south-central Ontario, Canada, during the summers of 1995 and 1996, collected in the Monitoring Acid Rain Youth Program (MARYP). Although others have assessed the validity of the precipitation and soil chemistry data collected in this program (Kumar et al. 2001), we include three additional tests of data robustness and consistency for samples collected. In addition, we explore the impact of the forest canopy on rainfall chemistry. Finally, differences in ion fluxes and pH of dustfall and throughfall between urban and rural sites are examined.

Methods

Data Collection

The pH and chemical composition of acid deposition collected in 18 forests of south-central Ontario (Figure 1) were determined (rainwater samples, throughfall and dustfall) as part of the Monitoring Acid Rain Youth Program (MARYP; Karagatzides et al. 1997*). The samples were collected during the months of July and August (1995 and 1996) at five locations, with two forests at each location. The Peterborough forests were sampled both years. Sample sites had a variety of forest cover: predominantly sugar maple; mixed deciduous; and mixed coniferous. At each forest site, four dust-

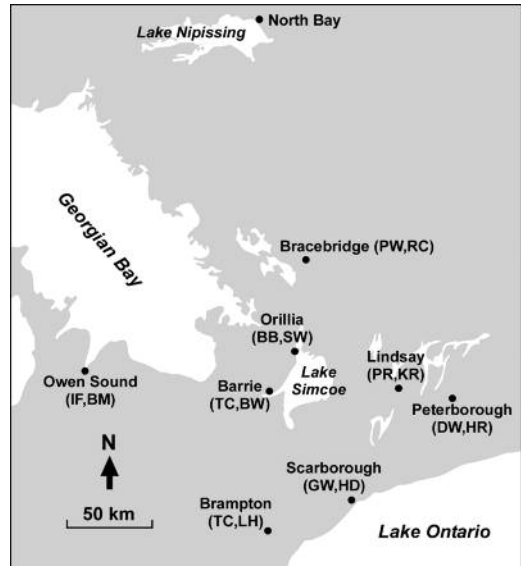


FIGURE 1. Map of MARYP sites in southern Ontario.

fall collectors and four throughfall collectors were installed and sampled weekly. The volume in each collector was recorded using a graduated container and pH measured using a portable pH kit. Composite dustfall and throughfall samples were produced, by pooling samples from the four throughfall and the four dustfall collection locations, for each forest. The result was that only one dustfall and one throughfall sample was chemically analyzed for each collection. The acidifying compounds (SO_4^{2-} , NO_3^- , Cl^- , F^- , and PO_4^{2-}) were analyzed by ion chromatography (Dionex 2010i), and base cations (K^+ , Ca^{2+} , Na^+ , Mg^{2+} , and Fe^{2+}) were measured by ICP-mass spectrometry (Perkin-Elmer ELAN 5000).

Samples were filtered through Whatman #42 immediately and frozen. Samples for ICP-MS were acidified with nitric acid to a final concentration of 2% HNO_3 . Analytical instruments were calibrated with NIST stock standards and the calibration curve checked with a different reference standard. Blind pH buffers of known concentrations were sent to all field assistants and results were always within ± 0.1 pH units.

Dustfall and throughfall fluxes, determined from elemental concentration and rainfall volume, were extrapolated to a per hectare basis and the total flux determined as the difference between dustfall and throughfall. The weekly fluxes were summed over the sampling period. Dustfall and throughfall samples from North Bay were mistakenly pooled into one composite sample containing rainwater from both dustfall and throughfall collection, so chemical analysis was not performed, only pH values were included in the

* See Documents Cited section.

data analysis.

Ion fluxes and pH of dustfall and throughfall were compared using paired, two sided t-tests. Statistical relationships among cations were explored by correlating base cation net concentrations (dustfall concentration – throughfall concentration) with H^+ and anion net concentrations. The net change in total anion charge and total cation charge were calculated by summing the net change in the concentration of each anion or cation weighted by the magnitude of its charge. The net changes in total anion charge and in total cation charge was compared. The magnitude of net ion fluxes were compared between Scarborough forests and the average of the 16 other sites to determine differences between urban and rural areas. Although Brampton could be construed to be an urban site, the Scarborough sites were directly downwind of the Greater Toronto Area. Differences were deemed significant if ion fluxes from Scarborough sites were outside the 99% confidence interval described by the other sites.

Data Analysis

CONSISTENCY CHECKS: Three separate internal consistency checks were performed. To determine whether the sample volumes collected were within the range of previous work, calculated interception losses for the canopies studied were compared to interception losses found in other studies. The other two checks, charge balance and ion correlation, were performed to determine whether the measured concentrations of ions in the dustfall and throughfall collectors were internally consistent. Differences between net rainfall concentration of H^+ , K^+ , Ca^+ , Mg^{2+} , Na^+ , SO_4^{2-} , NO_3^- , and Cl^- (ion concentrations of dustfall minus ion concentrations of throughfall) were correlated (Pearson multiple correlation).

Within each study site, pH differences for throughfall and dustfall were assessed using t-tests. Finally urban and rural differences were analyzed. Statistica was used for all statistical analyses.

Results and Discussion

Consistency Checks

RAINFALL INTERCEPTION: The average values for canopy interception loss of 14 +/- 9% and 15 +/- 9% (Tables 1 and 2) for 1995 and 1996, respectively, fall within the range (between 11 and 22%) of interception loss values from other studies performed in deciduous or mixed temperate forests of North America or Europe (Helvey and Patric 1965; Robson et al. 1994; Gash et al. 1995; Carlyle-Moses and Price 1999).

The Limehouse site in Brampton was not considered in the interception loss average since the measured rainfall volume in throughfall collectors exceeded the measured rainfall volume in dustfall collectors. The larger dustfall rainfall volume is either the result of spatial inhomogeneity of precipitation or measurement or analysis error. At this site the dustfall collectors were over 100 m away from the throughfall collectors, the largest separation in the study.

CHARGE BALANCE: Exchanges between rainfall and leaf surfaces can change the concentrations of positive and negative ions dissolved in throughfall precipitation. However, the associated charges of these ions must balance since the rainwater must remain neutral throughout the ion exchange processes. All sites except Tiffin Conservation (TC, Barrie) showed a net loss of both cations and anions from the canopy into the throughfall precipitation (Table 3). The gain of both anion and cation charge at this station is anomalous being suggestive of field sample contamination. Therefore, the average change in charge is calculated without the TC data. The net change in anion charge was 74% greater when the Barrie site was not considered. This suggests that the ions not measured in the analysis (mostly organic ions) were predominantly negatively charged. Lovett et al. (1985) found that organic anions had a significant effect on maintaining the charge balance and in countering cation leaching.

TABLE 1. Total rainfall volumes collected in both dustfall (DF) and throughfall (TF) gauges from all sites of the 1995 MARYP study. The percentage reductions in throughfall volumes due to interception are given for each forest.

Location	DW	HR	PR	KR	PW	RC	IF	BM	TR	LH	
DF (L)	2.6	1.9	1.9	1.4	2.6	3.2	2.3	2	2.5	1.7	
TF (L)	2.1	1.8	1.6	1.3	2.2	2.9	1.5	1.9	2.1	2.2	Average (9)
% Interception	19	5	16	7	15	9	35	5	16	-29	14 +/- 9

TABLE 2. Total rainfall volumes collected in both dustfall and throughfall gauges from all sites of the 1996 MARYP study. The percentage reductions in throughfall volumes due to interception are given for each forest. Data are not available for the North Bay forests.

Location	DW	HR	GW	HD	TC	BW	BB	SW	
DF (L)	1.1	1.7	2.1	1.5	1.5	3.5	2.5	2.6	
TF (L)	0.8	1.5	1.8	1.1	1.4	2.9	2.5	2.1	Average (8)
% Interception	27	12	14	27	6.7	17	0.0	19	15 +/- 9

TABLE 5. Difference in net ion fluxes (in kg/ha) of Cl⁻, Na⁺, Mg²⁺, and Ca²⁺ between the two Barrie forests and the average of the other 16 MARYP forests. The average net ion flux for the other 16 forests and the 99% confidence intervals (CI) of this dataset are also given.

Ion	Tiffin Conservation (TC)	Brigley's Woods (BW)	Average	99% CI of 16 Sites	
Cl ⁻	4.10	4.90	-0.75	-1.43	-0.66
Na ⁺	0.50	1.20	-0.20	-0.43	0.28
Mg ²⁺	0.60	0.70	-0.32	-0.56	-0.07
Ca ²⁺	-0.40	-0.30	-1.33	-2.24	-0.43

for the two sites, while Barrie and Orillia showed H⁺ ratios of about 2 (50% neutralization) (Table 7).

The highest throughfall pH values were observed in Brampton (LH) in 1995 (6.8) and at the two Scarborough sites in 1996 (6.3 and 5.8), while the lowest pH throughfall values were observed in North Bay (4.5), Lindsay (KR) and at the two Bracebridge sites (Figure 2). There appears to be a reduction in the pH of the throughfall precipitation with increasing latitude. The largest dustfall-throughfall differences in pH were observed at the two Scarborough sites (Figure 2) and may be attributed to increased deposition of SO₄²⁻ and NO₃⁻ (Figures 3 and 4).

CHEMICAL COMPOSITION OF IONS IN DUSTFALL VS. THROUGHFALL: Ion fluxes (dustfall – throughfall) were negative for K⁺, Ca²⁺, Mg²⁺, Fe³⁺, NO₃⁻, SO₄²⁻ and Cl⁻, positive for H⁺, and similar for Na⁺ (Table 6). Any percentages over 100 indicate a negative ion flux (i.e. throughfall greater than dustfall). Significant differences (t-test p < 0.05) were observed in both 1995 and 1996 for K⁺, Ca²⁺, and NO₃⁻, while significant differences were only observed in 1995 for Mg²⁺ and in 1996 for SO₄²⁻ (Table 6).

ACID CONTRIBUTING ANIONS: Nitrate fluxes were significantly greater in throughfall than in dustfall for 1995

and 1996 (Table 6), consistent with most studies which have found negative net NO₃⁻ fluxes (Prakasa Rao et al., 1995; Houle et al., 1999). Dry deposition was reported to be the largest contributor to NO₃⁻ deposition (Lindberg et al., 1986) compared to foliar leaching, which usually makes a minimal contribution to the negative net NO₃⁻ fluxes (Puckett 1990; Potter 1991; Liechty et al. 1993; Houle et al. 1999). Results for SO₄²⁻ and Cl⁻ were inconclusive. Significant negative SO₄²⁻ fluxes were observed for 1996; however, 1995 had a positive flux. The negative SO₄²⁻ fluxes are likely due to dry deposition onto leaf surfaces. Contributions to net sulphur concentration of throughfall from foliar leaching have been recorded to be as low as 3% (Cape et al. 1992; Granat and Hallgren 1992; Veltkamp and Wyers 1997). Cl⁻ showed significant negative net fluxes (Table 6) in 1995 but not in 1996. This may be related to the choice of locations which, differed from 1995 to 1996.

CATION ANALYSIS: The largest negative net cation flux was observed for K⁺. The large difference in K⁺ may be attributed to foliar leaching. Foliar leaching has been found to comprise nearly 70% of the net ion flux for K⁺ (Cappellato et al. 1993) but there was no significant correlation between H⁺ and K⁺ in the MARYP

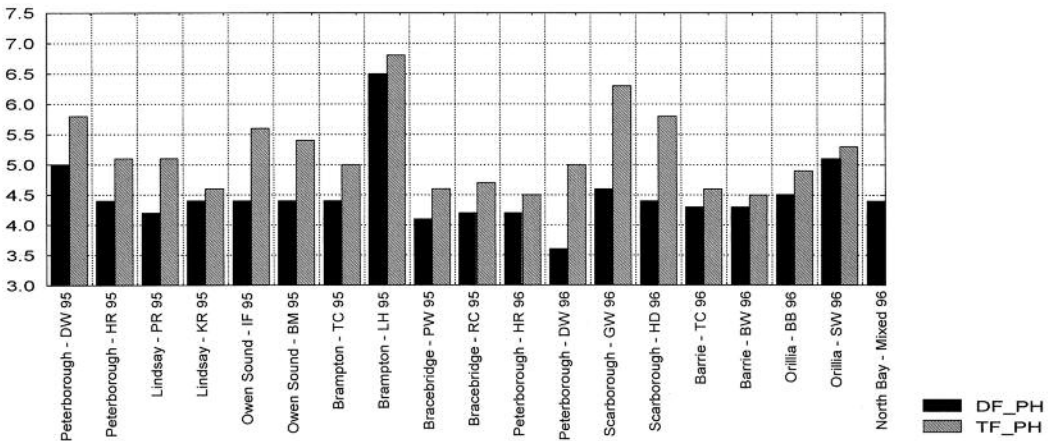


FIGURE 2. Comparison of pH between rainfall collected in throughfall and dustfall collectors in the 20 Ontario forests of the 1995-1996 MARYP study. The two letter acronyms below the pH columns represent individual MARYP sites.

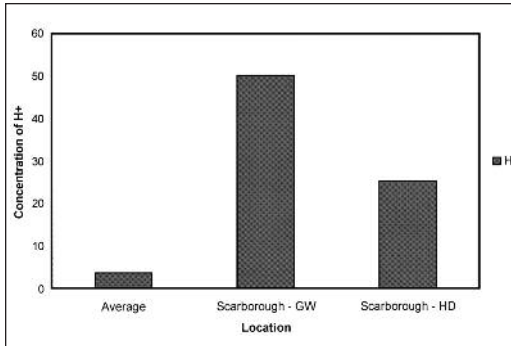


FIGURE 3. Ratio of dustfall to throughfall H⁺ ion fluxes for the average of 16 MARYP forests compared to the dustfall to throughfall H⁺ ratio for the two Scarborough forests. GW and HD represent the Scarborough forests Greenwood and Heber Down.

data ($p > 0.05$) (Table 4). Studies to determine relationships between H⁺ deposition and K⁺ leaching have given inconclusive results.

Both years showed significant differences between Ca²⁺ dustfall and throughfall deposition ($p < 0.05$) (Table 6). Canopy leaching makes a significant contribution (up to 60%) to the negative net canopy flux (Houle et al. 1999). Canopy leaching is believed to take place mainly by cation exchange (Mecklenberg et al. 1966; Gaber and Hutchinson 1988b; Gjengedal 1996).

The average Mg²⁺ flux was significantly greater in throughfall than in dustfall in 1995 ($p < 0.05$) (Table 6). Mg²⁺ fluxes are commonly larger in throughfall than in dustfall (Lindberg et al. 1986; Gaber and Hutchinson 1988b; Liechty et al. 1993; Neary and Gizyn 1994; Prakasa Rao et al. 1995; Houle et al. 1999).

Urban vs. Rural

The difference in chemical composition between throughfall and dustfall is strongly affected by dry deposition. To determine the location of sources of

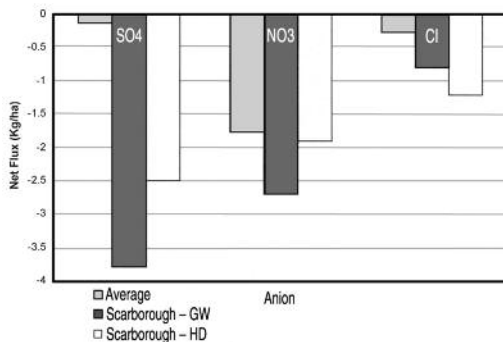


FIGURE 4. Net anion fluxes for the average of 16 MARYP forests compared to net anion fluxes for the two Scarborough forests. GW and HD represent the Scarborough forests Greenwood and Heber Down.

deposition, we examined the net ion deposition fluxes in sites near urban centres and in rural areas. Deposition of ions (particularly the acid contributing anions) is likely to be greater in urban areas resulting in larger ion fluxes if local point sources exist.

Net sulphate flux at the two Scarborough forests was more than 17 and 26 times as great as the average sulphate flux of the other forests in the study. Sulphate fluxes in Scarborough were outside the 99.9% confidence limits described by the other 16 sites indicating the likelihood of a point source for sulphates in the Greater Toronto Area. One possible source of sulphates is the large SO₂ emissions from the coal burning at the Lakeview Electrical Plant in Mississauga. Net fluxes of NO₃⁻ were also larger than average for the Scarborough sites but NO₃⁻ fluxes remained within the 99% confidence interval described by the other 16 forests. This is in agreement with Gough et al. (2002) who also found independent evidence of a sulphate source in the Greater Toronto Area using acid deposition data.

Scarborough forests had a much stronger buffering capacity than the more rural sites. The two Scarborough forests had dustfall/throughfall H⁺ deposition ratios of 25 and 50, while the average dustfall/throughfall H⁺ deposition ratio for all forests was only 6 (Table 7). This may be explained by the significantly larger dry deposition of sulphates at the Scarborough forests. (We assume that due to the close proximity of the dustfall and throughfall forests that the wet deposition for the two are identical). Larger sulphate dry depositions may result in greater ion exchange on leaf surfaces to neutralize the sulphuric and sulphurous acids formed when the sulphates dissolve in water on the leaf surface. Net fluxes of K⁺ and Ca²⁺ were significantly higher (outside the 99% confidence limits) at the Scarborough forests than the average for the other forests (Table 7). Increased exchange would likely increase the uptake of H⁺. Increased uptake of H⁺ by the canopy results in increased neutralization of dustfall as it passes through the canopy.

Conclusions

In this work we have examined throughfall and dustfall precipitation chemistry from 18 forests in south-central Ontario collected in the MARYP program during the summers of 1995 and 1996. Three internal consistency checks were performed on the data. For the most part the data were internally consistent. One anomaly arose when examining rainfall interception which had more throughfall rain volume than dustfall unlike all other locations and contrary to past observations. All other locations fell within published interception loss. This anomaly is likely due to either rainfall heterogeneity or possible sampling errors.

All sites with the exception of one of the Barrie sites showed a net loss of cation and anion charge from the canopy to the throughfall precipitation consistent with the scientific literature. The changes in anion

TABLE 6. Comparison of dustfall and throughfall deposition fluxes for eight major ions for 10 forests in 1995 (9 degrees of freedom) and for eight forest sites in 1996 (7 degrees of freedom). The comparisons are also given for pooled 1995 and 1996 data. P-values from two-sided dependent t-tests are given and the ratio of throughfall / dustfall is given as a percentage. $P < 0.05$ is designated with a *, $p < 0.001$ is designated with ***. All ions with a throughfall/dustfall percentage ratio above 100% are enriched in throughfall with respect to dustfall and have a negative net ion flux, and vice versa.

Year Ion	1995 (9df)		1996 (7df)		Average (17 df)	
	p-value	TF = % DF	p-value	TF = % DF	p-value	TF = % DF
K ⁺	0.000039 ***	478%	0.021 *	206%	0.000 ***	287%
Ca ²⁺	0.00060 ***	162%	0.025 *	154%	0.004 **	158%
Mg ²⁺	0.018 *	249%	0.63	124%	0.060	170%
Na ⁺	0.18	121%	0.95	99%	0.460	106%
Fe ³⁺	0.011 *	393%	0.027 *	135%	0.007 **	191%
SO ₄ ²⁻	0.50	93%	0.020 *	116%	0.754	103%
NO ₃ ⁻	0.020 *	194%	0.011 *	136%	0.000 ***	159%
Cl ⁻	0.028 *	148%	0.76	94%	0.710	106%

TABLE 7. Net ion fluxes of the average of 16 MARYP sites and the two most urban forests (Scarborough – Greenwood and Heber Downs). Ions with significantly different net fluxes at the Scarborough forests than from the average of the other forests are starred. H⁺ is given as a ratio of concentrations of dustfall and throughfall in moles per litre. The other ion fluxes are given as differences between dustfall and throughfall in kg/ha.

Ion	Average	99% Conf. Int.	Scarborough – GW	Scarborough – HD
H ⁺	9.39	0.74	18.0	25 *
K ⁺	-2.17	-2.66	-1.09	-5.9 *
Ca ²⁺	-1.23	-1.38	-0.40	-4.8 *
Mg ²⁺	-0.211	-0.44	0.16	-1 *
Na ⁺	-0.083	-0.43	0.29	-0.2
Fe ³⁺	-9.77	-3.07	-15.1	-15
SO ₄ ²⁻	-0.137	-0.89	1.37	-3.8 *
NO ₃ ⁻	-1.78	-2.67	-0.75	-2.7 *
Cl ⁻	-0.261	-1.55	1.42	-0.8

and cation charge were strongly and significantly correlated as expected. However they were not balanced suggesting the presence of negatively charged organic anions which were not measured in this work.

The ion correlations linked sulphate with the base cations K⁺ and Ca²⁺, suggesting greater cation exchange in more acidic environments. Similarly nitrate was significantly correlated to K⁺, Ca²⁺, and Mg²⁺. Sulphate and nitrate were significant correlated suggesting the pollutants were part of a plume passing through southern Ontario likely from the southwest consistent with Gough et al. (2002). Na⁺ and Cl⁻ were strongly correlated suggesting road salts were deposited on the forest canopies as dry deposition.

The forest canopy acts as a chemical buffer reducing the pH of the throughfall precipitation. This can arise due to dry deposition on the leaves or through foliar leaching (cation exchange). Throughfall fluxes significantly exceeded dustfall fluxes for K⁺, Ca²⁺, Fe²⁺, and NO₃⁻, while dustfall fluxes are greater than throughfall fluxes for H⁺, consistent with other studies. Much larger fluxes of base cations and Cl⁻ were observed for forests in Barrie, and nearby Orillia and Bracebridge sites, suggesting a source of base cations and Cl⁻ in this area.

Urban (Scarborough) forests had larger net sulphate fluxes and larger throughfall to dustfall H⁺ ratios than the remaining rural forests. This may be explained by larger dry deposition of sulphates and may indicate a point source of sulphates in the GTA consistent with Gough et al. (2002). Further studies making comparisons of net depositions of ions between urban and rural areas are needed to further explore this issue.

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