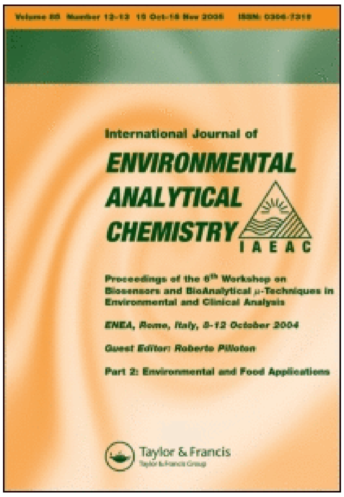

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Indoor-Outdoor Levels of Nitrogen and Sulphur Species and their Relation to Air Flow in Antigonish, Nova Scotia

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To cite this Article Méranger, J. C. , Brûlé, D. , Smith-palmer, T. , Wentzell, B. and Donini, J. C.(1987) 'Indoor-Outdoor Levels of Nitrogen and Sulphur Species and their Relation to Air Flow in Antigonish, Nova Scotia', International Journal of Environmental Analytical Chemistry, 29: 1, 61 — 72

To link to this Article: DOI: 10.1080/03067318708078411

URL: http://dx.doi.org/10.1080/03067318708078411

Intern. J. Environ. Anal. Chem., 1987, Vol. 29, pp. 61–72
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Printed in Great Britain

Indoor–Outdoor Levels of Nitrogen and Sulphur Species and their Relation to Air Flow in Antigonish, Nova Scotia

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(*Received August 26, 1986*)

A study was conducted in Antigonish, Nova Scotia, to determine the extent to which acid rain related pollutants are present in indoor ambient air. The pollutant study included: fine (0 to 2.5 μm) and coarse (2.5 to 10 μm) particulates, sulphates, nitrates, acidity (H_2SO_4 and HNO_3), SO_2 and NO_2. During the $3\frac{1}{2}$ month study, maximum levels of 173 n equivalent/m^3 fine sulphate and 55 n equivalent/m^3 H_2SO_4 were recorded for outdoor air within the town site compared to corresponding values of 110 n equivalent/m^3 and 13 n equivalent/m^3 for indoor air. Based on back trajectory analysis, wind direction, and sulphuric acid content, it was postulated that local or medium range pollution sources are predominant in the winter while long range transport originating from the United States produces the major episodes when SW winds are persistent.

INTRODUCTION

In recent years, there has been increased public awareness in Nova Scotia regarding acidic deposition. While a significant portion of this acid rain has been linked to the long-range transport of pollutants from the northeastern United States, recent studies have suggested that local sources are also important contributors.[1] In this study, conducted in Antigonish, a rural town in northern Nova Scotia, the aim was to measure the ambient levels of a range of nitrogen and sulphur compounds and correlate these levels with air flow. In order to differentiate between local and long-range pollution two sampling sites were chosen: one at the town's centre and one outside the town. Local pollution would usually be expected to be predominant at the centre town site. Indoor measurements were also carried out simultaneously at the town site. The area chosen for the study was Antigonish, a small university town near the sea surrounded by woodland with a local population of 6000. It is 50 km from towns to the E and W and 160 km NE of the industrial cities of Halifax and Dartmouth. The major local sources of pollution include an oil-burning plant at St Francis Xavier University fueled by low-grade Bunker C Oil and an oil burning plant at the local hospital as shown in Figure 1.

EXPERIMENTAL

The sampling site chosen in the centre of town was a 60 year old partly insulated house heated by a forced air oil furnace system. An electric stove was used for cooking. There were no smokers among the occupants. The houses in the neighbouring area use both oil and wood for heating. Ambient air samples were collected from both indoors and outdoors. The indoor air samples were collected in the dining room 1.5 metres above the floor level and 0.6 metres from a wall. The outdoor pollution levels were monitored in the back yard 1.8 metres from the NE wall and 2.7 metres above the ground level.

The cost of operating several control sampling sites surrounding the town to differentiate between long range and local pollution coming from different wind directions is prohibitive. Therefore, in the present study the control site was strategically placed at 3.5 km west of the town sampling site since it was anticipated that the highest sulphate episodes would be associated with SW winds. When such an episode occurs both the control site and the town sampling site will show high pollutant levels, while under periods of low wind the town site will predominate resulting in higher town site values.

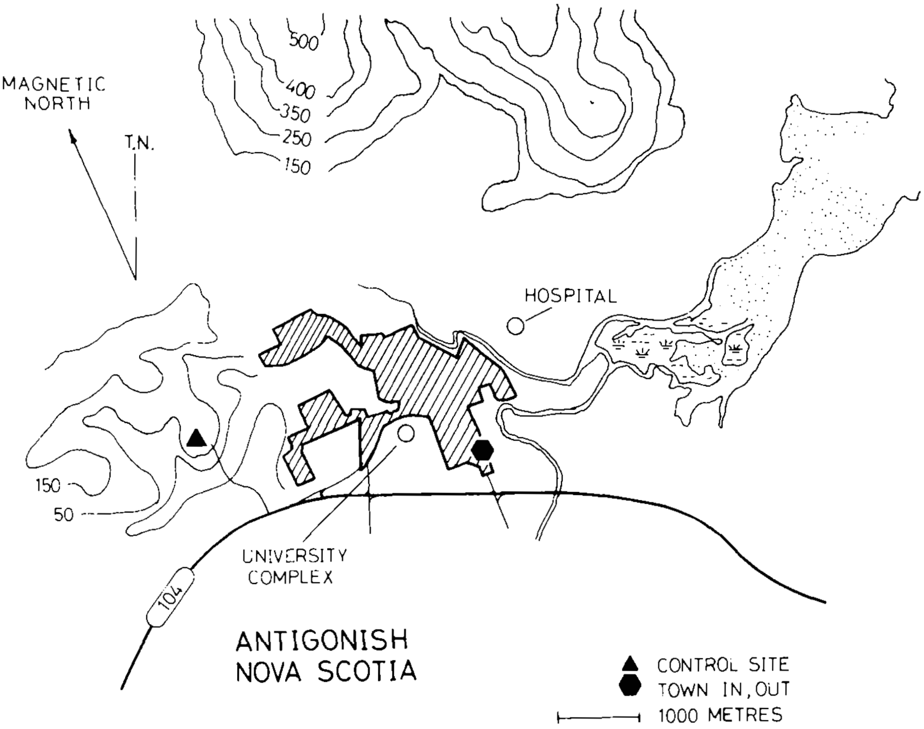

Figure 1 Location of sampling sites for indoor/outdoor monitoring.

This out-of-town sampling site was used to collect outdoor samples only. The instrumentation was housed in an insulated constant temperature room on the side of a warehouse. A continuous recording windspeed and direction monitor was also installed there, 15 metres above the ground, providing a clearance of 6 metres above the roof. Sulphates and free acids were continuously monitored at the control site with a Flame Photometric Detector–Thermal Analysis System (FPD–TA) provided by the Harvard School of Public Health.[9–11] Thermal analysis allows for the selective vaporization and detection of H_2SO_4 at 120°C, and ammonium bisulphate and ammonium sulphate at 300°C. Continuous monitoring of gaseous SO_2 was accomplished by the exclusion of particulate matter with a membrane filter prior to flame photometric detection. The system was calibrated weekly in the field using a calibrated SO_2

permeation tube coupled to a Monitor Labs Inc. model 8500 calibrator. The system was also calibrated in the laboratory prior to the field study using sulphuric acid, ammonium sulphate, and ammonium bisulphate aerosols. The detection limit for total sulphate determination was $0.6\,\mu g/m^3$.

Nitric acid and nitrates were sampled alongside the sulphate detector using the denuder difference technique[2,3] in conjunction with ion chromatographic analysis (IC). The ambient air was drawn through a 1/8″ (3.2 mm) internal diameter stainless steel tubing, and the flow was split to go through either a nylon filter or a diffusion denuder and nylon filter. The denuder consisted of twelve 90 cm long 4 mm inside diameter glass tubes coated with sodium carbonate. The 47 mm diameter nylon filters having a pore size of $0.45\,\mu m$ were obtained from Pall (Canada) Ltd. The filters were extracted ultrasonically in 10 ml IC buffer (3×10^{-3} M $NaHCO_3$ and 2.4×10^{-3} M Na_2CO_3), and duplicate aliquots were injected into a Dionex Model 12 ion chromatograph equipped with 5 × 250 mm anion separator and suppressor columns. Under these conditions, the detection limit attained was $0.11\,\mu g\,NO_3^-/m^3$. Particulate samples of indoor and outdoor air at the town centre were collected using two Sierra–Andersen dichotomous samplers equipped with a Model 246 $10\,\mu m$ inlet head to allow for the collection of fine particles (0–$2.5\,\mu m$) and coarse particles (2.5–$10\,\mu m$). The particles were collected over 24-hour periods on 37 mm diameter Teflon filters supported by polypropylene rings. Exposed filters and blanks were sealed in petri dishes and stored for the same length of time at −14°C prior to analysis. Filters were then placed on a Teflon holder and cut in half with a razor blade. One half was used to determine the chloride, nitrate and sulphate content by ion chromatography after ultrasonic extraction for 20 minutes with 10 ml of IC buffer. The method used was the same as previously described for nitrate determination. The detection limit attained was $0.1\,\mu g/m^3$ for sulphate and nitrate analysis and $0.04\,\mu g/m^3$ for chloride. The other half of the filter was analysed for total acidity as described previously.[4-6] The particulates were extracted ultrasonically for 20 minutes with 5 ml of a 3×10^{-5} N $HC1O_4$ solution. The samples were titrated with 5 ml increments of 5×10^{-3} N NaOH – 0.1 M KCl after bubbling with N_2 for 20 minutes. The equivalence point was determined using Gran's plot[7] and the strong acid concentration was determined by extrapolation of the linear portion of the plot. Ambient air samples for SO_2 and NO_2 determinations were collected with a simple diaphragm pump at a flow rate of 400 mL/minute for 48 hours according to EPA method.[8] The air flow was split by a manifold and bubbled through two impingers containing acidified H_2O_2 and two containing basic 0.1% w/v sodium arsenate. The oxidized SO_2 was determined as sulphate using IC (12). A standard calibration curve was prepared by adding known amounts of K_2SO_4 to the H_2O_2-HCl impinger solutions. The detection limit for SO_2 was 2.7 μg/m^3. NO_2 was converted to nitrite and analyzed as previously described[9,10] using a 2 cm cuvette for absorption readings. This procedure combined with the longer sampling time of 48 hours gave a detection limit of 2.2 μg/m^3 NO_2. The collection system was periodically calibrated using NBS traceable NO_2 and SO_2 permeation tubes and a Monitor Lab Inc. model 8500 calibrator.

RESULTS AND DISCUSSION

During the first 10 days of study, the FPD–TA system was used side by side with the dichotomous sampler to compare results originating from the two different instruments. The values for sulphate and acidity obtained with the dichotomous samples were slightly higher as shown in Figure 2. This may be explained by differences in the analytical measurement techniques used in both cases. The acid component of the FPD–TA system measures sulphuric acid whereas the Gran titration method also includes bisulphates. The lower total sulphate values may be attributed to the loss of larger particles by precipitation in the inlet tube of the FPD–TA system. Since the monitoring stations were close to the sea, there was a requirement to correct the sulphate values obtained for the sea spray component. To obtain this correction it was assumed that all the chloride detected resulted from this component. A molar marine sulphate/chloride ratio of 0.1 was used to apply the final correction.

Throughout the $3\frac{1}{2}$ month study period, the major atmospheric pollutant was sulphate. Several sulphate episodes of moderate size were detected during the cold months, but the largest episode was measured during the latter part of the study, when temperatures had risen and southerly winds were predominant (Figures 3, 4). Nitrates

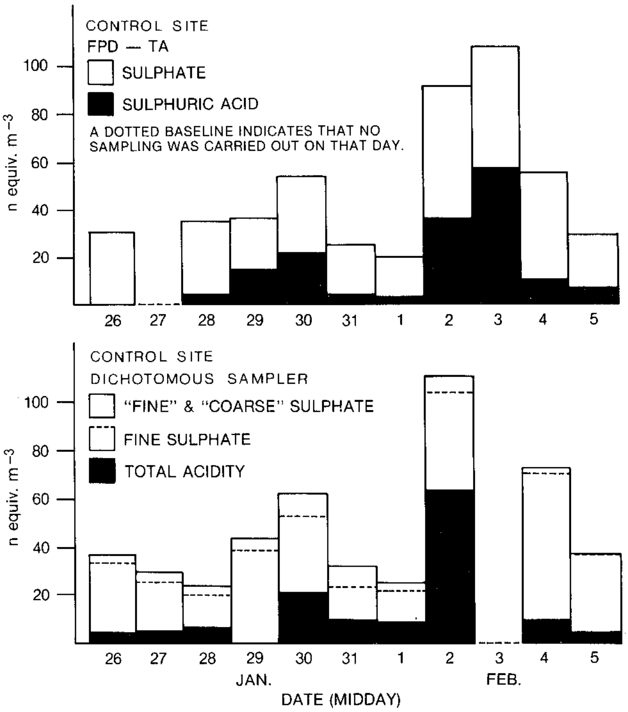

Figure 2 Comparison of continuous (FPD–TA) and dichotomous sampling for acidity, and total sulphate monitoring.

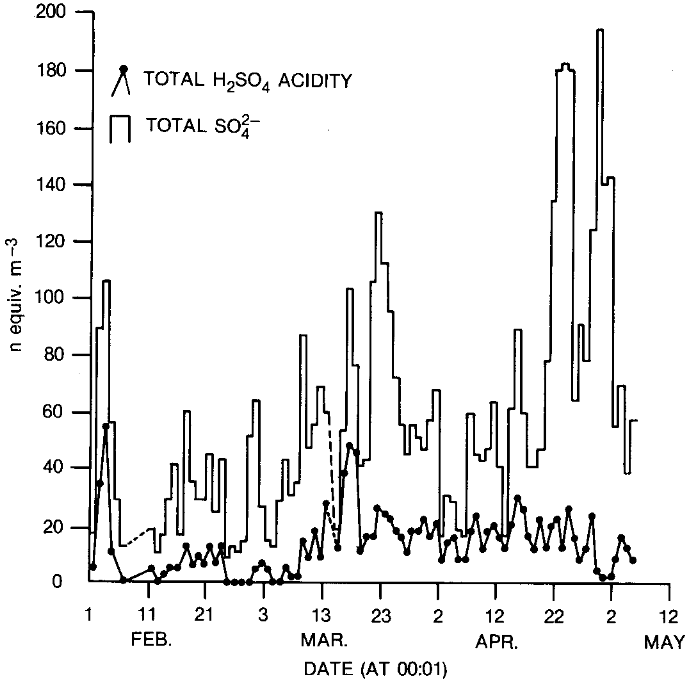

Figure 3 Daily outdoor total sulphate and sulphuric acid concentrations at the control site using the continuous (FPD–TA) system.

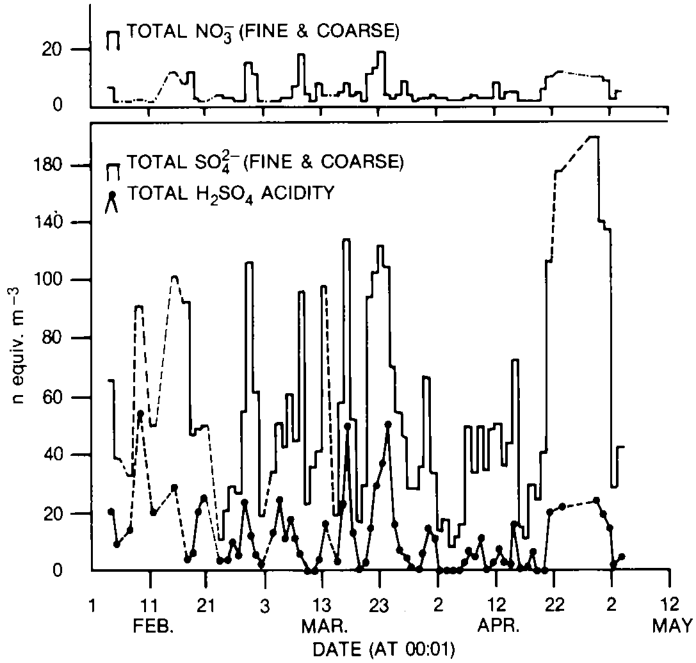

Figure 4 Daily outdoor total sulphate and sulphuric acid concentrations at the town site using dichotomous sampling.

(Figure 4) and free acids were minor contributors to the overall pollutant level, although increases were observed during most sulphate episodes. The airborne sulphate and free acid was predominantly found in the fine fraction i.e. 0–2.5 μm size (Figure 2). These particles are within the respirable range and as such are of greater significance from a health point of view. Nitrates were often more concentrated in the coarse fraction, and the ratio of nitric acid to total nitrate was considerably larger than the ratio of sulphuric acid to sulphate. Nitrate levels of up to 19 n equivalent/m^3 were recorded in outdoor air and at times the nitric acid accounted for some 30% of the total acidity. The SO$_2$ and NO$_2$ values were usually below 14 μg/m^3 (Figure 5) and did not correlate with the sulphate episodes as shown in Figures 3 and 4. The SO$_2$ levels were usually higher in town than at the control site with the exception of days when E winds prevailed, blowing local pollution towards the control monitoring station. Strong evidence of local NO$_2$ pollution was found

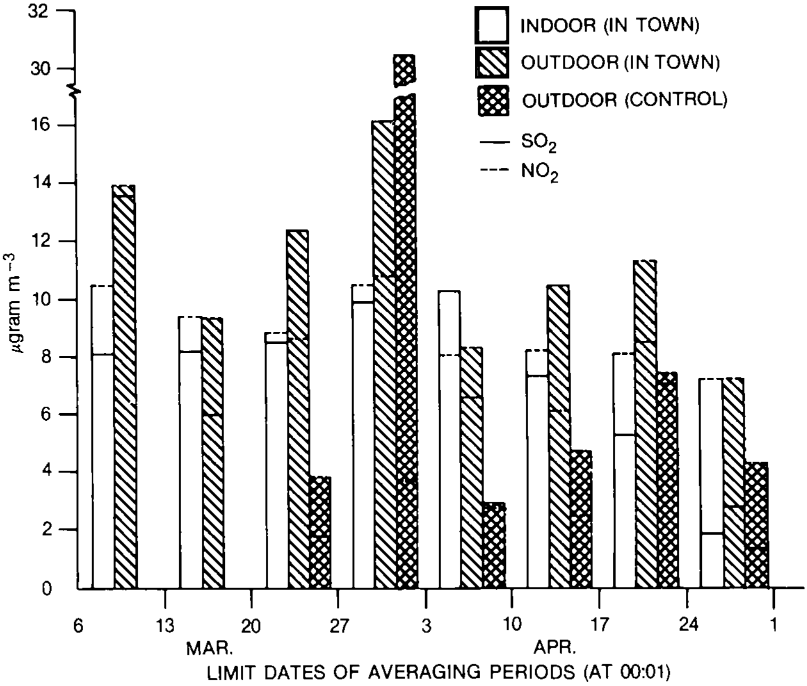

Figure 5 Average weekly indoor/outdoor SO_2 and NO_2 concentrations.

when in town control concentration ratios were examined. The ratio for NO_2 was above 1.0 at all times, pointing to local pollution.

The total sulphate and acidity values obtained at the control site are shown in Figure 3, and the town site values are presented in Figure 4. There was generally good agreement between the continuous sulphate recorded episodes and those recorded at the town site. There was also good agreement between the indoor and outdoor fine sulphate levels obtained at the town site as shown in Figure 6. During the course of the study, the major sulphate episodes were recorded in late spring when S winds prevailed. Five episodes resulted in sulphate values in excess of 100 n equivalent/m^3 as shown in Figure 3. On February 1 to 5, the episode originated from the NE and ended in a W direction. A maximum value of 112 n equivalent/m^3 was recorded at the control site and approximately 50% of this value was recorded as sulphuric acid acidity.

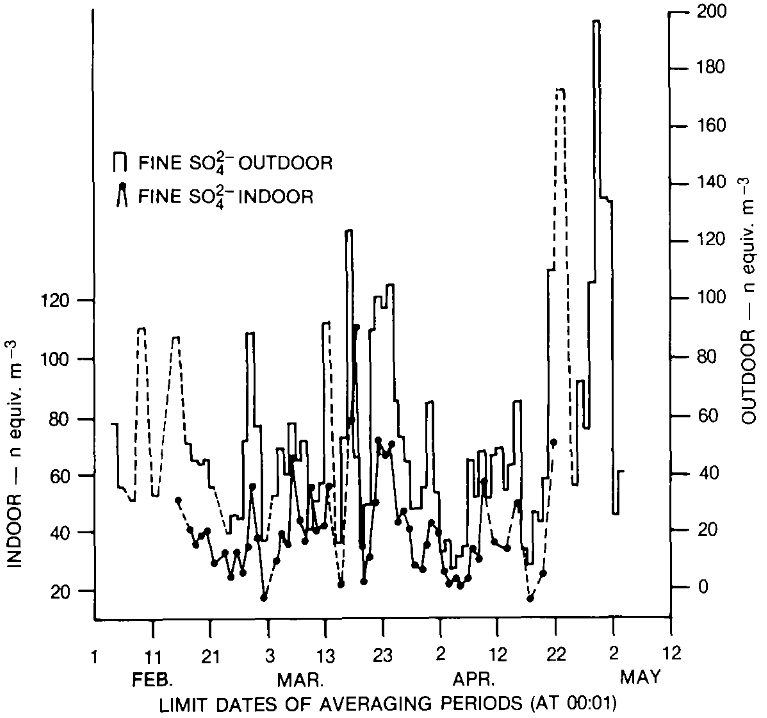

Figure 6 Daily indoor/outdoor fine particulate concentrations at the town site using dichotomous sampling.

On March 14 to 19, the winds predominated from the NE and a maximum value of 104 n equivalent/m^3 was recorded. This episode was again characterized by high acidity values (approximately 45% of the total).

As shown in Figure 7, air masses originating from the NE pass over the heavily industrialized Sydney area. The acid component present in both episodes suggests that medium range transport was a major factor. During the period of March 20 to 26, a maximum total sulphate of 131 n equivalent/m^3 was recorded when SW winds prevailed. Minimum values were recorded at the start of the episode under SE winds and at the end when NE winds dominated. The acidity was higher in the town site indicating that local pollution was the contributing factor. Although it is difficult to prove whether

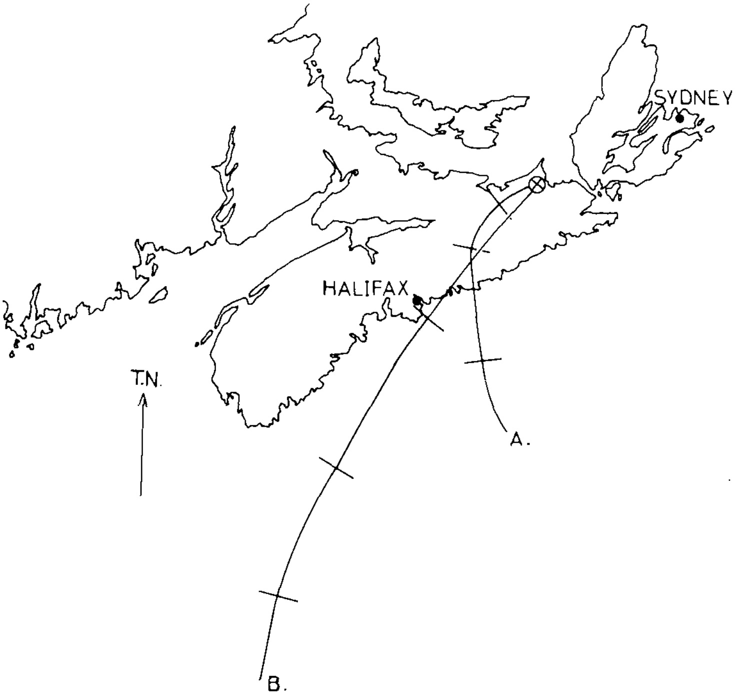

Figure 7 Typical back trajectory curves for sulphate episodes with a SW wind prevailing.

the sulphate source was from Halifax alone or whether the air mass was already polluted when it reached Halifax, the acid component suggests that medium range transport was a major factor.

The last two sulphate episodes occurred at the end of the study. On April 19 to 25, a maximum level of 183 n equivalent/m^3 total sulphate was recorded (Figure 3) with SW winds prevailing and minimum values were recorded with the SE winds. The April 27 May 2 episode had identical wind direction patterns with levels up to 195 n equivalent/m^3 total sulphate being recorded. The relative acidity levels during both of these episodes were lower than the first three major episodes.

Back trajectory analysis (B in Figure 7) showed air movements from a SW direction avoiding Halifax during the episode with winds from the SE direction (A in Figure 7) in the pre and post episode.

Therefore, the most likely explanation seems long-range transport from the United States with some acid component remaining mainly because of the largely marine path travelled. Sulphate episodes were recorded in Boston a day or two earlier as the air mass in question moved up from the United States to Nova Scotia bypassing Halifax.

In order to assess the effect of fluctuating outdoor pollution on indoor environments, simultaneous air pollution measurements were carried out with the dichotomous samplers and impinger systems for NO_2 and SO_2. The indoor sulphate pollution was concentrated in the "fine" particulates and generally followed the pattern of outdoor levels (Figure 3). There was less similarity found between indoor and outdoor acid content since acidity is often neutralized in an indoor environment.

As shown in Figure 5, except for the weeks of March 13 to 20 and April 3 to 10, the SO_2 levels were significantly lower indoors that outdoors. This is to be expected because of the high reactivity of SO_2 gases with household materials. On the other hand, the NO_2 levels were very similar indoors and outdoors, and were essentially identical during five of the eight weeks of the present study. The control NO_2 and SO_2 values were consistently lower with the exception of SO_2 during the week of March 27 to April 3. This higher SO_2 level coincides with the only persistent W wind in the study. The pollutants are likely not long range as evidenced by the relatively low total sulphate and acidity values for this period (Figure 3).

CONCLUSION

This study shows the types of fluctuations that are seen in sulphur and nitrogen species during winter months, and the effect these fluctuations have on the indoor environment. The indoor environment chosen would give us typical minimum levels; in households with pollution point sources, the levels would be expected to be much higher.

It is difficult to prove conclusively whether the pollution is long range or local without using tracer gases, but a variety of factors—local conditions, back trajectory analysis, and the composition of the aerosol have allowed us to make reasonable assessments of pollution sources. The most striking feature of the study is that during the colder months, the pollution appeared to be local or at most medium-range in origin, whereas in the warmer months, the prevailing S air flow tended to bring polluted air from further afield. In winter the prevailing wind is NW, and there are no obvious sources of long range pollutants in such an air flow, but in summer, the prevailing S to SW wind will often take air masses over Halifax before reaching Antigonish. The measurement of the speciation and size distribution of both sulphur and nitrogen pollutants helps assess the source of the pollutants, and, most importantly, their potential as health hazards. A variety of methods were used to provide data which was consistent and complementary. The results of this study confirm the opinion of Shaw[2] that, in Nova Scotia, local sources can be as important contributors to pollution as can long range pollution. A very general conclusion would be that, in winter months, local sources are major contributors, whereas in summer, the majority of the pollution tends to come by long range transport from the S and SW.

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