Trans-Tasman tropospheric transport of acid rain

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Rainwater samples collected at Karamea on the west coast of the South Island were analysed for pH and ionic composition. An attempt has been made to correlate rainwater samples with air mass origin using air mass back trajectories. Unexpectedly high levels of fluoride (> 1 ppm) were observed in rainwater event samples associated with air mass trajectories from Australia. Mean values for the observed ions were K+ 0.44 ppm, Na+ 4.7 ppm, Ca2+ 2.9 ppm, Mg2+ 0.31 ppm, F− 0.50 ppm, Cl− 12.0 ppm, NO3− 8.2 ppm and SO42− 10.1 ppm.

Keywords: pH, acid rain, fluoride, Westland

INTRODUCTION

It has long been assumed that acid rain is a problem only in the highly industrialised regions of the northern hemisphere, despite the fact that there have been very few reported studies of rainwater analysis in New Zealand to support this opinion. In 1986 Holden and Clarkson predicted that less than 3% of sulphur emissions from Australia will fall out over New Zealand. This was a theoretical proposal based on modelling of air mass volumes. A cruise in the northeastern Tasman Sea by an international SEAREX (Sea-Air Exchange) team found a positive correlation between air masses having crossed Australia and a decrease in rainwater pH. High rainwater nitrate concentrations were also observed at a site on Ninety Mile Beach (Pszenny and Duce, 1983; 1984). Rainwater samples collected at New Plymouth (Ayers et al., 1986) and at Kelburn and Lauder (Harvey and Clarkson, 1988) have shown pH values less than 5.6. This value is attributed to “natural” rainwater, which is the pH attained by pure water in equilibrium with atmospheric CO2 (Granat, 1972).

Fluoride ion has not been reported in New Zealand rainwaters, but has been identified as a possible pollutant from aluminium smelter emissions. The combined production of Queensland and New South Wales smelters could produce between 0.5 x 10^6 kg and 1.0 x 10^6 kg fluoride per annum (Bridgman et al., 1988).

This paper describes measurements of rainwater chemistry collected at a site on the West Coast of New Zealand. Sampling was carried out in conjunction with air-mass trajectory calculations in order to collect rain subject to Australian influence.

METHODS

Sampling and analysis

Karamea is situated on the northern west coast of the South Island of New Zealand, at latitude 41° 15' S and longitude 172° 7' E (357 950). The site chosen for sampling was 2 km south of Karamea township, 1.5 km inland from the coast, on a plateau known as The Terrace, elevation 50 m (NZMS 260 L27 358 933). It offers a 180° view of the Tasman Sea, and is backed by a mountain range to the southeast.

Rain samples were collected during May 1986 using 500 ml low density polyethylene bottles. The bottles were acid washed in aqua regia for a week, then twice rinsed with

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Deionised water from a Milli-Q system. For storage they were filled with deionised water, individually sealed in polythene bags and crated for transport. All handling and preparation of the bottles was carried out with gloved arms in the Otago University Marine Chemistry laboratory Class 100 clean room. A polythene funnel, diameter 30 cm, was fitted with a screw thread on the neck to receive the sample bottles. It was prepared for transport in a similar manner to the bottles. To prevent any splash-over at ground level, the collector was raised above the ground on a 3 m stand. Neutral filters rinsed with Milli-Q water were used to prevent particulate matter entering the sample.

Two separate rain events were sampled during late May 1986. The first event lasted from 0925 until 1700 on May 24. The second event lasted from 2300 on May 29 until 1200 on May 30. Once the sample was collected the pH was measured, then the bottle was returned to the polythene bag, dated, and stored in the dark at 4 °C. On return to the Otago University Chemistry Department the bottles were stored in the cool room at 4 °C. Ridder et al., (1985) have shown this to be the most satisfactory method for storage of precipitation samples.

Immediately after the collection of each rain sample the pH, wind direction, duration of collection and approximate sample volume were recorded. An Orion Research EA 920 ion analyser with a combination glass electrode was used to record the bulk rain sample pH. To measure the pH of the sample, it was agitated and then allowed to come to full rest so that the pH was measured in the quiescent solution. The value was not recorded until the electrode had reached equilibrium with the solution (Marinenko and Koch, 1984). The ions chloride, nitrate and sulphate were measured by ion chromatography on a Pye Unicam series 4000 liquid chromatograph. A 100 μl sample was injected onto a Vydac 302 anion column (250 mm x 4.6 mm ID) using potassium hydrogen phthalate (0.001 M adjusted to pH 6) as eluent. The U.V. detector was set to 267 nm. Magnesium and calcium were analysed on a Pye Unicam PU 9000 atomic absorption spectrophotometer. Sodium and potassium were analysed with an EEL flame photometer. Fluoride was determined by a colorimetric technique described by Bellack and Schouboe (1958). Zirconium salts of 2-(p-sulphophenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonate (SPADNS) form a red-coloured dye lake, which is discoloured by fluoride ions. The absorbances of the Zr-SPADNS-sample solutions were measured using a Schiradzu UV-240 U.V.-visible spectrophotometer set at 570 nm. Sulphate and sodium concentrations were corrected for sea-salt contribution. This was done by applying the correction described by Underwood et al. (1987), based on the seawater SO$_4^{2-}$/Cl weight ratio of 0.140 and Na'/Cl' weight ratio of 0.5565. The correction used to calculate non-sea-salt sulphate and non-sea-salt sodium based on weight ratios was:

$$\text{non-sea-salt sulphate} = \frac{[\text{SO}_4^{2-}]}{([\text{Cl}^-] \times 0.140)}$$

$$\text{non-sea-salt sodium} = \frac{[\text{Na}^+]}{([\text{Cl}^-] \times 0.5565)}$$

The contribution from sea salt aerosol to other ionic species was calculated to be negligible.

**Air-mass trajectories**

Air-mass trajectory maps were produced in order to pinpoint possible sources of contaminated air. The trajectories of two pressure levels (500 and 900 hPa) were plotted. The first rain event on Saturday 24 May 1986 lasted from 0925 through till 1700. Three samples were collected (sample 0925, collected between 0925 and 1230; sample 1230, collected between 1230 and 1500; sample 1500, collected between 1500 and 1700). Wind direction was southwest to northwest with steady rainfall throughout the sampling period.

The trajectory map for the event (1200 NZST, 24.5.89) showed the air-mass trajectories at both levels originating in the southern ocean (Fig. 1a), at approximately latitude 50°S. The following trajectory map (0000 NZST, 25.5.89) showed the 900 hPa trajectory in the same latitudes while the 500 hPa trajectory lay along latitude 40°S. Weather maps for the period showed an anticyclone covering the west coast of the South Island. The satellite maps showed rain cloud off the east coast of Australia, but only a belt of cloud covering the
Fig. 1 – 96 hour trajectories of air-masses arriving at Karamea at 900 and 500 hPa. Pressure heights are marked in kPa at 24 hour intervals.
(a) 1200 NZST Saturday 24 May 1986; (b) 0000 NZST Friday 30 May 1986.
The locations of aluminium smelters are shown by x.
(NZ Meteorological Service)
Karamea site. We therefore conclude that samples 0925, 1230, and 1500 are likely to be examples of typical oceanic marine aerosol.

Between 1200 NZST Thursday 29 May and 0000 NZST Friday 30 May the 500 hPa trajectories swept an area between 30°S and 35°S on the eastern NSW seaboard. During this time the 900 hPa trajectories remained stationary 300-400 nautical miles northwest of Karamea for the 48 hours before arriving at the Karamea coast. These trajectories originated in the southern ocean, and passed the south coast of the South Island 60 hours earlier (Fig. 1b).

During the morning of Friday 30 May the 500 hPa trajectory swept down the coast of New South Wales, originating 30 hours previously in Tasmania. At the same time the 900 hPa trajectory originated mid-Tasman and was not in contact with any land mass for the 96 hours before arriving at Karamea. The 500 and 900 hPa air mass trajectories for the rain events of 29 and 30 May 1986 were therefore divergent; the 500 hPa trajectories crossed Australia, and the 900 hPa trajectories originated in the southern ocean. During the 24 hours from 0000 Thursday 29 May till 0000 Friday 30 May, the prevailing wind at the Karamea site was from the west/northwest direction. During the following 24 hours the wind turned to the southwest and weakened considerably. This period also saw increased sunshine. Satellite photos indicate that during the night of 29 May there was considerable rainfall in the Tasman sea with heavy falls on the coast. This rain weakened during the following day, with much less rain falling at sea.

RESULTS AND DISCUSSION

Table 1 gives a summary of ionic species concentrations for the rain samples. Ionic Table 1 - Concentrations of ionic species. All concentrations are expressed as ppm (mg/ml). Sulphate and sodium values are corrected for sea-salt contribution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>K⁺</th>
<th>Na⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>F</th>
<th>Cl</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0925-24-05</td>
<td>0.86</td>
<td>13.9</td>
<td>8.5</td>
<td>0.45</td>
<td>nd</td>
<td>10.6</td>
<td>20.1</td>
<td>22.3</td>
<td>6.58</td>
</tr>
<tr>
<td>1230-24-05</td>
<td>0.17</td>
<td>1.1</td>
<td>1.3</td>
<td>0.10</td>
<td>0.18</td>
<td>4.8</td>
<td>4.1</td>
<td>3.4</td>
<td>5.21</td>
</tr>
<tr>
<td>1500-24-05</td>
<td>0.94</td>
<td>9.3</td>
<td>7.8</td>
<td>0.80</td>
<td>0.19</td>
<td>14.4</td>
<td>16.0</td>
<td>19.3</td>
<td>6.08</td>
</tr>
<tr>
<td>2300-29-05</td>
<td>0.85</td>
<td>0.1</td>
<td>1.9</td>
<td>0.15</td>
<td>0.39</td>
<td>11.6</td>
<td>7.1</td>
<td>8.4</td>
<td>5.48</td>
</tr>
<tr>
<td>0130-30-05</td>
<td>0.28</td>
<td>2.2</td>
<td>1.7</td>
<td>0.12</td>
<td>0.14</td>
<td>2.9</td>
<td>3.1</td>
<td>4.4</td>
<td>5.03</td>
</tr>
<tr>
<td>0400-30-05</td>
<td>0.09</td>
<td>0.5</td>
<td>0.4</td>
<td>0.13</td>
<td>0.26</td>
<td>5.0</td>
<td>3.9</td>
<td>4.4</td>
<td>4.64</td>
</tr>
<tr>
<td>0600-30-05</td>
<td>0.28</td>
<td>&lt;0.1</td>
<td>1.6</td>
<td>0.22</td>
<td>0.42</td>
<td>12.6</td>
<td>2.5</td>
<td>3.4</td>
<td>4.67</td>
</tr>
<tr>
<td>0815-30-05</td>
<td>&lt;0.01</td>
<td>6.8</td>
<td>0.4</td>
<td>0.19</td>
<td>1.19</td>
<td>26.9</td>
<td>6.8</td>
<td>8.4</td>
<td>5.28</td>
</tr>
<tr>
<td>1000-30-05</td>
<td>0.48</td>
<td>3.5</td>
<td>2.2</td>
<td>0.59</td>
<td>1.25</td>
<td>19.5</td>
<td>10.1</td>
<td>16.7</td>
<td>5.42</td>
</tr>
</tbody>
</table>

Mean | 0.44 | 4.7 | 2.9 | 0.31 | 0.50 | 12.0 | 8.2 | 10.1 |
S.D. | 0.34 | 4.6 | 2.9 | 0.24 | 0.42 | 7.2 | 5.8 | 6.9 |

nd = not determined.
imbalance is assumed to be due to ammonia, which was not analysed, and dust containing carbonate species.

High fluoride concentrations were recorded during the storm of 29-30 May 1986, with a high of 1.25 ppm recorded at 1000 hours on 30 May. These fluoride levels approach the upper recommended control limit for fluoride in drinking-water as laid out by the World Health Organisation (1971). Where the annual average of daily maximum temperature is in the range 14.7-17.6 °C, the recommended control limit for fluoride in drinking-water is 0.8-1.3 ppm F. The annual average daily maximum for the region is 15.8 °C. There are a considerable number of households in Karamea that rely on rainwater for domestic supply. The mean value of 0.50 ppm F is, however, well within the recommended limits. Also, the contribution of F towards lowering of rainwater pH can only be described as negligible.

The observation of fluoride was totally unexpected. The concentration of fluoride in seawater is typically 1.0-1.2 mg/L (ppt). Bewers and Hayson (1974) suggest that fluoride is actually depleted in marine aerosols, and that terrigenous dust can account for only a few percent of fluoride species in the atmosphere. The contribution of sea salt aerosol to the observed fluoride concentration in the rainwater samples is considered negligible. This leads to the suggestion that the high fluoride levels we observed could be attributable to anthropogenic emissions. When the associated meteorology of the rain events is considered, it does indeed seem possible that emissions from aluminium smelters on the eastern seaboard of Australia could contribute to the high levels of fluoride and sulphate observed in several rain samples.

One major difference can be identified between those rain events of low pH and high ionic concentration, and those rain events of higher pH and low ionic concentration: the origin of the 500 hPa air-mass trajectory. Those events with higher (normal) pH and low ionic concentrations are derived from air masses originating in the southern ocean. However, the events with low pH and high ionic concentrations, in particular fluoride, have air-mass trajectories which appear to have crossed Australia within 30 hours of being sampled at Karamea. It is not possible to establish absolute correlation between air-mass trajectories and anthropogenic transport of trace pollutants without a larger sampling base; errors in mapping air-masses over such large distances and time are large.

CONCLUSIONS

New Zealand is unlikely to suffer the large scale effects of acid rain as experienced in the Northern Hemisphere. While it is possible to show that there is some trans-Tasman transport of atmospheric pollutants, it is too small to warrant immediate concern, unlike the problems of global warming and the ozone hole. However, New Zealand does offer an ideal site to study the southern ocean, an as yet largely unpolluted source of marine aerosol. During winter in particular the air masses originate in the southern latitudes, providing solely marine aerosol. In order to establish positive correlations between air masses originating in Australia and low pH rainfall on the West Coast, further studies should be carried out. The role of the halides in particular requires further investigation.

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REFERENCES


