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Atmospheric chloride deposition and corrosivity at Judgeford, New Zealand

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Abstract

Atmospheric chloride dry deposition rates and the chloride content of rainfall have been measured over a five-year period at the Building Research Association of New Zealand (BRANZ) research station at Judgeford, New Zealand. Dry deposition collectors were placed at various locations on the 10 ha BRANZ site to assess the effects of topography and the proximity of trees and buildings on the measured deposition rates. The mean dry deposition rates measured from collectors in the open gave statistically indistinguishable results. Collectors in close proximity to buildings gave rates one-third of the rates measured from collectors in the open. The variation in dry deposition rates between collection periods was large. The chloride deposition results are compared with those obtained in other studies, and 'CLIMAT' atmospheric corrosivity measurements.

INTRODUCTION

Chloride deposition from the atmosphere is an accepted mechanism for the promotion of atmospheric corrosion of metals. Chloride deposited on a metal surface will provide the ionic content of an electrolyte, and since sodium chloride (the major component of sea-salt) is hygroscopic at relative humidities above 80%, the corrosion reaction may be sustained in the absence of rain or dew. Because New Zealand is an isolated chain of islands in which strong westerly winds create sea-salt aerosol and carry it in the atmosphere, and because relative humidities exceeding 80% for significant lengths of time are a characteristic of the New Zealand climate (Duncan 1985), high levels of deposited chloride can be predicted and will be a significant contributing factor to corrosion.

Most previous work on chloride deposition from New Zealand atmospheres has been by measurement of the chloride content in rain by the Department of Scientific and Industrial Research (DSIR) Soil Bureau (Blakemore 1953, 1973; Miller 1961; Claridge 1975). Claridge (1970) has also reported results of dry deposited salts collected at Taita in 1969 and 1970, which indicated that considerable amounts of chloride were included. Duncan & Whitney (1982) suggested that the best, although indirect, evidence available then for the relative levels of total chloride deposition throughout New Zealand was from the distribution of sodium in sweet vernal grass (DSIR 1962).

Building Research Association of New Zealand (BRANZ) has conducted a project to measure atmospheric chloride deposition and corrosion rates in New Zealand, with the principal aim of examining the relationship between chloride dry deposition rates and corrosivity (Ballance & Duncan 1985; Duncan & Ballance 1987). This paper reports the results of the work to validate the test methods, including the results of measurements made over five years at the BRANZ research station at Judgeford, New Zealand (41°07'S, 174°56'E).

EXPERIMENTAL METHODS

A chloride dry deposition collector design described by Cawse (1974) in which atmospheric aerosol is collected on a sheet of filter paper sheltered from rainfall was used (Fig. 1). Filter papers were recovered at nominally 28-day intervals, as proposed by Cawse. Longer collection periods were tried, but the amount of chloride collected during three-month collection periods was appreciably less than collected during the three concurrent one-month collection periods at an adjacent collector. Cawse (pers. comm.) advised against using three-month collection periods because of the possibility of chloride being blown off the surface of the collector. It is possible that deposition rates measured using this method are inversely related to the length of the collection period (i.e., a number of shorter collection periods will indicate a higher apparent deposition rate than a single longer collection period), but more sensitive analysis methods
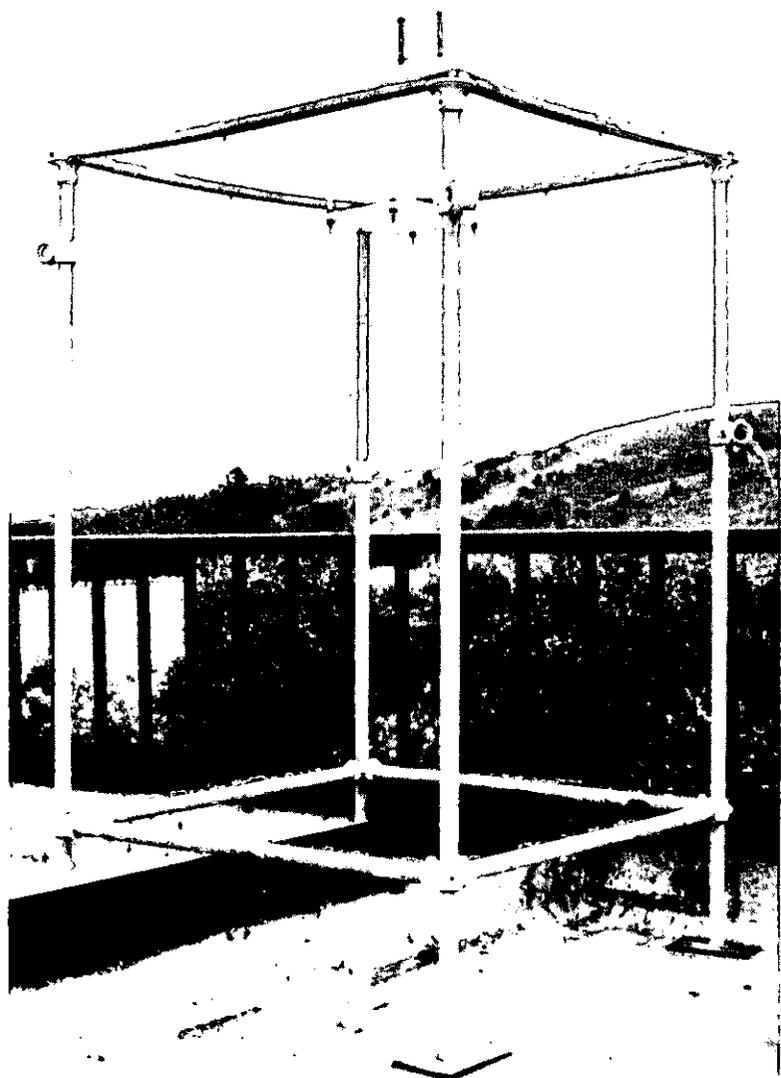
Fig. 1   Chloride dry deposition collector with CLIMAT test unit attached.

than those used would be needed to detect with acceptable precision the smaller amounts of chloride that would be collected in collection periods much less than 28 days.

The chloride was extracted from the filter papers after recovery from exposure by refluxing with deionised water in a Soxhlet apparatus. Initially the whole of the extract was titrated with mercuric nitrate after the method of Schales & Schales (Metson 1956), but this method did not give a very clear end point. The detection sensitivity was estimated at 400 μg, which is approximately equivalent to 10 μg/cm^2/yr for a collection surface of 500 cm^2 exposed for 28 days. After February 1984 a chloride-specific electrode was used; an initial problem with this method due to bromide interference was overcome by the addition of sodium bromate 10 minutes before measurement. The efficiency of the extraction method was checked using filter papers prepared with known amounts of sodium chloride. At intervals, unexposed filter papers were put through the analysis procedure to ensure that chloride contamination was not occurring.

Rainfall was collected in a 100 mm diameter glass funnel and retained in a glass winchester sheathed in aluminium foil. The volume of the rainfall was measured, and a sample was retained for chloride analysis by the same methods as were used for the filter paper extracts.

Atmospheric corrosivity was measured using CLIMAT test units. The test units comprise aluminium wires wrapped around studs of nylon, mild steel, and copper. The wire used was 0.9 mm diameter alloy 1350 (electrical purity), hard drawn. The studs were half-inch BSW threaded and were purchased from local suppliers. CLIMAT test units have been widely used to measure corrosivity both in New Zealand (Duncan & Whitney 1982) and overseas (Doyle & Wright 1982). The results are interpreted in terms of three 'Corrosivity Indices' (Doyle & Wright 1982). The general atmospheric corrosivity index for aluminium or Al–A.C.I. is the percentage weight loss of the wire wrapped on the nylon stud after 90 days exposure. Similarly, the marine corrosivity index (M.C.I.) and industrial corrosivity index (I.C.I.) are the percentage weight losses of the wires wrapped on the steel and copper studs respectively.

LOCATION OF CHLORIDE COLLECTORS AND CLIMAT TEST UNITS

The locations of collectors on the BRANZ research station are shown in Fig. 2. Initially collectors were placed at locations 1, 2, 3, and 4 to test for differences between collectors in the open with collectors in close proximity to buildings. The collectors at locations 1 and 2 were then moved to locations 5 and 6 and further collectors placed at 4 other locations on the site to examine the variability of dry deposition rates between locations. Collectors were placed on the top of a building (location 5), at the top of a hill (location 7), at the base of the same hill (location 8), and in open fields (locations 3, 4, 6, 9, and 10). The collector at location 10 was adjacent to a large tree. The CLIMAT test units were attached to the top of the dry deposition collector at location 3 from 13 May 1985. The rainfall collector was attached to an exposure test rack at the position shown in Fig. 2.

RESULTS AND DISCUSSION

The atmospheric chloride dry deposition results are presented in Tables 1, 2, and 3. The CLIMAT results are also presented in Table 3. The chloride in rain results are presented in Table 4. Selected data are graphically presented in Fig. 3–6.

The dry deposition results from September 1982 to August 1985 (Table 2) were used for analysis. It can be observed (Fig. 3) that the standard deviation among collectors for one collection period is proportional to the mean for that period (i.e., the data fit a log-normal distribution). For this reason a log transform of the data was used to stabilise variance (Box et al. 1978).

An estimate of the coefficient of variation for one observation is about 120%, most of which is due to the variability between collection periods (i.e., the variation
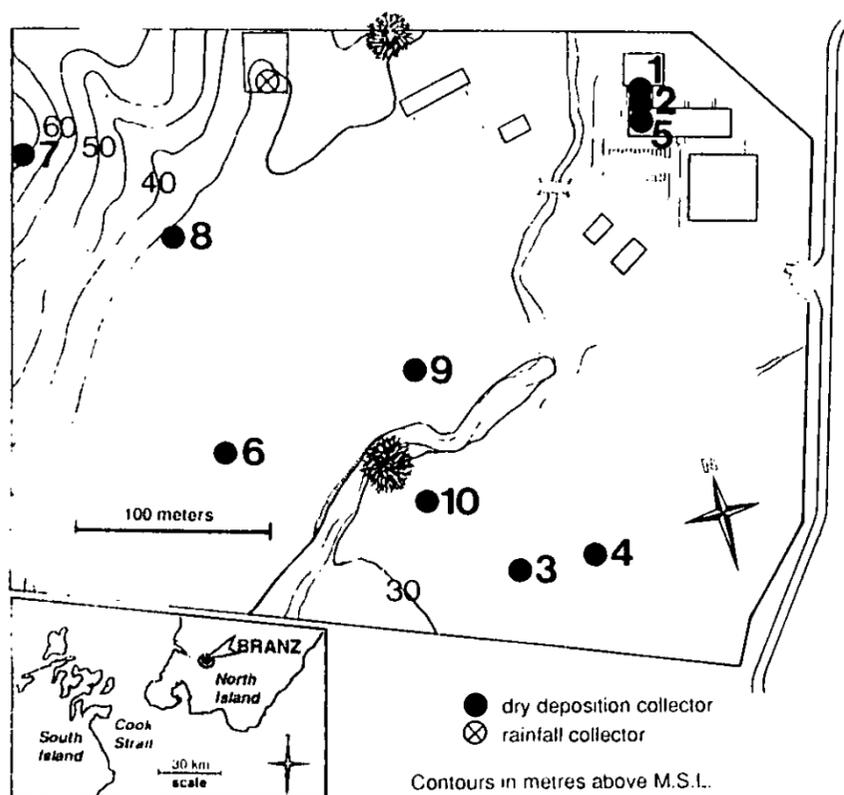
Fig. 2 BRANZ research station showing locations of chloride dry deposition collectors and rainfall collector.

Table 1 Chloride dry deposition ($\mu g/cm^2/yr$).

| Collection	Sheltered		Open	
Period	1	2	3	4
1981				
24 Jun–22 Jul	120	120	260	240
23 Jul–20 Aug	130	140	290	400
20 Aug–24 Sep	130	•	•	•
9 Oct–6 Nov	110	160	390	290
6 Nov–8 Dec	40	90	180	190
8 Dec–5 Jan	100	160	300	340
1982				
7 Jan–4 Feb	170	270	1090	920
5 Feb–5 Mar	80	90	•	•
10 Mar–7 Apr	60	60	210	70
16 Apr–14 May	140	170	630	540
17 May–14 Jun	160	220	670	620
14 Jun–12 Jul	30	30	140	110
12 Jul–9 Aug	190	240	680	550
9 Aug–6 Sep	•	•	87†	530
Mean	112	146	411	400

• = missing data.
† = 1/3 of 3-month collection value.
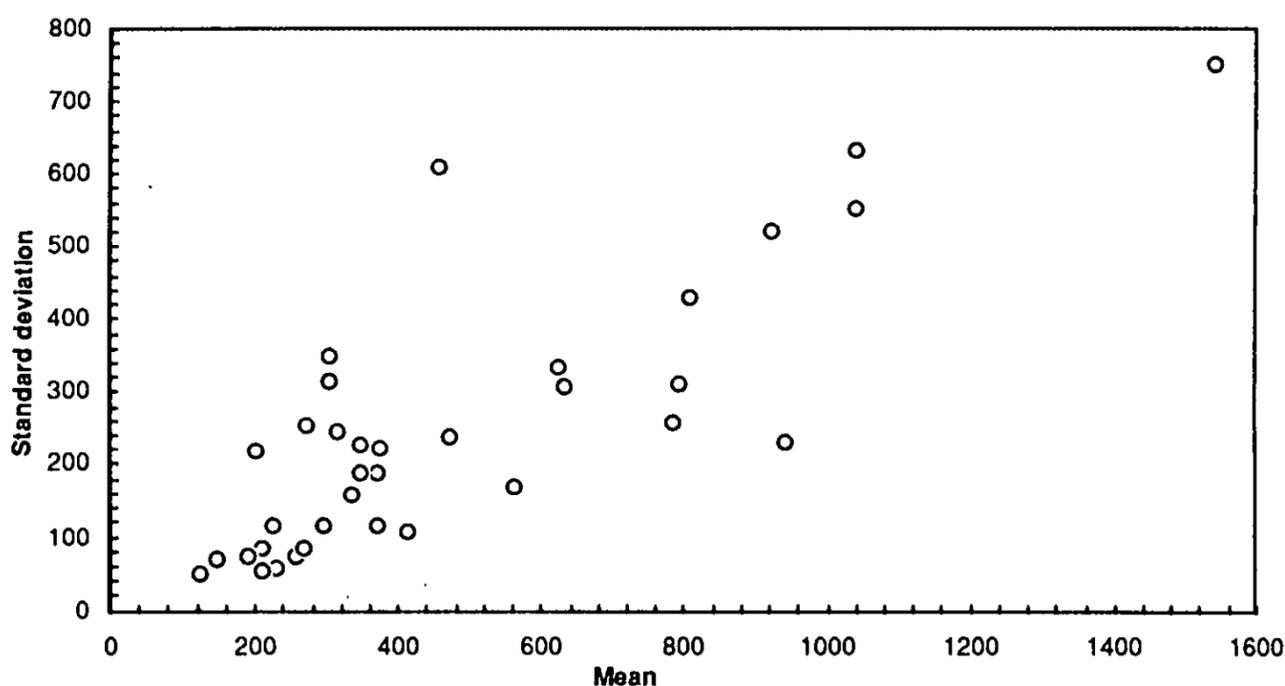
Fig. 3 Mean chloride dry deposition by variance for 36 collection periods, $\mu g\ cm^2/yr$.

between collection periods is much greater than the variation between collectors). The variability between collection periods is illustrated in Fig. 4, from which it can be seen that there is no apparent seasonal pattern in the dry deposition rates. This large variability between collection periods demonstrates that a single 28-day measurement is insufficient to reliably estimate average chloride dry deposition for a given location.

To compare the dry deposition rates measured at each collector location, the variation between time periods has been removed. A standard two-way analysis of variance was conducted on the data. The mean values for all locations are within two standard deviations of the overall mean (Fig. 5), showing that the results from collectors placed at different locations about the site are statistically indistinguishable. Thus it can be concluded that a dry deposition collector placed at any reasonably open location will give a good measure of the level of chloride deposition for the area.

The results from the collectors placed between the buildings (Table 1) were about one-third that of the collectors in the open, indicating that the amount of dry

Table 2 Chloride dry deposition (µg/cm²/yr).

Collection period	Rack location (refer Fig. 2)									
	3	4	5	6	7	8	9	10	Mean	s
1982										
6 Sep–4 Oct	87†	290	490	370	350	240	260	270	295	116
4 Oct–3 Nov	87†	260	70	140	830	380	340	400	313	246
3 Nov–1 Dec	320†	890	220	990	1420	1330	1300	1830	1038	552
1 Dec–29 Dec	320†	610	440	440	350	250	450	440	413	108
29 Dec–26 Jan	320†	1710	1590	920	510	390	1070	850	920	522
1983										
26 Jan–23 Feb	180	303†	320	130	160	110	180	160	193	77
23 Feb–23 Mar	1030	303†	300	880	490	390	670	1000	633	306
23 Mar–20 Apr	1330	303†	930	810	830	440	810	890	793	312
20 Apr–18 May	1820	147†	2020	1690	2640	1020	1180	1790	1538	751
18 May–15 Jun	750	147†	310	450	310	100	170	180	302	314
15 Jun–13 Jul	490	147†	990	680	1210	550	500	430	625	335
13 Jul–10 Aug	740	250†	690	540	550	390	590	730	560	171
10 Aug–7 Sep	460	250†	530	400	620	390	280	<10	368	189
7 Sep–5 Oct	960	250†	1320	*	720	340	730	1340	809	43
15 Oct–2 Nov	<10	70	<10	100	610	240	120	450	201	220
2 Nov–30 Nov	140	170	220	30	260	120	120	110	146	71
30 Nov–25 Jan	280	300	300	70	840	390	320	480	373	222
1984										
25 Jan–22 Feb	280	230	340	90	270	150	170	140	209	85
22 Feb–21 Mar	170	150	100	220	110	70	90	80	124	52
21 Mar–26 Apr	270	150	130	80	280	140	230	220	188	73
26 Apr–16 May	650	220	470	310	310	180	210	340	336	157
16 May–13 Jun	860	350	840	350	420	280	300	380	473	237
13 Jun–11 Jul	640	400	330	340	280	300	350	320	370	115
11 Jul–8 Aug	900	760	1380	660	660	700	600	630	786	258
8 Aug–3 Oct	540	170	430	290	690	210	210	240	348	187
3 Oct–31 Oct	1350	920	1130	940	1020	670	810	680	940	229
31 Oct–28 Nov	120	140	90	500	560	530	210	630	348	227
28 Nov–19 Dec	290	190	260	270	300	130	200	190	229	60
19 Dec–15 Jan	230	170	260	240	290	130	190	180	211	53
1985										
15 Jan–13 Feb	310	210	370	310	260	140	230	210	255	73
13 Feb–18 Mar	190	230	100	1160	150	270	180	160	305	349
18 Mar–15 Apr	540	280	140	1910	410	120	120	110	454	609
15 Apr–13 May	230	180	160	890	200	120	130	250	270	255
13 May–10 Jun	1630	1790	430	310	410	570	1430	1740	1039	663
10 Jun–8 Jul	160	460	190	260	140	140	130	330	226	117
8 Jul–6 Aug	270	300	230	310	440	190	190	210	268	84
Mean	527	381	504	525	553	336	419	511		

* = missing data.
† = 1/3 of 3-month collection value.

Table 3 CLIMAT and chloride dry deposition results.

Exposure period	A.C.I.	I.C.I.	M.C.I. (% Mass loss)	Chloride dry deposition, sum of 3 measurements (µg/cm²)
13 May 85–6 Aug 85	0.01	3.84	5.78	160
6 Aug 85–29 Oct 85	0.10	5.18	4.56	90
29 Oct 85–21 Jan 86	0.09	5.59	6.10	120
21 Jan 86–15 Apr 86	0.12	4.31	3.93	60
15 Apr 86–8 Jul 86	0.07	6.70	7.36	130
Mean	0.08	5.12	5.55	112

deposition occurring on at least some surfaces of structures may be considerably lower than anticipated from measurements made in the open.

The overall mean chloride dry deposition rate for the site of 482 µg/cm²/yr (based on all data for collector location 3) is considerably higher than might have been expected from overseas studies. Cawse (1974), for example, reported much lower values for sites closer to the coast than the BRANZ site. The levels measured at the BRANZ site are similar to the levels found at similar distances inland in Manawatu and Southland by Ballance & Duncan (1985).

The mean chloride deposition in rain of 3200 µg/cm²/yr is higher than levels measured at 9 sites, including two

Table 4 Chloride in rain.

Collection period	Rainfall (mm)	CI (mg/l)	CI (μg/cm²/yr)
1982			
1 Nov–29 Nov	139	25	4520
2 Dec–5 Jan	251	2	490
1983			
5 Jan–2 Feb	18	52	460
2 Feb–2 Mar	12	41	640
2 Mar–30 Mar	96	14	1800
30 Mar–28 Apr	168	9	1930
28 Apr–25 May	353	45	21450
25 May–22 Jun	81	29	3090
22 Jun–20 Jul	249	13	4130
20 Jul–17 Aug	111	22	3240
17 Aug–14 Sep	147	7	1260
14 Sep–12 Oct	152	3	550
12 Oct–10 Nov	284	1	390
10 Nov–7 Dec	47	11	720
7 Dec–4 Jan	187	5	1170
1984			
4 Jan–1 Feb	74	11	1020
1 Feb–29 Feb	42	1	20
29 Feb–28 Mar	105	3	360
28 Mar–26 Apr	54	9	570
26 Apr–23 May	106	17	2460
23 May–20 Jun	78	11	1150
20 Jun–18 Jul	316	13	5390
18 Jul–15 Aug	60	15	1160
15 Aug–12 Sep	83	7	790
22 Sep–10 Oct	109	16	2220
10 Oct–7 Nov	101	17	2220
7 Nov–5 Dec	98	12	1520
5 Dec–10 Jan	77	6	480
1985			
10 Jan–7 Feb	200	4	1100
13 Feb–18 Mar	86	11	1020
18 Mar–15 Apr	0	0	0
15 Apr–13 May	47	9	530
13 May–10 Jun	337	94	41290
10 Jun–8 Jul	175	5	1230
8 Jul–5 Aug	264	44	14950
5 Aug–2 Sep	144	9	1520
2 Sep–4 Oct	72	11	910
4 Oct–29 Oct	91	27	3630
29 Oct–25 Nov	94	26	3320
25 Nov–24 Dec	173	5	1090
24 Dec–21 Jan	69	6	490
1986			
21 Jan–17 Feb	173	2	490
17 Feb–18 Mar	115	6	800
18 Mar–14 Apr	64	11	920
14 Apr–12 May	72	8	720
12 May–9 Jun	89	26	3030
9 Jun–7 Jul	353	15	7000
Mean	132	16	3200

sites 0.5 km from the coast, in the southern part of the North Island of New Zealand (Blakemore 1953), and is three times higher than levels reported for Taita (41°12'S, 174°58'E), approximately 8 km south of Judgeford (Miller 1961; Blakemore 1973; Claridge 1975).

This is evidence of the strong marine influence at the Judgeford site.

The CLIMAT marine corrosivity index results are indicative of a 'moderate' to 'moderately-severe' marine environment according to the classifications proposed by Doyle & Wright (1982). The values of the industrial corrosivity index confirmed that the site is predominantly marine and not influenced by industry. The marine corrosivity index results correlated ($r=.78$) with the log sum dry deposition values for the corresponding time period, as shown in Fig. 6. The correlation equation,

marine corrosivity index =
$$-7.26 + 2.75 \ln (\text{chloride } \mu g/cm^2),$$

is similar to that reported by Duncan & Ballance (1987), who also used 28-day chloride collection periods. This is further evidence of the significance of dry deposited chloride as a corrosion stimulator in New Zealand, and supports the view of Duncan & Ballance (1987) that the CLIMAT test is a valid indicator of chloride dry deposition levels in predominantly marine-influenced sites. However, if the measured rate of chloride deposition proves to be dependent on the length of collection period, as indicated by the lower three-month rates obtained in this study, then the terms of the correlation equation will vary with the length of collection period. The CLIMAT results also correlated with the volume of rainfall ($r=.60$). This weaker correlation may be attributed to the complex effect of chloride-containing rain on the corrosion reaction. While sustaining the corrosion reaction during precipitation the rain will also dissolve and wash away accumulated salts and other surface contaminants such as corrosion products from the corroding surface (Duncan 1984), so reducing subsequent corrosion.

CONCLUSIONS

Methods to collect and measure atmospheric chloride dry deposition have been validated. Measurements made over five years at Judgeford, New Zealand have been analysed.

Higher levels of dry deposited chloride (482 μg/cm²/yr) than expected from overseas studies were found, in agreement with other work in New Zealand. There were large differences observed between collection periods, demonstrating that a number of measurements are necessary to reliably estimate the average deposition. No apparent seasonal effect was found. Collectors placed at different locations about the site gave statistically indistinguishable results; thus a collector at any reasonably open location should give a good indication of the likely highest levels of dry deposited chloride on exposed surfaces throughout an area. Collectors placed between buildings gave measures of deposition one third that of collectors in open locations.

The levels of chloride in rain (16 mg/l, 3200 μg/cm²/yr) were high compared to earlier studies at other places in New Zealand.
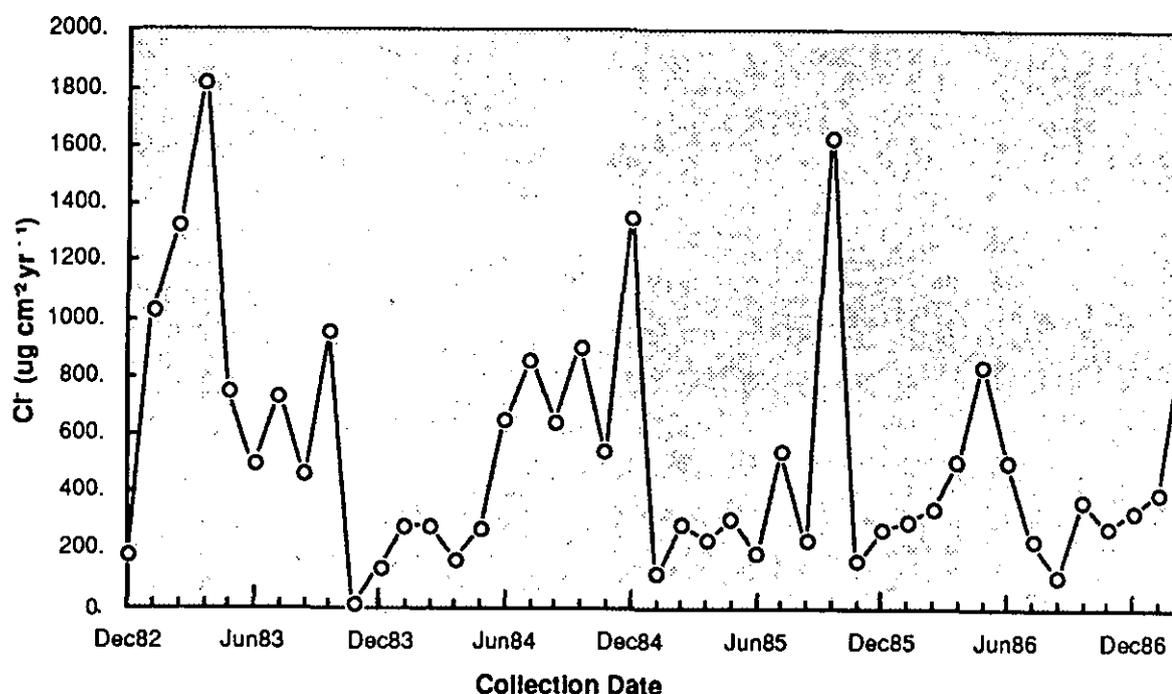
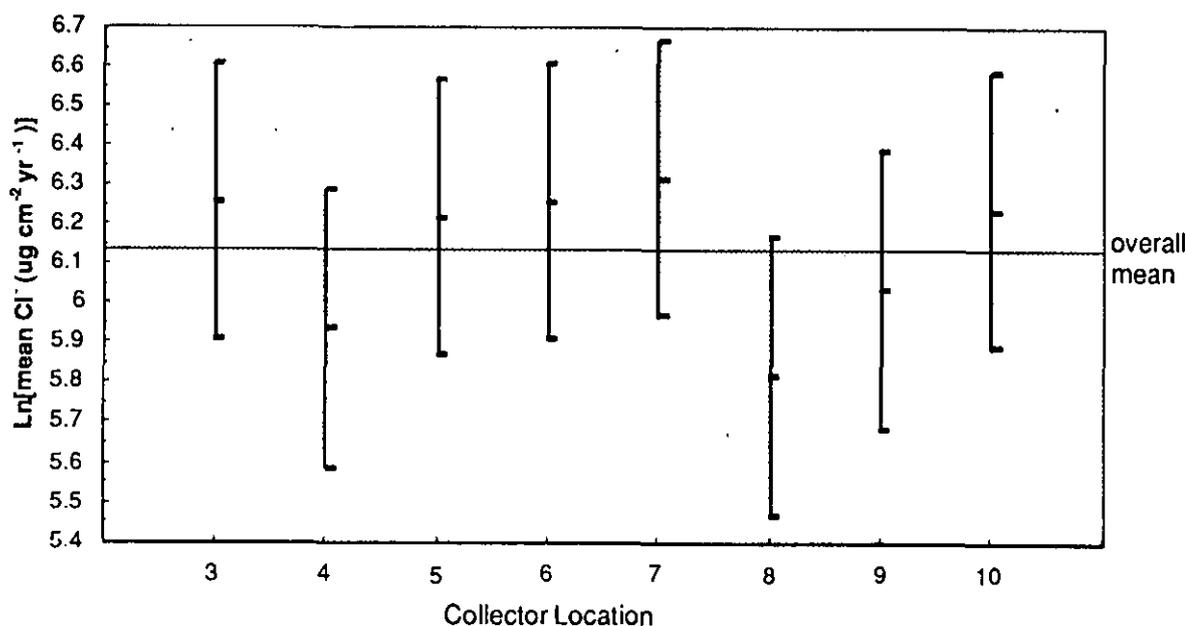Fig. 4   Chloride dry deposition rate by collection date, collector location 3.

Fig. 5   Mean chloride deposition rate by collector location (bars represent two standard deviations either side of mean).

The reasonable correlation of the CLIMAT results with chloride dry deposition confirms the significance of dry deposited chloride as a corrosion stimulator, and supports the validity of use of the CLIMAT test as an indicator of chloride dry deposition levels at marine influenced sites.

ACKNOWLEDGMENTS

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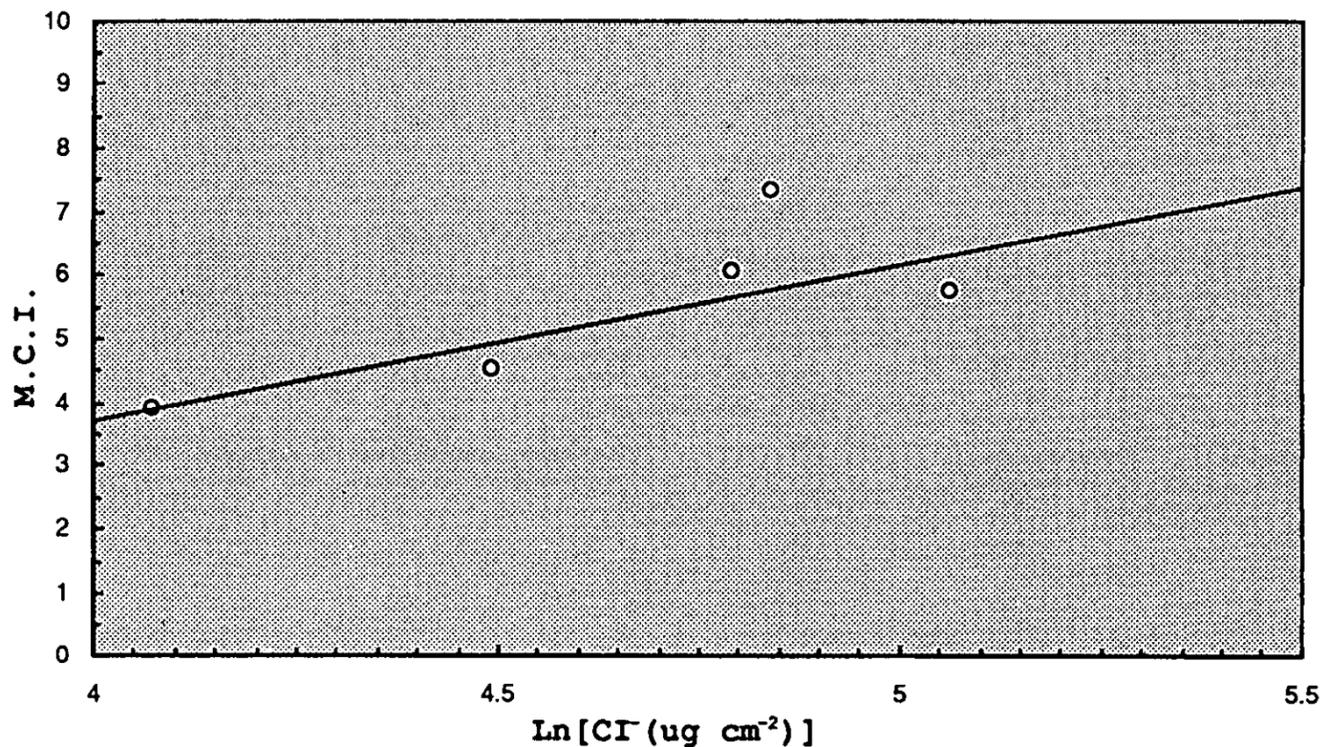
Fig. 6   Correlation of chloride dry deposition rate with M.C.I.

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