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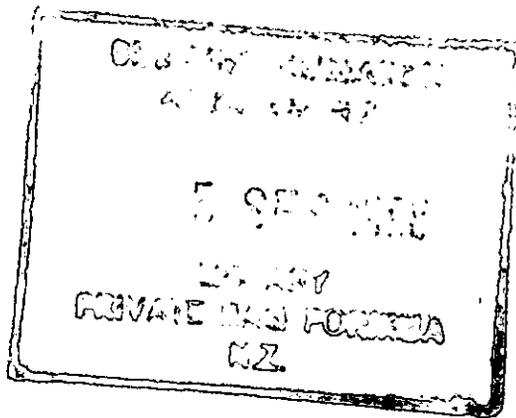
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# MARINE SALTS CONTRIBUTION TO ATMOSPHERIC CORROSION



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# Marine Salts Contribution to Atmospheric Corrosion

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**REFERENCE:** Duncan, J. R. and Ballance, J. A., "Marine Salts Contribution to Atmospheric Corrosion," *Degradation of Metals in the Atmosphere*, ASTM STP 965, S. W. Dean and T. S. Lee, Eds., American Society of Testing and Materials, Philadelphia, 1988, pp. 316-326.

**ABSTRACT:** The effects on atmospheric corrosivity of carriage of sea-salt inland from ocean coasts have been largely neglected by researchers except for regions within a few kilometers from the sea. In island nations, salt-affected zones can cover large percentages of total land area. The extent of carriage of sea-salt inland, and correlation to this of the corrosion rates of metals, is assessed in two areas of New Zealand. A sheltered surface collector is erected at each of 18 sites at up to 90 km inland. The site had been chosen to minimize the likelihood of industrial pollution. Each collection rack had attached to its top a test unit with an aluminum wire on a threaded stud (Climat test unit) and a rod holding a pair of steel coupons. There was very good correlation of the steel corrosion rate (48 weeks of exposure) to the log (chloride deposition), and to the 48-week average steel stud value in the 12-week Climat test. The Climat test, because of its ease of performance, thus seems to be a cost-effective means of assessing likely corrosion problems in purely marine environments. The results suggest that sea-salt mediated corrosion rates at distances 20 km and more inland are higher than might have been expected from published reports of studies on continental land masses.

**KEY WORDS:** aluminum, atmosphere, chlorides, corrosion, measuring, New Zealand, sea-salt, steel

The carriage of sea-salt inland from coasts has long been recognized as an important contributor to atmospheric corrosion problems in most maritime regions. The most thorough study of this subject reported is that by Ambler and Bain in Nigeria [1], though many textbooks and authors have based their statements on an earlier report [2] of a smaller set of values found in Nigeria. These studies found chloride deposition decreases with distance inland, with a consequent decrease in atmospheric corrosion. Most of the decreases occurred within a kilometer or two of the shore. But the authors seem to have mainly confined themselves to discussing this rapid decrease in corrosivity close to the shore, rather than looking deeply into the effects of sea-salt further inland. The rapid decrease is important in assessing the corrosivity variations to be expected at exposure sites within this distance of the shore if the comparability of results at different sites is to be understood. However, it has much less relevance to the precautions that must be taken in the design of a structure at a distance of, say, 20 km inland. The designer recognizes that if his structure is immediately adjacent to a beach, he will need to take special precautions, but he has much less guidance on how to assess his problems further inland.

Over 1984 to 1985, corrosion tests and measurements of the levels of chloride deposited by wind onto sheltered surfaces were performed at 18 sites at up to 90 km from the sea in two regions of New Zealand [3]. This work was undertaken because there seemed to be unexpectedly high atmospheric corrosion rates inland along the path of prevailing winds blowing from the

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sea. A characteristic of the climate of these regions is long periods of relative humidity exceeding 80%. Since sodium chloride can take up water from the atmosphere at these humidities, sea-salt deposits (especially on surfaces that are sheltered from rain) can pose severe durability hazards to metal building claddings.

Neutron activation analyses of the chloride collection surfaces showed that even 50 km inland, the ratio of sodium to chloride was still approximately correct for the chloride to have been of marine origin [3]. This paper discusses the correlations between amounts of chloride deposited and the corrosion measurements found in this recent study, and compares the relationship of corrosion rate to distance from the sea with that suggested by Ambler and Bain and other workers.

## Experimental Procedure

### *Selection of Monitoring Sites*

Monitoring sites for the study were in an approximate geometric progression of distance inland from coasts that had prevailing winds blowing off the sea onto the land, across fairly flat countryside at least for the first 30 km. The availability of reliable meteorological data was also taken into account. (It was hoped that wind run and gust data could be used as variables in the analysis of the results, but this proved impossible because there were insufficient sites with these data.) Sites were initially selected to try to avoid industrial pollution sources, which could be expected to interfere with the experiment. The locations are listed in Table 1.

TABLE 1—*Site locations and 28-day chloride dry deposition rate and rainfall data.*

Site	Distance from Coast, km	Chloride Dry Deposition Rate, g/m <sup>2</sup> /year		Rain in Test Period, mm <sup>a</sup>
		Mean	Maximum	
<b>Manawatu</b>				
Tangimoana	0.8	21.9	53.8	NR
Paraparaumu	1	11.3	25.1	913
Flockhouse	4.5	6.4	15.0	915
Clydesdale	7	6.0	16.3	NR
Levin	8	2.6	8.9	1007
Bulls	13.5	1.7	4.5	NR
Kairanga	20.5	4.0	8.2	725
Palmerston North	33	2.3	6.0	807
Ballantrae	52	3.1	6.3	NR
<b>Southland</b>				
Oreti Beach	0.6	34.1	108.6	NR
Tiwai Point <sup>b</sup>	5.5	28.5	64.3	808
Clifton	8	12.9	23.4	NR
Invercargill Aero	8.5	7.8	14.9	914
Myross Bush	16.5	2.4	6.0	NR
Woodlands	28	0.5	0.9	927
Brydone	49	2.2	3.9	NR
Gore	64	1.0	2.0	782
Tapanui	94.5	0.4	0.8	773

<sup>a</sup>Rainfall data collected by NZ Meteorological Service station. NR = not recorded at this site.

<sup>b</sup>On sandy harbour beach, 5.5 km from nearest ocean shore.

*Collection of Dry-Deposited Chloride*

The collector used is described by Cawse [4]. A horizontal sheet of filter paper (Whatman 541, 200 × 250 mm) supported on a perspex sheet of approximately the same size is mounted centrally beneath a one-m square perspex cover supported at each corner (to shield the paper from rain). This filter paper surface is approximately 1350 mm above the ground. The paper surface is collected and renewed each 28 days. On recovery, the chloride is extracted from the paper using a Soxhlet apparatus by refluxing with deionised water. The chloride concentration is determined in the resulting solution using a chloride-specific electrode. Control samples that were never exposed are put through the analysis procedure at intervals.

*Corrosion Rate Determinations on Steel Panels*

Projecting from the top of each chloride collection rack is a bracket with two steel coupons attached, with an insulated bolt through the centre of each coupon so that the coupons are held vertically, approximately 120 mm from the bracket. The coupons were produced from steel cast by BHP Research Laboratories in Australia to an alloy composition (Table 2) which corrodes at a rate relatively insensitive to minor variations in composition [5]. The steel was hot and cold rolled to 3.2 mm strip, which was then guillotined to 100 × 50 mm coupons. These were annealed and drilled with an identification pattern of four 1.59 mm holes at one edge of each coupon before supply to the Building Research Association of New Zealand (BRANZ).

Before exposure, the coupons are lightly rubbed with steel wool, degreased, then immersed in 5% hydrochloric acid solution at 80°C for ten min. They are then rinsed in cold running tap water for ten min, immersed in boiling water, and air dried. Each is weighed to 0.1 mg and stored in a dessicator until ready for exposure. The exposure period is 48 weeks. Upon retrieval, the coupons are immersed in a solution of 50 g stannous chloride per litre of concentrated hydrochloric acid to remove corrosion products, and rinsed thoroughly. The coupons are reweighed to 0.1 mg and the corrosion rate calculated as a function of the total exposed area of the coupon. (This follows the procedure adopted by King et al. [5].)

*Galvanic Corrosion Evaluation of Aluminum*

A Climat test unit [6] is attached to the top of each chloride collection rack. This comprises aluminum wire wrapped around 1.27 mm (0.5 in.) BSW threaded studs made of mild steel, copper and nylon, respectively, which are screwed into a solid base. The wire used is Alloy 1350 [7], 0.9-mm diameter hard-drawn, supplied by Alcan (NZ) Ltd.

Before assembly, the components are cleaned in petroleum ether, air dried, then rinsed in acetone and again air dried. The wire (approximately 900 mm long) was weighed to 0.1 mg, wound tightly around the stud, and held in place by short lengths of insulated wire. The exposure period was 84 days (to correspond to a multiple of 28 day periods of chloride collection). Upon retrieval, the wire is removed from the stud and immersed in a boiling solution of 20 g/L chromic acid, 40 g/L phosphoric acid for 10 min to remove the corrosion products. After rinsing in hot water, then acetone, the wire is reweighed to 0.1 mg and the percentage weight loss calculated. Unpublished studies at BRANZ have shown this method (modelled on that used by Doyle and Godard [8]) produces negligible weight losses on control samples.

TABLE 2—*Composition of steel panels.*

C	Mn	Si	P	S	Ni	Cr	Cu
0.16	0.61	0.05	0.01	0.026	0.27	0.12	0.22

## Results

The amount of chloride deposited onto the collectors differs widely from month to month. The mean and maximum 28-day chloride deposition rates at each site over the 48-week period of the study are listed in Table 1. The steel coupon corrosion rate and the mean aluminum wire percentage weight losses from the Climat units at each site are listed in Table 3. The steel coupon rates are the average from the two coupons at each site. The Climat values are the average for the single units at each site over the four test periods. Typical data are given in Table 4.

Figures 1 to 8 show some of the relationships found between the amounts of chloride deposited, the 84-day Climat tests, and the 48-week steel corrosion rates. Table 5 lists the correlation details for the complete data sets for chloride deposition, the 84-day mild steel stud Climat tests, and the 48-week steel corrosion rates. The steel stud results were chosen for use in this further development because this stud has been described as that most affected by a marine environment [6].

## Discussion

A very good correlation has emerged between the values found on the mild steel stud in the Climat test and the corrosion rates of the steel coupons. There has also been good correlation of the corrosion measurements using the mild steel stud in the Climat test to the logarithm of the deposited chloride, and very good correlation of the steel coupon corrosion rate to the logarithm of the deposited chloride.

These correlations are important in assessing the validity of using the Climat test in selecting materials or methods of protection against atmospheric corrosion. The Climat test is relatively cheap and simple to perform, and particularly so as compared with the analysis for chloride deposition, whether using the wet candle technique of Ambler and Bain or that used in the present study. There is very large variability from month to month in the dry deposition of

TABLE 3—Results of corrosion tests done at collection sites.

Site	Average Climat Test Results, %wt Loss			Average Corrosion Rate for Steel, $\mu\text{m}/\text{year}$
	Mild Steel	Copper	Nylon	
<b>Manawatu</b>				
Tangimoana	12.25	14.37	0.24	39.2
Paraparaumu	9.36	10.22	0.24	36.4
Flockhouse	8.62	8.52	0.14	31.6
Clydesdale	8.01	8.01	0.20	33.5
Levin	5.67	5.33	0.08	18.9
Bulls	5.46	5.67	0.14	22.6
Kairanga	6.76	5.72	0.15	26.4
Palmerston North	5.20	4.85	0.10	25.2
Ballantrae	5.50	5.17	0.10	25.3
<b>Southland</b>				
Oreti Beach	12.76	16.23	0.21	41.2
Tiwai Point	11.83	11.80	0.27	40.9
Clifton	10.32	12.32	0.20	37.8
Invercargill Aero	8.68	8.30	0.15	32.8
Myross Bush	5.77	5.55	0.09	20.9
Woodlands	2.97	3.40	0.08	12.2
Brydone	5.68	5.93	0.11	22.1
Gore	3.31	3.82	0.07	13.8
Tapanui	1.48	1.82	0.06	7.0

TABLE 4—Actual Climat values recorded for three sites in Southland, and rainfall data for the test periods.

Site	Test Period 1984-5			
	May to Aug.	Aug. to Oct.	Oct. to Jan.	Jan. to Apr.
<b>Tiwai Point</b>				
Climat units				
Mild steel	17.32	10.08	10.53	9.38
Copper	17.42	10.98	9.72	9.06
Nylon	0.33	0.26	0.34	0.14
rainfall, mm	158	216	194	241
<b>Invercargill Aero</b>				
Climat units				
Mild steel	9.78	8.23	8.95	7.75
Copper	9.36	9.08	8.02	7.94
Nylon	0.16	0.24	0.15	0.06
rainfall, mm	186	229	215	283
<b>Gore</b>				
Climat units				
Mild steel	4.54	3.20	2.90	2.58
Copper	4.94	4.01	2.90	3.42
Nylon	0.13	0.11	0.05	0.00
rainfall, mm	147	221	195	219

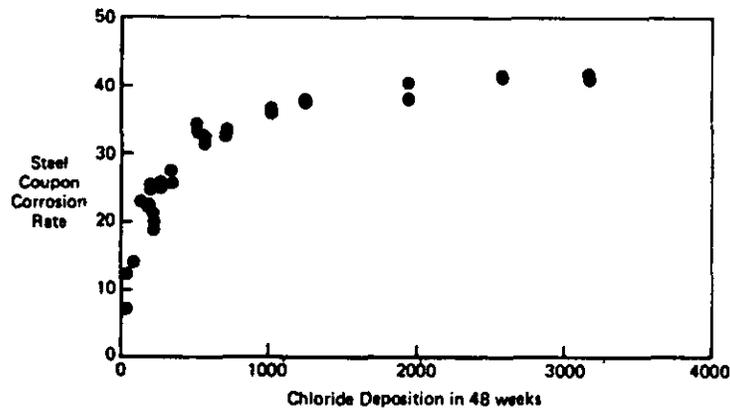


FIG. 1—Relationship of steel corrosion rate ( $\mu\text{m}/\text{year}$ ) to the 48-week total chloride deposition on the sheltered collector ( $\mu\text{g}/\text{cm}^2$ ).

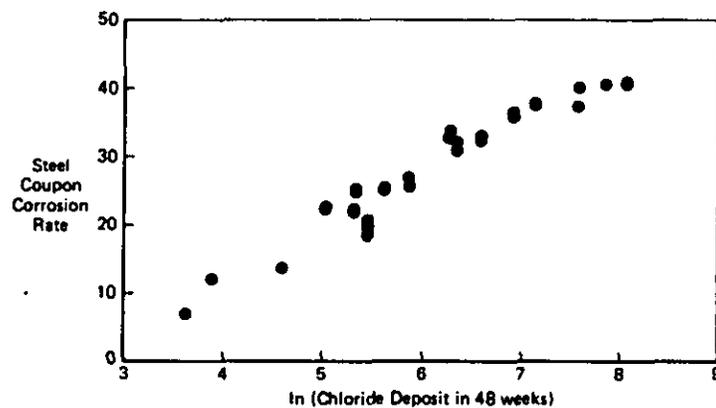


FIG. 2—Relationship of steel corrosion rate ( $\mu\text{m}/\text{year}$ ) to the logarithm of the 48-week total chloride deposition on the sheltered collector ( $\mu\text{g}/\text{cm}^2$ ).

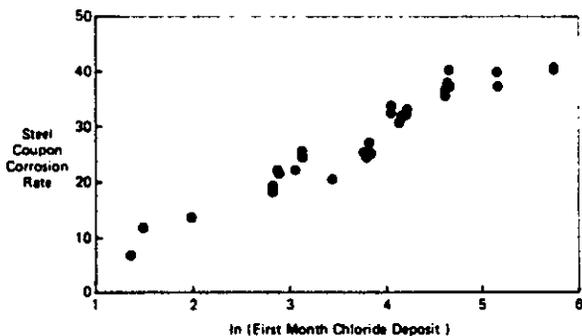


FIG. 3—Relationship of steel corrosion rate ( $\mu\text{m}/\text{year}$ ) to the logarithm of the first four weeks chloride deposition on the sheltered collector ( $\mu\text{g}/\text{cm}^2$ ).

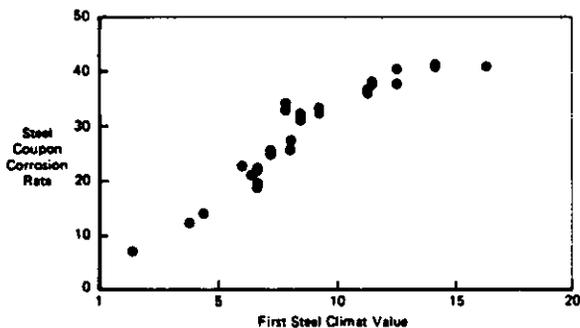


FIG. 4—Relationship of steel corrosion rate ( $\mu\text{m}/\text{year}$ ) to the percentage weight loss from the aluminum wire on the steel stud in the Climat test over the first twelve weeks.

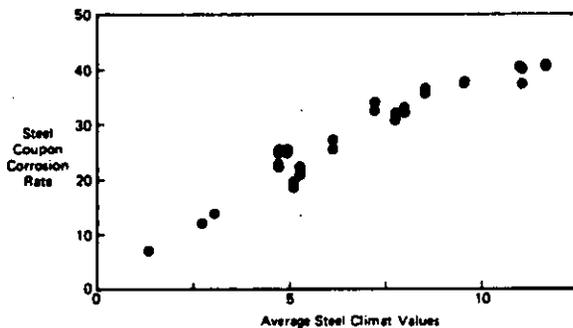


FIG. 5—Relationship of steel corrosion rate ( $\mu\text{m}/\text{year}$ ) to the average percentage weight loss from the aluminum wire on the steel stud in the Climat test over the four 12-week periods.

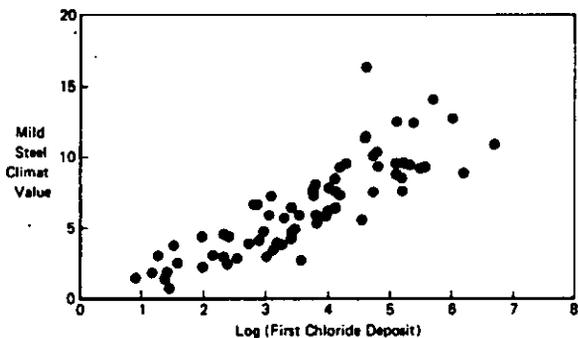


FIG. 6—Relationship of the percentage weight loss from the aluminum wire on the steel stud in the Climat test to the logarithm of the first four weeks chloride deposition on the sheltered collector ( $\mu\text{g}/\text{cm}^2$ ).

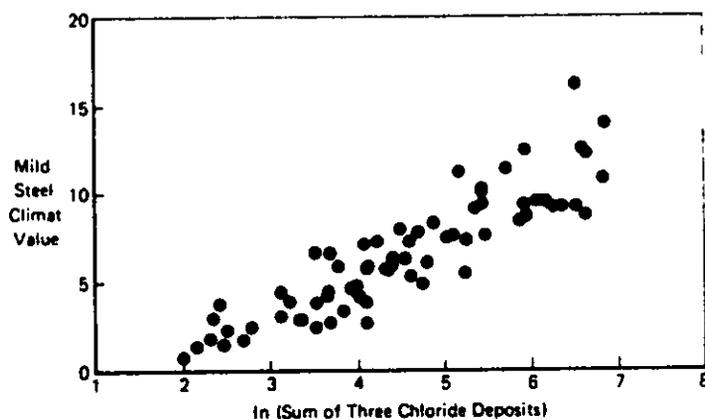


FIG. 7—Relationship of the percentage weight loss from the aluminum wire on the steel stud in the Climat test to the logarithm of the total twelve weeks chloride deposition on the sheltered collector ( $\mu\text{g}/\text{cm}^2$ ).

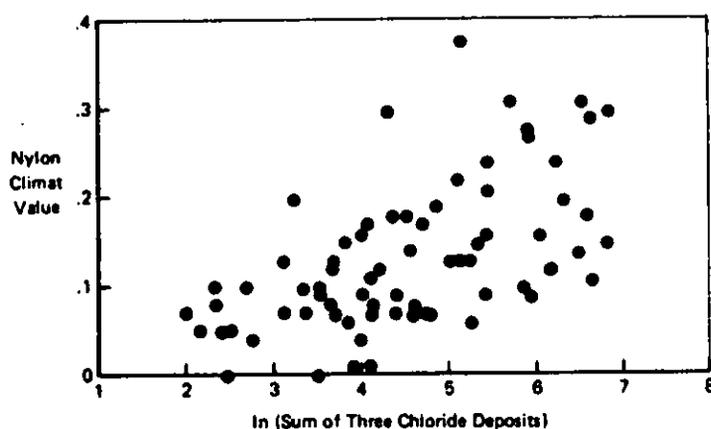


FIG. 8—Relationship of the percentage weight loss from the aluminum wire on the nylon stud in the Climat test to the logarithm of the total twelve weeks chloride deposition on the sheltered collector ( $\mu\text{g}/\text{cm}^2$ ).

chloride, as shown in Table 1. It would be unwise to categorize the possible corrosivity of a site on the basis of a single month's chloride deposition measurement. There is also the possibility on sheltered surfaces that will not be washed by rain that a single storm could deposit sufficient chloride to pose major corrosion hazards to these surfaces even in a less generally corrosive zone. Since this test has been done at many sites around the world (see, for example, the lists by Doyle and Wright [6]), it offers the possibility that a new site could be put into a wider context, and allows past experience at other sites to be used as a guide to the corrosion problems to be anticipated, provided it has a basic validity. This study, performed in two widely separated regions in New Zealand, suggests that the Climat test does have a basic validity, at least for sites which can be categorized as dominantly affected by sea-salt deposition. The variability from season to season of values in the Climat test (Table 4) has been observed by other workers also [6]. From the data in Table 4, it is obviously not related simply to rainfall in the present study. It probably is related to wind blowing from the sea, but this could not be proven conclusively from the weather data available.

The qualification regarding the dominant effects of sea-salt should be emphasized. The success of the correlation in this instance is possibly enhanced by the choice of monitoring sites, which were expected to be free of significant industrial pollution. Thus, for example, Ambler [9] found a similar drop in chloride concentration with increasing distance inland in United Kingdom as compared to that found in Nigeria, but did not find such a clear relationship between distance and corrosion rate as had been found in Nigeria. He attributed this difference to the effect of industrial pollution. Hayward (personal communication) had described how to

TABLE 5—Correlation equations and coefficients.

## FIG. 2

Steel Coupon Corrosion Rate =  $-19.7 + 7.88 \ln$  (total of twelve 4-week chloride deposition rates)  
Correlation Coefficient: r-squared is 95.1%

## FIG. 3

Steel Coupon Corrosion Rate =  $-2.66 + 8.27 \ln$  (chloride deposition rate in first 4 weeks)  
Correlation Coefficient: r-squared is 93.5%

## FIG. 4

Steel Coupon Corrosion Rate =  $5.61 + 2.59$  (first steel-stud Climat value)  
Correlation Coefficient: r-squared is 88.9%

## FIG. 5

Steel Coupon Corrosion Rate =  $5.23 + 0.832$  (sum of four steel-stud Climat values)  
Correlation Coefficient: r-squared is 93.6%

## FIG. 6

Steel-Stud Climat Value =  $-1.17 + 2.11 \ln$  (chloride deposition rate in first 4 weeks)  
Correlation Coefficient: r-squared is 72.0%

## FIG. 7

Steel-Stud Climat Value =  $-3.94 + 2.33 \ln$  (total of three 4-week chloride deposition rates)  
Correlation Coefficient: r-squared is 80.6%

## FIG. 8

Nylon-Stud Climat Value =  $-0.0354 + 0.0372 \ln$  (total of three 4-week chloride deposition rates)  
Correlation Coefficient: r-squared is 33.6%

NOTE: Steel coupon corrosion rate is in  $\mu\text{m}/\text{year}$ ; chloride deposition is in  $\mu\text{g}/\text{cm}^2$ ; Climat value is in percent.

correct the value for the A1/Cu stud, for the marine influence, so that it can be used to assess industrially generated atmospheric corrosivity, using the expression:

$$(\text{Industrial Corrosion Index}) = (\text{A1/Cu Value}) - 1.22(\text{A1/Mild Steel Value}) \quad (1)$$

Values below 0.5 are negligible. When this is done, only the Oreti Beach site in each of the first three periods gives significant values. The reason for this is not understood, since the collector was sited more remotely from roads, etc., than most of the other collectors.

It is interesting to observe the good correlation of the 48-week steel corrosion rate to the first four-week chloride deposition, which might be taken to confirm the warning of others [10] that the initial exposure conditions have a very important effect on the subsequent corrosion. However, there is also very good correlation of this corrosion rate to the total chloride deposited over the whole 48 weeks, and the four-week result may simply indicate that the initial four weeks were fairly typical of the whole year.

Atmospheric corrosion rates on fully rain-washed nonferrous metal surfaces in New Zealand are generally low compared to some other countries [11]. Though no nonferrous metal panels are used in the present study to assess the correlation of their corrosion rates to the chloride deposition rates, this general trend of low nonferrous metal corrosion rates is reflected by the fairly low values for the nylon stud when compared to some of the values listed by Doyle and Wright [6]. It will be noted from Fig. 8 that the correlation of values found for this stud to the

deposited chloride is fairly poor, and this is presumably because the rainfall (see Table 1) has regularly washed away the deposited chloride. In instances where metal roof claddings in eaves become perforated by corrosion in New Zealand, the corrosion is very frequently from the underside, reflecting this benefit from rainwashing. The atmospheric corrosion mechanism of mild steel differs from that of nonferrous metals in that on steel, the chloride aggregates at the metal/rust interface, while on the others, it is at the corrosion product/atmosphere interface [12]. Because of this difference in mechanisms, removal of chloride by rainwashing is much more difficult from corroding steel surfaces. In the present study, there was fairly comparable rainfall at all sites within each region over the course of the exposure test (Table 1), so that differences in rainfall have not been a significant contributor to the differences in corrosion rate. Presumably, this regular rainfall, which is an advantage in washing the surfaces of the nonferrous metals, has had the effect, in the present study, of simply increasing the time-of-wetness, and hence the corrosion, of steel. (Rainfall in New Zealand also contains a lot of dissolved chloride [11]. It might, therefore, be expected that a low residual level of chloride is left on the surface, even after rain.)

There have been very few reports of direct comparisons made between corrosion rate and chloride deposition. It has been customary, on the basis of the studies in Nigeria [1,2], to expect that the chloride concentration drops off rapidly with distance from the coast, and with it the corrosivity of the natural atmosphere. This view has probably been strengthened in European minds by the production of a report for the Commission of European Communities [13], which shows reduction to very low background levels within 5 km of the sea for many sites as part of an assessment of exposure test site severity. These "continental" measurements are, however, almost certainly not transferable to oceanic sites. In a paper which seems to have been largely ignored by corrosion scientists, Brierly [14] collated available data on total chloride precipitation at sites around the world and proposed four "atmosphere seasalts design criteria areas," into which he categorized all land masses. Brierly emphasized the importance of geography in determining the amount of seasalt deposited; thus, because the wind is predominantly westerly across Scandinavia, values of 12 kg/ha/year were found for chloride deposition in Norway, but only a few per cent of this on the eastern coast of Sweden. This is reflected in the greater corrosiveness of the atmosphere in Norway [15]. Oceanic islands, especially if they lie in strong wind flows that travel extensive distances across the sea, fall in Brierly's most severe zone, and the direction and strength of the wind is more important than the distance inland in determining the saltfall. Thus New Zealand, a chain of islands in a latitude belt of strong winds, might be expected to show rather different effects from Nigeria or Europe in the relationship of seasalt deposition to distance inland.

This geographic effect on atmospheric corrosivity zones on small islands has been reported previously for Cuba [16], where the chloride in the atmosphere was determined to be the major corrosive influence, and for Barbados [6]. The latter workers proposed a relationship between the cube roots of the corrosion rate (or the atmospheric salinity) and the distance inland, which they said fitted to the Ambler and Bain data from Nigeria and to data collected in the Republic of South Africa for distances up to 16 km inland. It is not clear from their paper whether it fitted to their data from Barbados. Application of this relationship to their data from South Africa and to the data from the two regions of New Zealand examined here is shown in Figure 9. The relationship appears to be of doubtful validity for the South African data, and to be invalid for the New Zealand data. The decrease in corrosion rate with distance inland is too slow.

## Conclusions

For an environment that can be expected to be fairly free of industrial pollution, the Climat test is well-correlated to steel corrosion rates and to the amount of chloride deposited onto sheltered surfaces. Because it is a relatively simple test to perform, this test is a cost-effective means of assessing the dangers of atmospheric corrosion in such environments. The extent of chloride

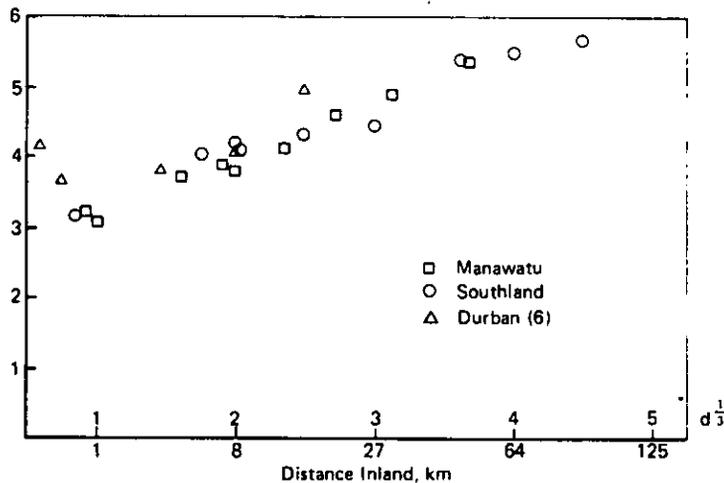


FIG. 9—Test of cube root relationship of the type  $(\text{distance from sea (km)})^{1/3} + (\text{average Climat value, mild steel stud})^{1/3} = \text{const}$  proposed by Doyle and Wright [6].

carriage inland, and hence the hazard of atmospheric corrosion, is higher on oceanic islands than might be predicted from the classic studies of corrosion versus atmospheric salinity made in Nigeria, or from the extensive studies made in Europe. The geography has a very important influence. This must be taken into account in specifying corrosion protection measures for structures in these environments.

#### Acknowledgments

Many people have contributed to aspects of this study. We especially thank the site owners/operators for their cooperation; the NZ Meteorological Service for assistance in selecting sites, obtaining access for us, and giving advice; and G. Wilson of BRANZ for help in the statistical analysis of the data.

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## DISCUSSION

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*R. Baboian<sup>1</sup> (discussion questions)*—Our work at Texas Instruments has shown that a correlation of chloride composition with corrosivity in the atmosphere is complicated by the presence of acid deposition. In the combination of acid deposition and chloride salts, HCl is formed which vaporizes off during dryoff periods. Subsequent analysis of the corroding system for chloride composition gives misleading results because of this behavior.

*J. Duncan (author's closure)*—We could believe that such volatilisation does occur. However, we are reasonably confident that the measurements of chloride deposition in this study were not affected by this factor because the collection sites were chosen to be away from likely sources of industrial pollution. We have not attempted to measure concentrations of chloride upon the actual corroded samples.

<sup>1</sup>Texas Instruments, Attleboro, MA.

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Marine salts contribution  
to atmospheric corrosion.

**BUILDING RESEARCH ASSOCIATION OF NEW ZEALAND INC.  
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The Building Research Association of New Zealand is an industry-backed, independent research and testing organisation set up to acquire, apply and distribute knowledge about building which will benefit the industry and through it the community at large.

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