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Salts in Rainfall and Dry Fallout Over Western Australia

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Introduction

"Cyclic" salt is relevant to the theme of this symposium from several aspects. Firstly, since rain scavenges soluble and insoluble aerosols from a large volume of air, analysis of rainfall and dry fallout provides a convenient sampling of atmospheric components. Secondly, establishment of background levels of elements cycling through the atmosphere is important in assessing levels of pollution. Establishment of these levels can only be done in regions which are to date remote from large scale industrial activity, and parts of Western Australia may fulfil this requirement. Thirdly an appreciation of the composition of cyclic salts may be important when considering reactions involving gaseous pollutants, dust, ash etc.

Western Australia (14°S to 35°S latitude, 113° to 129°E longitude) occupies about 2.6 million square kilometres, comprising a third of the Australian Continent. Sources of salts in precipitation proposed by many previous workers include oceanic spray, terrestrial dust, industrial emissions and emission from volcanic areas. In an area such as Western Australia aerosols produced from oceanic spray (Woodcock et al. 1953), and terrestrial dust are likely to be most important, relatively small and localised contributions may arise from industrial activity, and there is no volcanic activity. The main environmental characteristics of the state likely to affect the amount and nature of salts in precipitation are the climate, the elevation of the land surface and the occurrence of saline drainage systems and soils.

The cumulative effect of precipitation of elements from the atmosphere to the land surface on the salinity of soils and waters, the proportions of exchangeable ions in the soil and on soil nutrient status has been demonstrated for many parts of the world (e.g. reviews by Eriksson 1960 and Gorham 1961). In Western Australia the land surface has been stable for a long period in recent geologic history, in large areas drainage is usually uncoordinated, the input of cyclic salt is large and evaporation is high. The association of these factors not surprisingly results in the saline soils, groundwaters and surface waters, which are problems in much of the south west of the state particularly eastwards of the 550 mm rainfall isohyet (Northcote and Skene 1972).

In areas where drainage is more active the salts precipitated in rain play a different role. Here soluble nutrient ions, calcium, potassium and sulphur in rainfall may equal or exceed the amounts contributed to the soil by weathering. The input of these nutrients to the pool of nutrients in natural ecosystems on sands and lateritic soils could then be a substantial factor for survival and growth of plant communities.

This study of the regional variation in accession of salts from the atmosphere contributes to the understanding of the distribution of saline soils and waters, by providing a regional base for salt and water balances, which was not previously available. It will supplement data at present available for Western Australia (Hingston 1968) and other regions on the Australian Continent (Anderson 1941, Hutton and Leslie 1958).

Sampling

A total of 59 centres throughout the state returned monthly samples for analysis. The sampling was more intensive in settled areas in the south-west where studies of water and salt balances are in progress.

lide 1 Only broad-scale assessment was possible for remote areas.

The centres have been grouped according to regions:

1. Kimberley - North East and West Kimberley Divisions
2. North West - De Grey, Fortescue and West Gascoyne
3. Murchison - East Gascoyne and Wiluna
4. South West Coastal - North, Central and South Coastal Divisions
5. South West Coastal - Central North and Central South Divisions of the South West, and the South Eastern Division
6. Eucla - Eucla Division.

Polythene collection vessels and funnels were used to avoid contamination and precautions were also taken to protect the samples from contamination due to birds, insects, local dust and splash. The collection units were designed to minimise evaporation, and were located in the open with the top of the funnel 1.5 m from the ground surface. Rainfall was recorded from nearby gauges, which were read daily. For months without rain the funnels were washed and the washings analysed to determine dry fallout of salt and dust.

Samples collected monthly from January 1973 to December 1974 were analysed for chloride, but other major ions were only determined until June 1974. Complete data illustrating seasonal variation in the ionic composition of rain at all centres is available on application to the author.

Rainfall and dry fallout were also sampled daily at Floreat Park during 1973. These samples were all analysed for chloride and from May to September other major ions were also determined.

Analysis

Samples were filtered through a millipore filter (0.4 μm) and the amount of dust was estimated by weighing the oven dried material from the filter. The metal cations Na^+, K^+, Mg^{2+} and Ca^{2+} were determined by atomic adsorption. Chloride was determined by automated colorimetry and sulphate by reduction to H_2S followed by precipitation of bismuth sulphide. Bicarbonate was determined by titrating suitable aliquots to pH 4.5, and the pH was determined electrometrically using a glass electrode.

Uncertainties due to adsorption of ions onto the walls of sampling containers were anticipated and investigated. Experiments with the polythene vessels used for collection and transport showed that for the usual concentrations of ions in rainwater found in this survey (mg l^{-1} range) adsorption onto the polythene was not a serious problem. For concentrations in the μg l^{-1} range, found for a few samples from Camballin and Kununurra (Kimberley Region), adsorption onto container walls is an unavoidable uncertainty. At these centres some ions (e.g. Ca^{2+}, Mg^{2+} and K^+) may be underestimated due to adsorption, however measurements of Cl^- concentration should be relatively little affected because of its higher concentration. Adsorption is not considered to invalidate the interpretation of the overall estimates of regional precipitation of salts.

Analytical errors were estimated to be less than 5% for ions present at about 1 ppm level. The difference between the sum of the cations and the sum of the anions was less than 5%.

Results

Particulate Matter

Particulate matter consisting of dust from soils, plant debris etc., was trapped as dry fallout and as a component of rainfall. In monthly samples it was not possible to separate these two sources. The amounts collected ranged from 8 to 319 kg ha^{-1} for the year 1973. There was wide variation for individual centres but grouped on a regional basis the range for mean dust fall was as follows; Kimberley 53 kg ha^{-1}, North West 84 kg ha^{-1}, Murchison 119 kg ha^{-1}, South West Coastal 62 kg ha^{-1}, South West Central 117 kg ha^{-1}, Eucla 34 kg ha^{-1}. The inland regions returned samples containing approximately twice as much dust as the coastal regions.

Chloride

Large quantities of chloride (>100 kg Cl ha^{-1}) were precipitated annually at coastal centres in the south-western corner of the State. The quantity decreased to 50 kg ha^{-1} approximately 30 km inland. Less chloride was precipitated at coastal centres in the north (10-14 kg ha^{-1}) and also somewhat less towards the east on the southern coast. The amount of chloride precipitated in the inland areas of the south-west was generally higher (>10 kg ha^{-1}) than would be expected from consideration of distance from the coast and studies conducted elsewhere. The lowest precipitation of chloride (2-3 kg ha^{-1}) was at the inland centres of Mt. Newman, Fitzroy Crossing and Leonora. The general decrease of the mean chloride concentration in rainfall with distance from the nearest coast for 1973 is shown in slide 2. This shows the different relationships obtained for centres in the north-west (north of 24°S latitude) and the south-west of the state.

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lide 2

The saline drainage lines and salt lakes of the central region of the south west, the main river systems draining to the coast, and the locations of ranges of hills which may influence the precipitation of salt are shown in slide 3.

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Other Cations and Anions

The amounts of ions precipitated during 1973, varied widely with location. The amounts of sodium ranged from a maximum of 97 kg ha^{-1} at Donnelly River in the south west corner of the state to 2 kg ha^{-1} at some inland centres, and were closely correlated with the amounts of chloride precipitated. Excluding the few centres which did not return samples for a full year, accessions of other ions were as follows :-
magnesium, 0.2 to 14.6 kg ha^{-1}; calcium 0.8 to 35.3 kg ha^{-1}; potassium 0.3 to 13.9 kg ha^{-1}; sulphate 1.7 to 56.7 kg ha^{-1} and bicarbonate 0.7 to 105 kg ha^{-1}. Rainfall for the centres ranged from 127 to 1554 mm in 1973.

Daily Sampling at Floreat (3.2 km from the ocean)

Samples were taken from May to September 1973, showed that for 103 wet days the correlation between chloride content of rainwater and the logarithm of the rainfall was highly significant ($p<.001$). The relation was presented by the equation,

$$Y = 42.69 - 12.88 \ln X \qquad (1)$$

$$(r = 0.46,\ n = 103)$$

where $Y = Cl^-$ concentration ($mg\ l^{-1}$)

X = rainfall (mm)

This relationship accounts for 21% of the variation in chloride concentration in daily samples.

Mean daily dry fallout of fine days from January 1973 to March 1974, averaged for calendar months, ranged from 0.021 kg Cl^{-1} ha^{-1} (S.D.* 0.010 kg ha^{-1}) in May, June and July, to 0.058 kg ha^{-1} (S.D. 0.046 kg ha^{-1}) in April. The values were lower in winter than in summer, when the dry atmosphere and coastal sea breeze would be expected to favour wind transport of salt aerosol from the ocean inland. Variable but often strong equinoctial winds during April, August and September coincided with higher and more variable amounts of dry fallout on fine days.

The amount of salt trapped in the collector was a guide to the dry fallout contribution to total salt precipitated into funnels which were open continuously for monthly samples. In those months when no rain fell, the washed funnels gave the equivalent of about 1 kg Cl^{-1} ha^{-1} at Perth and Floreat. This value agreed with the monthly dry fallout of salt calculated from daily measurements which gave a total of 12.4 kg Cl^{-1} ha^{-1} deposited on fine days during 1973.

At other centres near the coast in the south west (Bunbury, Albany, Esperance) about 2 kg Cl^{-1} ha^{-1} $month^{-1}$ was collected as dry fallout. Inland, values ranging from 0.1 to 10 kg Cl^{-1} ha^{-1} $month^{-1}$ were obtained depending on the location of centres relative to terrestrial salt source areas. In the Kimberley Region 0.03 kg Cl^{-1} ha^{-1} $month^{-1}$ was found for inland centres and 0.3 kg Cl^{-1} ha^{-1} $month^{-1}$ for coastal centres. As

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* Standard Deviation

collection funnels are relatively inefficient compared with vegetation for trapping dry salt from the air, the amounts of salt quoted above are lower limits for dry fallout at the land surface.

The ionic composition of dry fallout as characterised by the ratios of cations to chloride, for daily samples differed significantly ($p<.001$)
lide 4 from rainfall salt, and from sea-salt, for all the major cations.

This difference affects the comparison of the composition of rainwater samples collected over a month and sea-salt, and also contributes to seasonal variation in ionic ratios for rainwater samples. Rainwater collected daily (containing less dry fallout) was closer to sea-salt in composition but still differed significantly ($p<.05$) in the ratios of Na^+, Ca^{2+} and K^+ to Cl^-.

Seasonal Variation in "Excess" Ions Precipitated in Rainfall

Seasonal variation in the ionic composition of dry fallout and rainfall relative to sea-salt can be used to indicate the source and mechanism of precipitation of salts. As an illustration, the ionic composition of fallout for Perth, the largest city in Western Australia (population 642,000) is compared with Yanchep in a centre located in a National Park about 50 km north of the city and 7 km from the coast.

ide 5

There are small excesses of sulphate, calcium and potassium over the amount expected from sea-salt aerosols, occurring throughout the year at Yanchep. Terrestrial inputs should be small and industrial activity is relatively remote from this centre. The excesses may arise as discussed previously from dry fallout e.g., $CaCO_3$ from calcareous dunes. However at Perth the excesses of sulphate and calcium are high and show correlation with rainfall, although excess of these ions were also precipitated in dry months. Comparison of the two centres suggests that sulphur dioxide or sulphuric acid, produced by combustion of fuels and firewood for urban and industrial use in Perth, is carried into the atmosphere where it reacts with finely dispersed dust from calcareous dunes which skirt the coast. The resultant calcium sulphate settles as dry fallout, but is more efficiently washed out of the atmosphere in rainfall. The difference between the two centres only 50 km apart is noteworthy. The excess potassium precipitated, was greater at Yanchep than Perth, with the highest values in April 1973 and, February and March 1974 at Yanchep. Potassium is commonly the ion present in greatest excess (compared with sea-salt) in the "throughfall" measured under eucalypt forest. Thus the larger amount of leaf detritus in the National Park compared with the city may be responsible for the greater potassium excess in rain at Yanchep during the period of greatest leaf fall.

Discussion

The World regional pattern of distribution of chloride in precipitation is inadequately defined since it has only been studied in detail in Europe and the United States of America in the Northern Hemisphere, and in Victoria and New Zealand in the Southern Hemisphere. However chloride precipitation seems to depend partly on wind direction and strength (correlated with latitude), rainfall (partly determined by topography) and distance from the coast. In these respects the results obtained for Western Australia fit with the general pattern, but there are strong regional influences on the amount and composition of salts precipitated at the land surface.

The Geographic Distribution of Chloride in Precipitation

Variation of chloride in precipitation was illustrated in the first slide. Other data (Hingston 1958) indicated that the mean annual concentration of chloride in rainfall varied by about 20%, and that this parameter was less variable than the total chloride precipitated annually.

South West Coastal Region

In the south west of Western Australia (32 to 35° S latitude) the climate is Mediterranean, the summers are hot and dry, about half the yearly rainfall is in winter (June to August) when the winds are westerlies.

On the coast, the annual chloride precipitation of about 100 kg Cl ha^{-1} is similar to that for the Victorian south coast at about 30°S latitude (Hutton and Leslie 1958). Values in excess of 100 kg ha^{-1} have been reported for New Zealand at about 40°S latitude (Blakemore 1953). These values are higher than those for the west coast of the United States (50°N latitude) where an annual precipitation of about 32 kg Cl ha^{-1} was recorded (Junge and Werby 1958), and are similar to values reported from the west coast of Ireland (Stevenson 1968) and the coast of Norway between about 45 and 60°N latitude (Eriksson 1960). Both in the northern and in the southern hemispheres the highest chloride precipitation was recorded at locations in the path of strong winds from the ocean. The subdued topography in south western Australia favours the transport of oceanic aerosols inland.

Kimberley Region

In the Kimberleys the climate is tropical with strong winds and heavy monsoonal rain associated with occasional cyclones in summer (December to March). The mean annual rainfall decreases from about 1200 mm on the far north coast to less than 250 mm inland.

A storm in January 1974 brought very heavy rain containing more chloride (6.8 ppm Cl^-) than usual for Broome but otherwise much less chloride (approximately 14 kg Cl^- ha^{-1} yr^{-1}) was precipitated at near coastal centres in the Kimberleys (14 to 21°S latitude) than further south. The chloride values for the north west are similar to those found in Florida (30°N) and the south-eastern region of the United States. Both the North West of Western Australia and south-eastern United States are influenced by winds associated with tropical cyclones. We suggest three possible regions for the lower chloride content of rainfall in the Kimberlies compared with the middle and high latitudes. Firstly, the higher intensity of rainfall from tropical thunderstorm activity may dilute the chloride washed from the atmosphere (see equation (1)). Secondly, a contributing factor related to thunderstorm activity may be the mixing of air from higher altitudes, containing low amounts of salts (Junge et al. 1961), with lower altitude air, giving on the average a more dilute salt source. Thirdly, salt aerosols may sediment more rapidly in the tropics because the humid atmosphere causes adsorption of moisture and growth of salt particles increasing their terminal velocity. Thus the equilibrium concentration of salt in tropical air may be considerably lower than in the air at higher latitudes.

The Geographic Distribution of Sodium, Magnesium, Calcium, Potassium, Sulphate and Bicarbonate in Rainfall

The same ions in rainwater may come from different sources which therefore cannot be identified simply from analysis. However the proportions of ions, considered in relation to the geographic distribution of collection sites, can be interpreted to suggest the relative importance of the possible sources.

An approximate method for apportioning the ions is to assume that the chloride in rain is solely of oceanic origin, and to calculate the excess or deficit of other ions relative to sea-salt composition (Eriksson 1960). This assumption is probably close to correct for sampling centres nearer the coast. A further assumption is that other ions in sea water are

South West Central and South Eastern Regions

In the central region of the South West and the South Eastern Region the salt drainage channels and lakes are sources of terrestrial salt which contribute substantially to the ions in precipitation. The region has mainly internal drainage, with channels interconnected but functional only in an occasional wet season, when the inland system is drained by incised streams cut back at its margin. Usually the lakes are sumps where surface and groundwater evaporate and salt accumulates. Redistribution of salty, calcareous, gypseous and silty soil materials is evidence of the considerably aeolian activity in the region. Hence present-day accession from the ocean is difficult to estimate. Within the region, there are large variations in rainfall salt content and composition both over short distances and at different times; probably related to variations in dryness of the lakes and intensity of winds. We suggest that the contribution of chloride from salt lakes is also a reason for the widespread higher chloride precipitation at inland centres in the south west, when compared with centres a similar distance from the coast on the same latitude in Victoria (Hutton and Leslie 1958).

North West and Murchison Regions

In the intermediate latitudes in the North West of Western Australia (20^{o} to 32^{o}S) the amount and seasonal distribution of rainfall is highly variable, as rain in this region is associated with the northern edge of the winter rainfall zone and the southern edge of the summer cyclones.

The chloride concentration in rainfall at near coastal centres is usually lower than in the south west, but it is variable, rain from Wiluna, Brickhouse and Carnarvon (near salt lakes) giving among the highest values in the state. Occasional storms bring high rainfall, and sometimes the chloride concentration in rain is as high as it is further south.

The lowest amounts of chloride precipitated annually (2-3 kg ha^{-1}) were at the inland centres Mt. Newman, and Leonora and are similar to those recorded for Katherine in the Northern Territory of Australia for arid areas of Israel and also for inland areas of Europe and the United States of America. However they are higher than the precipitation in Antarctica where <0.7 kg ha^{-1} has been reported (Boutron et al. 1972).

transported without separation of components resulting in changes in their proportions relative to chloride. Eriksson's treatment involves subtracting the contribution presumed to be from sea-salt, from the amount precipitated. The "excess" remaining is then considered to come from other sources. A summary of mean values for excesses is given in the next slide.

lide 6 Total sulphate precipitation is generally about 15 kg ha^{-1} on the south coast and decreases inland, but at some centres high amounts were recorded. The excess of sulphate is approximately 3 kg ha^{-1} over much of the state for 1973 but this is low by European standards (Eriksson 1960). Excess sulphate which seems to be widely distributed throughout the world and may be derived from a number of sources including the following :

(a) highly dispersed stratospheric sulphate (Junge _et al_. 1961), attributed to oxidation of SO_2 injected into the atmosphere by volcanic activity.

(b) release of small amounts of H_2S by biological action at land and sea surfaces (Eriksson 1960), with subsequent oxidation to SO_4^{2-} in the atmsophere.

(c) disintegrated algae and plankton which tend to be concentrated at the sea surface and dispersed into the atmosphere by drying sea spray, as suggested by Dean (1963) for high I^-/Cl^- ratios in rainwater,

(d) burning of fossil fuels, forests and grasslands.

(e) roasting of sulphides at mining centres.

(f) terrestrial aerosols from soils and plant debris.

A selection of centres with "excess" sulphate in precipitation illustrates
lide 7 the range of values obtained. Since the rainwaters were collected at monthly intervals and were not analysed for up to a month after collection the interpretation of pH values is very tentative. The values obtained ranged from 4.8 to 7.3 with most values between pH 5.5 and 6.0. Samples with higher excess sulphate in Perth and Kalgoorlie where industrial sources are probable, had lower pH. The lowest values approached those given for rain collected in the Lakes District in England (ph 4.0 - 5.8) by Gorham (1955).

Excesses of calcium ranged from 0.6 to 34 kg ha^{-1} in 1973. High values were found near coastal centres (e.g., Eucla, Esperance) where fine particles of lime from dune systems contribute to the ions in precipitation.

High values for calcium were also found at centres near salt lakes. The excesses of bicarbonate were correlated with the calcium excess, but it was evident that near salt lakes and industrial areas excesses of sulphate and calcium were also correlated.

Excesses of potassium generally ranged from 0.1 to 3.8 kg ha^{-1}. Contributions from smoke and ash from fires, and terrestrial dust (leaf material and surface soil) were probably considerable but other mechanisms for the modification of sea-salt ratios are possible.

Daily sampling near the coast at Floreat indicated that the imbalance of sodium and chloride relative to sea-salt composition, may be due to the higher amounts of calcium, potassium and chloride relative to sodium in "dry fallout" settling in the collection funnel on rainless days. This suggests partial fractionation of the sea-salt aerosol in the atmosphere possibly due to settling of larger, more hygroscopic particles because they contain a higher proportion of calcium chloride. It does not necessarily follow that a change in the ratios of Ca^{2+}/Cl^- and K^+/Cl^- with distance from the coast would be evident for this mechanism to apply, as the overall affect on the atmospheric aerosol may be extremely small when compared with addition of ions from other sources.

Excesses of magnesium were small and even negative, generally less than 1.4 kg ha^{-1} suggesting that the ocean is the main source of magnesium in rainwater. Exceptional values of 10.4 and 3.0 kg ha^{-1} were obtained at Wiluna and Norseman respectively, probably because of terrestrial contributions of carbonates from salt lakes.

Sodium excesses were less than 4.0 kg ha^{-1} and were confined to the Kimberley, Northwest and Murchison regions. The sodium values indicated an excess of chloride in rainfall sampled in the south-west. This may also be related to the composition of dry fallout as discussed above.

Regional Variation in Ionic Ratios

The ratios of precipitates ions, Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-} and HCO_3^- to Cl^- calculated for the years rainfall, provide an alternative means of considering the data.

The variation in ionic ratios and the ratios of sea-salt to dust collected in rainfall samples are useful indicators of the relative importance of sources of salts. The mean ratios of Ca^{2+}/Cl^-, HCO_3^-/Cl^- and SO_4^{2-}/Cl^- for the regions differ from sea-salt when the ratio sea-salt/dust is low (i.e., the proportion of dust in the samples is high) Mg^{2+}/Cl^- and K^+/Cl^- show a smaller tendency to vary in the same way, and Na^+/Cl^- ratios showed no clear trends.

Slide 8

Particulate matter consisting of find surface soil and plant debris in the form of dry fallout, or precipitated in rainfall, will affect the filtered rainwater sample by direct contribution of soluble ions.

In summer the salt concentration in the surface few mm of soil may be high but even for dust containing 5000 p.p.m. Cl^-, as might be found in saline soils, the contribution to rainwater is only 0.5 kg Cl^-/100 kg dust ha^{-1}. However as the variation in the ratios of ions indicate, contributions in dust cannot be ignored particularly for ions present at lower concentrations in rainwater, such as calcium, potassium, sulphate and bicarbonate. At the few centres (e.g., Wiluna and Norseman) close to extensive dry salt lakes, a large portion of ions in precipitation probably originate from the surface efflorescence on the lakes which, in addition to chlorides, contains gypsum and carbonates of calcium and magnesium of sufficiently small size to form aerosols.

Hutton (1968) has drawn attention to the contribution from plant debris in atmospheric dust of considerable amounts of chloride and other ions to precipitation. Analysis of samples from jarrah leaves (Eucalyptus marginata), a major tree species in the Darling Range, gave chloride contents ranging from 0.3 to 1.2%, sodium from 0.2 to 0.5%, calcium from 0.4 to 0.8%, magnesium from 0.4 to 0.5%, potassium from 0.3 to 0.9% and sulphur from 0.07 to 0.1%. These values are not unusually high for plant leaves and are in the range obtained for other native tree and shrub species in Western Australia.

Slide 9

The chloride, sodium and potassium are in a readily soluble form however sulphur and magnesium are probably combined in organic forms which would need to be decomposed to release soluble sulphate and magnesium ions. The concentrations of ions in plant leaves show that while leaf debris could be a significant source of ions in rainfall, the ratios of sea-salt/dust (0.3 to 4.8) suggest that the contributions from other sources (such as oceanic aerosols) are probably larger.

Conclusions

At most coastal and near coastal locations in the South West coastal region the contribution of ions from terrestrial dust to rainwater composition is small compared with that of sea-salt aerosols except possibly for Ca^{++} from calcite in dust from dunes. At locations near salt lakes, and generally in the Central South West and South Eastern Regions, contributions from terrestrial sources likely to be predominant, and in the Kimberley and North West the data suggests that terrestrial sources of ions are at least of equal importance to oceanic sources. Thus accessions measured in rainfall in these regions cannot be used directly to calculate the accumulation of salt with time. Some adjustment must be made for local recycling.

Accession of salt from the atmosphere is almost an order of magnitude greater in the south-west than in the north of Western Australia. How far oceanic salt moves inland from the coast is difficult to determine because no clear distinction can be made between terrestrial and oceanic contributions to ions in precipitation. Maximum accession from the ocean is equivalent to the measured precipitation, but net accession is probably considerably less.

The non-oceanic component of ions in precipitation, estimated by approximate methods from the ionic composition, can be explained by considering the location of sampling centres. Excess sulphur was found at centres where there was industrial activity, roasting of sulphides at mining centres, or near salt lakes. In some instances excesses of calcium, magnesium and bicarbonate may also be due to windblown minerals from coastal sand dunes and lake deposits. The distribution of potassium excesses showed a different pattern, being more generally distributed but slightly greater in the forested areas of the south west where plant leaf detritus and ash from fires may have contributed to the ions in precipitation. Smaller excesses of calcium, magnesium, sodium, potassium, chloride and bicarbonate found at inland and northern centres are suggested to originate from soil and plant debris derived aerosols, and wide distribution of organic debris from sea spray.

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References

Anderson, V.G. (1941). The origin of the dissolved inorganic solids in natural waters with special reference to the O'Shannassy River Catchment. J. Proc. Aust. Chem. Inst. 8, 130-50.

Blackemore, L.C. (1953). The chloride content of rainwater collected in the Wellington province. N.Z. J. Sci. Technol. 193-7.

Boutron, C., Echevim, M., and Lorius, C. (1972). Chemistry of polar snows. Estimation of rates of deposition in Antarctica. Geochim. Cosmochim. Acta. 36, 1029-41.

Dean, G.A. (1963). The iodine content of some New Zealand drinking waters with a note on the contribution from sea spray to the iodine in rain. N.Z. J. Sci. 6, 208-14.

Eriksson, E. (1960). The yearly circulation of chloride and sulphur in nature; meteorological, geochemical and pedological implications. Part II. Tellus 12, 63-109.

Gorham, E. (1955). On the acidity and salinity of rain. Geochim. et Cosmochim.Acta. 7, 231-239.

Gorham, E. (1961). Factors influencing supply of major ions to inland waters, with special reference to the atmosphere. Geol. Soc. Am. Bull. 72, 795-840.

Hingston, F.J. (1958). The major ions in Western Australia rainwaters. CSIRO, Div. of Soils Div. Rep. 1/58.

Hutton, J.T. (1968). The redistribution of the more soluble chemical elements associated with soils as indicated by analysis of rainwater, soils and plants. 9th International Congress of Soil Sci. Trans. Vol. 5, 313-22.