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THE CHEMICAL AND MINERALOGICAL CONTENT OF THE PLANTS OF THE LAKE HULEH PRESERVE, ISRAEL

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[Frontispiece; six microfiches in pocket inside back cover]

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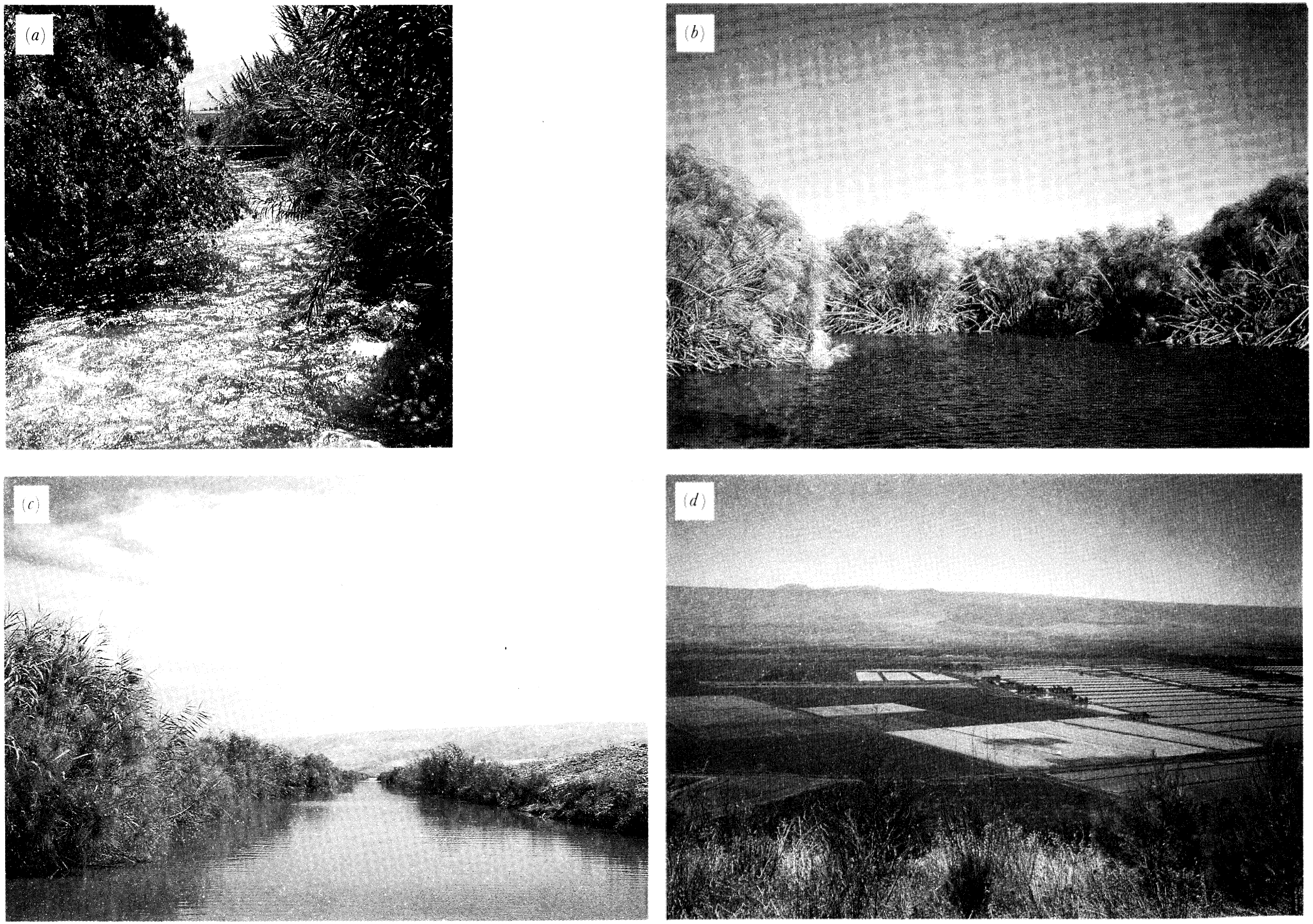

(a) The Jordan River as it enters the Lake Huleh Preserve.
(b) The papyrus swamp of the Lake Huleh Preserve.
(c) The Jordan River as it leaves the Lake Huleh Preserve.
(d) Overall view of the Lake Huleh basin with the Lake Huleh Preserve in the distance.

The Lake Huleh Project has involved as complete a biological, chemical and mineralogical study as possible with the intent that a biological and chemical history could be constructed of this basin, long thought to be one of the centres of origin of agriculture. The primary object of this aspect of the project was to gain some understanding of the chemical and mineralogical composition of the plant communities occupying the nature preserve and contiguous areas and what effect these communities have had on the chemical composition of past and present lake basins.

Lake Huleh, the first lake that the Jordan River used to form, was drained between 1951 and 1958. A small area of this lake was retained as a nature preserve. Twenty-nine plant families are represented here by 57 genera containing 71 species. On analysis, these species were found to be composed of 46 elements and 11 minerals. This paper is confined to these findings.

A comparison of the chemical composition of annual and perennial plants revealed that only Na, Si and Mn were significantly (beyond the 0.1 % level) taken up by perennials, while annual plants contained more K, Mg, P and Cl. A further subdivision relating habitat and chemical composition showed that aquatic plants contained significantly more Na, K, Si, S, P, Cl, Mn and opal minerals than their terrestrial counterparts. Rubidium, Cs, Li, Ag, Be, Hg, Ge, Pb, Se, Bi, V, F, Br, I, Fe, Co and the oxalate minerals exhibit the same pattern, but do not have concentrations statistically significantly different from those of land plants. Land plants were composed of more Mg, Ca, sylvite (KCl), calcite, quartz and gypsum than water plants. In addition, concentrations of Cu, Sr, Ba, Zn, Cd, B, Al, Sc, Y, La, Ce, Sn, Ti, Zr, Hf, Cr, Mo, As and Ni, though not statistically significantly different from those in water plants, followed the pattern observed in land plants.

One of the unexpected discoveries in this study was the variation of 29 elements within the leaves of the Cyperaceae, the Typhaceae and the Gramineae. Although only 10 of these elements exhibit variation that is statistically significant, the remaining 19 vary in a consistent fashion. The elements that concentrate in the margins of leaves of these families are Na, Ag, Be, Ca, Sr, Ba, B, Al, Ga, Si, Ge, Pb, Cl, Br, I, Mn and Fe, while those concentrated in the midsection are K, Rb, Cs and Li and those in the blade are Cu, Mg, Zn, Cr, Mo and P. It is proposed that the function of these distributions may lie in protection against inclement conditions and insect damage, while those elements that are structurally important may function to retain leaf shape or be instrumental in forming the shape itself.

A comparison was made between elemental composition and taxonomic position. It was found that K, Rb, P, Bi and F decrease with evolutionary time; that is to say the Nymphaeaceae contain more of these elements than the Gramineae. On the other hand, Si and Ti concentrations increase with time, the Gramineae containing larger amounts of these elements than the water lilies. These relationships were found to be significant at levels varying from 5.0 to 0.1 %. It is proposed that the structurally important Si and Ti may act as a defence mechanism in that high concentrations of either or both of these elements tend to make plants less palatable. Nutritionally important elements such as K and P may decline in concentration with time as plants through adaptation become more efficient in their use of essential elements. This kind of conservation may permit population expansion, thus ensuring the longevity, in the evolutionary sense, of the species. It is important to note that seven out of 46 elements are taken up in relation to their phylogenetic position.

Elemental content of the plants is subdivided into geochemically coherent groups.

Each group is compared with what is known of the particular association in similar species grown in other parts of the world. Pertinent ratios of elements in Huleh plants are contrasted with means of the same elements in land plants, Huleh soils, Huleh rocks and the earth's crust.

A comparison of the elemental composition of parasitic plants and their hosts is also presented. *Cuscuta planiflora* (Cuscutaceae) parasitizes the legume *Alhagi mannifera* (Fabaceae). Under normal circumstances, the former is an annual inhabiting swamps and the latter a perennial growing in waste places. *Cynanchum acutum* (Asclepiadaceae) parasitizes (usually is epiphytical) the grass *Phragmites australis* (Gramineae). Both plants are perennial in their life cycle; the former is an inhabitant of moist places and the latter is a swamp resident. *C. planiflora* has 28 elements more concentrated in its tissues than in those of its host and *C. acutum* has 31 more concentrated in the whole plant than in the leaves of the host plant. *C. planiflora* derives water and elemental nutrition through haustoria embedded in the stems of its host. Microscopic examination revealed that the vascular elements of host and parasite were close together. If a ratio is calculated between the elements in *C. planiflora* and *A. mannifera*, when the concentration in the former is greater than in the latter, only Bi and Mo have ratios higher than 2. In the reverse instance, only P and As have ratios greater than 2. It is suggested that these observations are characteristic of an efficient relationship between parasite and host.

The picture presented by *C. acutum–P. australis* is quite different from that of *C. planiflora–A. mannifera*. In the case where *C. acutum* contains higher concentrations than its host, the following ratios have been observed: 1–2, Rb, Li, Cu, Sr, Ba, Zn, Pb; 2–5, Na, K, Cs, Ag, Mg, Ca, P, S, F, Co; 5–18, Be, Hg, B, Si, Sn, Mo and Cl. In the reverse case, where the host contains higher concentrations than the parasite, the following ratios were noted: 1–2, As, V, Cr, Br, Al, Ga, La, Ce; 2–5, Fe, Mn, Y, Ti; 5–18, Ge. It is suggested that the lack of uniformity of the ratios between the two of parasite–host combinations is probably due to the fact that *C. acutum* is usually epiphytic on *P. australis* and becomes parasitic only under dire circumstances.

The mineralogical composition of Huleh plants may be divided into groups containing sylvite, oxalates, carbonates, siliceous minerals and finally, sulphates. Most plants form some oxalates, some carbonates and siliceous minerals. Sylvite (KCl) was detected only in the Urticaceae, Chenopodiaceae, Asteraceae and Typhaceae. It is suggested that an overabundance of light, in excess of that required by a particular species, encourages sylvite formation.

Magnesium oxalate dihydrate (α form) has no mineral name. Its distribution in Huleh plants was confined to the Nymphaeaceae, Chenopodiaceae, Amaranthaceae and Polygonaceae. It is suggested that the older plant families are more likely to form this mineral than those more recently evolved.

Gypsum was found to occur in the Urticaceae, the Tamaricaceae, Fabaceae, Asclepiadaceae, Cuscutaceae and Asteraceae. It was encountered in *C. planiflora–A. mannifera* and *C. acutum* but was not detectable in *P. australis*.

All data here described were analysed by linear and multiple correlation techniques. In addition, it was of interest to discover whether there was more chemical similarity between plants of different genera residing in the same area on the same soil than between plants of the same genera living in different regions. It became clear, with the aid of statistical methodology, that plants inhabiting some parts of the Huleh preserve reflect the chemistry of the soil more profoundly than their genetic differences, whereas in other parts the genetic factors were more pronounced.

1. INTRODUCTION

The first historical description of Lake Huleh is found in the works of Flavius Josephus (born in A.D. 37), who referred to this body of water as Lake Semechonitis (Traill 1862, pp. 46 and

53), the first lake made by the Jordan River. It has also sometimes been called 'Waters of the Merom'. Merom is noted in the Bible (Joshua xi–5–7) as the place where Joshua and Jabin, King of Hatzor, clashed; the battle probably occurred in the low plain west of the lake. The Huleh used to empty into the Sea of Galilee (Lake Tiberius, Yam Kineret or Gennesareth) (Traill 1862, p. 46), which eventually flows into the Dead Sea (Asphaltitis) (Traill 1862, p. 46). Lake Huleh was drained between 1951 and 1958 (Orni & Efrat 1964).

At present, the basin is largely occupied by enlarged irrigation canals (supplied by the Jordan River), carp ponds and fields of cotton, sorghum, wheat, oats and maize. The only portion of Lake Huleh that still exists is in a small preserve (the Nature Preserve) and is used to maintain the water of the carp ponds. When these ponds are drained, the water is allowed to enter the preserve, resulting in hypereutrophy.

During the summer of 1963 four cores of the lake mud, transecting the old Lake Huleh Basin, were taken (Cowgill 1969). At that time, the entire region from Metulla to Rosh Pinna (with the exception of the eastern hills) was sampled for water, shells, rock, plants, fossils and minerals. These materials, and that of the cores, have been subjected to a complete biological study and inorganic chemical analysis (46 elements) as well as a mineralogical investigation, with the intent that a biological and geochemical history could be constructed of this basin, long thought to be one of the centres of origin of agriculture. The primary object of this aspect of the Huleh project was to gain some understanding of the chemical and mineralogical composition of the plant communities occupying the Nature Preserve and contiguous areas and what effect these communities have had on the chemical composition of the past and present lake basins.

2. Site description

Background material of the region and this study has been previously described (Cowgill 1969, 1973*a*, 1975*a*, 1980, 1989*a*; Hutchinson & Cowgill 1973). At the time of plant collection the small body of water in the Nature Preserve, the only remains of the old Lake Huleh, had a maximum water depth of 35 cm. The area of the Nature Preserve is not known, as earth moving equipment was in constant use to increase the size of the area and widen the channels entering and leaving the preserve. Such activity had little effect on this study because it began after all samples had been collected.

The vegetation of the region has been the concern of many (Tristram 1884; Post 1932; Jones 1940; Zohary & Orshansky 1947). A review of their findings is presented in Cowgill (1969). It is noteworthy that the maximum water depth at the time of the Zohary & Orshansky (1947) study was 7 m. Many of the plant communities described by both Jones (1940) and Zohary & Orshansky (1947) have disappeared as a result of changes in water level and the encroachment of agriculture on the drained fertile soils of the Huleh Basin.

Much of the soil that erodes into the Huleh Basin is the slightly acid dark red terra rossa which covers the hard limestone. The valleys are characterized by a deep leached red soil, but in depressions, yellow soil or, in deeper horizons, yellow soils with brown mottling can still be found (Dan 1964; Reifenberg & Whittles 1947). The terra rossa of this region contains a high concentration of soluble salts. The climate of the region (Meigs 1953) is such that no rain falls in the summer and the mean annual rainfall, all of which falls in the winter, is 432 mm. As a result of the climatic conditions prevailing during the summer (and actually for most of the year), soluble products of weathering move upward in the soil profile so that during much of the year there is a lower elluvial horizon above which lies an accumulation layer or illuvial horizon. Chemical analysis of terra rossa and the surface Huleh Peat have been reported by Ravikovitch *et al.* (1960) and Reifenberg & Moshicky (1941), respectively. There are also examples of alluvial soil series in the region which support luxurious plant growth, noted by Zohary (1962, p. 14).

3. Materials and methods

(*a*) *Plants*

Plants were gathered from the Nature Preserve and from contiguous areas that extended no more than 800 m from its supposed boundaries. The town of Yesud Hama'ala and the adjoining Kibbutz Hulata are located within the boundaries of the Nature Preserve. Cultivated fields encroach on the boundaries of the Nature Preserve. Thus it appeared reasonable to attempt to collect members of all observable species within the area just described. For the purpose of chemical and mineralogical analysis, as well as the desire to obtain as representative a sample of the particular species as possible, an effort was made to collect at least ten plants of each species. All species that were collected had flowers and/or seeds sufficient for identification purposes, though often it was not possible to locate an adequate number of plants to provide enough material for analysis of individual plant parts. Thus, in some cases, only the whole plant could be analysed, while in other cases, plant parts were analysed.

Although this is not a treatise on analytical chemistry, it is important to note that blanks are always used during collection in the field. For example, triple glass distilled water was used as a water blank; highly purified starch was employed as a blank for plants. Blanks are always carried out in triplicate. New blanks are used for each area sampled. The same care was taken in the chemical analysis of blanks as in sample analysis. Blank corrections are extremely important when quantities near the detection limit are being measured. In such cases, a low-temperature asher (80 °C) was used to remove organic matter and the analyses repeated.

Plants were collected with gloved hands and individual plants were placed in plant presses, i.e. one plant between clean sheets of blotting paper, covered by more blotting paper and so forth. No one plant, once collected, was ever touched by any other; thus cross-contamination between samples was highly unlikely.

Identification of all plants was confirmed by comparing the Huleh Collection with plants deposited in the Herbarium of the Hebrew University and herbaria of both Yale University and Harvard University. The plant classification, life cycle and habitat are noted in Table 1.† The family sequence presented follows that of Cronquist (1981).

There are still many taxonomic difficulties with the flora of the Northern Jordan Valley. The binomials used to describe the plants collected are the most recent that could be found. It should be recalled, however, that the taxonomy of this flora still awaits extensive critical revision.

Table 2 illustrates the uses of the plants of the Nature Preserve. It is noteworthy that, with few exceptions, the plants gathered have important functions in the lives of Man and domestic animals. Because this region is thought to have been one of the centres of origin of agriculture, it is important to note that the plants that have survived are primarily those which are still useful. There is little doubt that the indigenous human populations which have lived in this

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† Tables 1–107 appear on accompanying microfiches.

region for 10000 years selected for better plants. Unpublished data on pollen analysis from the Lake Huleh cores indicate that plant breeding occurred: pollen grains become larger as time approaches the present century.

Nomadic people, called Bukharan, from the ancient city of Bukhara (Uzbek Republic, U.S.S.R.) annually visit the Huleh Basin to collect papyrus for the construction of mats and baskets. They also gather many plants growing in the Preserve. Although we had no language in common, they invited me to an evening party. They have parties like Georgians. The wicks of their ancient oil lamps originate from the stamen of *Ballota indulata*.

Recently, Yaniv *et al.* (1987), in a study of Israeli plants used for the treatment of diabetes, noted that *Ammi visnuga* and *Indula viscosa* are used in hypoglycaemic treatments. It is important to realize that insulin-like materials that resemble vertebrate peptide hormones have recently been isolated from aquatic plants (Collier *et al.* 1987).

Brotherson *et al.* (1980) note that *Amaranthus retroflexus* (nitrates), *Nerium oleander* (glycosides), *Xanthium strumarium* (hydroquinone), *Chenopodium album* (nitrates), *Melilotus albus* (dicoumarin), *Festuca arundinacea* (alkaloids) and *Solanum nigrum* (glycoalkaloids) all contain poisons (noted in parentheses) which undoubtedly were occasionally useful.

Table 3 shows the location of the plants collected and the number of specimens each sample analysed represents. Figure 1 shows a map of the region.

Once plants have been collected it is necessary to prepare them for chemical and mineralogical analysis. The surfaces of all plant specimens are contaminated by substances whose sources are not botanical. In arid regions such as the Huleh Valley, the preponderance of such materials is aeolian in origin. It has become an established procedure to clean all plant specimens, as soon after collection as possible, with a high-speed vacuum cleaner. This instrument is made of boron-free glass tubing attached to a trap which in turn is hooked up to a high-speed vacuum pump (1 HP motor, vacuum 0.1 μm). This method removes about 99% of the contaminating material. Adhering particles of colloidal size cannot be removed by this procedure. Washing specimens introduces error due to differential loss of elements from the specimens and is therefore not recommended. Past experience has indicated that contamination from adherence of colloidal-sized particles to plant specimens is minimal and is usually composed of Al, Si and Ca, three elements always abundantly concentrated in plants. On the completion of the cleaning procedure, plant specimens were air-dried in clean plant press assemblies. Once dry, plant specimens were divided into the smallest number of component parts that would provide samples sufficiently large for appropriate analysis.

Table 3 lists the number of specimens that each sample analysed represents.

(*b*) *Soils and rocks*

It was desirable to learn what the chemical contribution of the Huleh drainage basin was to the Nature Preserve. Thus, rocks and soils were sampled every 100 m from Metulla to the southernmost portion of the old Lake Huleh. Any stratigraphic change that appeared outside this sampling scheme was sampled as well. Vertical samples were collected from the uppermost regions of the hills to their valleys at a frequency of about every 15 m.

It was also of interest to learn what the chemical contribution of the Nature Preserve was to Lake Huleh. Thus the soil or mud beneath and associated with each plant collected was also sampled.

Small samples (approximately 1 kg) were collected. The soils were so dry that the use of a

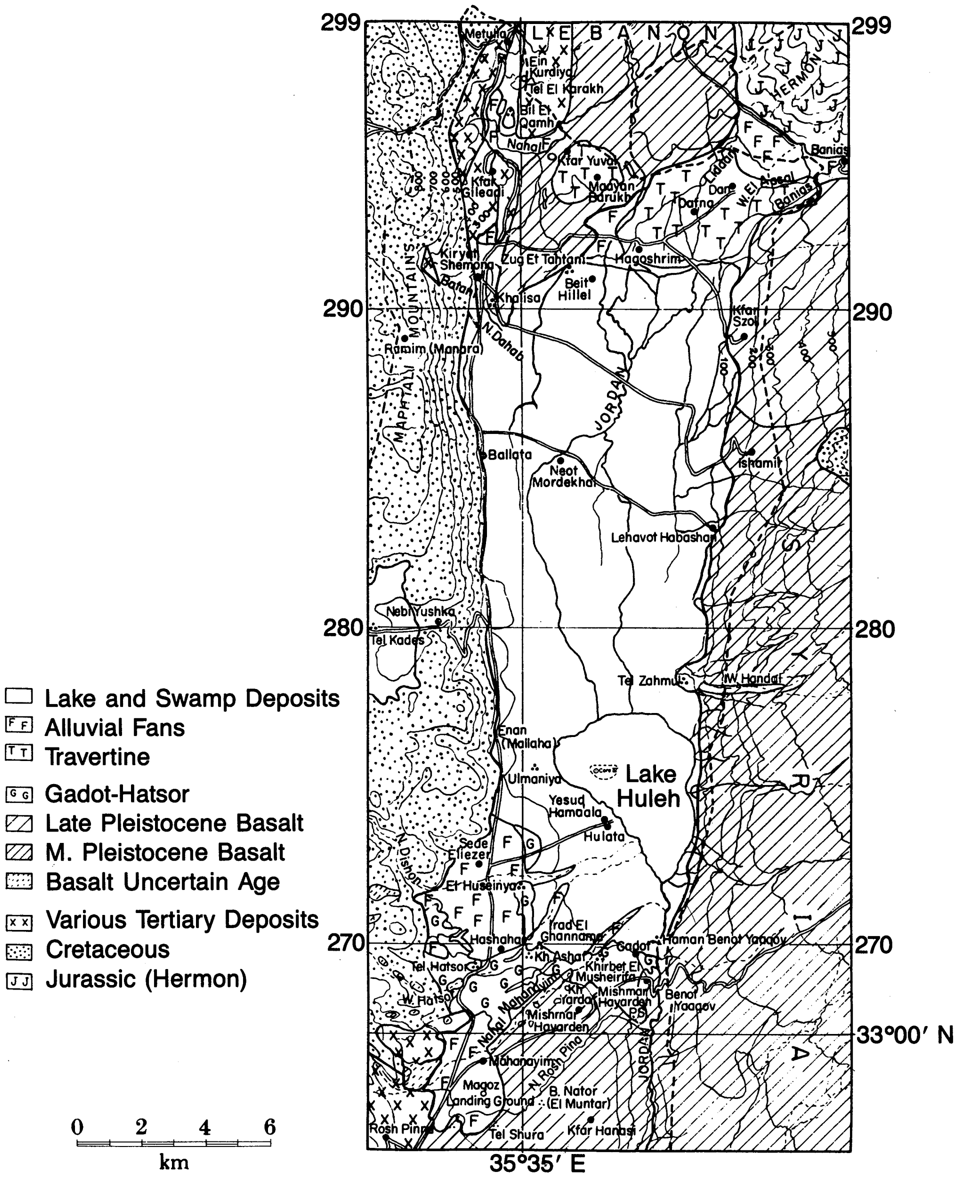

FIGURE 1. This map is part of one that was prepared by Picard (1963). It shows the geology of the region and the places referred to in the text of this paper as well as the outline of the Nature Preserve (dotted line in northwestern portion of Lake Huleh).

soil auger proved impracticable. A clean trowel was employed instead. The trowel was cleaned between samples with distilled water followed by acetone and ethanol and heated in the sun. Sampling encompassed the area to root depth. Rock samples (approximately 1 kg) were collected only from fresh faces and were removed from the hillsides with a geological hammer. All samples were placed in double plastic bags sealed with electrical tape.

(*c*) *Laboratory methods: chemical*

Each air-dried sample was ground in an agate mortar and pestle and then dried again at 60 °C for 72 h. The powdered material was then prepared for X-ray fluorescence analysis, optical emission analysis or atomic absorption analysis. All plant data were gathered from dry material and are reported on a dry mass basis.

Although data from soils and rocks are included only for comparative purposes, it is important to emphasize that data were gathered from dry material and are reported on a dry mass basis. Laboratory preparation has been described previously (Cowgill 1977).

Sample preparation and instrumental settings employed in X-ray fluorescence spectrometry have been previously reported (Cowgill 1970, 1973*b*). All X-ray tubes (Cr, Mo, Pt) were employed at maximum rating. A helium tunnel was used for all determinations. All net counts (peak minus background) for all elements studied by this technique were repeated three non-consecutive times. If the resulting three figures obtained for each element did not agree with each other within 1 %, the data were discarded and the element in question was subsequently monitored by another analytical technique.

Standardization was achieved by matrix simulation and the use of standard reference materials from the U.S. National Bureau of Standards, namely orchard leaves (NBS 1571), citrus leaves (NBS 1572) and tomato leaves (NBS 1573). Recovery was obtained within the limits specified for the particular reference material used for all the elements detected in the Huleh plants. When the reference material failed to have data for a particular element, such as Hf, then its concentration was estimated by matrix simulation and standard spiking procedures. Wherever possible elemental data have been confirmed by other techniques, usually a combination of wet chemistry and atomic absorption spectrometry.

Since the counting error for each element varies with the matrix in which it is studied, it is important to report standard counting error so that the precision of the data may be viewed in the context of conclusions drawn from such information. Table 4 contains precision data for the elements detected by X-ray fluorescence spectrometry. It should be noted that all elements whose precision of determination was in excess of 10 % were analysed not only on a dry mass basis but also on samples that had been ashed at a low temperature (low temperature, 80 °C, Tracerlab LTA 600). This procedure reduced the standard counting error by 50 %. These are the data that are reported in subsequent tables.

Optical emission spectrometry was used in this study to estimate the quantities of Na Li, Be, Bi, V, Sn, Co, Hg, Cd, B, Mo and Ag in air-dried plant samples. Details of sample preparation and instrumental settings have been described elsewhere (Cowgill 1972, 1973*b*). Suffice it to state that the instrument employed in this study is a direct reader equipped with a fine focus such that the limit of detection is 0.05 mg kg^{-1}. High and low concentrations and the relative standard deviation of the counts of each element are set out in Table 5.

The analysis for Ge, As and Se followed the general method of Rosenfeld & Beath (1964) which consists of an acid extraction followed by distillation in the presence of HBr and Br. This procedure extracts Se, As, Sb, Ge and Sn and separates this group from all others. The analysis is completed by use of the hydride generation technique with subsequent atomic absorption spectrometry. Concentrations of the elements studied by this method were of the air-dried as well as of the low-temperature ashed preparation. Only Se, As, Sn and Ge of this group were detectable. Limits of detection were 2.0, 1.0, 1.0 and 2.0 μg kg^{-1} respectively. Reproducibility, based on 40 duplicate samples, provided a relative coefficient of variation of less than 10 %. Specifics are shown in table 6.

(*d*) *Laboratory methods: mineralogical*

The X-ray diffraction study was done with an XRD-6 General Electric X-ray diffractometer. Tracings were made with Ni-filtered Cu radiation at 50 kV and 32 mA. Greater detail of instrument specifications may be found in Cowgill (1973*a*, 1973*d*, 1974*b*, 1975*b*). All peaks were scanned by employing the goniometer manually and counting three times with a 10 s count and then, once the peak was located, counting again with an average of three 100 s counts. Background positions were estimated from diffractograms and verified by hand-counting. All samples were scanned from $2\theta = 6$ to 70° with the 3° beam slit, and from $2\theta = 2$ to 10° with the 1° beam slit. Net counts (peak minus background) were used in all statistical analyses. No attempt was made to estimate percentage composition, because matrix effects were too complicated to achieve actual concentrations with any kind of confidence.

For purposes of positive mineral identification two different sample preparations were employed, both involving the use of the preferred orientation method. Sixty milligrams of oven-dried plant material (60 °C, 72 h), ground to 200 mesh (75 μm), were weighed into a 50 ml beaker to which 3 ml of dimethyl sulphoxide had been added. Because states of hydration become variable when exposed to laboratory conditions, it was found that dimethyl sulphoxide as a liquid in which to disperse powdered plant material was vastly superior to water. The mixture was magnetically stirred for one hour. With the use of a medicine dropper, the resulting solution was evenly distributed on a glass slide that was placed on a levelled sheet of plate glass. These slides were allowed to dry at laboratory atmosphere (21 °C, 50 % relative humidity). All plant samples that were analysed were also examined mineralogically by employing this straight glass slide preparation. By using the preferred orientation method, plant samples that had been used to determine the percentage loss on ignition (low-temperature asher, 80 °C to constant weight) were prepared, and patterns from these slides were subsequently obtained.

(*e*) *Statistical methods*

Program A was designed to determine all possible linear correlations among the 46 elements, loss of mass on ignition and the net counts of the major peaks of all minerals encountered in the plant samples studied.

Program B was developed to determine multiple correlation coefficients of the individual linear correlations obtained between pairs of elements, pairs of major mineral peak counts or any combination of element and major mineral peak. Only linear correlation coefficients that were significant at the 0.5 % level or better were used in this program. The significance of partial correlation coefficients was also determined. This program was repeated several times to obtain all significant partial correlation coefficients and to discard obvious spurious ones.

It was also of interest to discover whether different genera are chemically more similar when living together in the same small area on the same soil type than are the same genera living in different regions. To answer this question the Nature Preserve was divided into eight regions. Only analyses of the whole plant samples were compared. The complete chemical analysis of each plant sample was compared with the chemical analysis of all the other plant samples by calculating linear correlation coefficients. The *r* values (correlation coefficients) were transformed to *z* values and average *z* values were calculated for genera from each region. All the mean *z* values were then compared statistically. Statistically significant differences for mean *z* values suggest that plants of a given genus reflect the geology of the different regions rather than their taxonomy or inherent chemical composition. A lack of statistical significance suggests that the inherent chemical composition of a genus overrides the influence of edaphic chemistry.

4. RESULTS

Table 7 shows the mean mineral matter, the loss of mass on ignition (low-temperature ash preparation, 80 °C), the total and the range for each of these categories, the standard deviation and the percentage coefficient of variation (standard deviation divided by mean (100)). These data suggest that all the detectable elements have been adequately accounted for and that the high-speed vacuum cleaner had done an efficient job of removing adhering edaphic materials from the plant samples.

The chemical results are divided into groups of elements following the general scheme that Goldschmidt (1954) used in his book on geochemistry.

In all the subsequent tables, root analyses are shown but have not been included in any arithmetic compilations owing to the possibility that not all edaphic materials have been successfully removed. In addition, whole plant analyses represent all plant parts except the roots.

All plant, soil, sediment and rock chemical data are reported as mg kg^{-1} on a dry mass basis. The water analyses are recorded as the composition of the water at the time of collection and are expressed as mg l^{-1} or µg l^{-1}.

In the following chemical data sections, each section is divided into a discussion of the concentrations of the elements in question and their variation in relation to family sequence, cycle and habitat. This follows the scheme shown in Table 1. Distribution of elemental concentration compiled as to plant parts, following the list shown in Table 3, is also included. A summary of available comparative data concludes each of the chemical sections.

Before proceeding further, it is important to note how the arithmetic compilations were calculated. Variation in chemical composition in regard to taxonomic position was such that elemental concentrations of all plant parts within a family were weighted equally to obtain the mean. For the plant cycle, component parts of each species were averaged, then each of these averages was summed and divided by the number of species, to achieve a grand mean. *Centaurea iberica* was the only plant collected whose cycle is biennial. Although this sample consisted of 10 plants it is hardly representative of biennials as a group and thus is included for comparative purposes only. Division by habitat (lakes (6), swamps (15), moist places and banks (14), wadis (7) and waste places (29)) was calculated in the same way as that for plant cycle. Mean composition of plant parts was arrived at by weighting the particular elemental concentration for each plant part equally (flowers and seeds (21), leaves (6), leaves and stems (17), woody stems (8), stems and woody stems (5) and whole plants (47)).

It is important to note that a number of investigators (Kovalevskii 1971, 1973, 1978, 1984; Malyuga 1947, 1950, 1951, 1954, 1958*a*, *b*; Brooks 1960, 1968, 1972; Brooks & Lyon 1966) have used plant analysis to predict concentrations of elements of economic value in the subsurface. Although these works are quite important, they report analytical values as ash mass; these values are not comparable to data in the present work, which are reported on a dry mass basis.

(a) *Plant mineralogy*

It is well known that aquatic plants contain more Na than their terrestrial counterparts (Nelson & Palmer 1938; Botkin *et al.* 1973; Cowgill 1974*a*). In this study, two aquatic species, *Nuphar lutea* and *Alternanthera sessilis* (Cook *et al.* 1974) had the highest mean Na content, namely 6820 mg kg^{-1} and 9003 mg kg^{-1} respectively. The latter plant was not rooted in the mud; thus the origin of its Na content must have been the water (see tables 8 and 9), implying a concentration factor of 769. The lowest Na concentration in plants encountered in this study belongs to the Salicaceae, which exhibited a mean of 1006 mg kg^{-1}.

There does appear to be some enrichment of K relative to Na in the Huleh plants (Na:K 0.21) when this ratio is compared with that in either the Huleh Basin rocks (Na:K 1.01) or the earth's crust (1.1) (Bowen 1979). The Na:K ratio for Huleh soils (0.51) is not very different from that proposed by Bowen (1979) for median soil (0.36) and both cases show an enrichment of K relative to Na when contrasted with either the ratio for Huleh's rocks or that for the earth's crust. Figure 2 shows a plot of mean Na in plants against mean K in plants. The lower envelope contains 16 plants that accumulate K in relation to Na. These plants exhibit a Na:K range of 0.034–0.110. Muenscher (1951) has observed that some plants can be made poisonous by application of KNO_3, which is then sorbed from soil or water. Such plants may accumulate K in any case. He lists *Chenopodium album* of the Chenopodiaceae and *Amaranthus retroflexus* and *A. graecizans* of the Amaranthaceae as having such properties. *C. album* and *A. graecizans* in the present study accumulate K in relation to Na in excess of the general plant Na:K mean.

There are five plants that accumulate Na in relation to K well in excess of the plant mean (0.208). These plants are noted in the legend to figure 2. Their ratios range from 0.591 to 0.934.

When the ratios of Rb:K in Huleh soils (5×10^{-3}), in Huleh rocks (7.7×10^{-3}), in Huleh mud (6.4×10^{-3}) and Huleh Preserve water (12×10^{-3}) are compared with that found in the earth's crust (4.3×10^{-3}) (Bowen 1979) an enrichment of Rb to K is apparent. However, the Rb:K ratio for median soils (10.7×10^{-3}) (Bowen 1979) suggests that Rb is likely to be enriched in edaphic materials. The Huleh plants show a definite enrichment of K relative to Rb (0.8×10^{-3}).

The ratio Cs:K (water 1.4×10^{-4}, soils 2.2×10^{-4}, rocks 1.3×10^{-4}) in various substances of the basin does not differ very much from that of the earth's crust (1.4×10^{-4}) (Bowen 1979). The ratio found in Huleh soils is similar to that proposed for median soil (2.9×10^{-4}) (Bowen 1979). Plants, however, appear to discriminate against Cs in favour of K ($Cs:K = 0.02 \times 10^{-4}$ in Huleh plants; terrestrial plants, 0.06×10^{-4}–0.13×10^{-4}) (Bowen 1979). Caesium is vastly enriched relative to K in the mud (6.8×10^{-4}). Presumably this observation reflects the element's affinity for organic matter (see Cowgill 1980).

The Huleh soils exhibit a Li:K ratio (9.7×10^{-4}) similar to that encountered in the earth's crust (9.5×10^{-4}). However, this ratio is 19.8×10^{-4} for rocks and 67.6×10^{-4} for mud, showing a progressive enrichment of Li relative to K when the ratio is contrasted with that for the Huleh soils. The Huleh plants apparently exclude some Li from their tissues as their Li:K ratio is 0.04×10^{-4}.

Of the families that are represented by more than one plant species, the Amaranthaceae contain the highest mean concentration of K (26017 mg kg^{-1}) in their tissues and the Fabaceae exhibit the lowest amount (8526 mg kg^{-1}). A comparison of species shows that *C. album* of the Chenopodiaceae contains both the highest K (41179 mg kg^{-1}) and the highest

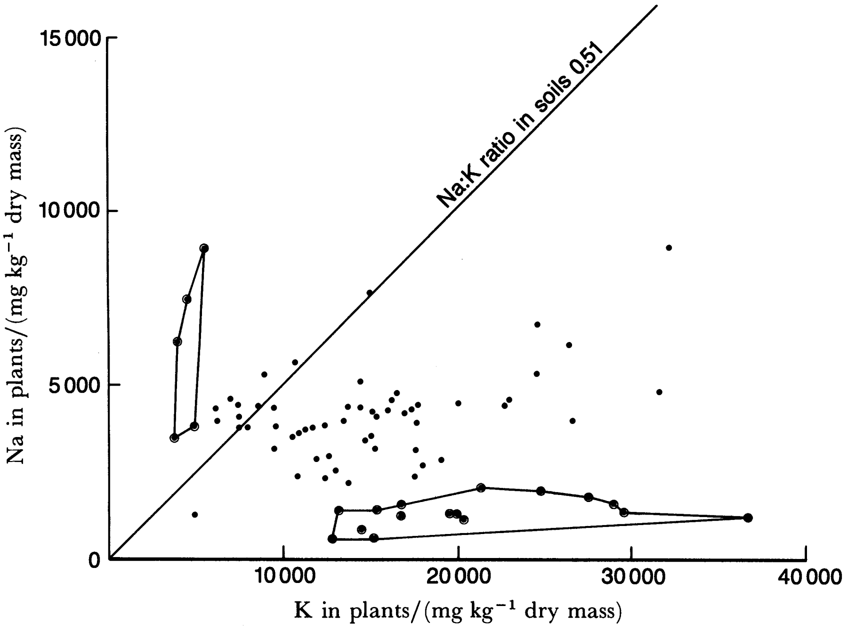

FIGURE 2. A plot of Na concentration against K concentration in plants, showing a group of Na accumulators close to the y axis and a second group of K accumulators near the x axis. The Na accumulators are *T. fragiferum. A. mannifera*, *E. angustifolia*, *C. mariscus* and *P. australis*. Their Na:K ratio varies from 0.9 to 0.6. The K accumulators are *A. rosea*, *C. album*, *Am. albus*, *Am. graecizans*, *P. senegalense*, *P. arenastrum*, *P. acuminatum*, *P. lapathifolium*, *S. acmophylla*, *N. oleander*, *S. nigrum*, *V. agnus-castus*, *G. elongatum*, *M. tripartita*, *X. strumarium* and *P. vaginatum*. Their Na:K ratio varies from 0.110 to 0.034.

Rb (35.2 mg kg^{-1}) of any plant studied in this collection; the lowest K (4923 mg kg^{-1}) concentration found was in *Phragmites australis* of the Gramineae and the lowest Rb content was in *Cyperus michelianus* ssp. *pygmaeus*, of the Cyperaceae (6.9 mg kg^{-1}). *Nuphar lutea* contained the highest Cs content (0.061 mg kg^{-1}) and *Cyperus alopecuroides* the lowest Cs quantity (0.008 mg kg^{-1}). For Li, *Alternanthera sessilis* accumulated the highest concentration of any plant studied (0.53 mg kg^{-1}) while *Polygonum lapathifolium* contain the least amount of Li (0.023 mg kg^{-1}).

Table 10 shows a comparison of the quantities of alkali metals in plants divided according to their life cycle. Rubidium, Cs and Li exhibit no statistically significant variation in relation to cycle, but both Na and K show a marked difference in concentration between annuals and perennials. Potassium is concentrated by the annuals studied here ($\chi^2 = 345.6$, $p < 0.001$) while Na is accumulated by the perennials ($\chi^2 = 10.8$, $p < 0.005$).

It was of interest to discover whether any correlation between elemental composition and taxonomic position might be apparent. Figure 3 shows such a relation with K and figure 4 with Rb. The families (y axis) are numbered from 1 to 29 in assumed evolutionary order, with Nymphaeaceae being number 1 (oldest or most primitive) and Gramineae number 29 (most recent or advanced). The relationship for Rb is more significant than that for K. The theoretical line for Rb includes all the families, whereas that for K suggests that families 24–29 survive with a minimum amount of K in their tissues. However, the oldest families contain more K and Rb than those more recently evolved. It is perhaps rather presumptuous to make such comparisons with so few plant species represented, and therefore the data presented should be viewed in a most tentative manner. It is nevertheless interesting that of all the alkali metals only K and Rb, which are coherent in nature anyway, exhibit such a remarkable

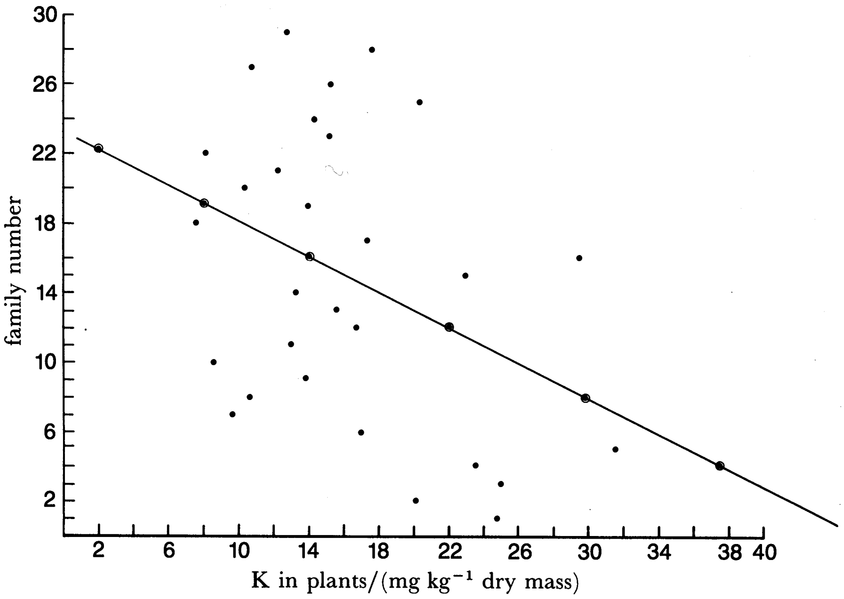

FIGURE 3. Potassium content of plants in relation to their family position. Families are designated as 1–29 with 1 being Nymphaeaceae and 29 being the Gramineae. The linear correlation coefficient is -0.382 ($p < 0.05$, $n = 29$) and the regression line which is depicted on the graph is $y = 23.45-0.005x$.

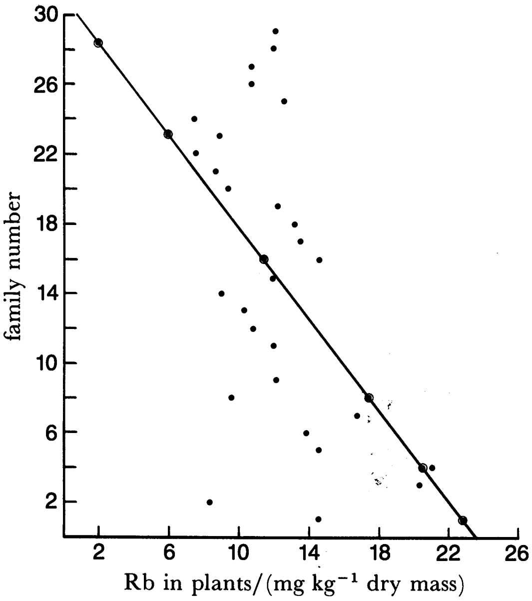

FIGURE 4. Rubidium content of plants in relation to their family position. Families are designated as in figure 3. The linear correlation coefficient is -0.5 ($p < 0.002$, $n = 29$), and the regression line depicted on the graph is $y = 30.88-1.309x$.

relation. Kovalevskii (1973) noted that an increase of K content in soils failed to result in an increase of these elements in plant communities. This may suggest that since K is taken up by plants in relation to their phylogenetic position, additions of more K to the soil failed to show any change in plant composition. This presumes that the original K content of the soil was sufficient for plant growth.

It is curious that Cs failed to follow K and Rb in their taxonomic relationships. The cause for this phenomenon may be found in the sources for the three elements: the ratios of the three elements may vary such that the amount of Cs entering the Huleh Basin is more constant than that of K and Rb.

Table 11 illustrates the concentration of alkali metals in Huleh plants subdivided according to their habitat. As has already been observed, Na is more prevalent in aquatic species than in terrestrial ones. Potassium and Rb are less concentrated in plants inhabiting moist places than residing in lakes. Caesium and Li fail to show any discernible trend.

The distribution of alkali metals in plant parts is shown in table 12. The mean composition of whole plants is added for comparison. Potassium, Rb and Cs are least concentrated in the leaves while Li is highest in this plant part. Sodium and Li are lowest in woody stems. Potassium, Rb and Cs are high or highest in flowers and seeds. The most Na was found in non-woody stems. There is usually a good deal more K in plant tissues than Na. Rubidium tends to follow K. The variation exhibited by Cs is so small that any meaningful comment concerning its distribution is not possible. Lithium is high in the whole-plant category, primarily because of high concentrations (in mg kg^{-1}) in *Alternanthera sessilis* (0.53), *S. nigrum* (0.113), *V. officinalis* (0.25), *P. lagopus* (0.18), *K. spuria* (0.13) and *C. michelianus* ssp. *pygmaeus* (0.103).

Potassium is most concentrated in the midrib and midsection of the leaves of Cyperaceae, Typhaceae and Gramineae. Rubidium, Cs and Li follow the same pattern but the observed variation is not statistically significant. The variation exhibited by K is enormously significant, well beyond the 0.1 % level. Sodium has a pattern of its own with the leaf margin concentrating the most and the midsection the least. This variation is statistically significant beyond the 0.1 % level in all three families. Though the leaves of other families were examined, no consistent pattern was observed. The data are given in table 12. Jones (1970) has noted a similar type of pattern for K in *Zea mays* leaves.

Among the alkali metals the vast majority of published plant analyses relate to Na and K. Few data are available on the distribution of the rarer alkali metals. Table 13 contains available comparative data, subdivided into 'aquatic and swamp plants', and 'terrestrial plants'. It should be borne in mind that much of the variation observed is probably reflective of samples that represent variable ages and different populations (Boyd 1970*b*, *c*; Gaudet 1977; Cowgill 1974*a*; Sugiyama *et al.* 1984).

There are no available comparative data for *Typha angustata*. Thus, *T. latifolia* and *T. angustifolia* figures are presented. With the exception of the low K figure, the K data are reasonably concordant (CV = 19). The Na information is much more variable. This has also been noted by Hutchinson (1975). Sodium is usually present in smaller amounts, is more difficult to analyse than K and the contamination problem associated with sampling is more pronounced than with K (although the Huleh plant samples were collected with gloved hands). These observations also contribute to the observed variation.

Phragmites australis analyses indicate considerable variation with Na and K data from various portions of the globe. Riemer & Toth's (1968) values appear to be lower than expected for Na and higher than expected for K. Clearly, many different populations are represented here.

The data presented by Bowen (1979) for terrestrial plants show that the latter appear to concentrate Li more than their aquatic relatives, though the data of Cowgill (1974*a*) uncovered an aquatic Li accumulator, *Pontederia cordata* L. The leaves of this plant contained 4.2 mg Li per kilogram dry mass. Plants of the Huleh basin contain less Li in their tissues than the range suggested by Bowen (1979). The rest of the alkali metals, with the exception of Na, appear to fall within the range he proposes.

The Na data reported by Botkin *et al.* (1973) are some of the lowest in the literature. However, Lake Superior water (see table 13) in the vicinity of Isle Royal is rather low in its Na content, which presumably is at least part of the explanation. The Lake Huleh Preserve contains about 7 times more Na than does the study area of Botkin *et al.* (1973). Arid region plants would normally be expected to contain more Na than north temperate zone plants, primarily owing to the lower availability of water.

Table 13 shows some Russian data on Li in plant families (Borovik-Romanova & Belova 1974*a*, *b*). Calculating correlation coefficients between these figures and those obtained for Huleh plants of the same families provides an r value of 0.841 ($p < 0.01$), which suggests that the order is followed in both studies, though the Soviet values are an order of magnitude greater than the Huleh ones. There is a suggestion that Li may exert some control over chlorophyll production in certain plants (Ezdakova & Tilavova 1972). Should this observation be universally the case, it would be expected that geographical variations might occur.

(*b*) *Copper and silver*

Polygonum patulum contains the highest amount of Cu (208 mg kg^{-1}), in its leaves and stems, of any plant examined in the study (see tables 14 and 15). The seeds of this plant, however, contain normal quantities of the element. Ten different specimens were examined for their Cu content. The leaves and stems all contained high amounts of Cu (mean 208 ± 12.5 mg kg^{-1}). This plant has not been identified as a Cu accumulator. The lowest amount of Cu encountered in the study was 6.1 mg kg^{-1}; this quantity was found in a number of plant parts as well as whole plants (*C. michelianus* spp. *pygmaeus* of the Cyperaceae and *P. vaginatum* of the Gramineae).

Silver is not known to have any biological function in plants, yet it is ubiquitous and appears to be taken up by water plants. Part of the reason for its apparent universal presence in plants is the increasing use of AgI in cloud seeding (Hodge & Folsom 1972) to encourage the production of rain and snow. Silver is often a by-product of galena (PbS) mining (Thrush 1968; U.S. Bureau of Mines 1980). It is quite possible that some Ag was globally distributed when Ag containing galena was being smelted. In the present study, the highest concentrations were found in the leaves (0.16 mg kg^{-1}) of *Salix acmophylla* and the leaves and stems (0.128 mg kg^{-1}) of *Amaranthus graecizans*; the lowest silver concentration was found in *Polygonum lapathifolium* (0.029 mg kg^{-1}). Gibbs (1974) reported 0.28 mg kg^{-1} Ag in *Salix* leaves.

Relative to the Ag:Cu ratio in the earth's crust (14×10^{-4}) there is an accumulation of Ag relative to Cu in Huleh plants (48.7×10^{-4}), Huleh soils (129×10^{-4}) and Huleh rocks (198.3×10^{-4}). The ratio found in Huleh plants (48.7×10^{-4}) falls within that proposed by Bowen (1979) for terrestrial plants (20×10^{-4}–533×10^{-4}).

Table 16 shows a comparison of Cu and Ag in plants divided according to their life cycles. There is no discernible difference in the accumulation of Cu and Ag by plants in relation to their life cycles.

These two elements show no relation between their concentration in members of a family and the taxonomic position of that family.

Table 17 shows the distribution of Cu and Ag in plants subdivided by habitat. The results of this compilation are unremarkable.

Table 18 shows the distribution of these two elements in plants subdivided according to plant parts. If the Cu content of *P. patulum* is not included, the concentrations in all plant parts are similar, the lowest being found in stems. Silver barely varies at all.

For the Cyperaceae, Typhaceae and Gramineae, Cu is most concentrated in the blade, Ag in the leaf margin; although the distribution is quite consistent, it fails to be statistically significant. Sayre (1952) found that tagged Ag concentrated in leaf margins, and Jones (1970) found that Cu was equally concentrated in the margin and the blade of *Zea mays* leaves.

Table 19 shows what comparative data exist for Cu and Ag in plants and other pertinent materials. Hutchinson (1975) showed that among water plants the concentration factor for Cu declines with increasing Cu content of the water, as would be expected from an essential element. Data from Chiaudani (1969) on Cu concentration of various parts of *Phragmites australis* living in various lakes in Italy suggest the existence of genetically different physiological races which accumulate different quantities of Cu from the mud. The data for Cu shown in table 19 are highly variable. The data for Ag are too scant to warrant any discussion.

Silver can substitute for K sites in membranes, inhibiting the sorption of other cations by the roots (Hendrix & Higinbotham 1974). The range of Ag in plant foods is 0.07–2.0 mg kg^{-1} dry mass (Chapman 1972). Horowitz *et al.* (1974) noted that plants of the same species contained less Ag in their tissues in the summer than those gathered in May. It was found in Linsley Pond water that Ag all but vanished in the summer (Cowgill 1972) and was at its highest level in the winter, apparently owing to the use of AgI by the Canadians to produce snow for the skiers in Quebec.

(*c*) *Beryllium*

The highest Be concentration was found in *Alternanthera sessilis* (1 mg kg^{-1}) and the lowest in *Nerium oleander* and *Polygonum patulum* (0.041 and 0.042 mg kg^{-1}, respectively).

The mean Be: Li ratio for Huleh plants is 2.82; that for Huleh soils and rocks is 0.31 and 0.27 respectively. It would appear that Be moves more easily from the source materials to the plants than does Li. Beryllium is also enriched in the plants relative to Mg ($Be:Mg = 34 \times 10^{-6}$) and to a lesser extent relative to Ca ($Be:Ca = 8.4 \times 10^{-6}$).

Table 16 shows the distribution of Be in plants divided according to their cycle. No discernible difference in accumulation of Be by plants in relation to their cycle was observed.

Beryllium failed to exhibit any relationship between concentration in members of a family and the taxonomic position of that family.

Table 17 shows the distribution of Be in plants subdivided by habitat. The results are unremarkable.

Table 18 depicts the variation of Be in relation to plant parts. Beryllium is higher in leaves and stems than other parts, the latter all containing about the same concentration.

For the Cyperaceae, Typhaceae and Gramineae, Be is most concentrated in the leaf margin; however, even though the distribution is quite consistent, it fails to be statistically significant. No comparative data for Be were located in the published literature.

Table 19 shows what comparative data exist for Be in plants and other pertinent materials. The figures for Be are too scant to warrant any discussion.

Some plant species in the Fabaceae and Brassicaceae families have an ability to accumulate Be in their tissues (Gribovskaya *et al.* 1968). Sorption mechanisms of Be by plants appear to be similar to those involved in Mg and Ca uptake (Krampitz 1980). The range reported in plants is 0.001 to 0.4 mg kg^{-1} dry mass. This does not include accumulator species. Asami & Fukazawa (1981) found the Be concentration in plants from unpolluted regions to have a mean of 0.001 mg kg^{-1} but in polluted ones the range was 0.023–0.69 mg kg^{-1}. Nikonova (1971) found concentrations in plants of the U.S.S.R. to range from a trace to 3 mg kg^{-1}, but found the element in only 34% of her plant collection.

(*d*) *The alkaline earths*

The Mg:Ca ratio in Huleh plants is 0.245, which suggests an accumulation of Mg in reference to Ca when the ratios for Huleh soils (0.050) and Huleh rocks (0.033) or mud (0.046) are considered (see table 20). Six plants have Mg:Ca ratios in the range of 0.5–0.9, implying Mg accumulation (*A. rosea* (0.561), *C. opulifolium* (0.795), *Am. gracilis* (0.670), *P. salicifolium* (0.859), *F. oxyphylla* (0.522) and *Cy. alopecuroides* (0.716)). There are also seven plants that show Mg:Ca ratios below 0.150 (*P. euphratica* (0.147), *F. vulgare* (0.147), *E. angustifolia* (0.106), *P. lagopus* (0.141), *I. graveolens* (0.127), *P. echiodes* (0.147) and *C. iberica* (0.129)). In absolute terms, *A. gracilis* contains the highest concentration of Mg (12029 mg kg^{-1}) and *S. acmophylla* the lowest (2420 mg kg^{-1}).

Ophel & Fraser (1970) reported on the ability of some water plants to accumulate Sr, notably *Nuphar variegata* (194 mg kg^{-1}), and of others to discriminate against Sr, in particular *Nymphaea odorata* (5 mg kg^{-1}). This capability has also been noted by Cowgill (1974*a*) in the Linsley Pond study and by Leinert (1979) in his study of Ca, Sr and ^{90}Sr uptake by aquatic plants. The uptake of Sr depends on how much of the element is present in the environment, the plant's ability to take up Ca and the tendency to discriminate in favour of or against Sr. Figure 5 shows a plot of the mean Sr concentration in Huleh plants against the mean Ca concentration in the same plants. It is clear that there are at least two populations with respect to Sr uptake. The Sr:Ca ratio in Huleh plants is 23.1×10^{-4}, about the same as the ratio in Huleh soils (23.7×10^{-4}). The highest concentrations of both Ca and Sr were found in *Echium angustifolium* (Sr:Ca = 41×10^{-4}) (see table 21). The upper envelope in figure 5 surrounds plants that exhibit a Sr:Ca ratio in excess of 34.6×10^{-4}. These plants discriminate in favour of Sr uptake. The line shows the Sr:Ca ratio in Huleh soils. The vast majority of plants fall below the line. The Sr:Ca ratio of *Nuphar lutea* is 19×10^{-4}, which suggests some Sr accumulation with reference to Ca, as the Sr:Ca ratio of the mud in which it grows is 14.4×10^{-4}.

There is also a small population of plants that discriminate against Sr. Their Sr:Ca ratio lies between 10.2×10^{-4} and 13.3×10^{-4}. These plants lie in the lower envelope on figure 5.

The range of Sr:Ca ratios calculated for Huleh plants is 10.2×10^{-4} to 58.2×10^{-4}, which is much smaller than that noted by Ophel & Fraser (1970) (5.3×10^{-4}–89.8×10^{-4}). It is important to realize that the Sr:Ca ratio in Huleh water (56×10^{-4}) is the same as that of Perch Lake (57×10^{-4}) although in the Huleh study soils and mud must be considered as well.

As with Sr, the Ba:Ca ratio in the Huleh plants (20×10^{-4}) is a good deal lower than the geochemical ratio in the earth's crust (122×10^{-4}) (Bowen 1979) or median soil (333×10^{-4}) (Bowen 1979). However, the plants accumulate a little more Ba relative to Ca in their tissues when the plant Ba:Ca ratio is compared with that of the source materials (soils 13×10^{-4}; rocks 5.8×10^{-4}). The highest quantity of Ba was found in *Calystegia sepium* (56.7 mg kg^{-1}) and the smallest quantity in *Megalodonta tripartita*. Both these quantities lie within the range proposed by Bowen (1979) for terrestrial plants (see table 25) (8–150 mg kg^{-1}).

The variation of alkaline earths in plants according to their cycle is shown in table 22. Calcium, Sr and Ba show no significant difference when annuals and perennials are compared.

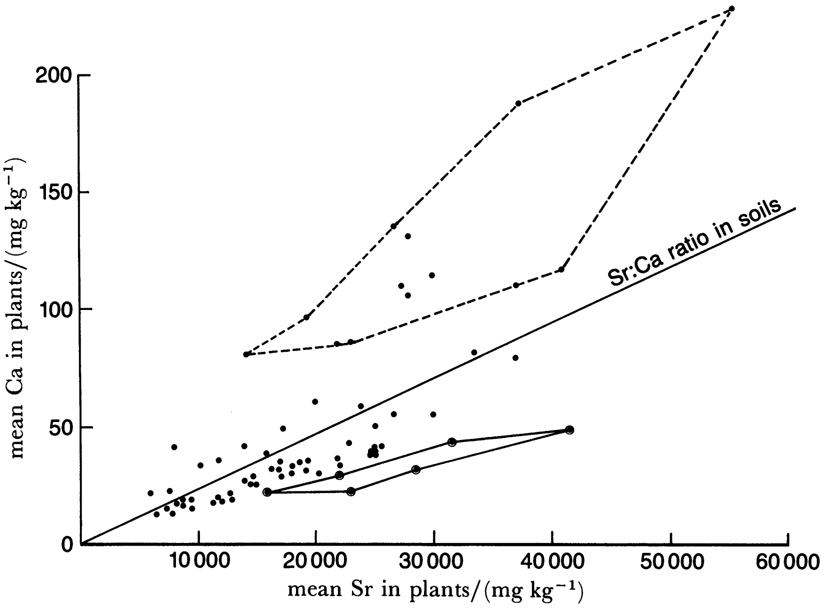

FIGURE 5. A plot of Sr in plants against Ca in plants, showing two different groups of plants, Sr accumulators and Ca accumulators. The former include *S. acmophylla*, *P. euphratica*, *H. incana*, *T. fragiferum*, *A. mannifera*, *A. visnuga*, *N. oleander*, *C. planiflora*, *E. angustifolia*, *V. officinalis*, *S. oleraceus* and *C. mariscus*. The Sr:Ca ratios vary from 37.2×10^{-4} to 58.2×10^{-4}. Ca accumulators include *Am. retroflexus*, *H. supinum*, *B. undulata*, *F. oxyphylla*, *I. graveolens*, *Cy. michelianus* ssp. *pygmaeus* and *P. vaginatum*. Their Sr:Ca ratio varies from 10.2×10^{-4} to 13.9×10^{-4}.

The Ca:Sr ratio for annuals is 417; that for perennials is 412, hardly a difference. However, a χ^2 test shows a highly statistically significant difference in their Mg content ($\chi^2 = 215.4$, $p < 0.001$) with annuals containing more. This is curious as Kiss (1975) noted that additions of $MgSO_4$ increased the longevity of plants. It would be expected, therefore, that perennials would contain more Mg in their tissues than annuals.

There was no obvious correlation between the concentrations of alkaline earths and the taxonomic positions of the plants. Generally, Ca is found to be highest in the Plantaginaceae and lowest in the Typhaceae. Strontium was highest in the Cuscutaceae, lowest in the Chenopodiaceae and Typhaceae. Bowen & Dymond (1955–6) noted that in their study the grasses generally contained the least Sr. In the Huleh study Ba is found to be the least concentrated in the Gramineae and highest in the Convolvulaceae. Amaranthaceae contained the most Mg and Typhaceae the least.

Variation of alkaline earth concentrations in relation to habitat is shown in table 23. Calcium and Mg are least concentrated among lake plants and most concentrated among wadi plants. Strontium more or less follows Ca. Magnesium is highest in swamp plants. Barium fails to show any trend with habitat.

Table 24 shows alkaline earth concentration distribution in relation to plant parts. Magnesium and Ca are concentrated in leaves and stems, Sr in leaves and Ba in flowers and seeds. Barium and Sr may be essential for mammals (Rygh 1949); however, their function in plants is poorly understood. It is difficult to believe that these two elements fail to have some important function, especially when Ba accumulation by the Brazil nut *Bertholletia excelsa* (4300 mg kg^{-1}) (Robinson *et al.* 1950; Seaber 1933; Wagner 1936) and Sr accumulation by *Anisantha madritensis* (18600 mg kg^{-1}, Bowen & Dymond 1955–6) are considered.

The lowest concentrations of Mg, Ca, Sr and Ba are found in woody stems, stems and woody stems, stems and woody stems and woody stems, respectively.

Plant leaves were examined for the distribution of alkaline earths within leaves. Only Cyperaceae, Typhaceae and Gramineae showed any consistent reproducible pattern. Barium and Sr distribution demonstrated the same pattern as Mg and Ca but failed to be statistically significant. Magnesium is more concentrated in the blade ($\chi^2 = 154.8$, $p < 0.001$) than in the leaf margin. The midrib–midsection of the leaf and the whole leaf contain less Mg than the blade. This is true of the leaves of all three families. The leaf margin contains the most Ca and the midsection contains the least. Both Ba and Sr follow this pattern; the latter element is characteristic of Cyperaceae, Typhaceae and Gramineae. The data are presented in table 24. Similar data have been noted in *Zea mays* leaves by Jones (1970).

The most curious phenomenon in these data is that Sr is concentrated in the midsection–midrib rather than margin, as is Ca. Even more curious is that the variation in Sr across the leaf is not significant while the difference between margin and midrib–midsection in Ca concentration provides a χ^2 of 1745, $p < 0.001$, significant well beyond the 0.1 % level.

The function of these concentrations in relation to leaf section is not known. There may be a seasonal component here, in that the Huleh plants were all collected at a time of either full bloom or seed production. There does not seem to be any information on seasonal distribution of the observed phenomenon.

Sayre (1952), using radiochemical tags, found that B, Cl, Co, Ag, Sb and Ir accumulated in the maize leaf margins.

These observed distributions were characteristic of Cyperaceae, Typhaceae and Gramineae. Though these phenomena were sought in other families nothing conclusive could be elucidated.

With the exception of B, an hypothesis could be put forward that these phenomena may relate to the reproductive function. In maize plants (Jones 1970, 1963; Sayre 1952) these phenomena have been described only in leaves after tasselling (emergence of stigmas).

Comparative data are shown in table 25. The results are highly variable for the plants listed and probably reflect age and seasonal variations in chemical content (see, for example, Boyd 1970*a*). The rarer alkaline earths are too poorly represented to make any meaningful discussion possible.

(*e*) *Zinc, cadmium and mercury*

Shacklette (1972), in his review of the Cd content of plants, suggested that Cd may enter the atmosphere through the combustion of hydrocarbons. Cowgill (1975*a*) showed a concentration of Hg in Huleh surface sediments, the origin of which was proposed to be the burning of fossil fuels (see also Joensuu 1971). Thus, the concentration of these elements in plants and surficial materials (table 26) must also be viewed as having an atmospheric contribution, the quantity of which is unknown.

Recently, Kuboi *et al.* (1986) noted that Cd accumulation has a familial dependency. These investigators discovered high Cd accumulation among the Chenopodiaceae, Brassicaceae, Solanaceae and Asteraceae, medium Cd accumulation among the Gramineae and low uptake among members of the Fabacea. High soil Cd promotes greater Cd uptake in the Brassicaceae.

The mean Zn:Cd ratio in Huleh plants is 88.6. Three plants (table 27), *N. lutea* (3.95), *H. incana* (8.71) and *G. elongatum* (3.97) discriminate in favour of Cd in contrast to Zn. If the effect of these plants is removed, the mean Zn:Cd ratio then becomes 392, suggesting an accumulation of Zn over Cd. This ratio is smaller than the mean for Huleh soils (494) or the earth's crust (682) (Bowen 1979), but considerably greater than that for Huleh rocks (97.5).

The mean Hg:Cd ratio in Huleh plants is 0.94. Apart from the above-mentioned plants high in Cd, *Al. sessilis* (7.49), *E. erecta* (4.7) and *Cy. latifolius* (16.9) all contain high amounts of Hg (greater than 1.91 mg kg^{-1}). If the effect of these plants is excluded from the ratio, the Hg:Cd ratio rises to 3.27, implying an accumulation of Hg in preference to Cd.

The plants containing the highest Zn concentrations are *P. patulum* and *X. strumarium*. The lowest Zn concentration was encountered in *U. hulensis*.

An examination of Zn distribution in grass leaves showed the Zn to be more concentrated in the leaf blades (mean = 35 mg kg^{-1}) than in the midrib section (mean = 18 mg kg^{-1}). The mean Zn concentration for leaf analyses of the Huleh grasses was 23.5 mg kg^{-1}. Grasses that were past the seed production stage of their cycle contained less Zn (mean = 17) than those in the process of seed production (mean = 32) or just prior to it (mean = 28). Panin & Panina (1971) have also observed that Zn is highest at flowering stage. Such observations have been also noted in *Zea mays* (Gorsline *et al.* 1965; Jones 1970). This observation was not noted in any other family, though it was sought.

No obvious relationship between Zn, Cd and Hg content of Huleh plants and their taxonomic position was noted.

Table 28 shows the distribution of Zn, Cd and Hg in plants separated in reference to their life cycle. There is no statistically significant difference in the concentrations of these three elements between annuals and perennials.

When concentration in reference to habitat (see table 29) is examined, the oscillations of Zn suggest higher concentrations as water availability declines. Cadmium and Hg fail to exhibit any discernible trend; however, Hg appears to be concentrated in lake and swamp plants, whereas Cd is high in lake plants and those that inhabit waste places.

Zinc is concentrated in leaves and stems, woody stems and flowers and seeds, while Cd is maximal in flowers and seeds. Mercury, like Zn, is highest in stems and woody stems, leaves and stems and flowers and seeds (see table 30).

It is interesting to compare the mean Zn, Cd and Hg content of Huleh plants with the ranges proposed by Bowen (1979) for terrestrial plants. Zinc and Cd in Huleh plants fall at the low end of the terrestrial plant range but Hg in Huleh plants is an order of magnitude higher than the range suggested for this element by Bowen (1979). It should be noted that the Hg data for Huleh plants have been confirmed by several different analytical methods and by two different analysts (see Cowgill 1974*a*). It has been noted elsewhere that Hg tends to be higher in surface lake sediments than in buried ones (see Cowgill 1975*a*) but there is a suggestion (Siegel *et al.* 1974; Kozuchowski & Johnson 1978) that gaseous Hg is emitted through plant tops. Such a phenomenon, were it universal, would suggest a cycle much like that of Se, with precipitation bringing the volatilized Hg back into the soil during the short but intensive rainy season experienced in the Huleh valley.

Comparative data (see table 31) for Cd and Hg are sparse. Kovalevskii (1986) examined 255 types of plant tissue for their Hg content and found only ten that took up Hg in a linear relation to the concentrations in the soils supporting them. It has been noted that in some aquatic plants Cd appears to increase with age (Cowgill 1974*a*). Again, much of the variation in Zn is most probably due to seasonal distribution, the particular population, the total amount of available Zn and the life-cycle stage at which material was collected.

(*f*) *Boron, Aluminium and Gallium*

Boron ranks twelfth in abundance among the dissolved elements of the sea. Its mean concentration is thought to be about 4.6 mg l^{-1} (Goldberg 1965). The vapour pressure of H_3BO_3 over the surface of the sea is about 2 mmHg (Gast & Thompson 1959). Thus the element may be picked up in droplets of sea spray by the atmosphere and transported over the landscape (Gast & Thompson 1959). Plants located on land tend to contain less B in their tissues than those growing in the vicinity of the sea. The mean B content of the Linsley Pond plants was 40.6 mg kg^{-1} (Cowgill 1974*a*); those of the Huleh Preserve (see table 32) contained on average 32.8 mg kg^{-1}. Linsley Pond is very close (less than 1 km) to the sea. Lake Huleh, or what remains of it, is the recipient of a strong but persistent Rift valley wind that moves across the Mediterranean Sea, northwards over the Dead Sea and finally across the Huleh Valley. The B content of plants varies according to the species, the plant part analysed and the time of sampling within the plant's life cycle (Chapman 1966; Jones 1967; Neubert *et al.* 1969).

When the analyses of these Huleh Preserve plants first began, a small pilot project was carried out to discover whether there existed any variation of statistical significance in elemental composition across a leaf surface. All members of the Cyperaceae, Typhaceae and Gramineae contained higher B concentrations in the marginal areas of leaves than in the midsections. All other plants were checked for the presence of this phenomenon but only the families noted above exhibited it. The results are shown in table 33. The concentration of B in marginal areas of leaves, principally in maize plants (*Zea mays*), has also been observed by other investigators (Sayre 1952; Kohl & Oertli 1961; Jones 1970). In addition, it has been noted that genetic variability occurs among maize hybrids in their ability to take up B and concentrate it in the leaves (Gorsline *et al.* 1968). It is generally believed that the dry matter of plants containing less than 15 mg kg^{-1} B is B-deficient (Chapman 1966; Jones 1967; Neubert *et al.* 1969). This is interesting since the Gramineae contain the lowest amount of B of any of the families studied (9 mg kg^{-1}) yet none of these plants showed any symptoms typical of B deficiency (see Chapman 1966). Philipson (1953), Ylaranta & Sillinpaa (1984), Lounamaa (1956), Katalymov (1955), Stiles (1961), Panin & Shchetinina (1974) and Shive (1941) have all noted that B is low in the Gramineae. In addition, Shive (1941) found the Brassicaceae to be rich in B and that dicotyledons generally take up more B than monocotyledons. Despite this apparently deficient state, the marginal areas of leaves of the grasses appear to contain adequate amounts of the element. The function or advantage of this phenomenon remains obscure. Lee & Aranoff (1967) noted that B deficiencies in plants permitted the accumulation of phenolic acids, which ultimately brought about the death of the plant. Borate in the plant functions in partitioning metabolism between the glycolytic and pentose-shunt pathways. However, there is no apparent relation between this phenomenon and the concentration of B in marginal areas of leaves of plants belonging to some families. Considering the taxonomic position of these families, this differential accumulation of B in leaves must be a relatively recent evolutionary phenomenon. Tanada (1974, 1978*a*, *b*, *c*) has proposed that B is required to stabilize a positive electrostatic charge in the plasma membrane that is generated by the actions of gravity and phytochrome. Boron has also been identified as necessary for auxin transport in plants (Dela Fuenta *et al.* 1986).

The B:Al ratio in Huleh plants is 568×10^{-4}. Relative to Al, B is vastly enriched in the plants when this ratio is compared with that of the source materials (Huleh soils 13.3×10^{-4}; Huleh rocks 9.1×10^{-4}), median soil (2.8×10^{-4}) (Bowen 1979) or the earth's crust (1.2×10^{-4}). However, the range for B and Al proposed by Bowen (1979) for terrestrial plants provides a B:Al ratio from 1222×10^{-4} to 2642×10^{-4}, suggesting that plants in general sorb B preferentially in contrast to Al.

Boron is concentrated in *Xanthium strumarium* (Asteraceae) and is lowest in the grasses. Amanova & Kinzikaeva (1973) noted that B tended to be high in desert Chenopodiaceae.

The Ga:Al ratio in Huleh plants is 13.7×10^{-5}. In terrestrial plants (Bowen 1979) this ratio oscillates between 11.1×10^{-5} and 37.7×10^{-5}. The ratio in Huleh rocks (19.9×10^{-5}) is similar to that in the earth's crust (22×10^{-5}) (Bowen 1979). Thus the Ga content of Huleh plants relative to Al is impoverished when the Ga:Al ratio in Huleh rocks is considered. The ratio for Huleh soils (9.5×10^{-5}) suggests that the plants sorb a bit more Ga relative to Al than would be presumed from the Huleh rock ratio.

Galium elongatum and *Ludwigia stolonifera* exhibit Ga:Al ratios 2–3 times that of the Huleh plant mean (36.7 and 28.1, respectively) (see table 34). *Paspalum vaginatum* (Gramineae) has the lowest Ga:Al ratio of any of the plants examined (3) (see table 34).

The Ga and B concentrations of Huleh plants fall within the range proposed by Bowen (1979) for land plants but the Al concentration exceeds the mean suggested by Bowen (1979). The Al concentration of *L. stolonifera* (242 mg kg^{-1}) is the lowest encountered; the highest concentration was found in *P. vaginatum* (1744 mg kg^{-1}). No plants studied fall into the Al accumulator types in the sense of Chenery (1948). The lowest Ga concentration was found in *P. vaginatum* (0.055 mg kg^{-1}) and *Am. sessilis* (0.055 mg kg^{-1}) and the highest in *H. supinum* (0.099 mg kg^{-1}) and *A. gracilis* (0.099 mg kg^{-1}).

There is no obvious correlation between Al, B and Ga concentration in plants and their taxonomic position.

There is no apparent relationship between the amounts of these three elements and annual and perennial plants (see table 35).

Boron increases in concentration in relation to decreasing water availability (see table 36) and the r value obtained ($r = 0.97$, $p < 0.005$) by enumerating lakes as 1 and waste places as 5 is highly significant. Neither Al nor Ga follows this trend or any other apparent trend. Aluminium is most concentrated in wadi plants and lowest in those inhabiting moist places and banks. The concentration of Ga is too invariate to make any discussion meaningful.

Table 37 shows the distribution of B, Al and Ga in plant parts. The highest B concentration is in flowers and seeds and the lowest in woody stems. Aluminium is most concentrated in leaves and least in leaves and stems. Gallium is highest in flowers and seeds; the rest of the plant parts contain about the same mean Ga content.

Contrary to the way in which B concentrates in the margins of leaves, Al and Ga concentrate in the blade and are minimal in the midsection. The Al variation is significant beyond the 0.1% level. Gallium follows Al but its variation is not significant.

There are relatively few available comparative data for B, Ga and Al (see table 38). It is interesting to note that the Linsley Pond plants (Cowgill 1974*a*) contain an order of magnitude more Ga than do the Huleh plants. The data are too few to offer any meaningful comment.

(*g*) *Scandium, yttrium, lanthanum and cerium*

The data for Sc, Y, La and Ce in plants are very sparse. Little is known about the behaviour of these elements in living things. Table 39 contains the Huleh means for plants and various other materials; table 40 shows mean concentrations of various elements in plants and soils. It is clear from the concentration ratios of plants:soils that Sc, Y and La are enriched in plants considerably when this enrichment is compared with Al, Ga and Ce, which are absorbed to only a moderate degree.

Scandium, Y, La and Ce are most concentrated (mg kg^{-1}) in *E. angustifolium* (0.528), *C. murale* (28.4), *S. nigrum* (1.72) and *G. lotoides* var. *dictamnoides* (14.6) respectively. These four elements are, respectively, least concentrated in *R. dentatus* (0.055), *C. acutum* (0.53), *G. lotoides* var. *dictamnoides* (0.53) and *M. tripartita* (0.34).

Rare earths beyond Ce were not detectable in plants or any of the various source materials of the basin. No accumulators of the sort Robinson *et al.* (1958) or Cowgill (1973*c*) have described were encountered (see table 41).

No obvious correlation occurs among the concentrations of these elements in plants and the latter's taxonomic position.

No variation in Y, Sc and Ce concentration was noted in annuals and perennials, but La is higher in annuals than in perennials (see table 42).

Table 43 shows the distribution of Sc, Y, La and Ce in plants in relation to their habitat. Scandium is least concentrated in lake plants and most concentrated in those inhabiting wadis. In a rather irregular fashion Sc tends to increase with declining water availability. The variation exhibited by Y and La is too small to make any comment meaningful. The wadi plants appear to contain high quantities of Ce but this is misleading since *G. lotoides* var. *dictamnoides* contained the highest amount of Ce found (14.6 mg kg^{-1}) and it is a wadi plant. Removal of the effect of this plant provides a wadi average of 0.6 mg kg^{-1}. In a general way Ce tends to increase in concentration as the available water decreases.

Both Sc and Y tend to concentrate in leaves or leaves and stems, which was also noted in the Linsley Pond plants (Cowgill 1973*c*). Lanthanum and Ce tend to be highest in flowers and seeds and woody stems (see table 44).

There are very few data on this general subject (see table 45). Goldschmidt & Peters (1933) found these elements concentrated in coal ash and assumed that they had originally been concentrated by plants. The occurrence of La in ferns has been published by Erametsa & Haukka (1970) though the amounts they report are less than those encountered in Linsley Pond plants (Cowgill 1973*c*). Bryophytes are also reputed to contain some of the rare-earth elements (Shacklette 1965, 1966).

Timperley *et al.* (1970) found that trace elements essential to plants produced hyperbolic plots when the ratio of the concentration of the element in the plant to that in the soil was plotted as a function of the quantity of the element in the soils. Non-essential trace elements, when this procedure was applied, produced a line parallel to the x axis. Hyperbolic plots were obtained for Y, La and Ce, but not for Sc, when the Linsley Pond data were handled in this fashion (Cowgill 1973*c*); however, sufficient data are lacking in the preserve plants to make such an approach meaningful.

Duke (1970) did a study of plant foods of the Choco Indians and found the Sc content to vary from 0.002 to 0.1 mg kg^{-1} and Y from 0.01 to 3.5 mg kg^{-1}. Laul *et al.* (1979) reported 0.07 mg kg^{-1} Sc in grasses. Erametsa & Yliroukanen (1971) found the range for Y in mosses and lichens to vary from 2 to 200 mg kg^{-1}. The concentration of lanthanides in plant tissue decreases with increasing atomic number (Cowgill 1973*c*; Laul *et al.* 1979). Comparative data are limited to a few studies. Laul *et al.* (1979) reported a concentration of 0.17 mg kg^{-1} La and 0.33 mg kg^{-1} Ce in *Bromus* sp. (cheatgrass).

(*h*) *Silicon, germanium, tin and lead*

There are very few recent comparative data for Si. Most of the old data are probably high owing to soil or sediment contamination. Silica occurs in many plant cells as opaline phytoliths. It is common in the Gramineae and Cyperaceae (see Takahashi & Miyake 1976; Takahashi *et al.* 1981 *a*, *b*). These two families contain the highest mean amounts of Si encountered in this study and are known to be Si accumulators (Bowen 1979) in any case. In some grasses, such as *P. australis*, bulliform cells in the leaves often become silicified (Parry & Smithson 1958, 1964; Sangster 1970). Mineralogical forms of silica will be discussed in §4(*p*).

The mean Si:Al ratio in Huleh plants is 3.32 (see table 46); that in Huleh soils is 2.25 and that in Huleh rocks is 5.22, owing to the high amounts of quartz and flint in the Huleh region. This ratio in the earth's crust (3.38) (Bowen 1979) is no different from that in the plants.

The Huleh plants contain two extreme groups: those that markedly accumulate Si (see table 47) in contrast to Al, namely those with Si:Al ratios in excess of 9 (*E. angustifolium* (10.73), *G. elongatum* (15.05), *C. mariscus* (12.46) and *P. australis* (9.55)) and those that are Al accumulators, namely those with a Si:Al ratio of 1.25 or below (*R. dentatus* (0.89), *P. arenastrum* (1.25), *E. crispus* (1.00) and *P. vaginatum* (0.75)). The plant with the highest Si concentration is *C. mariscus* (6693 mg $\mathrm{kg^{-1}}$); that with the lowest is *R. dentatus* (388 mg $\mathrm{kg^{-1}}$).

Next to nothing is known about the distribution of Ge in Nature. The concentrations encountered in the Huleh plants are extremely small, with *C. canadensis* containing the highest (1.78 mg $\mathrm{kg^{-1}}$) and *C. acutum* having the lowest (0.06 mg $\mathrm{kg^{-1}}$).

The Si:Ge ratio in Huleh plants is 1844.2, considerably smaller than that encountered in the Huleh source materials (soils 74183, rocks 594071) or the earth's crust (153889) (Bowen 1979). The mean plant ratio lies in the range proposed by Bowen (1979): land plants Si:Ge 400–25000.

There is probably some enrichment of Sn in the water of the Huleh Preserve owing to the use of solder in the connection of sections of irrigation pipe and pipe used to transport water between the carp ponds and to the Preserve. There is a great enrichment of Si relative to Sn in the plants (87182 Si:Sn) and in the Huleh rocks (104115) but the ratio in plants is more than twice that of soils (38946). The highest concentration of Sn was found in *Al. sessilis* (0.148 mg $\mathrm{kg^{-1}}$) and the lowest in *P. vaginatum* (0.001 mg $\mathrm{kg^{-1}}$).

Automobile traffic at the time of sampling, as well as earlier, was always sparse. It is generally held that the combustion of leaded petroleum is responsible for distributing Pb over the landscape. The continuous border war that has been raging for more than three decades has no doubt contributed to Pb contamination. This war involved not only Pb bullets, but trucks, tanks and aeroplanes, to a large extent utilizing fuels containing tetraethyl lead. In the absence of armed conflict, the Huleh Preserve region was exposed to two cars or trucks per hour. When a border war erupted, the area was exposed to tanks and trucks carrying soldiers at the rate of about 100 vehicles per hour. Planes overhead were continuous. Bullet shells and unspent bullets could be found all over the preserve. Thus, war was considered a major source of Pb contamination. The highest Pb content was found in *L. salicaria* (34.1 mg $\mathrm{kg^{-1}}$) and the lowest in *L. stolonifera* (14.5 mg $\mathrm{kg^{-1}}$). Bowen (1979) proposes that for land plants the Pb content should vary from 1 to 13 mg/kg.

The matter of Pb analysis needs to be considered here. As was previously noted, the plants were carefully cleaned. Analysis for Pb in plants was carried out on low-temperature (80 °C) ashed samples. X-ray emission data were confirmed with atomic absorption and graphite furnace data and found to be in excellent agreement (within 2% of each other). There is little doubt that the analytical data for Pb represent contamination, the source of which has been suggested as war. It is also a matter of considerable importance that the analysis of material removed from plants (by the vacuum cleaner technique mentioned earlier) contained, aside from Al, Si and Ca, a mean Pb content of 7 ± 2.3 mg kg^{-1}. This figure was confirmed by atomic absorption–graphite furnace methodology. It is presumed that the source is tetraethyl lead originating from the combustion of fuels. In other studies of plant elemental composition, Pb has not been detected in the material removed by the vacuum cleaner technique.

There is no statistically significant difference in the Ge, Sn and Pb concentrations found in annual and perennial plants (see table 48). However, there is a pronounced difference ($\chi^2 = 56.76$, $p < 0.001$) between the Si concentrations in annuals and perennials, the former containing the lower amount.

Figure 6 shows the relationship between Si concentration by family and taxonomic position, the more recent families containing the most Si.

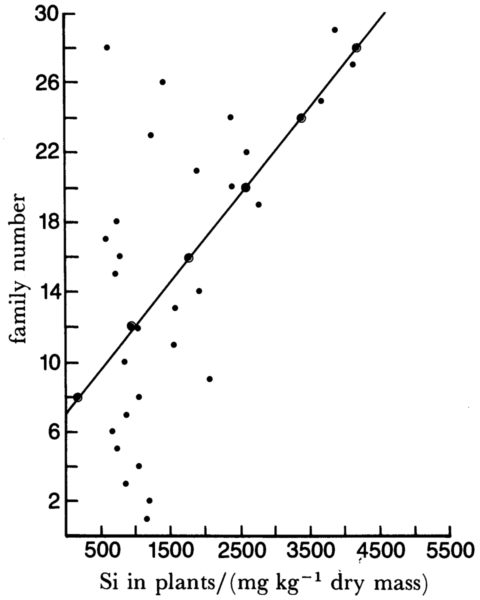

FIGURE 6. The relation between Si content in plants and their taxonomic position. The linear correlation coefficient is 0.592 ($p < 0.001$, $n = 29$) and the regression line on the graph is $y = 7.13 + 0.005x$.

Swamp plants accumulate the most Si and lake plants the least (see table 49). The figures are too small for Ge and Pb to permit any comparative comment; Sn seems to be highest in wadi plants and lowest in those inhabiting moist places and banks.

Silicon is highest in leaves and lowest in woody stems (table 50). Germanium, Sn and P are lowest in woody stems. Both Ge and Pb are highest in flowers and seeds; Sn is most concentrated in leaves and stems.

Silicon is highest in whole leaves but when leaf sections are examined Si is concentrated in the leaf margins. No other element detected exhibited this type of pattern. The pattern is highly significant (whole leaves × blade or leaf margin × blade). Germanium follows the pattern of Si but its distribution is not significant. The variation in Sn distribution is barely discernible. Lead is concentrated in the margins and is almost as high there as in the blades; it follows the pattern exhibited by Ca. Although the pattern shown by Pb is consistent, the variation is not statistically significant (see table 50). Jones (1970) noted that Si concentrated in the margins of *Zea mays* leaves.

With the exception of Pb, there are no available comparative data for these elements in the plant specimens of interest. Most of the Pb concentrations reported in table 51 are less than 13 mg kg^{-1}, which Bowen (1979) feels represents unpolluted vegetation.

The mean Si content of grasses in New Zealand may range from 3000 to 12000 mg kg^{-1}, whereas for clover it may vary from 400 to 1300 mg kg^{-1} and in alfalfa 1000–2000 mg kg^{-1} dry mass (Metson *et al.* 1979). Rice plants and nettles (*kozim* in Hebrew) have been identified as Si accumulator plants (Lovering 1959; Russell 1961; Okuda & Takahashi 1964; Jones & Handreck 1967; Van Soest & Lovelace 1969).

Duke (1970), in his study of the food of Central American Indians, found Ge concentrations in their food to range from less than 0.01 mg kg^{-1} to somewhat less than 0.1 mg kg^{-1}. Matsumoto *et al.* (1975) discovered that rice plants, given the opportunity, may accumulate Ge up to 10000 mg kg^{-1} ash mass in the tops. It has always been assumed that there exists an interaction between Ge and Si such that plants that require Si for growth exhibit unexpected sensitivities to lack of Ge in their environment (Sankla & Sankla 1967), although under most circumstances, Ge has been shown to inhibit plant growth (Sankla & Sankla 1967).

Duke (1970) found Sn to vary from somewhat less than 0.04 mg kg^{-1} to nearly 0.1 mg kg^{-1} in the food plants of the Central American Indians he studied. Chapman (1972) found 2.9 mg kg^{-1} Sn in maize kernels and reports a range of 0.2–1.9 mg kg^{-1} in grasses. The mean for Huleh plants was 0.022 mg kg^{-1}.

The mean Pb content of Huleh plants was 21 mg kg^{-1}. Bowen (1979) proposes a range of 1–13 mg kg^{-1}. In 1976, Cannon suggested that uncontaminated plants range from 0.1 to 10 mg kg^{-1}. Although the automobile traffic is minimal the effects of war are not and this is probably the principal source of Pb contamination in the Huleh region.

(*i*) *Titanium, zirconium and hafnium*

Generally speaking, Ti may be considered a convenient guideline to the amount of contamination contributed by source materials to the analyses, primarily because it is the element most resistant to erosion. The mean Ti content of Huleh's plants is 8.9 mg kg^{-1} (see table 52); that of the soils is 4854 mg kg^{-1}, providing a ratio of 1.8×10^{-3}. Multiplying this figure by the mean concentration of Si in the source material (105021 mg kg^{-1}) (table 46) results in an estimated Si concentration of 193 mg kg^{-1} in the plants which might be contributed as a contaminant from the rocks and soils of the basin. Because the mean Si content of plants is 1918 mg kg^{-1}, this implies that 89.9% of the Si is biologically involved. Bowen (1972), studying Si–Mn interaction in Sudan grass, concluded that if Si were essential to this plant then only 0.025 mg kg^{-1} would be required. This conclusion fails to negate 'luxury' consumption of Si and the advantages of precipitating siliceous minerals as a protective device against predators.

The same type of calculation applied to Al shows that the contamination due to source material is 61 mg kg^{-1}; this result again implies that 89% of the Al is biologically involved. If we repeat this calculation with other elements, it appears that the contamination due to source materials is 0.31 mg kg^{-1} for Zr, 0.003 mg kg^{-1} for Hf, 0.003 mg kg^{-1} for Sn and 0.001 mg kg^{-1} for Ge. There is an enrichment of all these elements relative to Ti; furthermore, all these elements are found in the plants at concentrations above those that would be expected on the basis of contamination alone.

The highest concentration of Ti was found in *P. vaginatum* (58.3 mg kg^{-1}, Gramineae) and the lowest quantity was in *Polygonum salicifolium* (0.76 mg kg^{-1}). The highest Zr found was 7.8 mg kg^{-1} in *Calystegia sepium* and the lowest, 2 mg kg^{-1}, in *Cuscuta planiflora*. Hafnium varied very little, the maximum being encountered in *Pulicaria dysenterica* (0.087 mg kg^{-1}) and the minimum in *Nerium oleander* (0.004 mg kg^{-1}). A number of workers (Pais 1979; Pais *et al.* 1978, 1979) have observed that spraying with 1 mg l^{-1} Ti increases the sugar content, chlorophyll production and elemental concentration of some plants. They indicate that Ti may be needed by some plants.

The Si:Ti ratio in Huleh plants is 215.5, a considerably higher ratio than in either of the source materials (16.5 in soils; 32.7 in rocks). The highest ratios were encountered among members of the Cyperaceae (*C. mariscus* (1969) and *C. alopecuroides* (1878)) and Gramineae (*P. australis* (1750)). The lowest ratio was found in *P. vaginatum* (22.4) of the Gramineae.

The Zr:Hf ratio in Huleh plants is 108.1, no different from that for Huleh soils (110.5). The highest Zr:Hf ratios were found among the Gramineae (*P. vaginatum* (633) and *E. colona* (733)) and Apocynaceae (*Nerium oleander* (700)). The lowest was found in *C. canadensis* (47) of the Asteraceae (see table 53).

There is no significant variation shown by Ti, Zr and Hf in relation to plant life cycle (see table 54).

Titanium concentration in plants seems to be related to their taxonomic position, with the more recent families containing more of the element than the older ones (figure 7).

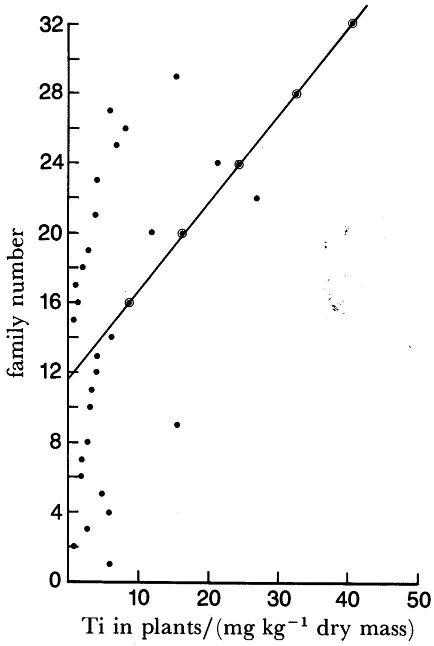

FIGURE 7. The relation between Ti content in plants and their taxonomic position. The linear correlation coefficient is 0.373 ($p < 0.05$, $n = 29$) and the regression equation depicted on the graph is $y = 11.95 + 0.489x$.

Titanium increases in concentration with decreasing water availability, the drier wadi plants containing more Ti than the lake plants (see table 55). Zirconium and Hf fail to exhibit any discernible trend in relation to plant habitat.

Table 56 shows the variation of Ti, Hf and Zr concentrations in plant parts. Titanium is highest in leaves and stems; Zr and Hf are maximal in flowers and seeds. Hafnium is lowest in leaves, as is Zr, but Zr is also minimal in stems and woody stems. Titanium is least in woody stems.

Table 57 shows what available comparative data exist. The figures of Petkova & Lubyanov (1969) appear quite high when compared with plants from the Huleh Preserve. Lounamaa (1956) proposed a mean Zr concentration of 1 mg kg^{-1} for land plants in a study of terrestrial plants from Finland.

Duke (1970) reported a range of 0.2–80.0 mg kg^{-1} Ti in the food plants (edible portions only) of the Choco Indians he studied. His data for Zr content for the same food plants varies from 0.005 to 0.2 mg kg^{-1}. Furr *et al.* (1980) in a study of the effect of sludge ashes used as a soil amendment, and the ultimate chemical composition of the plants grown in such an environment, noted that Hf was taken up by plants from such a substrate and that the latter contained about 3 mg kg^{-1} Hf.

(*j*) *Phosphorus, arsenic, bismuth, vanadium and niobium*

A comparison of the P, As, Bi, V and Nb content of Huleh plants with the concentration of these elements in soils shows that (see table 58) Nb, Bi, P and As (Plant:soil 283×10^{-2}, 181×10^{-2}, 162×10^{-2} and 65×10^{-2}, respectively) are greatly to moderately accumulated by the plants, whereas V appears to be largely excluded (plant:soil 0.9×10^{-2}). Total soil P is a poor measure of plant uptake, the ratio above is added only for comparison.

E. erecta of the Asteraceae contains the highest P concentration (9274 mg kg^{-1}) whereas *C. planiflora* of the Cuscutaceae accumulated the lowest amount (247 mg kg^{-1}). Arsenic concentrations in Huleh plants varied from 6.4 mg kg^{-1} (*E. colona* of the Gramineae) to (*P. dysenterica* of the Asteraceae) 0.43 mg kg^{-1}. There appears to be a relation between As and Se values (Cowgill 1981) such that As sets the flowering of non-selective plants. Water plants (see table 59) generally, appear to contain more Bi in their tissues than land plants. *Nuphar lutea* of the Nymphaeaceae contained a mean quantity of Bi of 3.6 mg kg^{-1} whereas *Al. sessilis* of the Amaranthaceae contained 3.7 mg kg^{-1}. Vanadium varied from 1.3 mg kg^{-1} (*P. lagopus* of the Plataginaceae, *I. graveolens* of the Asteracae) to 0.033 mg kg^{-1} (*Cy. alopecuroides* of the Cyperaceae). Very little is known of Nb distribution in nature. The concentration in Huleh plants is considerably greater than the amount proposed by Bowen (1979) for land plants (0.3 mg kg^{-1}).

A comparison of the composition of annuals with that of perennials (see table 60) shows that As, V and Nb vary hardly at all between the two types of cycles, but P is significantly more concentrated ($\chi^2 = 35.2$, $p < 0.001$) in annuals than in perennials and Bi is higher in perennials than in annuals ($\chi^2 = 18.4$, $p < 0.001$). Again it should be noted that the biennial category represents ten specimens of one plant and therefore any comment on biennials as a whole is not possible.

Arsenic, V and Nb show in their distribution in plants no apparent trend in relation to taxonomy. However, P (see figure 8) and Bi (see figure 9) are both negatively related to family position, indicating that more recently evolved plants contain less P and Bi than those that have been with us for a longer period of time.

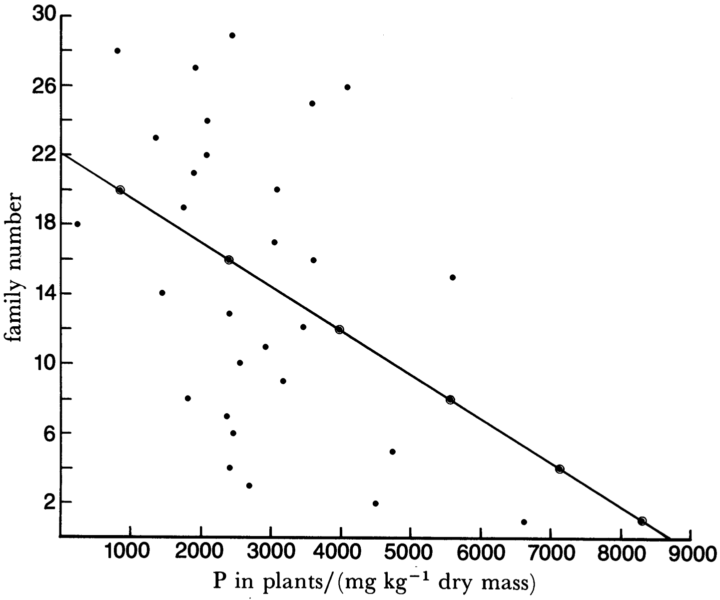

FIGURE 8. Phosphorus content of plants in relation to their family position. The linear correlation coefficient is -0.412 ($p < 0.02$, $n = 29$), and the regression line depicted on the graph is $y = 22.2 - 0.003x$.

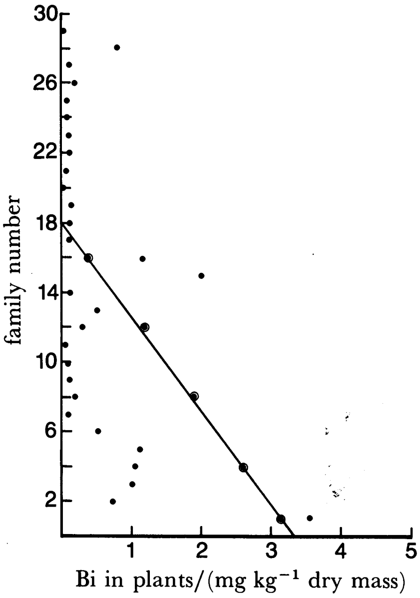

FIGURE 9. Bismuth content of plants in relation to their family position. The linear correlation coefficient is -0.465 ($p < 0.01$, $n = 29$), and the regression line depicted on the graph is $y = 18.2 - 5.378x$.

Processes connected with drainage and aeration, i.e. oxidation and lowering of the redox potential, may have an effect on the concentration of some elements in marsh plants. An excellent review of this subject may be found in Khalid *et al.* (1977) and Gambrell *et al.* (1977). Huiskes & Nieuwenhuize (1986) noted that lowering of the redox potential resulted in higher levels of Cd, Zn, Pb, As, Cu and Mn, whereas Fe tended to occur in higher levels in plants when the salinity was higher and drainage poorer. It should be emphasized that, in the strict sense of the term, there are no soils in the Huleh Preserve. The substrate of the preserve is lake mud. For ten to eleven months out of the year the substrate is dry; the preserve is seasonally flooded only one to two months out of the year. Because the mud is aerobic for all of the year (Cowgill 1980) the consideration of reduced states of various elements is not pertinent.

Niobium concentrations hardly vary at all when plants from various habitats (see table 61) are compared. Phosphorus and Bi are most concentrated in lake plants and tend to decline in concentration with declining water availability; As is most concentrated in plants inhabiting moist places and banks, and V in those from swamps. Vanadium and Bi are least concentrated in wadi plants, As in lake plants and P in those inhabiting moist places and banks.

The distribution of these five elements in plant parts is shown in table 62. Phosphorus and Nb are most prevalent in flowers and seeds, As in flowers and seeds and leaves, Bi in leaves and stems and V in leaves. Niobium is least concentrated in leaves and stems; the lowest concentrations of P, Bi, As and V are found in stems and woody stems.

Phosphorus is most concentrated in the blade of Cyperaceae (2759 mg kg^{-1}), Typhaceae (1019 mg kg^{-1}) and the Gramineae (2800 mg kg^{-1}) and is least prevalent in the midsection (Cyperaceae 1062, Typhaceae 440, and Gramineae 1000). These differences are all statistically significant beyond the 0.1% level. Neither As, V, Nb or Bi showed any consistent pattern. Jones (1970) noted that P is concentrated in the blade portion of *Zea mays* leaves.

Comparative data for Bi, V and Nb in plants (dry mass) are sparse and largely confined to the work of Cowgill (1974*a*) and Petkova & Lubyanov (1969). Arsenic has received considerable attention in recent years, largely owing to the fact that water plants have an ability to accumulate the element from geothermal waters feeding into the lower sections of natural and man-made lakes (Reay 1972; Lancaster *et al.* 1971). At about the same time as these New Zealand studies were being published, it was discovered that submerged aquatic plants were able to keep water free of As (Cowgill 1974*a*).

Phosphorus concentrations vary enormously (see table 63). Various studies on *P. australis* are reasonably concordant if the low results are excluded. Hutchinson (1975) presents a rather extensive discussion on the role of P and N in fresh waters. He suggests that, all other requirements being met, N below 1.3% in the presence of abundant P will limit plant growth, and P below 0.13% is limiting in the presence of adequate N. These figures are specific for freshwater plants.

As a rule, plants usually contain more N and P than these amounts. It is not clear whether Hutchinson's (1975) figures apply to swamp plants. However, an examination of the data of Bernatowicz (1969) suggests that water plants of Lake Warniak (Poland) are limited by low P concentration.

Bowen (1979) cautiously suggests 0.06 mg kg^{-1} Bi for edible vegetables. Erametsa *et al.* (1973) reported a range of slightly less than 1–11 mg kg^{-1} Bi in *Lycopodium*, but the element was not detectable in all plants.

Dobritskaya (1969) proposed 1 mg kg^{-1} V as a mean for higher plants; Tyutina *et al.* (1959) suggest the same value for Nb. The latter authors report that some plants have great ability to extract Nb from soil.

It should be noted that nitrogen fixers generally contain more V and Mo in their tissues than non-fixers (see tables 63 and 69).

(*k*) *Sulphur, selenium, chromium and molybdenum*

In 1957 Ravikovitch & Margolin reported a region north of the nature preserve called Naot Mordechai (see figure 1) as being seleniferous and supporting toxic Se accumulator plants (Tristram 1884; Barneby 1964; Eig 1955; Cowgill 1979, 1981). The soils of this region are alkaline (Ravikovitch & Margolin 1957; Cowgill 1980), having about the same range of pH as has been found for the waters of the northern Jordan Valley (Cowgill 1980, 1989*a*). Ravikovitch & Margolin (1957) found the highest Se concentrations in the soil profile in the upper layers, presumably associated with organic matter. These workers found that 7.5–30% of the total Se was water-soluble.

Because no seleniferous rocks could be found in the drainage basin of Lake Huleh, it was decided to examine the rainwater to discover whether this might provide a source of Se. The element is barely detectable in rainwater originating from Israel (U. Cowgill, unpublished data, winter rain samples 1963, 1964, 1969), Denmark (Gissel-Nielsen 1974) and the U.S.A. (Kubota *et al.* 1975).

In an effort to counteract the toxic effect of Se sorbed by domestic plants growing in the northern Jordan Valley, which subsequently would be consumed by livestock, Ravikovitch & Margolin (1959) found that additions of $BaCl_2$ to the soil inhibited the uptake of Se by domestic crops. Ba–Se complexes formed in the soil, presumably as a result of this treatment. These complexes are only sparingly soluble and hence reduce the availability of Se to plants. Four years after this treatment (Cowgill 1980) there was no indication of Se being a regional problem and though members of the genus *Astragalus* were sought, even non-seleniferous ones could not be located.

Seleniferous regions do not occur in areas of adequate rainfall (over 25 cm per year). It is therefore reasonable to suppose that irrigation alone over time would at least have removed the water-soluble portion of the total Se. It is interesting to note that the relation between Se and Ba in the top 387 cm of Core II (Cowgill 1969; U. Cowgill, unpublished data) of Lake Huleh is positive but statistically insignificant. Selenium is still a problem north of the Dead Sea on the Jordanian side (Abuereish & Lahham 1987), where members of the Fabaceae, Gramineae and Brassicaceae contain high quantities (over 4 mg l^{-1}) of Se.

The Se:S ratio in Huleh plants (see table 64) is 19.2×10^{-6}. In relation to S, Se is impoverished in these plants when the same ratio is examined in the Huleh source materials (soils, 391×10^{-6}; rocks, 270×10^{-6}). There is little question that irrigation practices and periodic flooding of the Huleh plain in midwinter effectively reduces the Se concentration in plants. The S quantity (see table 65) varies from 14417 mg kg^{-1} (*C. acutum* of the Asclepiadaceae) to 1415 mg kg^{-1} (*T. angustata* of the Typhaceae). Sulphur is generally high among the Brassicaceae; this has also been noted by Panin & Grishin (1975). The Se concentration is greatest in *C. planiflora* of the Cuscutaceae (0.22 mg kg^{-1}) and lowest in *P. vaginatum* of the Gramineae (0.05 mg kg^{-1}). The Se:S ratio in Huleh plants varies from 4.2×10^{-6} (*C. acutum*) to 53.7×10^{-6} (*T. angustata*); the former nearly excludes Se in relation to S and the latter, again in relation to S, sorbs quantities of Se.

The Cr:Mo ratio in Huleh plants is 4.8 (see table 64). Molybdenum is enhanced in plants relative to Cr when this ratio is examined in Huleh soils (19.6) and Huleh rocks (35.7). The Cr content of plants varies very little, from 2.4 mg kg^{-1} (*N. oleander* of the Apocynaceae) to 1.07 mg kg^{-1} (*C. latifolius* of the Cyperaceae). Molybdenum is high in the leaves and stems of two of the Chenopodiaceae (*A. rosea* 5 mg kg^{-1}; *C. album* 5.4 mg kg^{-1}). The highest mean concentration was found in *M. alba* (Fabaceae) (4.4 mg kg^{-1}) and the lowest in *E. colona* (Gramineae) (0.006 mg kg^{-1}). The Cr:Mo ratio in plants (see table 65) varied from 0.51 in *M. alba* (Fabaceae) to 538 in *P. vaginatum* (Gramineae). Evidently *M. alba* excludes Cr relative to Mo and *P. vaginatum* clearly accumulates it. It is interesting to note that Johnson (1966) would view the concentration of Mo in *E. colona* as highly deficient, since his proposed lower limit of Mo quantity in plant tissues is 0.1 mg kg^{-1}. Again, no deficiency symptoms were noted in any of the plants collected in the Huleh study.

The Mo concentration varies significantly within a leaf. The Mo concentration in leaves of the Huleh grasses is lower in the marginal areas and the midrib and higher in the leaf blade. This was also noted among the Cyperaceae and Typhaceae but the differences observed were not statistically significant. These observations have also been noted by Jones (1970) and Stout & Meagher (1948).

Sulphur, Se, Cr and Mo show no concentration trend in relation to the taxonomic position of the plants. Similarly, these elements show no statistically significant difference in concentration when annuals are compared with perennials (see table 66). When plants are divided according to their habitat (see table 67), S and Se are most concentrated in swamp plants and Mo in those of waste places, and Cr is highest in those inhabiting moist places and banks. The mean Cr concentration in wadi plants is also similar for Se. Molybdenum is least prevalent in wadi plants and Cr in swamp plants. The majority of the 'soils' of the waste places are actually dried lacustrine mud. The mud of these waste places has a fairly high Fe content, thus probably accounting for high Mo content, although the latter should be viewed only in the comparative sense (see Gorham 1964).

Selenium and Mo are most concentrated in flowers and seeds (see table 68). Sulphur is concentrated in leaves and stems. Chromium is concentrated in stems and woody stems. Sulphur and Se are least concentrated in woody stems, Mo in stems and woody stems and Cr in leaves and stems. The variation exhibited by Cr is hardly significant.

Both Mo and Cr tend, in an absolute sense, to be more concentrated in the blade than elsewhere in the leaf but the results are not significant and appear to be confined to leaves of the Gramineae.

Comparative data are given in table 69. During the past several decades the S content of water bodies has increased as a result of the combustion of fossil fuels (Cowgill 1968). Thus, concentrations of S in plants may reflect a component of pollution that should not be ignored. The S variations shown for the same plant growing in various parts of the world reflect in part the time of sampling, the age of the plant and the chemical composition of the environment from which it comes.

The data presented in table 69 for Se, though hardly extensive, tentatively suggest that water plants contain more of the element than non-seleniferous land plants. Alfalfa and grasses contain less than 1 mg kg^{-1} and usually less than 0.5 mg kg^{-1} unless they are supported by seleniferous soils.

Comparative Cr data are too sparse to permit much comment, other than that the present figures suggest that the mean amount of Cr in plants is less than 2.5 mg kg^{-1}. For Mo, normal quantities are said to be less than 30 mg kg^{-1} (see Kubota *et al.* 1961). Submerged water plants as a rule tend to contain more than this amount in their tissues (Cowgill 1974*a*).

(*l*) *The halogens*

Relatively little is known about Br in Nature. There is much evidence to suggest that an enrichment process occurs in the Huleh Preserve which may be attributed to some sort of sorption or ligation by organic matter (MacKereth 1965, 1966; Cowgill & Hutchinson 1966, 1970; Cowgill 1980). Chlorine in this shallow aerobic system is slightly sorbed by the mud in the littoral zone but is not sorbed by the mud in the open water region. Iodine, in this system, is sorbed by the mud but moves with a ferric hydroxide type of scavenger instead of organic matter (Cowgill 1980). This process is probably responsible for the lake plants' containing the most Cl, Br and I of any of the habitats studied.

A function for Br in plants has as yet not been described, although the fact that its distribution in plants is ubiquitous would suggest that it has some importance for organic life. Selivanov (1939*b*, 1944) reported a mean of 6.5 mg Br per kilogram of soil, with a range of 1 to 20. Bromine was higher in peats than in soils low in organic matter. A general correlation of its prevalence with the quantity of organic matter was noted. Halophytes of the family Chenopodiaceae were reported to contain as much as 100 mg Br per kilogram dry matter. Gibbs (1974) also observed that Br is high in some genera of the Chenopodiaceae. Duke (1970), in his Central American study, reports a range of 0.2–1.0 mg Br per kilogram dry mass in edible plants. Wilkins (1978) suggests a range of 17–119 mg Br per kilogram dry mass in grasses.

Selivanov (1939*a*, *b*, 1944, 1946) also studied the Br content of rain and snow and reported that the amount of Br received by the land surface was 0.0005–0.007 mg Br per square centimetre per year. Storms originating in the southern end of the Rift Valley and passing over the Dead Sea (Br 2.37 %, Rankama & Sahama 1950) could conceivably bring more Br to the Huleh region than the amount proposed by Selivanov. Selivanov also measured the Br content of water and reported a mean for rivers to be 0.021 mg l^{-1} and lakes 0.0045 mg l^{-1}.

The highest concentrations (see table 71) of the halogens found in Huleh plants were in *Glinus lotoides* var. *dictamnoides* (F 7.8 mg kg^{-1}), *Cynanchum acutum* (Cl 18910 mg kg^{-1}), *Chenopodium opulifolium* (Br 36.2 mg kg^{-1}) and *Echium angustifolium* (I 0.59 mg kg^{-1}). The lowest concentrations were in *Cladium mariscus* (F 1.5 mg kg^{-1}), *Vitex agnus-castus* (Cl 370 mg kg^{-1}), *Amaranthus retroflexus* (Br 6.4 mg kg^{-1}) and *Centaurea iberica* (I 0.15 mg kg^{-1}).

The F : Cl ratio for Huleh plants (see table 70) is 6.2×10^{-4}; for soils, 2800×10^{-4}, for rocks 13400×10^{-4} and for the earth's crust 73100×10^{-4} (Bowen 1979). Thus, relative to Cl, F is impoverished in the plants as well as the source materials of the basin when this ratio in the earth's crust is considered.

The Cl : Br ratio for Huleh plants (see table 70) is 544; for the source materials soil and rock it is 50 and 29, respectively, and for the earth's crust it is 351 (Bowen 1979). Chlorine is clearly vastly enriched in plants, relative to the source materials, although the ratio in plants is similar to that of the earth's crust.

The highest F : Cl ratio (see table 71) in Huleh plants was in *Vitex agnus-castus* (91.1) and the lowest in *Sonchus oleraceus* (19). The maximum Cl : Br ratio was in *Cynanchum acutum* (2307), the minimum in *V. agnus-castus* (47).

Chlorine, Br and I show no correlation between plant concentration and taxonomic position. However, as figure 10 illustrates, F concentration does show such a relation. Thus, from an evolutionary point of view, the older families contain more F than those more recently evolved.

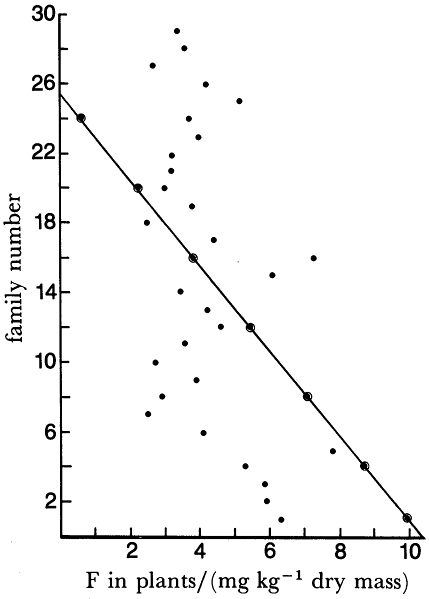

FIGURE 10. The variation of F in plants in relation to their taxonomic position. The linear correlation coefficient is -0.413 ($p < 0.02$, $n = 29$) and the regression line depicted on the graph is $y = 25.6 - 2.48x$.

Chlorine is more concentrated in annuals (see table 72) than in perennials ($\chi^2 = 47.4$, $p < 0.001$); F, Br and I do not exhibit any statistically significant difference between the two life cycles (see table 71). This is especially interesting since it has been previously noted that Cl concentration in plants tends to increase with age (Eaton 1972).

Chlorine, Br and I are most concentrated in lake plants, whereas F is highest in those inhabiting swamps. The lowest Cl and Br concentrations are found in wadi plants, the lowest I in plants of waste places and the lowest F in plants of moist places and banks (see table 73).

The halogen distribution in plant parts is shown in table 74. Fluorine is highest in leaves and stems, while Cl and Br are concentrated in stems and woody stems. The I variation is too small to make any meaningful statement possible. Woody stems contain the lowest amounts of Cl and Br; F is lowest in stems and woody stems.

In the leaves of Cyperaceae and Gramineae, all the halogens concentrate in the leaf margins rather than in the blades. However, only the difference between the Cl concentrations in leaf margins and blades is significant at the 0.1% level. Sayre (1952), doing radiotracer work, noted that Cl accumulates in leaf margins. Ulrich & Ohki (1956) noted essentially the same kind of distribution in sugar beet plants.

Comparative data for the halogens (see table 75) in plants are not extensive. The variation exhibited by the Typhaceae is probably due to the presence of different populations. *Phragmites australis* analyses are at least of the same order of magnitude and it might be suggested that this plant generally contains less Cl than do various populations of *Typha*. Iodine appears to be much lower in concentration than the range proposed by Bowen (1979), although the rest of the figures he proposes are of the same order of magnitude as the data from the Huleh plants. Sinitskaya & Chupakhina (1970) and Filippova *et al.* (1978) report similar I concentrations in plants from various areas in the U.S.S.R. and the northeastern Mongolian territory.

Before closing this section, it is interesting to comment on Na:Cl and K:Cl ratios. The former is 0.5 in Huleh plants while the latter is 2.41. Both Na and K are vastly impoverished in Huleh plants with reference to Cl when these ratios are compared with those of the source materials (Na:Cl, soils 8.2, rocks 16.8; K:Cl, soils 16.1, rocks 16.6) or the earth's crust (Na:Cl, 177; K:Cl, 162) (Bowen 1979). The Na:Cl ratio varies from 2.44 to 0.14 in Huleh plants and the K:Cl ratio ranges from 34.9 to 0.33. As will be noted in the mineralogy section, these ratios are of some importance in mineral precipitation in plants.

(*m*) *Iron, manganese, cobalt and nickel*

As shown in table 76, the concentrations of Fe and Mn in Huleh plants are about the same, providing a Mn:Fe ratio of 0.99. This ratio in mud and water is 0.013; in the source materials it is 0.02 (soils) and 0.03 (rocks), about the same as in the earth's crust (0.023) (Bowen 1979). Manganese is vastly enriched relative to Fe when the Mn:Fe ratio in the source materials is examined.

At one time it was widely held that Mn concentrations in excess of those of Fe were typical of land plants (Mayer & Gorham 1951; Robinson *et al.* 1917). Iron was expected to be in excess of Mn, as is the case in the Huleh source materials, and in water plants. Hutchinson (1975) suggests that rooted water plants are in contact with reduced sediment in which Fe and Mn are present in ratios not much different from those in the lithosphere. However, in hypereutrophic lakes where Mn is in excess of Fe in the water (see, for example, Cowgill 1970), it is conceivable that aquatic plants could contain Mn in excess of Fe in their tissues. The data are still too few to make any clear-cut comparison between water and land plants. Bowen (1979) proposes a Mn:Fe range of 0.29–1.0 for land plants. However, the range among the Huleh plants varies (see table 77) from 42.4 mg kg^{-1} (*Typha angustifolia*) to 0.19 mg kg^{-1} (*Paspalum vaginatum*), with the highest Fe concentration being found in the latter and the lowest in the former. Manganese concentration is maximal in *T. angustifolia* (3394 mg kg^{-1}) and minimal in *R. dentatus* (288 mg kg^{-1}). Lonergan (1975) analysed a number of plant species living on the same soil and found the Mn to range from 30 mg kg^{-1} (*Medicago truncatula*) to 500 mg kg^{-1} (*Lupinus albus*). Such differences were not noted in Fe and Co in the same plants (see table 77).

An examination of Fe, Mn and Co distribution within leaves showed that both elements concentrated in the marginal areas in contrast to the leaf blades. This phenomenon was observed in Cyperaceae, Typhaceae and Gramineae. The Fe and Co variations between marginal regions and the leaf blade were not statistically significant. The variation in Mn is shown below (in mg kg^{-1}).

	marginal	leaf blade	χ^2
Cyperaceae	1650	810	287
Typhaceae	165	60	12.3
Gramineae	1586	850	222

The differences are all significant beyond the 0.1 % level.

Sayre (1952) noted that tagged Co accumulated in the marginal areas of grass leaves. Jones (1970) reported that Fe and Mn accumulated in the leaf margins of *Zea mays*. Neubert *et al.* (1969) notes that Fe and Mn concentrations less than 50 mg kg^{-1} and 20 mg kg^{-1}, respectively, indicate deficiencies in these elements. No figures this low were observed in this study.

The Ni:Co ratio in Huleh plants is 4.5, which is essentially the same figure for Huleh rocks (4.2) and the earth's crust (4) (Bowen 1979). This ratio in Huleh soils (14.7) shows an enrichment of Ni relative to Co when the Huleh rocks' ratio is compared. This ratio varies from 11.6 for *Xanthium strumarium* to 1.2 for *Populus euphratica*. Nickel is always more concentrated than Co in Huleh plants, as well as in land plants (Bowen 1979). Recent evidence (Anke *et al.* 1986; Horak 1985; Eskew *et al.* 1984) strongly suggests that Ni is required for the life of higher plants. Lee *et al.* (1978) hypothesizes that Ni may be tied up as nickel citrate in some plants.

There does not appear to be any obvious correlation between Fe, Mn, Co and Ni concentrations in plants and taxonomic position.

Manganese is more concentrated in perennial plants (table 78) than in annual ones ($\chi^2 = 143$, $p < 0.001$); Ni, Co and Fe fail to show any concentration difference between the two life cycles (table 78).

The Mn:Fe ratio of plants divided according to habitat (see table 79) declines in relation to water availability from lake plants to waste plants, the ratio of the latter rising slightly. Manganese is in excess of Fe in lake plants, swamp plants and those inhabiting moist places. The reverse is true of plants from the two drier habitats. Cobalt and Ni show barely any variation in relation to habitat. Manganese is maximal in lake plants and minimal in those from wadis; Fe is most concentrated in wadi plants and least in those from waste places.

Manganese is highly concentrated in leaves and lowest in stems and woody stems (see table 80). On the other hand, Fe is highest in stems and lowest in woody stems. Nickel and Co are minimal in stems and woody stems and maximal in leaves and stems. As may be noted from the data of Lathwell *et al.* (1973), there is a considerable amount of variation in Fe content through the growing season of *Typha*. Less variation is noted in Mn concentration in Typha (table 81). Iron is reasonably concordant in *P. australis* and *Cy. papyrus* but the values for Mn are not. With a few exceptions, the Co and Ni data are all of the same order of magnitude. Hill *et al.* (1953) reported Co concentrations of 0.20 mg kg^{-1} for *Amaranthus retroflexus* and 0.08 for *Chenopodium album*. It could be proposed that some populations of *Typha* undergo a nearly Fe-deficient phase at some portion of their growth cycles.

It should be noted, before closing this section, that the edaphic substrate here is aerobic throughout the year; hence the reduced forms of Mn and Fe, and their ultimate effect on Fe and Mn concentrations in plants, are not pertinent here (Cowgill 1980, 1989*a*).

(*n*) *Loss of mass on ignition*

The percentage loss of mass on ignition, the percentage mineral matter and the total for each plant studied is set out in table 82. The organic elements (N and C), an essential portion of this study, are represented by the loss of mass on ignition. The lowest loss of mass on ignition, and therefore the highest amount of mineral matter, among the families was exhibited by the Brassicaceae, specifically *H. incana*. This is interesting because in the Missouri Project (Conner & Shacklette 1975), concerning entirely different species but some of the same plant families, the Brassicaceae had the highest amount of mineral matter (range 7.0–35% with means from three studies being 19%, 21% and 9.4%) and the lowest loss of mass on ignition. These authors studied 14 vegetable species and 18 native plant species. Therefore it might be suggested that high mineral matter content is characteristic of the Brassicaceae. *Nerium oleander* (Apocynaceae) contains the lowest percentage of mineral matter of any plant or family examined.

Table 83 examines mineral matter content in relation to plant life cycle. It would be expected that perennial plants over the years would accumulate more mineral matter. The highest percentage of mineral matter found among the annuals was in *H. incana* (12.16 %) Brassicaceae, *Inula graveolens* (Asteraceae) (11.91 %) and *Eclipta erecta* (Asteraceae) (12.54 %). However, the highest mineral matter found among the perennials belonged to *Cynanchum acutum* (14.46 % Asclepiadaceae). The numbers shown in table 83 are not statistically different from each other.

The percentage of mineral matter and plant taxonomic position are not significantly related. The Cyperaceae and Typhaceae tend to have less mineral matter in their tissues than the Nymphaeaceae.

The relation between mineral matter and habitat is shown in table 84. Statistically speaking the numbers for any given column are all the same. In the absolute sense, plants inhabiting moist places and banks contain the least mineral matter and those living in 'waste places' contain the most. This observation is rather curious when it is considered that the plants of the Huleh Preserve are supported by 'soils' of lacustrine origin, the area having been drained between 1956 and 1961 (Orni & Efrat 1964). Thus, all the plants examined in this study are supported by lake mud, dried or wet. Variations observed that are edaphically determined merely reflect the chemical variation found from place to place at the bottom of Lake Huleh.

Table 85 shows the mineral content of plant parts. There is no statistically significant difference among these plants, but in the absolute sense woody stems contain the least mineral matter and leaves and stems the most.

(*o*) *A comparison of the elemental composition of parasitic plants and their hosts*

Cuscuta planiflora (Cuscutaceae) parasitizes the legume *Alhaqi mannifera* (Fabaceae). Under normal circumstances *C. planiflora* is an annual that inhabits swamps while *A. mannifera* is a perennial that is usually found in waste places. *Cynanchum acutum* (Asclepiadaceae) parasitizes the grass *Phragmites australis* (Gramineae). Both plants are perennial in their life cycle. The parasite is often found in moist places and banks, whereas *P. australis* inhabits swamps. These two perennial plants were collected from a swamp habitat. *C. planiflora* was collected from *A. mannifera* growing at the interface of the Huleh swamp and the contiguous 'waste places'. Table 86 presents the pertinent data and includes, for comparative purposes, the mean composition of Huleh plants.

C. planiflora has 28 elements that are more concentrated in its tissues than in those of its host *A. mannifera*. It has been noted elsewhere (Malicki & Berbeciowa 1986) that parasitic weeds are on the average richer in major constituents than their host plants. Renaudin *et al.* (1980) observed that K, P and occasionally S, Cl and Ca were higher in concentration in the parasite than in the host. Wolswinkel (1978) noted that in another species of *Cuscuta* higher concentrations of K, P and Mg were found near the haustorial coil, and the host had a greater quantity of Ca than its parasite. These citations suggest that each parasite–host relationship has its own peculiar chemistry. The Huleh observation is statistically significant at about the 7 % level (+28, −6, the same 2, $\chi^2 = 3.3$, $p < 0.07$). *C. acutum* has 31 elements more concentrated in the whole plant than do the leaves of the host *P. australis* (+31, −13, the same 2, $\chi^2 = 7.2$, $p < 0.01$) which is significant beyond the 1 % level. The two parasitic plants clearly have a higher percentage of mineral matter in their tissues than do their hosts (see table 86).

The two host plants contain higher quantities of Ga, Y, La, Si, Ge, As and Br than their parasites. In addition, *A. mannifera* contains more Cu, Ca, Ba, Zn, Zr, P, Nb, Cl and I than its parasite while *P. australis* holds more Al, Ti, V, Cr, Fe and Mn than does its parasite.

C. planiflora parasitizes *A. mannifera*. The former presumably derives more water and at least elemental nutrition through haustoria embedded in the stems of the host. On microscopic examination, a close orientation of the vascular elements of host and parasite was revealed. The particular samples of *C. planiflora* that were collected contained some chlorophyll, as evidenced by the greenish-white leafless stems of the parasite.

Zohary (1962) reports transpiration data measured from hydrophytes living in the Huleh swamp. The plant that lost the most water through transpiration was *C. acutum*. The loss was 2268 mg water per gram of fresh mass per hour. Plants of this species were tightly wound around *P. australis* leaves. Five such plants were collected. The ten leaves of *P. australis* that *C. acutum* appeared to have invaded were also gathered. *C. acutum* is usually found as an epiphyte. However, in this small sample *C. acutum* appeared to be parasitic. In most instances only one or two spots on the *P. australis* leaves appeared to be parasitized by *C. acutum*. Microscopic examination of these spots revealed some orientation of vascular elements of the host and parasite. In addition, *C. acutum* is not a very big plant but *P. australis* is and thus the observed parasitism might well account for the huge loss of water through transpiration.

If a ratio is calculated between the elements in *C. planiflora* and those of *A. mannifera* when the concentrations in the former are greater than in the latter, only two elements, Bi and Mo, have ratios higher than 2 (Bi 2.97, Mo 4.7). In those instances where the host contains more of the element than the parasite only P (8.17) and As (2.05) have ratios greater than 2. Perhaps what is being observed is the efficient relationship of a parasite with its host.

If we repeat this series of calculations with *C. acutum* and *P. australis*, the data do not resemble those just noted above. In the case where the parasite contains higher concentrations than its host, the following ratios have been observed:

1.00–2.00	Rb, Li, Cu, Sr, Ba, Zn, Pb
2.00–5.00	Na, K, Cs, Ag, Mg, Ca, P, S, F, Co
5.00–18.00	Be, Hg, B, Si, Sn, Mo, Cl
2000	Bi

In the reverse case, the following ratios may be noted:

1.00–2.00	As, V, Cr, Br, Al, Ga, La, Ce
2.00–5.00	Fe, Mn, Y, Ti
5.00–18.00	Ge

The picture is quite different from that presented by *C. planiflora*. It is possible that the lack of uniformity of the ratios is typical of the epiphyte that may, under dire circumstances (lack of water, high heat, etc.), become parasitic. It may be suggested that, if this parasite continues to accumulate as much as the data suggest, it may end up killing its host, which is not the sort of pattern to be expected from an efficient parasite.

Given the data presented here it is difficult to imagine that the parasite gains all things and the host is entirely passive. In the case of *C. planiflora–A. mannifera*, a well-known parasite–host relationship, it might be suggested that the elements that are more concentrated in the host than in the parasite, have received some contribution to their observed quantities from the parasite. Small additions of S will reduce Mo uptake by plants. Stout *et al.* (1951) were of the opinion that this phenomenon was the direct result of competition of two divalent anions of similar size. Sulphur and Mo are most concentrated in the parasites of these two plant relationships. Phosphorus, on the other hand, appears to enhance the sorption and translocation of Mo (Stout *et al.* 1951) and in this instance the host has the higher concentration of P. These data suggest that the parasitism in this case has some symbiotic component that is not apparent until ratios are calculated.

In the *C. acutum–P. australis* relationship the only major constituents that are more concentrated in the host are Fe and Mn. The P concentration in the parasite is 4.4 times higher than in the host. High P concentration may inhibit Fe movement (the host Fe concentration is twice that of the parasite) and this phenomenon (Biddulph 1953) becomes more pronounced at higher pH. The pH of the mud in which *P. australis* was growing was 8.1 at the time of collection (cf. Cowgill 1980). Thus P in *C. acutum* may control Fe movement in *P. australis*.

It is probable that in these host–parasite relationships organic compounds may play a significant role. However, data on this subject are sparse and inconclusive.

(*p*) *The alkali metals*

Eleven minerals were detected in the Huleh plants. These were: sylvite (KCl); oxalate minerals (whewhellite-Ca oxalate monohydrate, weddellite-Ca oxalate dihydrate, Mg oxalate dihydrate alpha form); this last has no mineral name but the pattern of d spacing follows ASTM card 26-1223; carbonate minerals (calcite-$CaCO_3$, aragonite-$CaCO_3$ and dolomite $CaMg(CO_3)_2$); siliceous minerals (quartz, low form opal-cristobalite, low form opal-tridymite) and sulphate minerals (gypsum $CaSO_4 \cdot 2H_2O$). It should be noted that the minerals encountered are not merely the result of plant dehydration since wet leaves examined mineralogically show the major peaks of the minerals found in dried plant tissue (Cowgill 1975*b*).

Table 87 shows the distribution of sylvite in plants. A comparison with Na, K (see table 9) and Cl (see table 71) shows no statistically significant relationship between the mineral and the analysis of the plant that produced it. Even if it is assumed that all the Na is present as NaCl and this calculated Cl is subtracted from the total Cl obtained by analysis, leaving the amount of Cl available to form KCl, the resulting correlations are still insignificant. Partial correlations, though not significant, are illuminating. Comparing net counts per second of the main peak of sylvite with K, excluding the effect of Cl, in essence holding Cl constant, provides a partial correlation coefficient of -0.801. This suggests that K may be present as the chloride but is also present in conjunction with some other ion or ions. Since it is not clear what this might be, further calculation is not possible. All of these plants are swamp residents with the exception of *C. opulifolium*, usually found in 'waste places'. All are annuals with the exception of *U. hulensis* and *T. angustata*. All of these plants are luxury consumers of both K and Cl. Elsewhere (Cowgill 1974*b*, 1975*b*) it has been suggested that minerals may be formed by plants as storage products to be depended upon in the event of hard times or as excretory products. Without specimens representative of the two climatic seasons typical of the Huleh Valley this aspect of the study cannot proceed further.

Sylvite (KCl) was detected in the Urticaceae, Chenopodiaceae, Asteraceae and Typhaceae. The presence of sylvite in *X. strumarium* has also been noted by Bisht & Singh (1978, 1979). A number of other studies noting its presence either naturally (Chen *et al.* 1975; Wieneke *et al.* 1987; Yang *et al.* 1981) or induced by exposure to high salt content (Smith & Raven 1974) have been reported. In addition, Helal & Mengel (1981) have pointed out that plants grown under high light intensity tended to exclude Na and Cl and accumulated Ca, K and Mg to a greater extent than plants grown under low light intensity. Possibly the development of sylvite may result from excessive light for the particular species.

The K:Cl ratio in the plants that form sylvite varies from 0.52 to 2.64 and is negatively related to the net height of the main peak of sylvite ($r = -0.89$, $p < 0.05$, d.f. = 3). Furthermore, there are plants that contain enough K and enough Cl such that sylvite formation would be expected but was not found. These observations tend to lend credence to the hypothesis of overabundant light in excess of the particular species requirement causing or encouraging sylvite formation in the affected species.

If a comparison is made between the net counts per second and the taxonomic position designated by number, the correlation coefficient obtained is $r = -0.986$, $p < 0.005$. Although the data are sparse, the hypothesis could be put forward that the formation of sylvite is more common among the older families.

Calcium oxalate minerals have been known in plants for a very long time; in fact, it is believed that their first description comes from a letter written by Leeuwenhoek on August 14, 1675 to Mr H. Oldenberg (Rijnberg & Heringa 1939). At that time Leeuwenhoek described the raphides, presumably Ca oxalate monohydrate, in *Arum*. Despite this antiquity, there is no general agreement as to the mechanism by which these deposits develop in plants, nor as to their function. In the case of submerged aquatic macrophytes (Cowgill 1975*b*) it has been suggested that these compounds are excretory products which increase in quantity with the age of the plant. There does not appear to be any relation between Ca and the net counts per second of each or all of the Ca minerals totalled. Table 88 shows the distribution of oxalate minerals in Huleh plants. Magnesium oxalate dihydrate alpha form is most prevalent in the Chenopodiaceae. It occurs sporadically among the Amaranthaceae and the Polygonaceae and was noted in leaves and stems of *Nuphar lutea*. It was not detected in any of the other plants studied. Magnesium oxalate dihydrate alpha form has no mineral name. Based on this limited amount of information it might be suggested that the older plant families are more likely to form this mineral than those more recently evolved.

Wilson *et al.* (1981) report the location of Mg oxalate dihydrate beta form present as an extracellular precipitate in the thallus of the lichen *Lecanora atra*. It was derived from the decomposition of Mg silicates, particularly chrysolite, by the oxalic acid secretion by the lichen. These authors report that the precipitation of this mineral occludes large amounts of heavy metal ions into its structure, thus providing the lichen with a favourable means of survival in polluted atmospheres.

The Mg oxalate dihydrate alpha form in the Huleh plants shows a high number of significant correlations with Mg, K, Br, F, Rb, Sn, Bi, Mo, Cl, Na and P. Multiple correlation techniques showed this mineral to be closely related to Br, Rb, F and Mg. These elements are hardly indicative of polluted conditions. Their occlusion in the Mg oxalate structure may be fortuitous. For further information on this mineral, see Cowgill (1989*b*).

The lack of literature on the presence of Mg oxalate dihydrate in plants is not particularly significant; the absence of information may merely reflect a lack of scrutiny rather than the absence of the mineral.

Whewhellite is more prevalent (mean 561 counts per second (c.p.s.)) than weddellite (mean 376 c.p.s.) when the mean is calculated for those plants that contain these two oxalates. Plants belonging to the Tamaricaceae, Brassicaceae, Asclepiadaceae and Plantaginaceae did not contain any detectable oxalates. The limit of detection for most minerals by X-ray diffraction is about 5%. It is not possible to estimate the oxalate mineral concentrations as the levels of hydration are reduced by exposure to the X-ray beam, and thus their apparent concentration may vary due to loss of water. There does seem to be some argument concerning the presence of Ca oxalate crystals in Gramineae. These were first reported by Benecke (1903). This discovery has been disputed by Metcalfe (1960, p. XXXL) and confirmed by Lersten (1983) and this study. None of the oxalate minerals bear any relation to taxonomic position of the plants in which they were found.

Table 89 shows the distribution of carbonate minerals in Huleh plants. The various crystallographic forms of $CaCO_3$ are widely distributed in a variety of plant tissue and it is generally believed that $CaCO_3$ is an extracellular substance. It usually forms as a result of photosynthetic activity; the insoluble salt may precipitate in the cell, in the cell wall or extracellularly. Ruttner (1953) reported on *Elodea canadensis* living in water surrounded by limestone; in 10 h of sunlight, 100 kg of fresh plant material could precipitate 2 kg of $CaCO_3$. Much of the mineral is shed by the plant. Ruttner believes that the process is without cellular control. Plants growing in the same water (Cowgill 1974*b*) with the same chemical composition will vary in their ability to produce calcite. In the Huleh plants, the majority of all members of the following families fail to produce detectable quantities of calcite: Chenopodiaceae, Amaranthaceae, Polygonaceae, Tamaricaceae, Salicaceae, Fabaceae, Apiaceae, Asclepiadaceae, Convolvulaceae, Cuscutaceae, Rubiaceae and Typhaceae. In this plant collection calcite is only sporadically produced.

Calcium carbonate may be found in three crystalline varieties: calcite, aragonite and vaterite. Which type precipitates depends in part on the temperature (Faivre 1946) and the dielectric constant of the solution: a low dielectric constant and the presence of salts of Sr, Mg, Pb, Ba or gypsum in the medium favour aragonite (Harada & Goto 1957). Aragonite was found in the whole plant preparations of *P. lagopus* of the Plantaginaceae and in the roots of *P. australis* of the Gramineae. The mean Sr content for Huleh plants was 47.1 (see table 20); that found in *P. lagopus* was 109.5. It would be expected that this quantity would be enough to favour aragonite formation.

It should be noted that $CaCO_3$ crystals can be produced by bacteria (Boquet *et al.* 1973) and by diatoms (Lanz 1940; Hustedt 1930; Heinzerling 1908). It is always possible that these organisms may be involved in crystal production in association with some plants, especially their roots. It is also possible to transform calcite in plants to aragonite in plants at room temperature under atmospheric pressure by severe and lengthy grinding (U. Cowgill, unpublished data).

Dolomite was found in three plants of the Asteraceae and in one belonging to the Gramineae. This is a rather curious phenomenon since plants growing side by side do not contain the same minerals in their tissues. A comparison between the net c.p.s. of these four plants with their Ca content provides a correlation coefficient of -0.930 ($p < 0.10$), suggesting that the higher the c.p.s. the lower the concentration of Ca. The patterns are quite close to those of dolomite (ASTM card 11-78). The Mg concentrations of these plants show no relation to the net dolomite counts. The data are too few to carry this discussion any further.

None of the carbonate minerals are related to taxonomic position of the plants in which they are found.

The crystallographic nature of silica in higher plants has been identified as opal and quartz by Lanning *et al.* (1958). Swineford & Franks (1959) have identified two major forms of opal in the Ogallala formation in Kansas. One of these is classified as a diatom or biogenic type and the second is referred to as a low-cristobalite-tridymite type. The former is characterized by a lack of cations other than SiO_2 and the shape of the X-ray reflections may be attributed to a very low degree of crystallinity. Frondel (1962) notes that in opal the three-layered sequences of SiO_2 are dominant and are those of opal-cristobalite. With increasing disorder due to the entrance of cations such as the alkalis, and possibly also of H_2O, the diffractogram becomes more diffuse and the stronger diffraction lines of low tridymite appear. Thus a pattern develops which in varying degrees resembles the structure of both low-cristobalite and low tridymite. Neither the genesis nor the function of these minerals in plants is apparent. It should be noted that it is quite easy to change opal into quartz at ordinary room temperature and atmospheric pressure merely by putting the sample under pressure of 1055 kg cm^{-2}. The sample must be at least 0.4 cm thick. The entire process, using a marine sponge as a sample, takes 5 min (U. Cowgill, unpublished data).

Quartz was found in *N. lutea* flowers, *H. incana* whole plants, and in *P. vaginatum* whole plants. All plants studied contain varying amounts of both the low form opal-cristobalite and opal-tridymite. The mean concentrations of these two minerals tend to be similar (1485 and 1486 mg kg^{-1}, respectively). The highest concentration was found in *L. salicaria* (Lythraceae) (2434 and 2426 mg kg^{-1}, respectively) (see table 90). The lowest concentration was found in *C. acutum* (Asclepiadaceae). Despite the fact that Si concentration in plants bears a relation to taxonomy, these siliceous minerals fail to do so. This is the case whether their relation to family position is examined individually or collectively. In addition, no correlation of any significance was obtained between any given mineral and Si content or all the siliceous minerals and Si content. It is quite clear that a significant amount of Si is not involved in crystal formation.

The distribution of gypsum in Huleh plants is shown in table 91. Five of these plants are perennials and two are annuals. One is a lake plant, three inhabit swamps, and the remainder (one each) inhabit moist places and banks, wadis, and waste places. The net counts per second of these gypsum peaks bear no significant relationship to the Ca content or the S content of these plants. In addition, these few figures do not distribute in any systematic way to show any sort of taxonomic correlation with the mineral figures.

It is interesting to note the distribution of minerals in the two parasitic plants and their hosts (see table 86). *C. acutum* contains only the opal-cristobalite (756) and the opal-tridymite (779). The leaves of *P. australis* around which *C. acutum* is wound contain the two minerals at nearly three times the concentration of the parasite but in addition also contain whewhellite (431) and weddellite (275). The host, *A. mannifera*, contains the same minerals as its parasite except that weddellite is missing in the host. However, the host contains gypsum, the opal-cristobalite and the opal-tridymite at levels 1.2 to 1.6 times more concentrated than that of the parasite and has whewhellite at a concentration 1.5 times that of the parasite. Generally, it appears that the minerals formed by host plants are more concentrated than the same minerals in the plants that parasitise them. It is interesting to note that these two pairs of plants form no detectable carbonate minerals.

Table 92 shows the distribution of minerals in Huleh plants in relation to the plant life cycle. Dolomite was not encountered among the perennial species. Sylvite, whewhellite, weddellite, Mg oxalate dihydrate alpha form, opal-cristobalite, opal-tridymite, quartz and gypsum are more concentrated in the perennial species; calcite and aragonite are more concentrated in the annual ones.

The greatest concentration of whewhellite, weddellite, opal-cristobalite and opal-tridymite was found in lake plants (see table 93). The observation that oxalates tend to be more concentrated in aquatic plants than terrestrial ones has also been noted by Stephens *et al.*

(1973). The smallest amount of Mg oxalate dihydrate alpha form and calcite was found in lake plants. Weddellite declines in concentration with declining water availability. The opal minerals are least concentrated in plants that inhabit waste places. The highest Mg oxalate dihydrate alpha form was found in plants inhabiting swamps. The two Ca oxalates were least prevalent in swamp plants and those plants living in waste places. Table 94 shows the distribution of minerals in plant parts. The smallest quantity of the two opal minerals and the two Ca oxalates were found in flowers and seeds and the highest quantity of these were encountered in stems and woody stems. The data are too scanty for sylvite, Mg oxalate dihydrate alpha form and the carbonate minerals to offer any meaningful comment on plant part distribution.

5. STATISTICAL ANALYSIS OF RESULTS

Correlation coefficients were calculated between all possible combinations of 70 variables. This results in 2310 correlation coefficients. Of this number, a certain percentage will be spurious. To reduce this percentage, only linear correlation coefficients that are significant at or beyond the 0.5 % level will be accepted. It should be noted that with 2310 correlations, by accepting a level of significance of 5 %, it would be possible to accept 116 spurious correlations; to put it another way, 116 would be significant at this level by chance alone. Accepting 0.5 % and 0.1 % reduces this chance to accepting 12 and 2 correlations that may be significant as a result of chance alone. Thus, this approach reduces the chance of accepting a spurious correlation as being significant, but it does not eliminate it.

When all possible variables in a sample have been analysed the 100 % problem presents itself. When one variable increases, another, by definition, decreases. The best solution to this dilemma is to calculate multiple correlation coefficients and then determine the level of significance of the partial correlation coefficients (thus, only pertinent multiple correlation results will be shown). For example, Cl is significantly related to Br, S, Na and F at or beyond the 0.1 % level. It is also related, at the same level of significance, to the net counts per second of the major peak of sylvite as well as to the position of this peak. A multiple correlation coefficient relating Cl to Br, S, Na and F results in $R = 0.7429$ with a sample size of 118. This means that 55.19 % (R^2) of the variability observed in Cl is due to its relationship with Br, S, Na and F. With the F test, this multiple correlation coefficient is significant beyond the 0.1 % level ($F(4, 113) = 34.78$, $p < 0.001$). In essence, this means that the observed variability in Cl is controlled by the variability in Br, S, Na and F. An examination of the partial correlation coefficient reveals that Cl × Br, holding constant all the other variables (i.e. S, Na and F) are highly related to each other beyond the 0.1 % level. The same holds true for the relationship between Cl and S and Cl and Na. The relationship between Cl and F, however, is significant only at the 1 % level. Continuing this example, the multiple correlation among Cl, the position of the sylvite line and the net counts per second of the major peak of sylvite results in a multiple correlation coefficient significant beyond the 0.1 % level. Chlorine is also instrumental in determining the exact position of the sylvite line but not its height above background. If the same calculation is repeated for K, the net counts per second of the major peak of sylvite and the position of the major peak, the multiple correlation is significant beyond the 0.1 % level but the partial correlation coefficient between K and the position of the sylvite line (major peak) is significant only at the 1 % level, suggesting that K is intimately involved in other processes.

Multiple correlation coefficients involving the alkali metals are shown in table 95. The expected correlations, i.e. Na × Cl, K × Rb, hold true when subjected to the scrutiny afforded by partial correlation analysis. Sylvite is highly related to Cl and K and these relations also hold true when examined by multiple/partial correlation technique (see table 101). Sodium is clearly involved in many processes since only about 42.89 % of its variation can be accounted for utilizing the linear correlation coefficients with which it is significantly involved. It is interesting that 70.38 % of the variation exhibited by K can be attributed to its relationship with F and Rb (see table 95). Similarly, 70.23 % of the Rb variation can be accounted for by a large number of elements (14), the Mg oxalate line position and its net counts per second, but in reality the majority of the variation may be attributed to its intimate relationship with K, Mg and Rb. Caesium has no significant partial correlations, but nearly 50 % of its variation may be explained by its concordance with 13 elements. Lithium is concordant with As, Sn, Be, V, Bi, Fe, and weakly associated with Na.

The multiple correlation coefficients involving Cu, Ag, Be and the alkaline earths are given in table 96. Copper is clearly involved in many processes that are not discernible by correlation techniques, since only about 42 % of its variation can be accounted for and this appears to be controlled by Pb and Zn. In addition, Cu and Hf are closely related but, surprisingly, not Zr.

A certain portion of the Ag enters the Huleh Valley through rain and aerosols. Thus it is interesting that the only significant partial correlation observed for Ag is with B. Boron may be viewed in this context as a wind and rain indicator. Only 36 % of the variation in Ag can be attributed to its relations with six elements.

Beryllium has a vast number of relations and nearly 94 % of its variability can be explained by only a few elements. It is related at various levels of significance to K, Hg, Bi, Li and Cd. Beryllium is a divalent cation whose ionic radius is quite small (3.4 nm) (Goldschmidt 1958) and thus can replace divalent Zn in 4-coordination as well as trivalent Al. The fact that Be is highly related to both F and Li might suggest the existence of very small amounts of Li_2BeF_4 (see Goldschmidt 1954).

An examination of the statistical analyses of the alkaline earths reveals expected linear correlation coefficients, i.e. Mg × Ca, Ca × Sr, and, interestingly enough, Ba × Se (see Se discussion in §4*k*). Strontium is closely related to Ca but no significant partial correlation between the two elements could be found. Franceschi & Schueren (1986) noted that an increase of Sr in the growth medium brings about a concurrent rise of Sr incorporated in Ca oxalate crystals. Statistical attempts to correlate this relation failed to elucidate the possibility of such a phenomenon in Huleh plants. This suggests that enough plants take the two elements up at somewhat different rates so that gross correlations are apparent but no partial relationship can be ascertained. The Mg × Ca and Ba × Se hold true and produce significant partial correlation coefficients. It has been noted elsewhere (Garten 1976) that the relation Mg × Ca × K is true in plants (see table 96); it certainly holds true in this study.

Table 97 contains the multiple correlation coefficients for Zn, Cd, Hg; B, Al, Ga; Sc, Y, La and Ce. Zinc is strongly related to Cu and Cs and this accounts for nearly 49 % of its variability. No other multiple correlations involving significant linear correlations were significant. Cadmium oscillates at the same rate as the net height of the main quartz peak. It is a curious relationship since so few plants contain any quartz. However, the variation exhibited by Cd is relatively small and this probably accounts for the relationship since most plants contained no quartz. In any case only 37 % of the variability of Cd can be accounted for and this is related to P, Be, Hg, Bi and the net height of the main quartz peak.

Nearly 90% of the variation in Hg is due to the oscillations of P and Be though Hg is significantly related to 12 other elements that fail to exhibit significant partial correlations.

Boron is significantly related to elements of which a major component is contributed by wind and rain, namely Cl, S, I and Ag. As there are several sources for this element external to the Huleh Valley it is difficult to account for much more than 41% of its variability. It is also related to the oxalate minerals and the siliceous ones, excluding quartz. Since the partial coefficient is negative, one possible hypothesis might be that the lack of rain encourages mineral formation in plants.

Aluminium is significantly related to Ti and Fe and the former exhibits a highly significant partial correlation coefficient. The partial with Fe is not statistically significant, although the linear relation is. Aluminium is clearly coherent with Ca, Ti, Si, Fe, Sc, As, Hg, Co, V and Li, although the technique of partial correlation was unable to discern these relations any more closely.

Gallium does not have a significant partial correlation with Al. Gallium varies hardly at all in the plants. It may be that there is more than one major source of Al in the basin that has a different Al:Ga ratio and thus the relation is not discernible. Gallium is related to Hf and Ge, two elements, like Ga, that exhibit hardly any variability in plants.

Scandium is coherent with Ca. An investigation carried out by Goldschmidt & Peters (1931) revealed that Sc was more closely related to Mg and ferrous iron than to the rare earths.

In the multiple correlation that accounts for 93% of the variability exhibited by Sc, both Mg and Fe are highly related but no significant partial could be discerned. According to Goldschmidt (1954) the behaviour of Y is identical to that of rare earths Gd–Lu. No rare earths beyond Ce were detected in any substance studied that was gathered in the Huleh project. Yttrium appears to be taken up by plants in relation to Ca, Si and Ce, three elements with which it is concordant in Huleh plants. These account for about 64% of its observed variability. No significant partial correlation coefficients were found for La. The two elements, La and Ce, are highly related, as revealed by their linear correlation coefficient, but no significant partial correlation could be ascertained. The only significant positive partial for Ce was with Y. However, 63% of its variability is accounted for by its relationship with 14 elements, only one of which has a significant partial correlation.

Table 98 shows the significant multiple correlations for Si, Ge, Sn, Pb, Ti, Zr and Hf. Ninety-six per cent of the variation shown by Ti is due to its close relationship with Al and Fe. Zirconium is strongly associated with Hf, as would be expected, and is concordant with Ti, Si, Al and Fe. However, these associations explain only 23% of its variability. Hafnium exhibits these same relations and, in addition, is strongly related to Cu. About 48% of the variability shown by Si is due to its relation to Al, Sc, Y and the position of the quartz line. It is always difficult to elucidate the behaviour of major components, since the vast majority of variables have been ascertained, when one variable increases another must decrease. This is the most likely explanation for negative partial correlations.

Eleven per cent of the variation noted in Ge is due to its concordance with Ti, Si and Al, which is to be expected. No significant partial correlations were found for this relationship. Fourteen elements control the variability of Ge but only Ga has a significant partial correlation with the element.

Tin is concordant with Mg, B, Bi and Li in Huleh plants and this concordance accounts for nearly 74% of the observed variation. Lead is one of those elements external to the geology of the basin. Like Hg, Pb is transmitted climatically throughout the globe. For example, in the extremely long lake core (600 m) taken from Japan's ancient Lake Biwa, the beginning of smelting of lead during the Neolithic in Yugoslavia was noted (S. Horie, personal communication). In highly populated regions, the majority of Pb found in the landscape originates from cars, trucks, planes and diesel powered engines (tetraethyl lead). As noted earlier, the automobile traffic in the Huleh basin is sparse. However, the contaminants of war have been continuous in this region since the British Mandate. Lead is concordant with I and Cu and 46% of its variability is accounted for by 13 elements.

Multiple correlation coefficients of P, As, Bi, V, Nb; S, Se, Cr and Mo are shown in table 99. Phosphorus is concordant with K, S, Hg and Cd in Huleh plants. Again, the difficulty encountered with major components mentioned earlier prevails with P. Sixty-nine per cent of the variation exhibited by As is largely due to its concordance with Fe and Li. The relation with Fe is to be expected. Its origin within the basin is presumably basalt (Goldschmidt 1954). Nearly 84% of the variation exhibited by Bi is due to its association with K, Na, Sn, Be and Cd. Not very much is known about the distribution of Bi in living things. The variation noted for V is entirely due to its association with Fe, which is to be expected (Goldschmidt 1954) and Li. Niobium moves with 14 elements and is significantly and positively related to percentage loss of mass on ignition. It shows no other statistically significant partials.

Sulphur bears a relation to the principal oxalate minerals and the two opals. This relation may be fortuitous: the same minerals bear a gross relation to Ca and some portion of the S in plants is tied up as gypsum. Sulphur is concordant with Cl and P. The majority of its variability cannot be explained by the usual statistical methods.

When Se is used as the dependent variable it is concordant with S and Pb. Selenium and S are expected to be closely related. Were this a region where galena (PbS) was common, the Pb–Se association would not be unusual (see U.S. Bureau of Mines 1980). However, this not being the case, the association is unexpected. Selenium is also associated with Ti, Si, Al and V. The majority of this element's variability has not been accounted for by these statistical methods. Much of the Se is probably still tied up with Ba, which was added to solve the problem of highly seleniferous soils (Ravikovich & Margolin 1957, 1959).

Chromium is concordant with Ba and Ge in Huleh plants and is highly associated with loss of mass on ignition. These relations account for 51% of its variability. Molybdenum has no significant partial correlation. Only 16% of its variability can be accounted for and Fe, interestingly enough, is not among the four elements involved. It appears that Mo is associated with the development of Mg oxalate dihydrate.

Multiple correlations involving the halogens, Fe, Mn, Co, Ni and the percentage loss of mass on ignition are shown in table 100. As would be expected, Cl is concordant with Na, S, Br and F. Bromine is closely associated with Cl and this is the only significant partial correlation found with Br. It is curious that F has no significant multiple correlations, though it has many highly significant linear correlation coefficients. Its strong relationship with K and Cl suggests that it might be occluded in the formation of sylvite. Iodine is not associated with the other halogens. Its variation in the plants is slight and its concentration small. Forty-five per cent of its variation is accounted for by percentage loss of mass on ignition and 12 elements.

Eighty-four per cent of the variation exhibited by Fe is due to its close association with Ti and Al, though the partial correlation with Al is negative, as it is also with Mn. Iron is concordant with As and V. Manganese has no statistically significant linear correlations but nearly 12% of its variability is due to its concordance with Si, Al and Fe. Cobalt is taken up at the same rate as Sr by plants and it is related to nine other elements but exhibits no significant partials with any of them. Nickel is related to Ti, Si, Al, Fe, Sc, Be, V and the position of the quartz line, which accounts for 20% of its variation. It is also related to 11 other elements and percentage loss of mass on ignition. No significant partial correlations were found for Ni.

The loss of mass on ignition is related to the majority of major constituents and this accounts for 90% of its variation.

The multiple correlation coefficients involving minerals are shown in table 101. Sylvite is highly related to Cl, Br, K, P, F and Na. Pertinent multiple correlations essentially confirm that sylvite is composed of K and Cl. Whewhellite and weddellite are closely related to each other; this result suggests that plants form those two oxalates at the same rate. Weddellite is also related to the net height of the major peaks of the two opals. These statements are supported by multiple correlation analysis.

Magnesium oxalate dihydrate alpha form is correlated with Mg, Br, Rb, F and K. Significant partial correlations (see table 102) were obtained between the position of the major peak, Mg and Br and net height of the major peak with Rb and F. These relations suggest that Br, Rb and F may be occluded when the mineral is being formed by plants.

Pertinent multiple correlations for the carbonate minerals are shown in table 103. Because calcite is highly related to Ca, all the relations previously noted that involve Ca are also observed with calcite. Aragonite is so poorly represented that no relations for this carbonate were noted. Dolomite line position and height are significantly associated but no multiple correlations were found. Seventy per cent of the variation noted in calcite is due to its association with the sum of the intensities of the major peak of all Ca-bearing minerals and Al. Calcite is concordant with Al and Ti, largely because Ca is concordant with these two elements.

Quartz, although infrequently encountered in Huleh plants, is intimately related to Si (see table 104) when multiple correlation techniques of analysis are applied. The two opals did not exhibit any statistically significant multiple correlations. They are largely related to each other, the major oxalates and Cr and Pb, which may be occluded during their formation.

Gypsum is made of Ca and S and both linear correlations and multiple correlations confirm this fact. There is a suggestion that Se may be occluded during its formation (see table 105).

It is interesting to note that statistical methodology such as that applied here to minerals largely does no more than confirm the elemental composition and point to some elements that may be occluded during mineral formation.

To answer the question as to whether plants of different genera are chemically more similar living in the same small area on the same soil than plants of the same genera and species living in different regions (Ylaranta & Sillanpaa 1984), the plants are divided into eight regions.

(i) East of Hulata: shore of dry lake.
(ii) East of Yesod Hama'ala: dried lake.
(iii) Northeast of Yesod Hama'ala: dried lake.
(iv) Northwest of Yesod Hama'ala.
(v) West of Yesod Hama'ala: Jordan Canal.
(vi) Northwest of Huleh Preserve.
(vii) West of Preserve.
(viii) Northeast of Preserve.

Each plant is represented by 118 variables. The chemistry of any given plant sample is compared with the chemistry of all the other plant samples and linear correlation coefficients are calculated. Because it is of interest to discover whether these correlation coefficients are part of the same population or whether they come from different populations, each correlation coefficient is transformed to a z value (Snedecor & Cochran 1980). The z values that represent plants living in a particular area are then averaged. The mean z values representing two different areas are then subtracted from each other and the significance of the difference between the two z values is then examined by use of a t-test. A lack of significance implies that the two means come from a common population, i.e. the chemistry of the plants living in two different areas is more genera dependent than edaphically so. High levels of significance ($p < 0.001$) suggest that the means (z values) are drawn from different populations, implying that the plant chemistry is more edaphically determined than generically so.

Table 106 shows the correlation coefficients obtained by calculating the relations of all whole plant analyses from those inhabiting the northwest of Yesod Hama'ala section with the remaining seven regions. The following table (see table 107) shows the mean z values of plants in each region in contrast to those living in the area northwest of Yesod Hama'ala. Region G (northeast of Huleh Preserve) is significantly different for all the plants from the region northwest of Yesod Hama'ala, suggesting that the plants of both regions reflect the edaphic factors in their chemistry more strongly than the genetic ones. The same may be said for regions F and D, west of the Huleh Preserve and west of Yesod Hama'ala. It is interesting to note that *Alhagi mannifera* (variable no. 10) shows significance in all regions studied.

Concluding this section, it is clear that plants inhabiting some sections of the Huleh Preserve reflect the chemistry of the soil more profoundly than their genetic differences, while in other sections the genetic factors are more pronounced.

6. Discussion

During the coring process (Cowgill 1969) it was possible to identify the Cyperaceae in the more recently deposited peat (A7, A5, A4) layers. Thus it was of interest to compare the composition of peat in zones A7, A5, A4, A3 and A1 (cf. Hutchinson & Cowgill 1973) with that of members of the Cyperaceae and Typhaceae found growing in the Huleh swamp. However, elemental ratios in the peat are not in the least reminiscent of those in the Cyperaceae or Typhaceae.

Another query that should be posed concerns perennial plants and the elements they tend to take up or accumulate over the years. Curiously enough, restricting the differences to limits in excess of a level of significance of $p < 0.001$, only Na, Si and Mn are significantly higher in the perennials than in the annual plants, while annuals contain significantly more ($p < 0.001$) K, Mg, P and Cl. It may be suggested that the annuals in this little preserve function to recycle elements that are crucial in the life of aquatic organisms. This ability to recycle nutrients has also been noted in shrubs living in arid regions (Romney *et al.* 1980).

One of the unexpected discoveries in this study is the variation of 29 elements within the leaves of the Cyperaceae, Typhaceae and Gramineae. Although only 10 of these elements exhibit variation that is statistically significant ($p < 0.001$), the remaining 19 vary in a consistent fashion. Jones (1970) has made the point that leaf sampling of domestic crops to measure the adequacy of crucial elemental concentrations is severely hampered by the observed variation. He suggests the use of leaf punches as a sampling technique. He offers no comment as to the function of such variation.

Only Cyperaceae, Typhaceae and Gramineae show this variation. Leaves of species of other families were examined but no consistent variation was noted. Though the sample studied here is too small to offer any conclusive statement, it may be suggested that the more recently evolved groups exhibit these elemental distributional phenomena.

Jones (1970), Sayre (1952), Neubert *et al.* (1969) as well as the data referred to here involve sampling at a time of flowering, tasselling or seeding. It is not known whether these phenomena occur in plants prior to their reproductive period. Similarly, it is not known whether these concentration distributions are related in some way to the reproductive period. In the group of species examined some are perennial, some are annual, some are swamp plants and some inhabit waste places.

The elements that concentrate in the margin of the leaf are Na, Ag, Be, Ca, Sr, Ba, B, Al, Ga, Si, Ge, Pb, Cl, Br, I, Mn and Fe; those accumulated in the midsection are K, Rb, Co and Li, and those in the blade of the leaf are Cu, Mg, Zn, Cr, Mo and P.

An examination of the elements concentrated in the leaf margins reveals some that are thought to be structurally important. Their presence may reduce the incidence of wind damage, in particular the shearing effect of wind. In addition, this group of elements may function either to retain leaf shape or possibly even to be responsible for shape itself. It is also possible that quantities of elements, or their peculiar distribution, may induce leaf epinasty and inhibit hyponasty or the reverse, depending on the taxonomic character of the particular plant. Such phenomena are delayed by inhibitors of ethylene synthesis and toxic amounts of some elements (Salisbury & Wheeler 1981). The presence of some elements in the leaves may exert control on such processes.

The alkali metals except Na are concentrated in the midsection of the leaves while those usually placed in the 'essential for life' category are found in the blade. This distribution may direct insect damage to an area of the leaf that would least damage the plant (Huber 1980). In an arid region such as the Huleh Basin there are ample sources for Na but not as many for K or P which, in tropical areas, tend to be in short supply anyway.

It is not immediately obvious why elemental uniformity should be viewed as the norm. All measured concentrations, after all, must be associated with a standard deviation not only because of the inherent variability intrinsic in all chemical methods, but the natural variability found in the plant as well. It is clear that this whole area of elemental distribution within plant parts needs further attention. It should be realized that the divisions into which leaves were separated were entirely arbitrary. Boron was examined first and found to concentrate preferentially in leaf margins. It was then thought that the midsection and the blade might be reasonable divisions to examine chemically. If, instead, the leaf had been divided into equal thirds, some other sort of periodic distribution might have been noted. Unfortunately, there was not a large enough sample to pursue this idea; however, still smaller divisions might prove illuminating.

Elements concentrated in plants that are positively or negatively related to the taxonomic position are K, Rb, Si, Ti, P, Bi and F. Thus K, Rb, P, Bi and F decrease with time; that is to say the Nymphaeaceae contain more of the given element than the Gramineae. On the other hand, Si and Ti concentrations increase with time, the Gramineae containing larger amounts than the water lilies. These relations were found to be significant at levels varying from 5.0%

to 0.1 %. Considering the small size of the sample, it is unusual to find even seven elements that show such a significant response. It is curious that elements that are structurally important (Si, Ti) increase with time while those that are nutritionally important (K, P) decrease with time. The structurally important Si and Ti may act as a defence mechanism (Lanning & Eleuterius 1983, 1985) in that high concentrations of either or both elements tend to make plants less palatable. Nutritionally important elements such as K and P may decline in concentration with time as plants through adaptation become more efficient in their use of 'essential to life' elements. This kind of conservation may permit population expansion, thus ensuring the longevity (in the evolutionary sense) of the species.

The question of habitat and chemical composition has received little attention in the published literature, with the exception of Na, which is far more concentrated in aquatic plants than in their terrestrial relatives. The lake plants and swamp plants are not as clearly differentiated here as they may be in some locations, as the Huleh Preserve is naturally flooded in the winter and often flooded during other times of the year when the water from the carp ponds is drained into the preserve. The chemical composition of lake and swamp plants was therefore averaged and compared with the average of plants inhabiting moist places and banks, wadis and waste places. Aquatic plants contain significantly more ($p < 0.001$) Na, K, Si, S, P, Cl, Mn, low-opal-cristobalite and low-opal-tridymite in their tissues than do terrestrial plants of the Huleh Preserve. Although not significant, Rb, Cs, Li, Ag, Be, Hg, Ge, Pb, Se, Bi, V, F, Br, I, Fe, Co, percentage mineral matter, whewhellite, weddellite and Mg oxalate dihydrate follow this pattern of being more prevalent in aquatic plants than in land plants. Land plants contain significantly ($p < 0.001$) more Mg, Ca, sylvite, calcite, quartz and gypsum in their tissues than water plants. In addition, Cu, Sr, Ba, Zn, Cd, B, Al, Sc, Y, La, Ce, Sn, Ti, Zr, Hf, Cr, Mo, As and Ni, although not statistically significant, follow this pattern.

There is little question that mineral formation in plants is due to the need to store nutrients, possibly for use in expected poor times. Sometimes these minerals are simply excretory products. Nevertheless, there is growing evidence that the oxalates (Ellis *et al.* 1983; Rodriguez Mejia *et al.* 1985) and the siliceous minerals (Lanning & Eleuterius 1983, 1985), at least, act as a defence mechanism against animal and insect damage.

The field work was carried out during the time I was a member of the Biology Department of Yale University. The laboratory work was completed during my tenure in the Department of Biological Sciences of the University of Pittsburgh. This work was supported by a series of National Science Foundation grants awarded to Professor G. E. Hutchinson of Yale University and/or to U.M.C. The statistical aspect of this study was done on the computer of the U.S. Steel Corporation Research Laboratory of Monroeville, Pennsylvania and supervised by Mr F. A. Sorensen. The manuscript was written during my stay in Midland, Michigan. I thank Professor G. E. Hutchinson for all his assistance, encouragement and helpful comments on this manuscript. I am grateful to all the people acknowledged in previous papers relating to the Huleh project. Finally, sincere appreciation is owed to Rafi Roth, the naturalist at the Lake Huleh Preserve, who assisted this study in many ways, and to Professor John Reeder, Curator of the Yale University Herbarium, for his help in confirming the identity of the Huleh plants and ascertaining their most recent scientific names.

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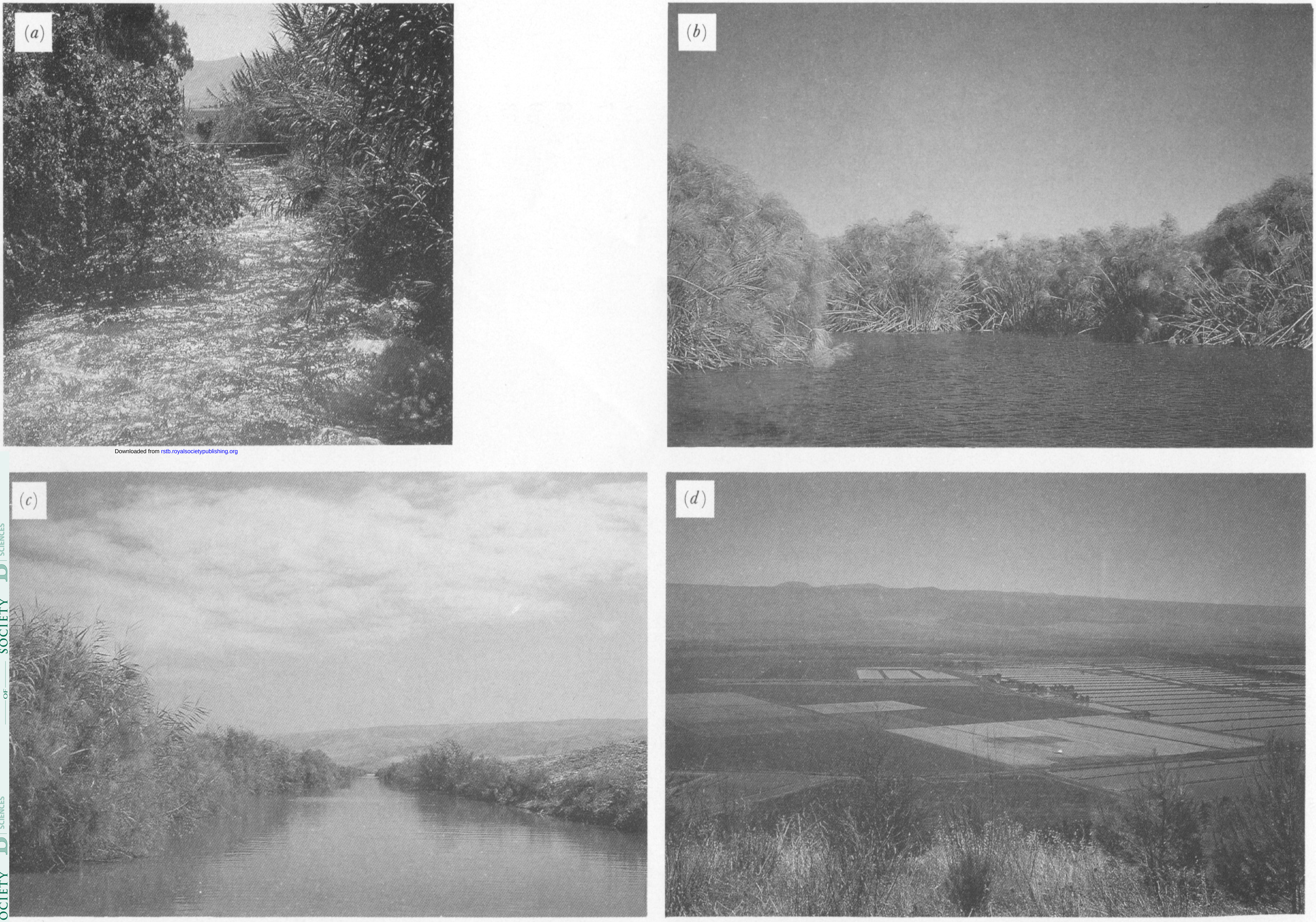

(*a*) The Jordan River as it enters the Lake Huleh Preserve.
(*b*) The papyrus swamp of the Lake Huleh Preserve.
(*c*) The Jordan River as it leaves the Lake Huleh Preserve.
(*d*) Overall view of the Lake Huleh basin with the Lake Huleh Preserve in the distance.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES