

SEDIMENT GEOCHEMISTRY  
OF  
FLATHEAD LAKE, MONTANA

by

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## PREFACE

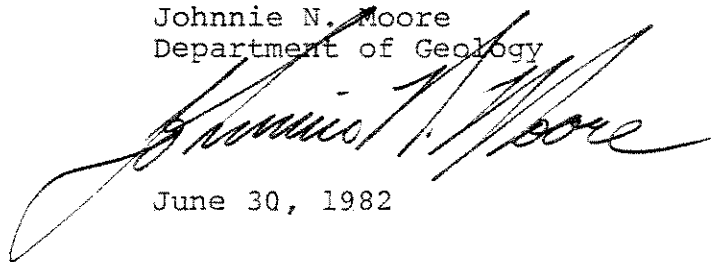
This report is the final statement on a study of the nutrients and metals in the sediment of Flathead Lake, Montana. We initiated this work on June 15, 1982 with funding from the U.S. Environmental Protection Agency managed through the Flathead River Basin Environmental Impact Study. The purpose of this work was to establish the distribution of phosphorus and the pathways and mechanisms controlling phosphorus migration. Because the grainsize, organic content and heavy metal concentrations of the sediment affect phosphorus migration, we also determined the sedimentologic and geochemical framework of Flathead Lake sediments.

Because Flathead Lake is a popular recreation resource and the drainage is expected to be modified by future mineral, petroleum, and timber production, it is essential to have detailed baseline data to monitor future changes. Aesthetically, Flathead Lake seems completely pristine, and its waters have been classified A-open-D1, the highest water quality rating of the Montana State Department of Health and Environmental Sciences. But recent aquatic chemistry suggests that the lake lies at the boundary of the Oligo-mesotrophic (Stanford, et al., 1981). If this is correct, any changes in the nutrient budget could have significant effect on the lake biota, chemistry and water quality and, therefore, recreation potential. The basic goal of this sedimentation study is to determine the history of sedimentation in the lake and the relationships between nutrients and metals in

the sediments. We have developed models that explain nutrient and metals distribution as well as establishing baseline data on physical and chemical properties. This data will allow changes in sedimentation, nutrient input and trace metal concentration to be monitored and responses of the lake predicted. In the last chapter of this report I discuss possible future scenarios based on our present understanding of sediment-nutrient interactions.

The fieldwork and analyses presented here result from two years of work by faculty, staff and students of the Geology Department of the University of Montana. We thank all the people and agencies that aided in these two years of research. The scientists and staff at the University of Montana Biological station gave us logistical and analytical support and many hours of helpful discussion. The secretarial, professional and computer center staff of the University of Montana helped throughout data collection and report preparation. Specific thanks to: J. Bibley, S. Vuke, B. Wall, G. Thompson, L. Hanzel, T. Stewart, T. Qamar, J. Stanford, B. Ellis and R. Cooper. Finally, we thank the U. S. Environmental Protection Agency and especially the Flathead River Basin Environmental Study for funding this research and supporting us throughout the two years of work.

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A large, stylized handwritten signature in black ink, which appears to read "Johnnie N. Moore". The signature is written over the typed name and department information.

June 30, 1982

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## Chapter One

### INTRODUCTION AND SEDIMENTARY FRAMEWORK

J.N. Moore

#### Geologic and Environmental Setting

Flathead Lake is the largest freshwater lake in the United States west of the Mississippi River and covers an area of 510.2 square kilometers. The lake occupies the southern end of the Rocky Mountain Trench (Fig. 1), a depression that extends from British Columbia into northern Montana.

The Rocky Mountain Trench is bounded on both sides by normal faults that continue into Flathead Lake basin (Stickney, 1980), and Seismic activity around the lake is similar to other areas of the intermountain Seismic Belt with many small earthquakes and microearthquake swarms. Although most earthquakes are small, two recent magnitude five earthquakes occurred in 1952 and 1975 (Qamar and Breuninger, 1979). Microearthquake swarms have been located on the southwestern side of the lake (Sbar, et al., 1972; Stevenson, 1976) and other small earthquakes identified with faults in the Kalispell Valley to the north (Stickney, 1980).

During the Pleistocene, the Rocky Mountain trench guided lobes of Pleistocene ice sheets south into the Rocky Mountains, and multiple glacial events left a complex record of tills, moraines and lake deposits. During the last advance in Pinedale time into the Flathead Valley, Polson moraine formed, damming Flathead Lake. Since that time, approximately 10,000 to 14,000 years ago (Stoffel, 1980), the lake has received sediments from

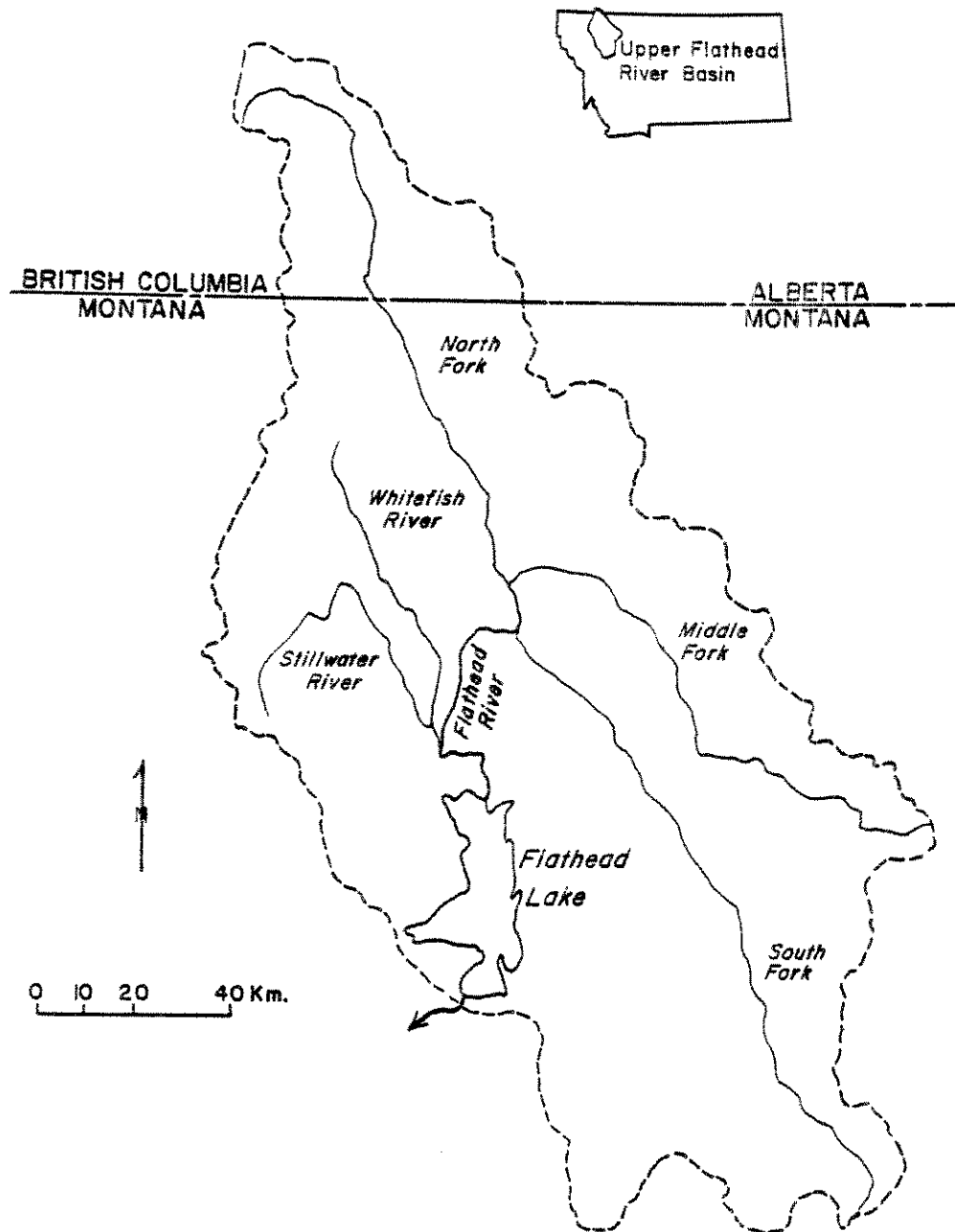


Figure 1

an extensive drainage (18,378 km<sup>2</sup>) dominated by the Flathead River and other less important sources. The level of the lake lowered from a high immediately following the retreat of the glacier, to the present low, as the outlet river cut through the moraine (Johns, 1970). The level is now artificially maintained by Kerr Dam, constructed in 1938.

The Flathead watershed encompasses mixed forest and agricultural lands in northwestern Montana and British Columbia, drained by six major river systems. The Flathead River is the major sediment source for the lake (Stanford, et al. 1981) supplying 90% of the water (Potter, 1978) the bulk of the suspended sediment and probably most of the bedload sediment annually.

The bedload is deposited adjacent to the inlet forming a large deltaic complex extending over 5 km into the lake. Suspended load is carried into the lake as a sediment plume during spring runoff in late April to June. The coriolis force drives the plume against the western shore concentrating suspension sedimentation there. Rivers and streams entering the lake supply the bulk of suspended sediment during the maximum spring runoff. During the remaining months the rivers flow clear, supplying only a small amount of organic debris.

Flathead Lake contains several distinct bathymetric provinces (Fig. 2). The eastern part of the lake is underlain by a deep trough (110m deep) extending the entire length of the lake. This trough connects to shallower shelf to the west, where depths range from 24m to 45m. Polson Bay, at the southern end of



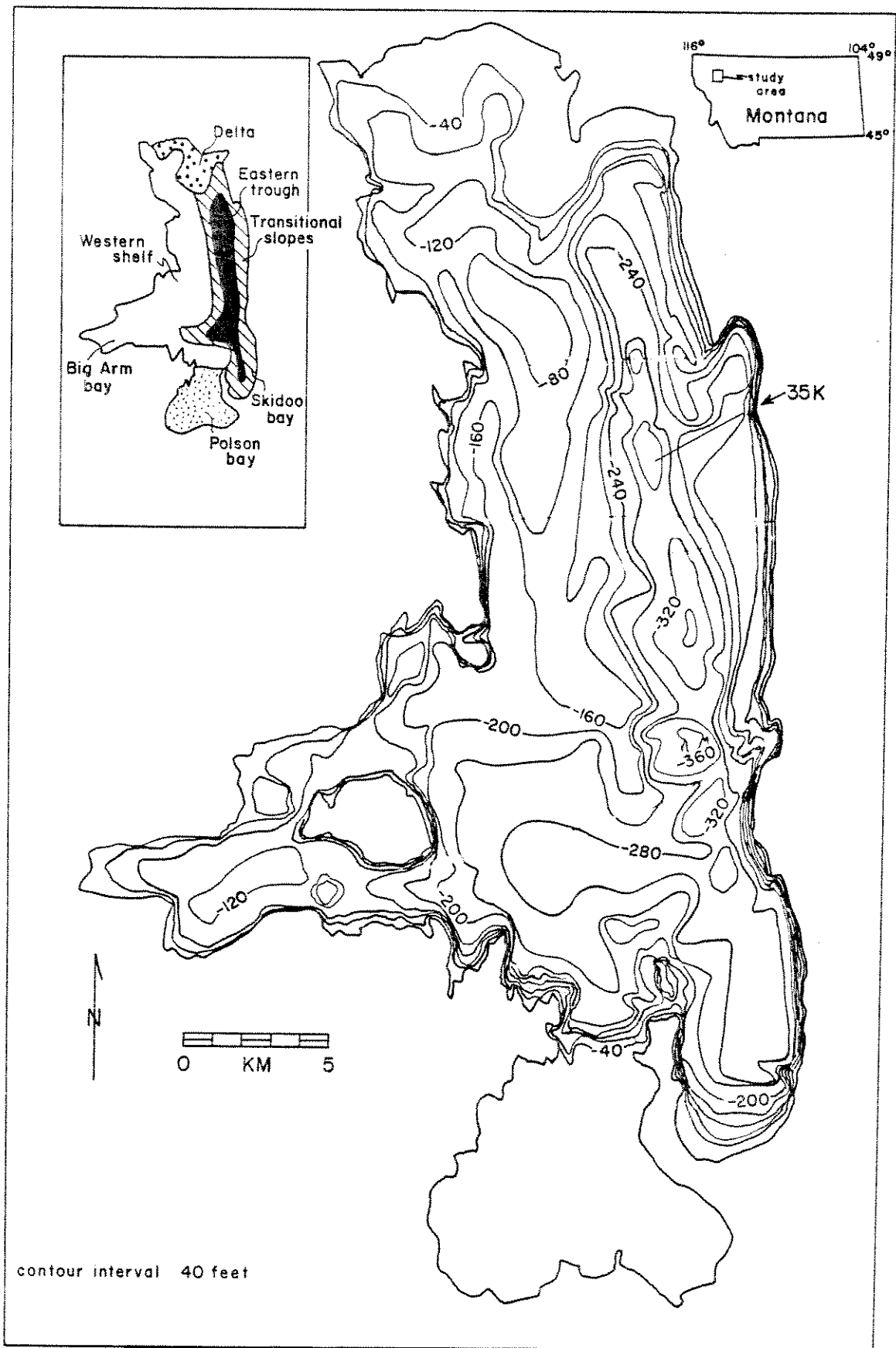


Figure 2

the lake, is isolated from the main lake by a narrow inlet. With depths less than 8m this bay forms the most extensive shallow area in the lake. At the extreme north end of the lake the present active delta and an older inactive delta combine to form a shallow platform with depths from 2m to 5m.

The drainage basin of Flathead Lake encompasses several major mountain ranges and a complex geologic terrane. Rocks of the Precambrian Belt Supergroup cover the majority of the basin (approximately 80-85%, Price 1965; Harrison, 1972). The Belt terrane is covered locally by a veneer of Tertiary sedimentary rocks or Pleistocene till which were mostly derived from the Belt rocks. Paleozoic rocks are exposed in the far eastern, and Mesozoic rocks in the northern parts of the basin.

The Mesozoic strata of British Columbia contain large quantities of coal that is slated for development at Cabin Creek and Sage Creek. This development was the initial impetus for the Flathead River Basin Environmental Impact Study and remains as the largest potential contributor to change within the basin as resources are developed.

One problem that may emerge in the Flathead drainage in response to natural resource development is the increase of heavy metals in the environment. Even residential sewage sludge not containing large amounts of industrial effluents usually contains enriched amounts of copper, cadmium and zinc which might enter the environment by leeching as residential development increases on the shoreline and within the drainage basin of Flathead Lake.

Because of the possible increases in heavy metals, it is important to understand the sources, pathways and sinks

controlling their distribution. The primary purpose of the heavy metal study (Chapter 2) is to determine the geochemical factors controlling distribution of heavy metals in Flathead Lake sediments and their associations with the limiting nutrient, phosphorus (Chapter 3). This type of study has been used as an effective tool in determining the levels and sources of heavy metal pollution in a basin (Forstner, 1979) and should add considerable baseline data to monitor the condition of the Flathead River Basin.

The major background source of metals in the Flathead drainage are the rocks of the Belt Supergroup. All metal deposits are stratiform and occur as disseminated grains and blebs in argillite, quartzite and oolitic carbonate (Harrison, 1972; Lange and Moore, 1981). These deposits are a source of heavy metals and could supply copper, silver, mercury and lead. However, because they are tightly bound in the lattice of mineral grains (Harrison and Grimes, 1970) considerable weathering is needed to release them in soluble forms. Mining operations increases leaching of metals from tailings and may significantly alter the concentrations formed by weathering of undisturbed rock. In the unaltered state probably only a small amount of heavy metals in solution is derived from erosion of Belt bedrock, and it is unlikely that this natural background contributes significant heavy metals to the biota.

Mining, ore processing, waste disposal, fuel consumption, and fertilizing can drastically change the normal concentrations of metals and nutrients within the basin. The large coal mining

operations proposed on the North Fork of the Flathead River offer a source for soluble metals. Coal use releases heavy metals at many stages, including mining, cleaning, processing, transportation and burning. Changing the geochemical environment of the coal and overburden causes release of metals into surface and sub-surface waters (U.S. Comm. for Geochem., 1980). These chemical changes are most effective in the large volumes of solid waste produced by strip mining and coal production. For that reason, the U.S. Committee on Geochemistry (1980) and the Committee on Accessory Elements (1979) considered solid wastes the most environmentally hazardous facet of coal use.

Agriculture, including forestry, can also contribute to heavy metal and nutrient increases by the application of fertilizers and pesticides. Fertilizers commonly contain phosphorus and enriched amounts of cadmium, arsenic and uranium (Forstner, 1979); pesticides may contain significant amounts of arsenic (Shukla, et al., 1972). Because of the large amount of agricultural activity in the Kalispell Valley and on the slopes surrounding Flathead Lake, such inputs are expected.

Domestic sources potentially add significant amounts of heavy metals and nutrients to drainage systems. In urbanized areas sewage effluents, storm runoff and refuse disposal supply most of the leachable metals and phosphorus (Wittman, 1981). Sewage effluents and sludge are often enriched in copper, lead, zinc and cadmium, mainly from the corrosion of pipes (Preuss and Kollman, 1974). Storm runoff commonly flushes lead, copper and zinc into the drainage system (Malmquist, 1975). These sources may add significant quantities of metals to Flathead Lake as the

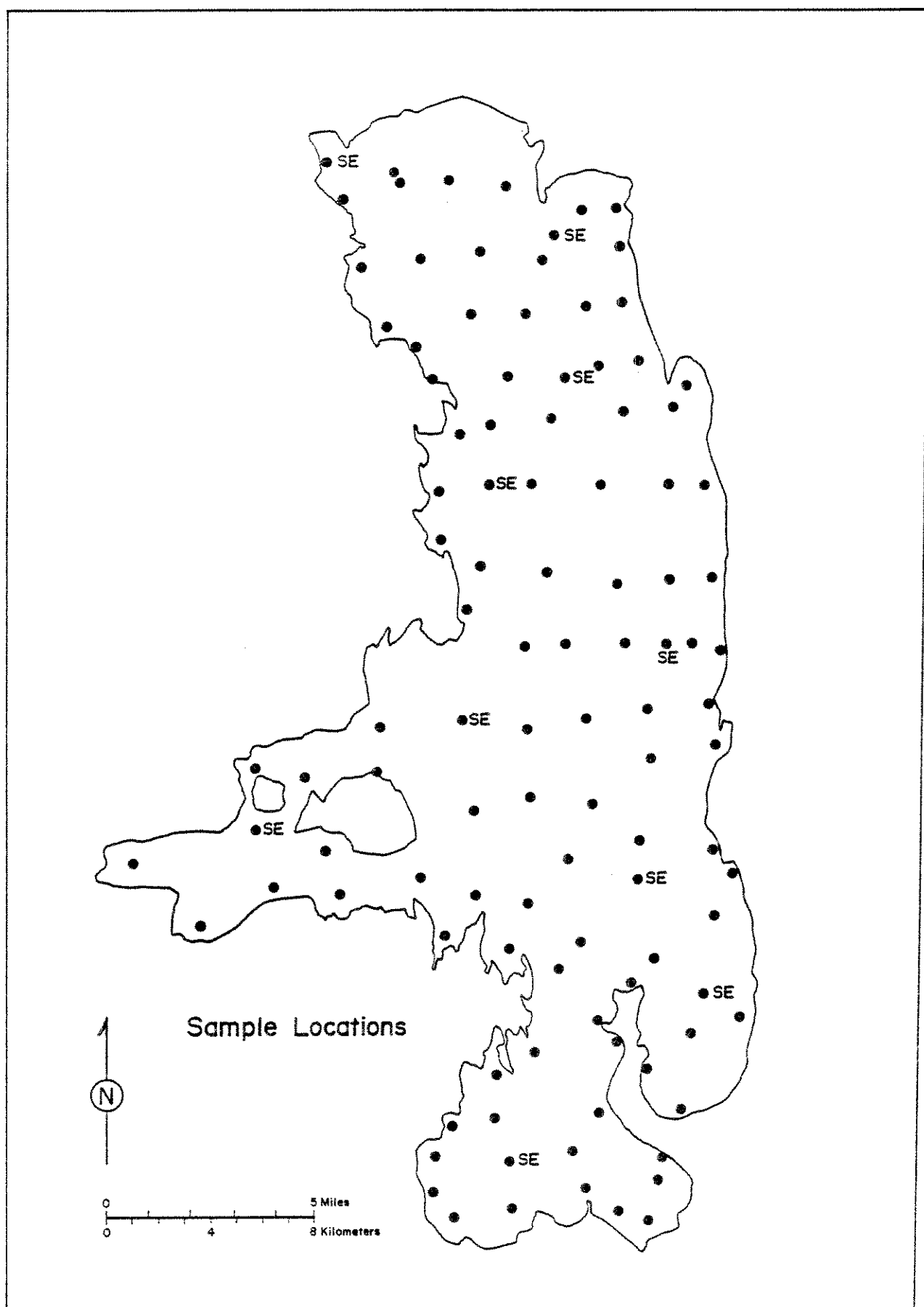


Figure 3

shoreline and basin is developed, and urban and suburban disposal sites contaminate groundwater with copper and zinc and excess phosphorus (Forstner and Van llerde, 1979).

#### Suspension Sedimentation

Grab samples and cores of sediment in Flathead Lake (Fig. 3) show well-oxidized sediment at the sediment-water interface. This upper, oxidized layer is forms a distinct light-yellowish brown band from several millimeters to a centimeter thick, at the top of most cores and grab samples. Beneath the oxidized layer, the sediment is reduced to light gray and contains streaks and laminae of black organics. Grain size analyses of both these layers were performed by seiving (sand fraction) and pipet analysis (silt and clay fraction). The resulting grain-size distribution is presented in figures 4 and 5.

The percentage of silt in surface sediments decreases systematically southward from the mouth of the Flathead River (Fig.4). Noticable highs in Polson Bay and on the east shore that deviate from this trend probably result from waves reworking shoreline sediment. The percent of clay in surface sediments show opposite trends to the distribution of silt. Clay content increases away from the source at the Flathead River because silt settles out first from the spring sediment plume and clays carried farther. Because of the differential settling within the plume. sediments in the northern half of the lake are silt rich (40-80%) and those in the southern half clay rich (greater than 60%).

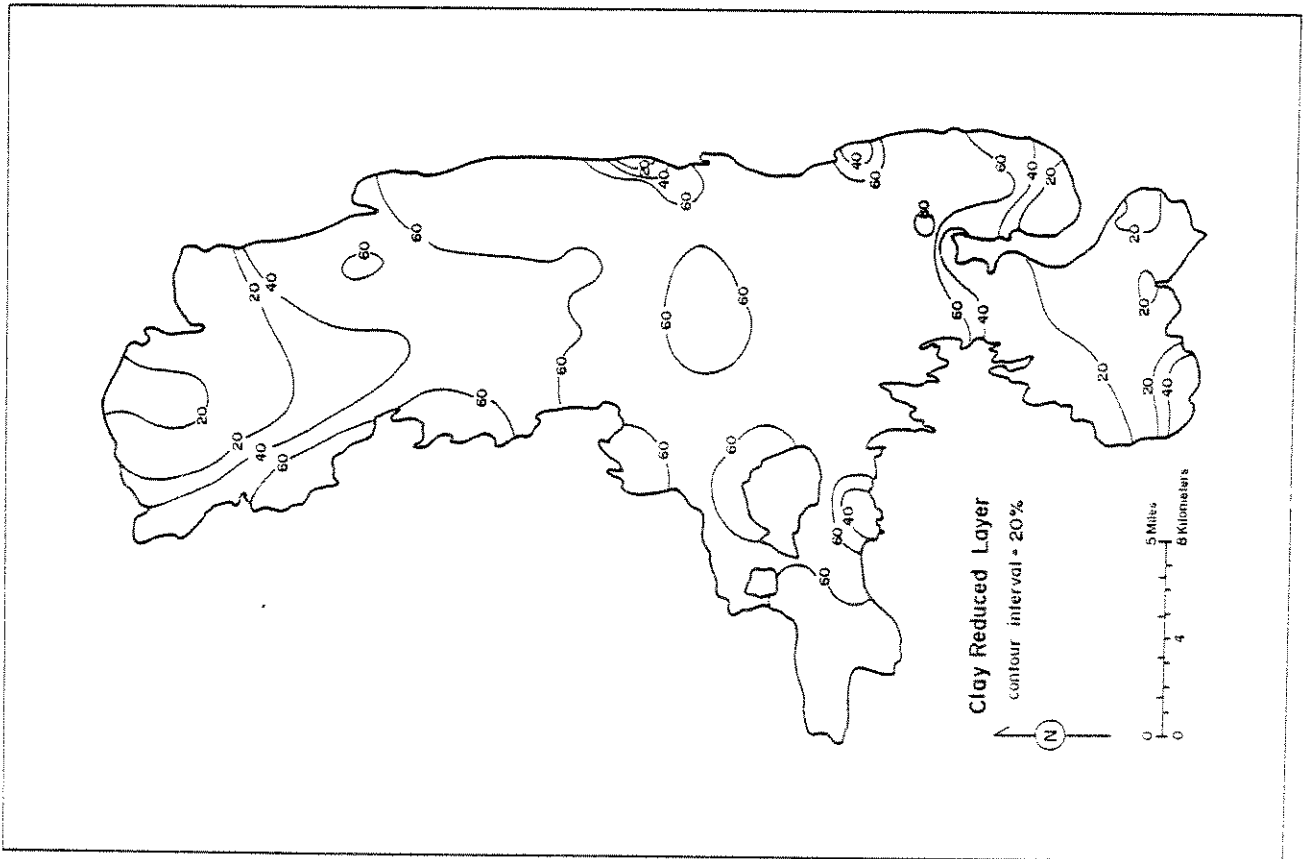
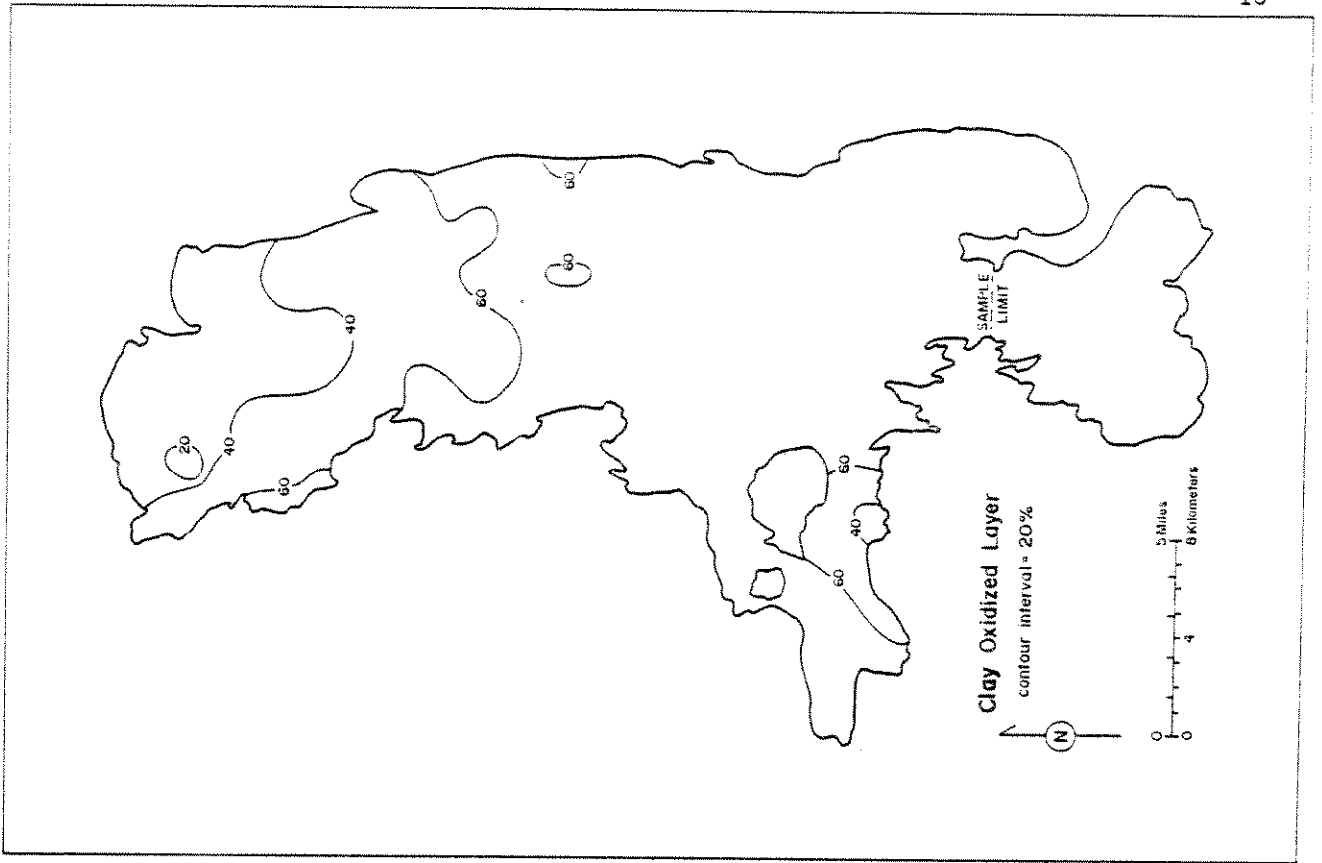


Figure 4

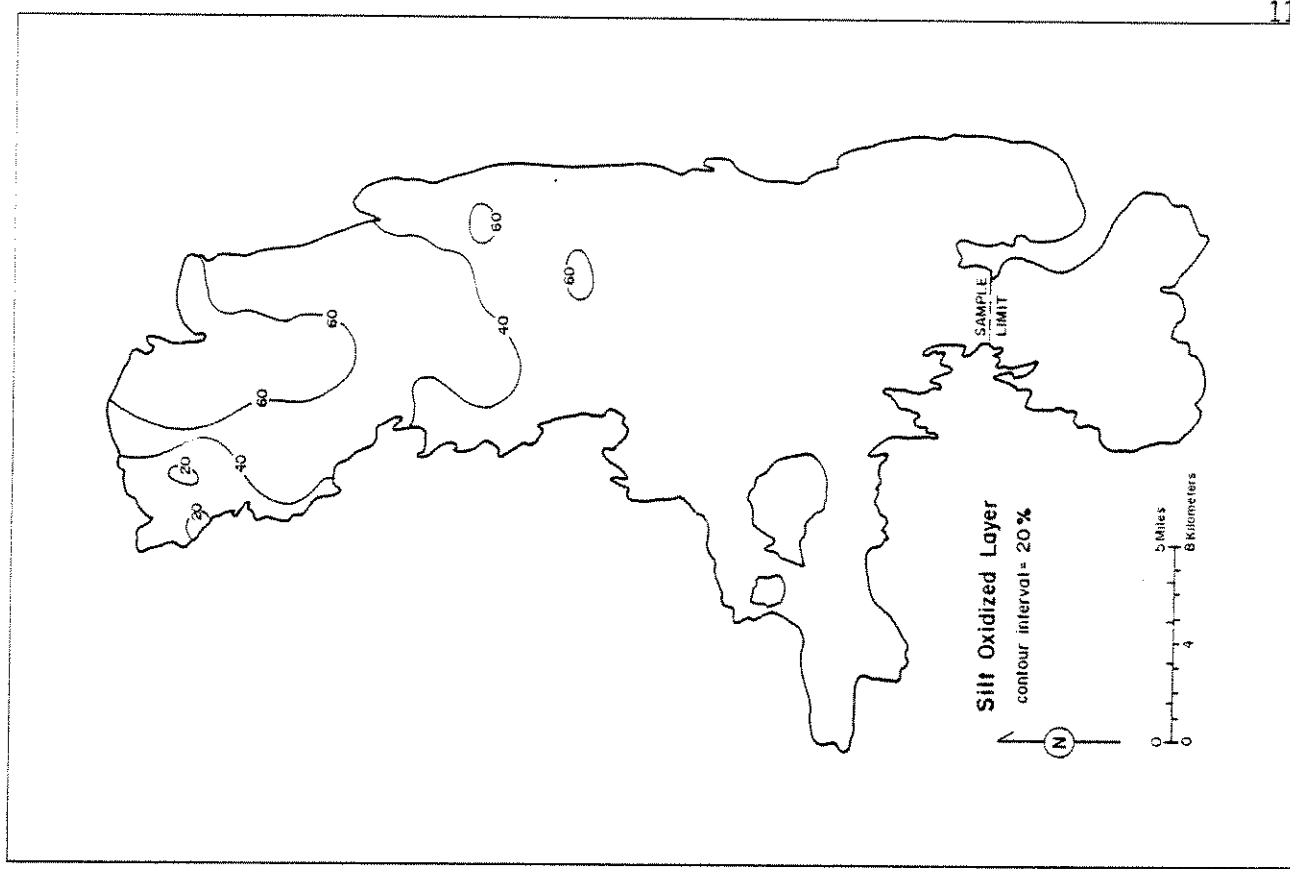
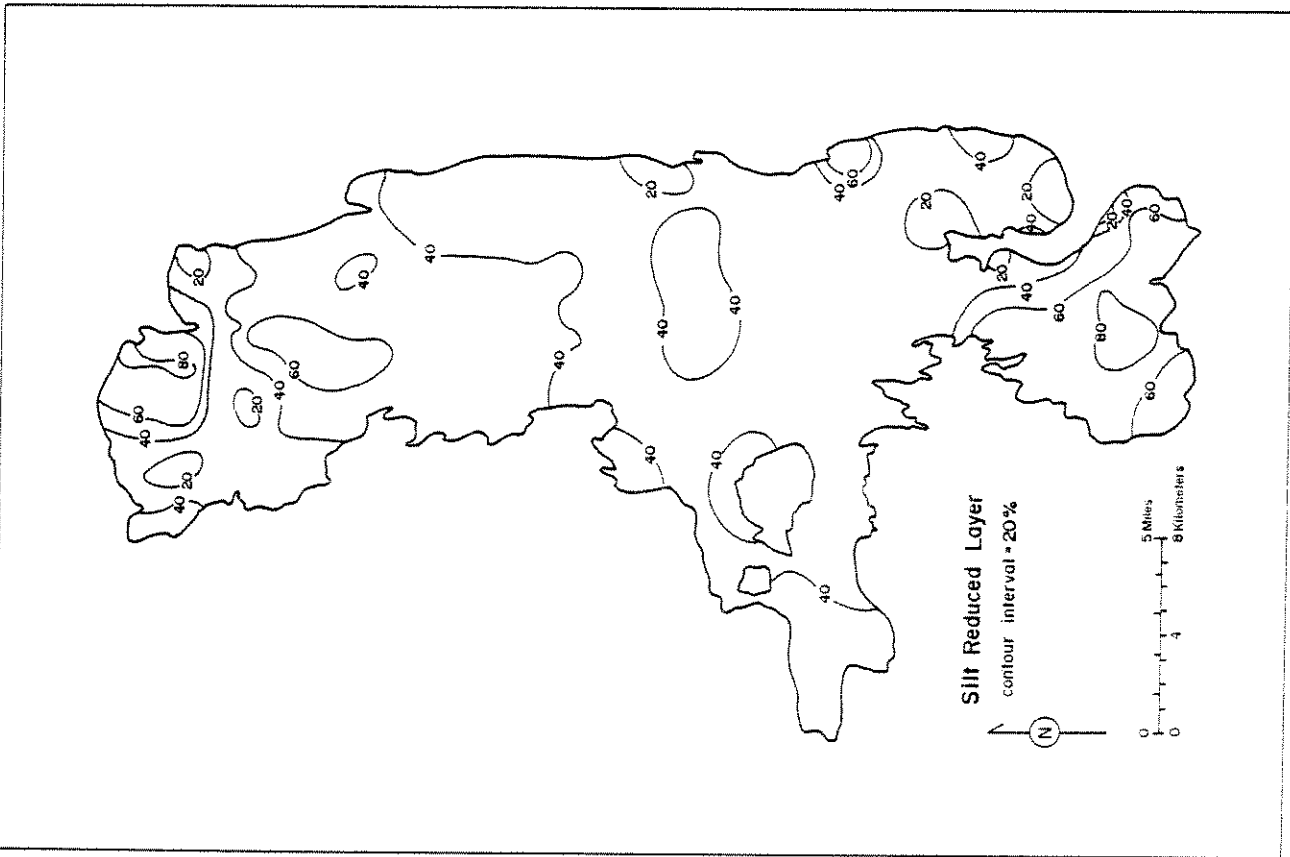


Figure 5



Sand and coarser-grained sediment is not controlled by the sediment plume but instead by river and wave processes. These processes are limited to shallow water so coarse-grained sediment accumulates only along the margin of the lake, on the delta and in shallow bays (eg., Polson Bay). Isolated grains and patches of sand and gravel are transported into deeper areas at the bases of steep slopes adjacent to shallow-water areas by gravity sliding and ice rafting.

The grain-size difference between surface oxidized sediment and the underlying reduced sediment is minimal (Fig. 6). However, oxidized sediment contains a slightly higher percent of silt than reduced sediment. A trace of sand accompanies this increase, even in localities far removed from a sand source. In smear slides of the coarse fraction of oxidized samples, volcanic ash makes up these coarser grains. Ash is absent, however, in reduced sediment. The ash is identical to that deposited by the May 1980 Mt. Saint Helens eruption when several millimeters of ash fell in and around Flathead Lake. The presence of Mt. Saint Helens ash accounts for the slightly coarser distribution in the oxidized layer which represents the most recent sedimentation.

During normal spring runoff sediment settles out from the spring plume. By mid-summer all this sediment has reached the bottom and the yearly algal bloom supplies organic material to the lake (Stanford, et al., 1981). This alternating sedimentation results in interlayers of silt-clay and organics. These laminae are generally less than 1mm thick and form a distinct rhythmic layering that records sediment influx and algal productivity. The organic and sediment laminae also contain

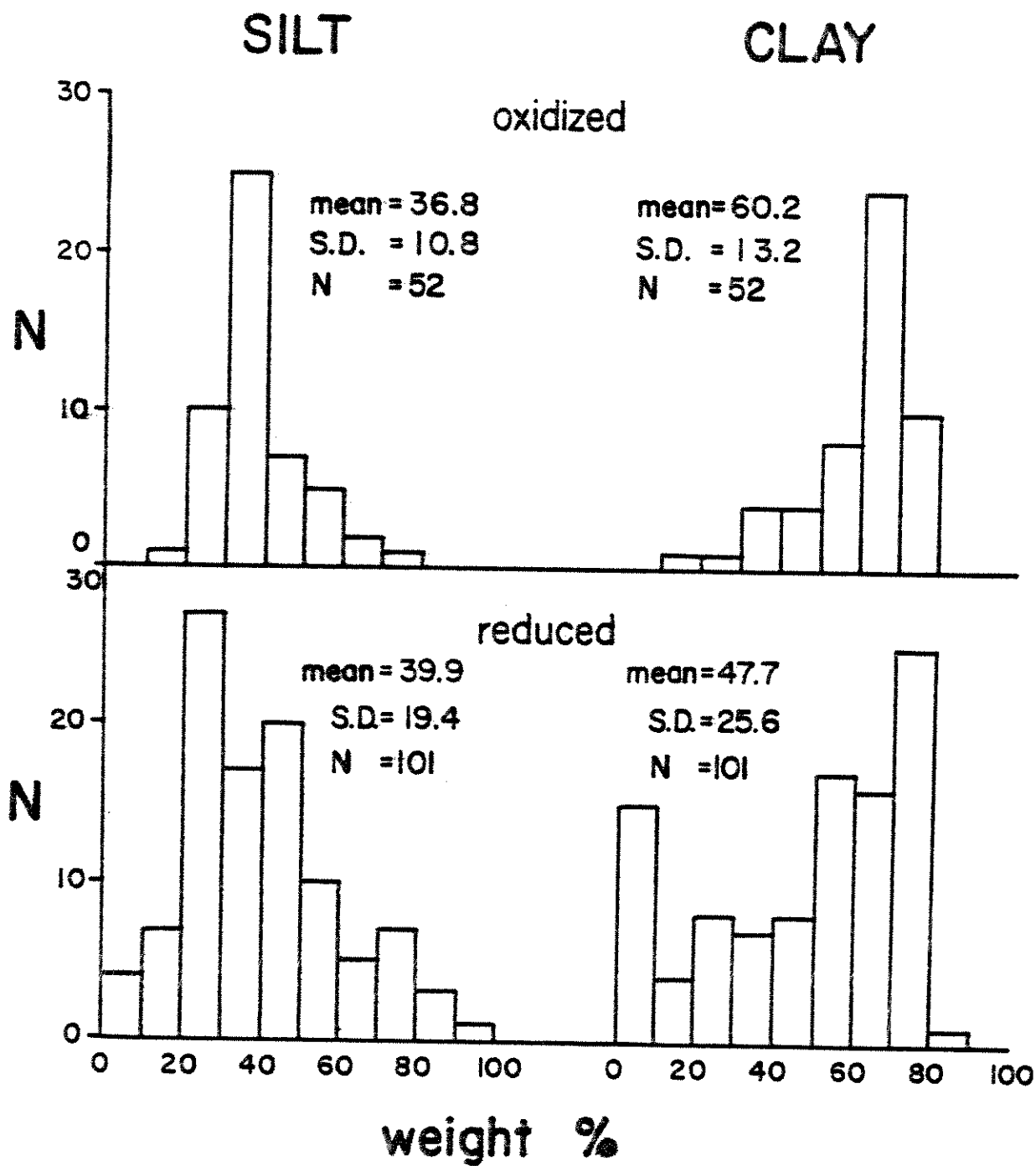


Figure 6

detritus washed in from the drainage. This material includes plant fragments and charcoal.

Unfortunately, the sediments do not continuously record yearly events because the spring plume often does not cover the entire lake, is non-existent or very small or may have more than one pulse. So, even though laminae are formed by periodic, annual processes, they are not proper varves and cannot be used to date sediment. In general though they record changes through time in both the lake and the drainage basin.

The thickness of sediment between distinct organic laminae increases downward in sediment collected by coring in the central lake (Fig. 7). This thickening is accompanied by an increase in the thickness of the organic laminae themselves, representing both a change in organic material and sediment supplied to the bottom through time.

Thickness and composition of laminae also vary laterally. Sediment accumulating on the western shelf, along the main path of the plume, contains thicker laminae than sediment on the east side of the lake. Sediment in the deeper areas on the eastern side of the lake, where the sediment plume reaches last, also contain slightly higher concentrations of organics. Sediment laminae also increase towards the delta as the grain size increases

Although suspension sediment in Flathead lake does not contain true varves they do contain ashes that are correlative to dated volcanic eruptions in the Cascade Range. In cores from the central lake, where sedimentation is fairly low, ash from Mt.

Depth (cm) from top of core

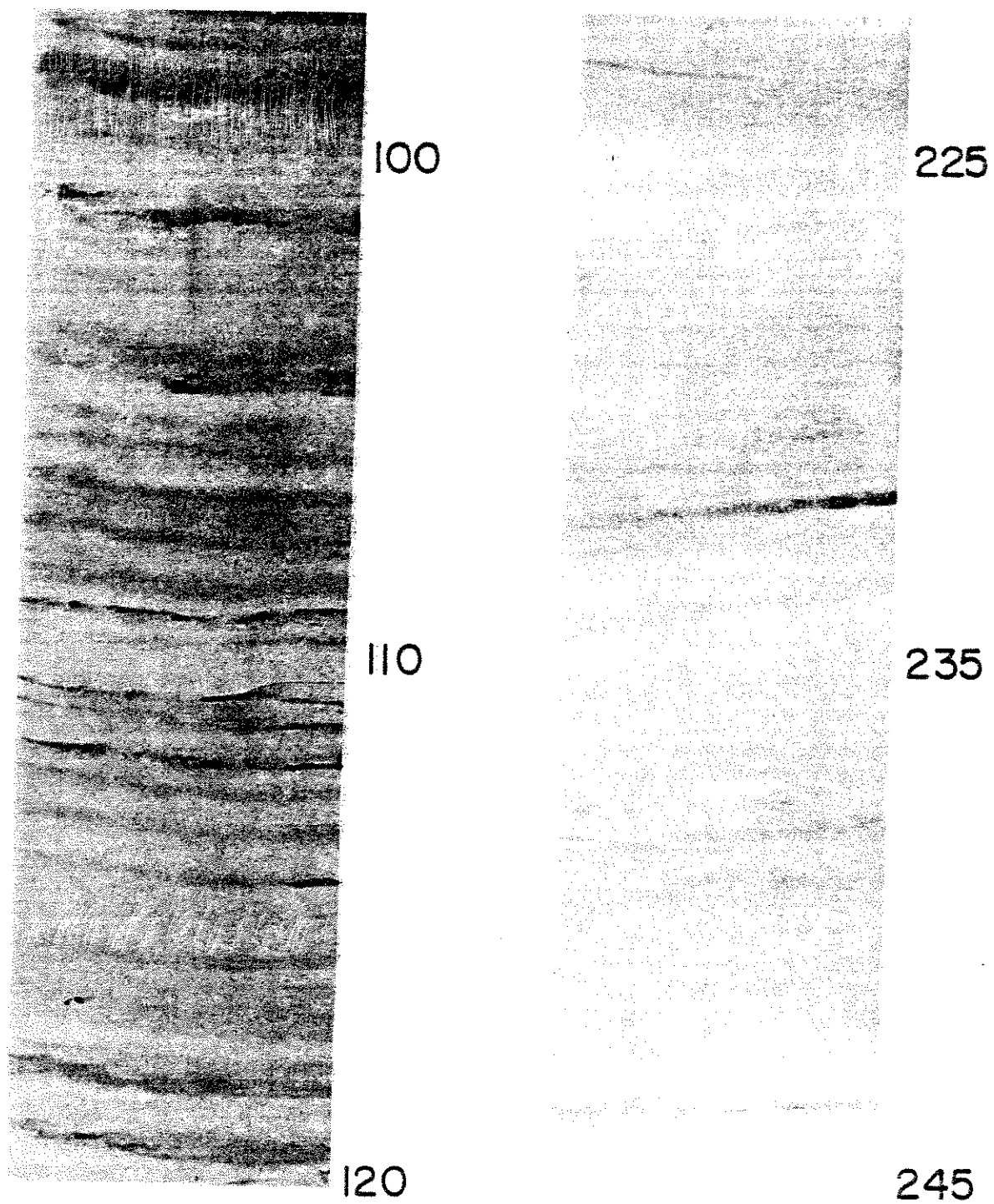
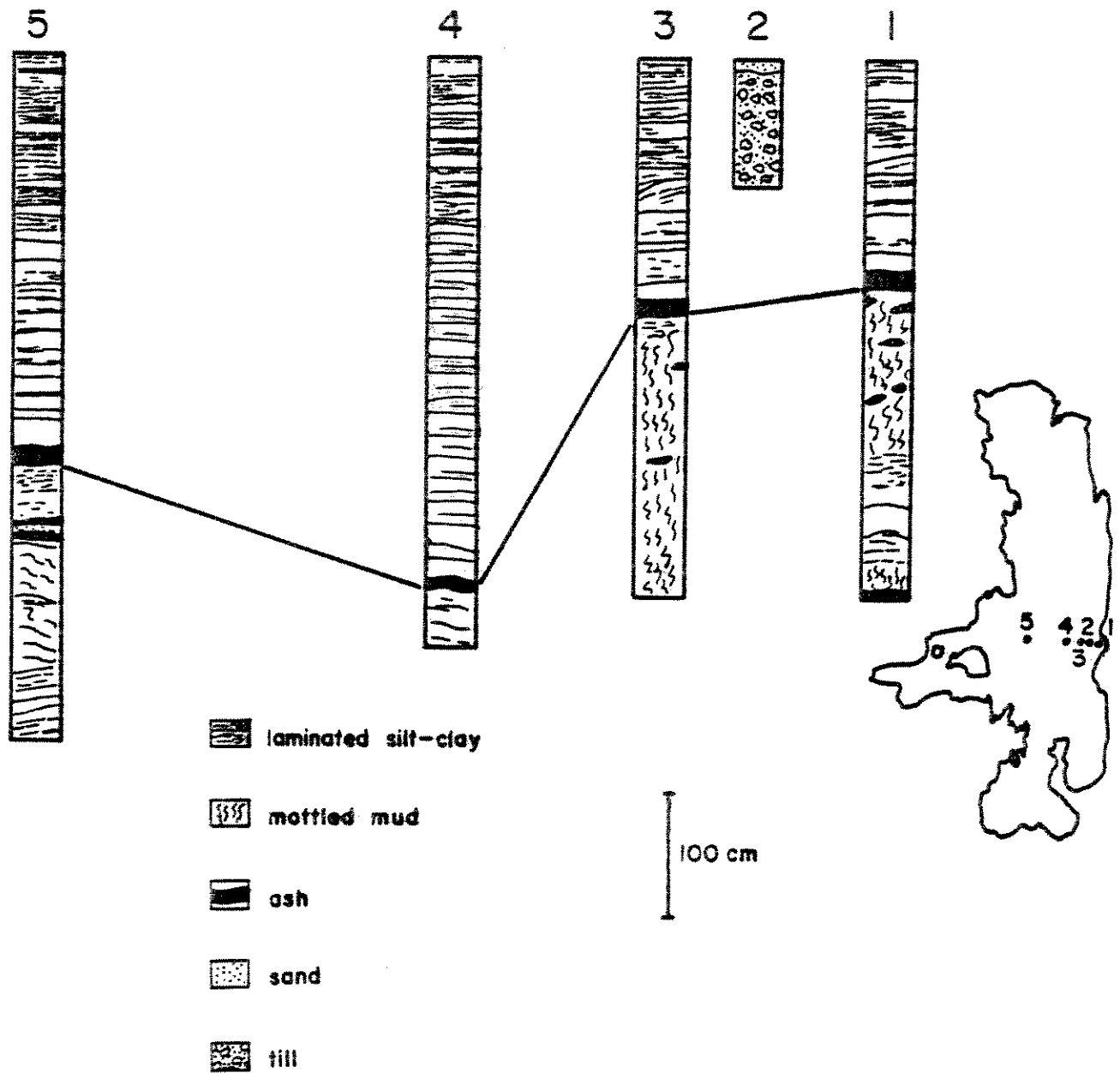


Figure 7

Figure 8  
Stratigraphy of Cores



Mazama (6600 years before present) was found at 1.8 to 3.3m below the surface (Fig. 8). The ash was deeper in cores from the western shelf where sedimentation rate averages 0.5 mm/year over the last 6600 years. In cores from the eastern trough, the rate of accumulation averaged 0.3 mm/year. These differences in sedimentation rate result from the path of the sediment plume.

Using these average sedimentation rates we can estimate the age of sediments accumulating under conditions similar to those in Flathead Lake today. Seismic profiles of Flathead Lake sediments show an undisturbed package of sediment from 2 to 9m thick (Fig. 9) overlying an older package of horizontal and/or disrupted sediment (Kogan, 1981). Assuming 0.3 to 0.5mm/year sedimentation rate, in most places this drape represents undisturbed sedimentation for approximately 12,000 to 30,000 years. This timing coincides well with the last withdrawal of Pinedale glaciers from the Flathead Valley (Stoffel, 1980) 12,000 to 14,000 years ago. Because sediments in cores from the drape have nearly identical characteristics throughout their length, they must have accumulated under very similar conditions. This data suggests that Flathead Lake developed its present configuration, both chemically and sedimentologically, approximately 12,000 to 14,000 years ago and has not changed appreciatively since.

Although the major processes affecting sedimentation have varied little since the lake formed, sediments recovered by deep coring reveal changes in relative quantities of organics and sediment through time. Older organic events (deeper in core) were larger (thicker organic laminae) and occurred less frequently

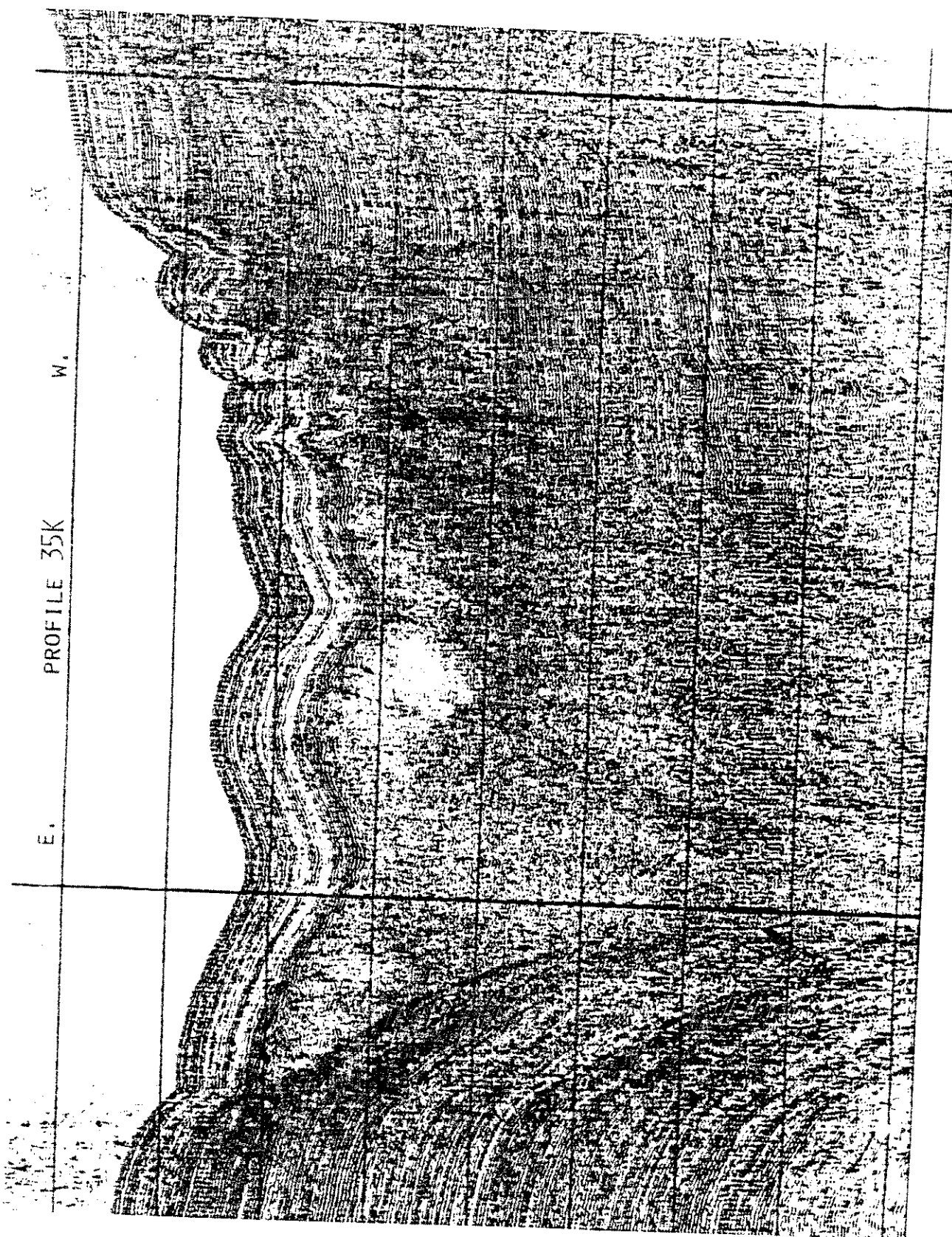


Figure 9  
Seismic Profile of Stratigraphic Units

(greater spacing). More recent deposition shows that more frequent and less voluminous events supplied organics to the lake. If the organic laminae formed entirely from algal blooms these differences suggest the productivity of the lake has evolved from fewer, larger blooms to more frequent, smaller blooms. The same characteristics could also be controlled by sediment influx. If sediment were supplied faster in the past and decreased more recently, then only the larger blooms would be preserved as organic laminae because the smaller ones would be mixed with the sediment. However, because the sediment laminae are thicker and the organic laminae are very distinct it seems likely that these older sediments record changes in lake productivity associated with climatic warming since the last glacial retreat. Suspension sediments also record more detailed changes as well as these general trends.

Throughout the lake shallow cores contain a distinct horizon at a depth of from 15 to 20cm below the sediment surface. The horizon is composed of a pinkish gray mud underlain by brown clay. Locally, an organic layer is sandwiched between these two layers. Assuming a sedimentation rate of 0.3 to 0.5mm/year, this horizon represents an event that occurred 400 to 500 years ago, which correlates to a well established climatic event in northwestern North America.

The climate of the Rocky Mountain region cooled approximately 500 years ago and alpine glaciers advanced in their valleys throughout the Northwest (Stoffel, 1980). This "mini ice age" led to more precipitation and erosion and hence more



sediment. Because open lake sedimentation is dominated by suspension sediment supplied by the Flathead River and other streams around the lake, these climatic changes were faithfully preserved in the sediment of Flathead Lake.

In summary, suspension sedimentation in Flathead Lake has continued since the formation of the present system initiated by the final retreat of Pinedale glaciers. Sedimentation is dominated by annual influx of sediment from the Flathead River and from algal blooms within the lake. These processes have changed only in relative magnitude over the last 12,000 to 14,000 years because sediment characteristics show no major modifications, but do record detailed climatic and productivity changes.

### Deltaic Sedimentation

The delta complex formed by the Flathead River as it flows into the north end of the lake covers over 20 square kilometers (including submerged portions). To the west of this active delta older deltaic deposits form an extensive submerged plain approximately half the size of the present active delta. This ancient delta formed when the Flathead River flowed into the lake along the western side of the Flathead graben. The river's shift to the eastern side of the valley to form the present delta possibly resulted from the rapid tilting of the graben and migration of the river until it met bedrock on the east (Stickney, 1980; Hlebicheck, 1981).

Deposits of the recent delta consist of interlayered fine- to medium-grained sand and mud. Sand layers are from 2 to 25cm thick with subordinate layers of mud from 1 to 3cm thick. Lakeward from the delta plain, percentage of mud increases and mud dominates the delta slope and prodelta sediments (Dobos, 1980). Sand supplied by the Flathead River is reworked by waves and transported lakeward forming a large, sandy delta plain. At the edge of this plain a sharp break in slope marks the front of the delta (Fig. 10). Slumps and turbidity currents carry sediment down this steep front into the deep eastern trough and onto the western shelf where it accumulates in a hummocky pile (Joyce, 1980; Kogan, 1981). The magnitude of this reworking is unknown but a significant amount of sediment is probably transported into deeper water by these processes.

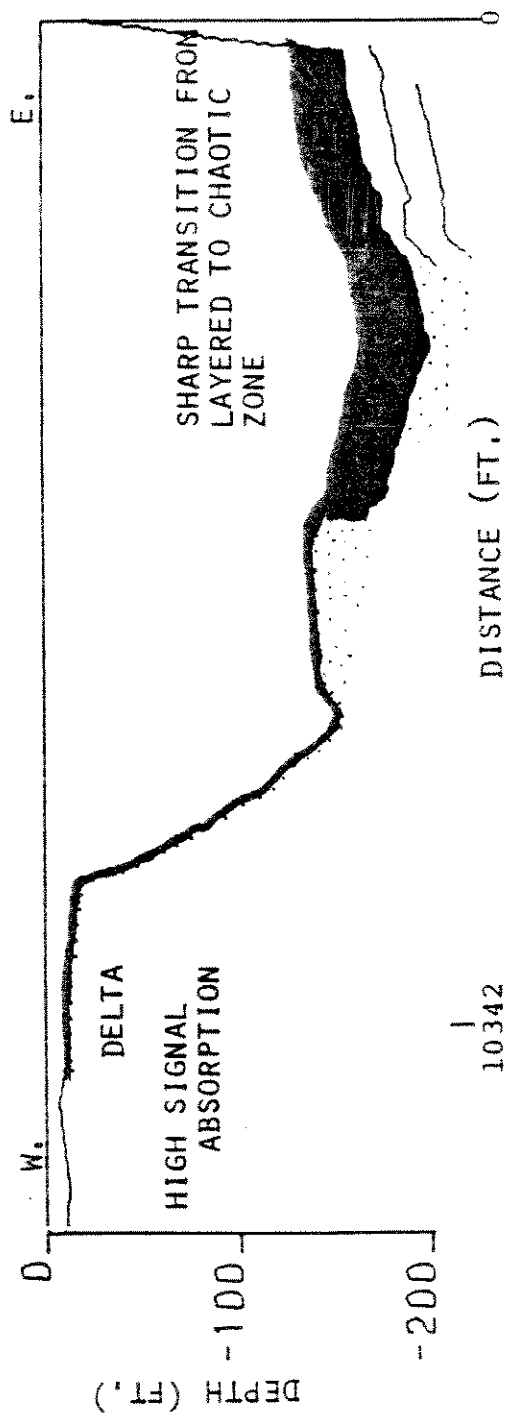


Figure 10

Flathead delta forms a large wedge of sediment that dominates sedimentation in the northern lake, but it has very few features characteristic of deltas forming in other temperate lakes. The form of lacustrine deltas is generally controlled by river processes because sedimentation always overpowers other lake processes. This results in deltas that fill their inlet with sediment so that complex channel systems develop on vegetated deltaic plains. These plains remain emergent throughout most of the year and flood only during maximum spring runoff, establishing excellent habitat for waterfowl and other wildlife. Although Flathead delta once contained all these characteristics it no longer does.

The vegetated portion of Flathead delta forms only a small percentage of the delta plain. At high water level (which is maintained throughout most of the year) a narrow cusp-shaped peninsula extends into the lake next to the Flathead River channel. When the lake level is lowered a broad sandy plain extends for 3 km into the lake away from this upper vegetated surface. So, the main active delta lobe is subaqueous and not covered with wildlife habitat. This odd morphology has developed in the last forty-four years and is not a natural situation for the lake (Fig. 11).

When Kerr Dam was built and lake levels controlled in 1939 the processes affecting the delta changed drastically. Before 1938 (Fig. 11) lake levels responded to yearly runoff, staying low during most of the year and then raising briefly during the spring runoff. The delta plain formed a large vegetated lobe

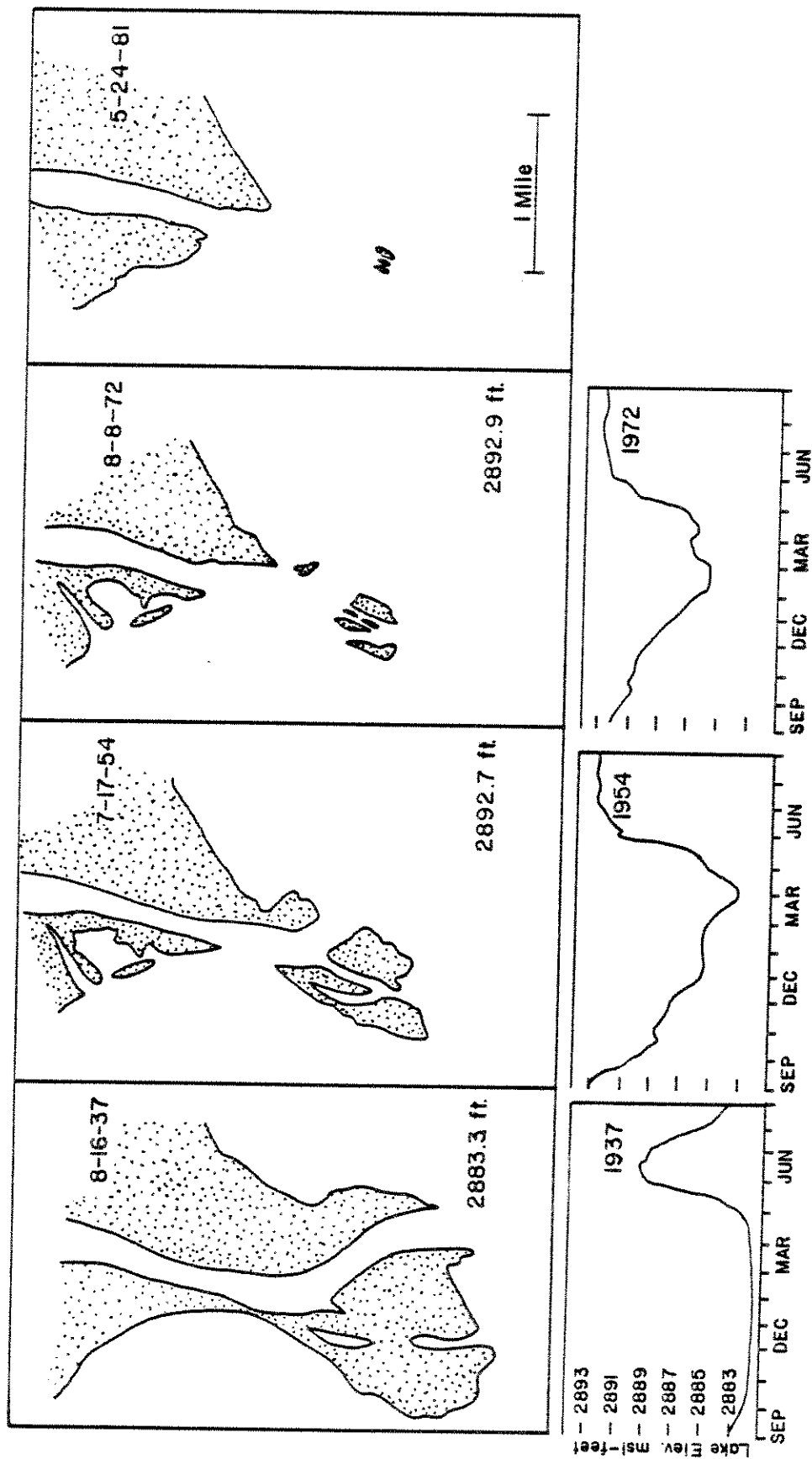


Figure 11

extending into the lake and flooded only during the spring. Low lake levels and the forested surface protected the lobe from destruction by fall and winter storm waves. Since 1938 artificially high lake levels have allowed storm waves to erode the delta plain. The waves transport sand lakeward, forming the broad submerged sandy delta plain, and mud to the open lake. These processes have removed up to 1.5 m of sediment vertically from the delta plain and reduced the vegetated area from 10 to less than 2 square kilometers. This erosion has significantly reduced the wildlife habitat on the delta since the construction of Kerr Dam and in the last three years has destroyed at least two osprey and one bald eagle nesting sites as well as many goose and duck nesting. Skeletons of tree stumps are the only remains of this once extensive habitat.

Summary

We can make several generalities based on the data collected from grab samples and cores of Flathead Lake sediment:

- 1) Sedimentation in the lake is dominated by suspension sediment supplied by the spring sediment plume.
- 2) Sediment at the sediment-water interface is oxidized, that below reduced.
- 3) Sedimentation rates average from 0.3 to 0.5 mm/year with higher rates of accumulation on the western side of the lake.
- 4) Similar processes have acted in the lake for the last 12,000 to 14,000 years, since the last retreat of Pinedale glaciers.
- 5) Since the formation of the present lake system, input of organic sediment has become more regular and shorter lived, presumably the result in changes of productivity.
- 6) Erosion of the delta results from artificially high lake levels which has drastically decreased the habitat available for wildlife.
- 7) Some unknown amount of sediment is reworked by wave action on the delta plain and along the shoreline.

Within this system heavy metals and nutrients are collecting along with sediment and organics. Grain size distribution and sediment composition affect the storage and migration of metals and nutrients within the sediments, so the sedimentary framework presented in this chapter is important in considering the metals and nutrient models considered in subsequent chapters.

Chapter Two

HEAVY METAL DISTRIBUTION IN THE SEDIMENTS  
OF FLATHEAD LAKE, MONTANA

by  
Christopher J. Murray

Presented in partial fulfillment of the requirements for the degree of

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## INTRODUCTION

Flathead Lake is a large freshwater lake, covering 462.3 sq. km. in the Rocky Mountains of northwestern Montana (Potter, 1978). The drainage basin of the lake occupies 18,400 sq. km. (Potter, 1978) in Montana and southeastern British Columbia (Fig. 1). Argillites, quartzites, and carbonates of the Proterozoic Belt Supergroup dominate the bedrock geology of the drainage basin. Cultural development of the basin has been slow, with a small population, and an economy based on logging, farming, and catering to the tourist industries. Flathead Lake is the largest natural freshwater lake west of the Mississippi River (Joyce, 1980). Considering its size and long history of use, the lake remains largely unpolluted.

Recently, however, development in the drainage basin has increased dramatically. Exploration for coal, oil and gas are underway throughout this part of the Rocky Mountain Overthrust belt. Development of known energy resources has either begun, or is in the planning stage. For example, Rio Algom Ltd. has applied for permission to begin strip mining coal at its Cabin Creek property on a tributary of the Flathead River in British Columbia. Minerals companies have been exploring the drainage basin for base and precious metals, economic deposits of which have been found in the sedimentary rocks of the Belt Supergroup west of the Flathead Lake drainage basin. These activities, along with the general trend of population growth in the

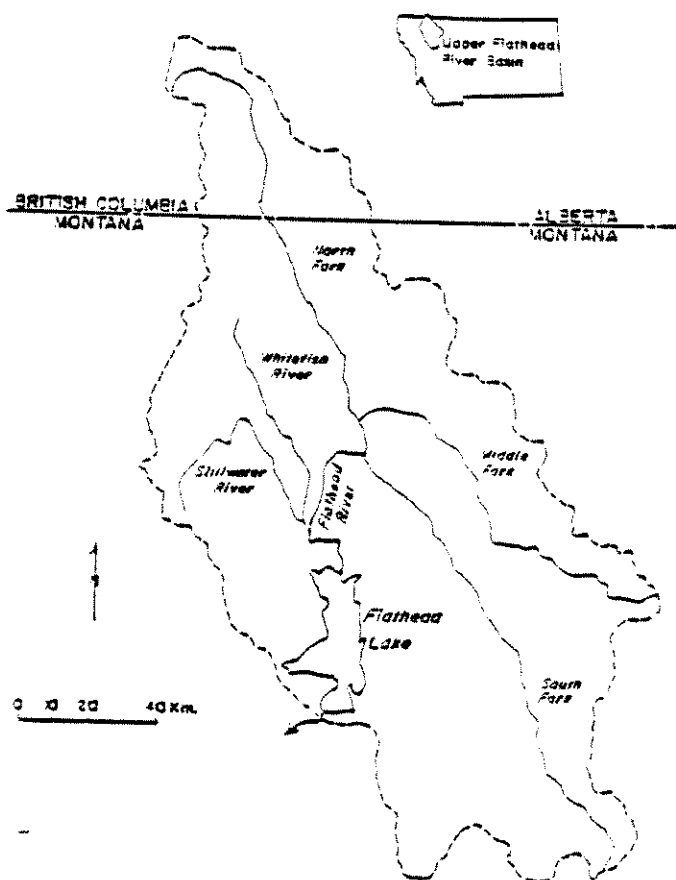


Fig. 1. Location of watershed draining into Flathead Lake.

Rocky Mountains, have increased residential pressure on the area, with concomitant increases in sewage, automotive pollution, and erosion (Potter, 1978).

The study of sediment metal contents has been used previously to monitor the environmental health of aquatic systems (Forstner, 1982b; Crecelius et al., 1975; Goldberg et al., 1981). The study of extractable metals is particularly applicable. Extractable metals reflect the metal content of the sediment that is readily available to the biota. The purpose of this study was to document the present levels of extractable Fe, Mn, Cu and Zn in the lake sediments, and to interpret the geochemical factors controlling their distribution. That knowledge may be useful to future researchers in studies of Flathead Lake and its drainage basin, and in monitoring the effects of present and future development.

## METHODS

### Sampling and Preparation

Sampling was performed at 110 sites during the summers of 1980 and 1981 (Fig. 2). Surface sediment samples were taken with a Peterson clamshell dredge. Wherever possible, subsamples were taken from the upper oxidized sediment layer, and the lower reduced layer. These layers were recognized by a distinctive color change from gray in the reduced layer to a rust brown color in the oxidized layer (Price, 1976; Berner, 1981). The separation of these subsamples was usually not possible in coarser, sandy areas, such as the Flathead River delta. The samples were stored in clean polyethylene containers, and refrigerated at approximately 4° C.

### Extraction

After drying, the samples were extracted with a solution of 20% acetic acid. The metals released by this extraction are weakly bound to the sediment, for example, in pore water, cation exchange sites and carbonates, and physically adsorbed to mineral and organic sediment. The metals bound in this fashion are assumed to be readily available to the biota if the chemical environment of the sediment changes (Skei and Paus, 1979). The extraction was performed by placing one gram of sediment with 25 ml of 20% acetic acid in a Nalgene Screw-Cap test tube, which was then placed on a mechanical shaker for 12 hours. After centrifuging, the supernatant was decanted into Nalgene bottles, which were kept at 4° C until the samples were analyzed.

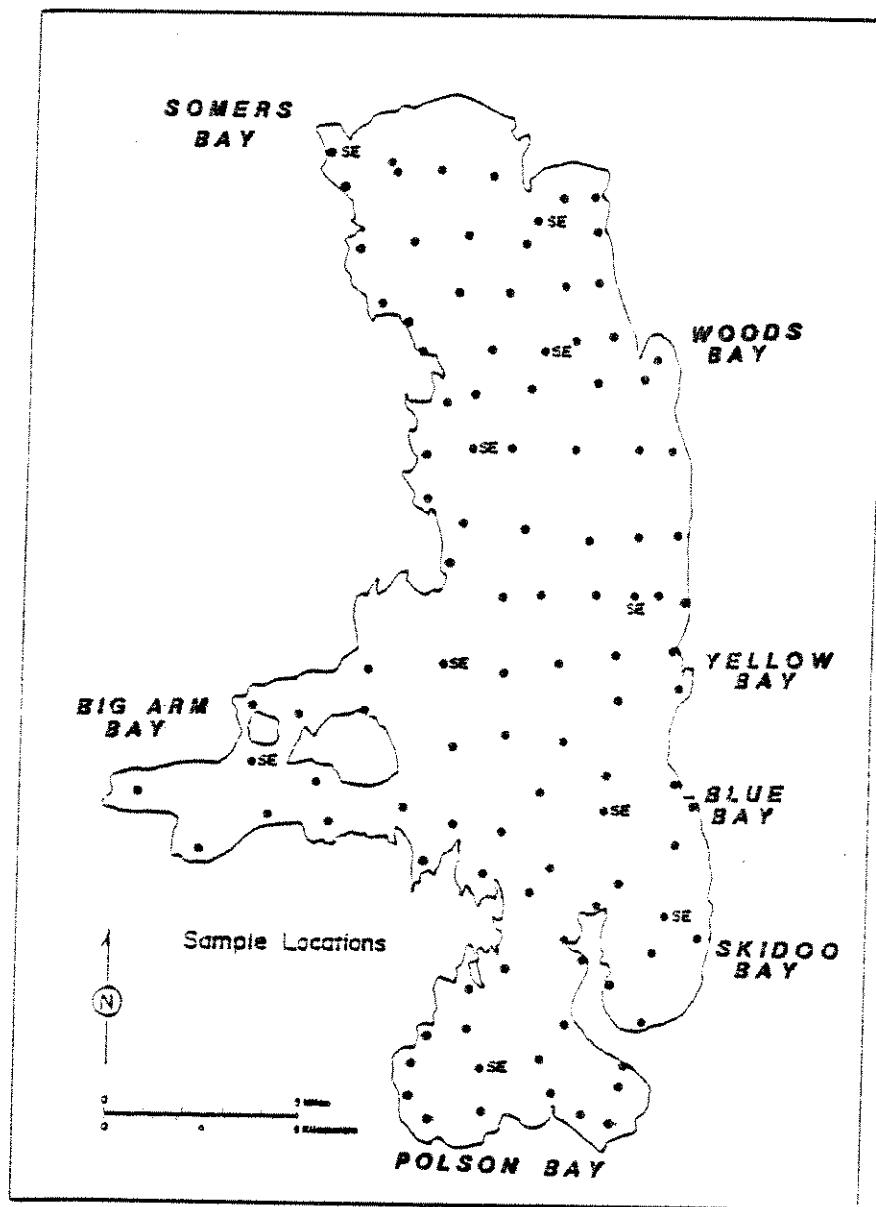


Fig. 2. Sample locations in Flathead Lake. Samples taken at sites marked SE were sequentially extracted (see text).

### Sequential Extraction

A small number of the samples (Fig 2) were selected for a sequential extraction (Chester and Hughes, 1967; Gupta and Chen, 1975; and Forstner, 1981). The extraction scheme used in this study was a simple, two step extraction.

The first step was identical to the acetic acid extraction previously described. After the sample was centrifuged, the residue was washed and dried, and a 0.25 gm. subsample was taken. The subsample was fused with 1.25 gm. of sodium carbonate in a platinum crucible at  $1100^{\circ}\text{C}$  for 15 minutes, and then dissolved with 5.0 ml. of concentrated nitric acid and deionized water. The resulting solution was then diluted to 50.0 ml. (Jeffery, 1975).

The second step of the extraction process removes residual metals that are more tightly bound to the sediment than the metals removed in the acetic acid extraction. These residual metals include metals bound in silicate lattices, coprecipitated in oxide phases that are not readily reducible, and metals that are tightly bound to organic materials. The metals bound in this fraction should not be available to the biota, under most conditions.

### Analysis

Solutions were analyzed for Fe, Mn, Zn, and Cu using a Perkin-Elmer 5000 atomic absorption spectrophotometer in flame mode, using the standard analytical conditions for that machine (Perkin-Elmer,

1976). Reagent blanks were prepared and duplicates or spikes of every fifth sample were analyzed. Standard solutions were made up with compositions that duplicated those in the sample solutions. Reagent grade materials were used throughout.

#### Other Analyses

Besides the metals analysis, samples were analyzed for extractable and total phosphorus (both organic and inorganic), total carbon, nitrogen, hydrogen, and grain size, and for the mineralogy of the sand, silt, and clay size fractions. Statistical analysis of the data was performed using the SCSS software package (Nie et al., 1980).

## RESULTS

### Iron

Extractable Fe in the oxidized sediment layer has a mean of 3820 ppm (S.D.=1200, N=70). In the reduced layer the mean is 3430 ppm (S.D.=1530, N=110). Results of the sequential step extraction indicate that only a small percentage of the total Fe is extractable (Fig. 3). In the oxidized layer an average of 7.7% is extractable, and in the reduced layer, 7.3%.

The average total Fe in the sediment samples that were sequentially extracted (Fig. 3) is very close to the average recent lake sediment value (43,000 ppm), and to the global shale standard (46,700 ppm) (Forstner, 1981a, p. 136).

Contour maps of the distribution of extractable Fe data for oxidized and reduced layers show that the highest concentrations of extractable Fe occur in four different areas (Fig. 4). In two of these areas (northeast and southwest areas of Big Arm Bay) we found crusts of nodular Fe similar to those found by Cronan and Thomas (1972) in the Great Lakes, and to cases reported by Calvert and Price (1977). These crusts form a hard pavement at the sediment-water interface. A Peterson dredge with attached lead plates, weighing nearly sixty pounds, had difficulty penetrating the crust. The crusts appear to have a lateral extent of about 20 square meters. They grade into areas



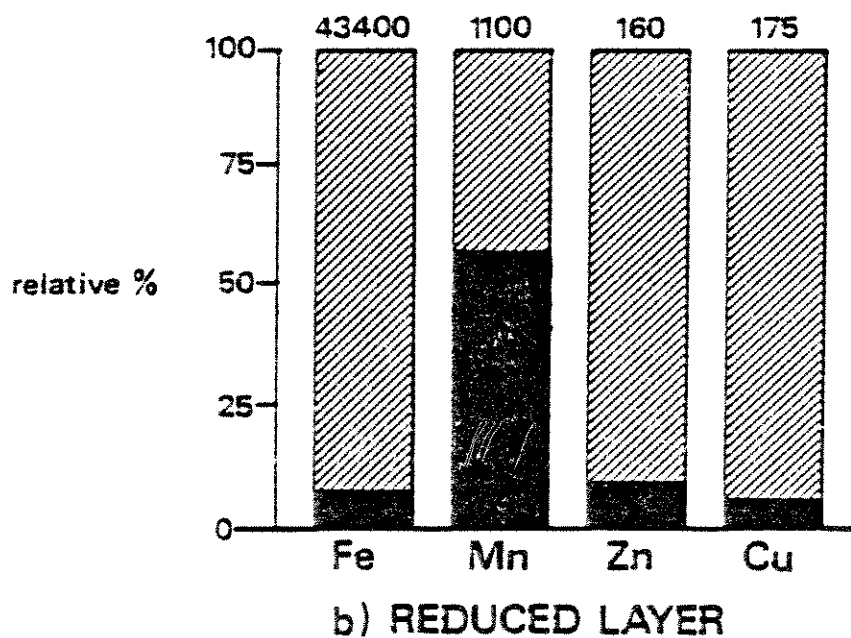
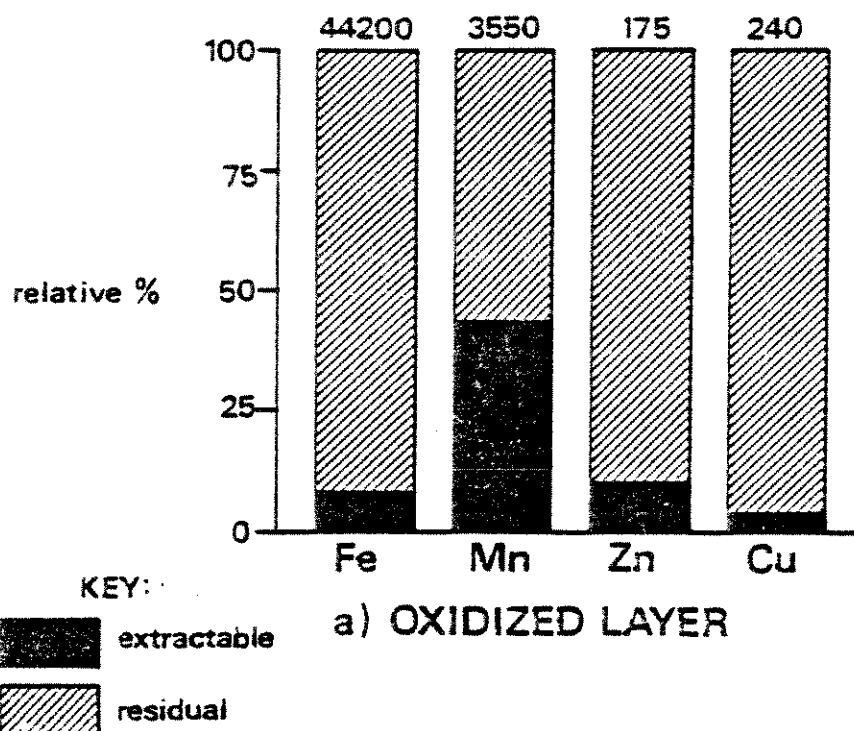


Fig. 3. Histogram depicting results of the sequential extractions for the oxidized and reduced layers. At the top of each bar, the average total amount of each metal is posted, in parts per million.

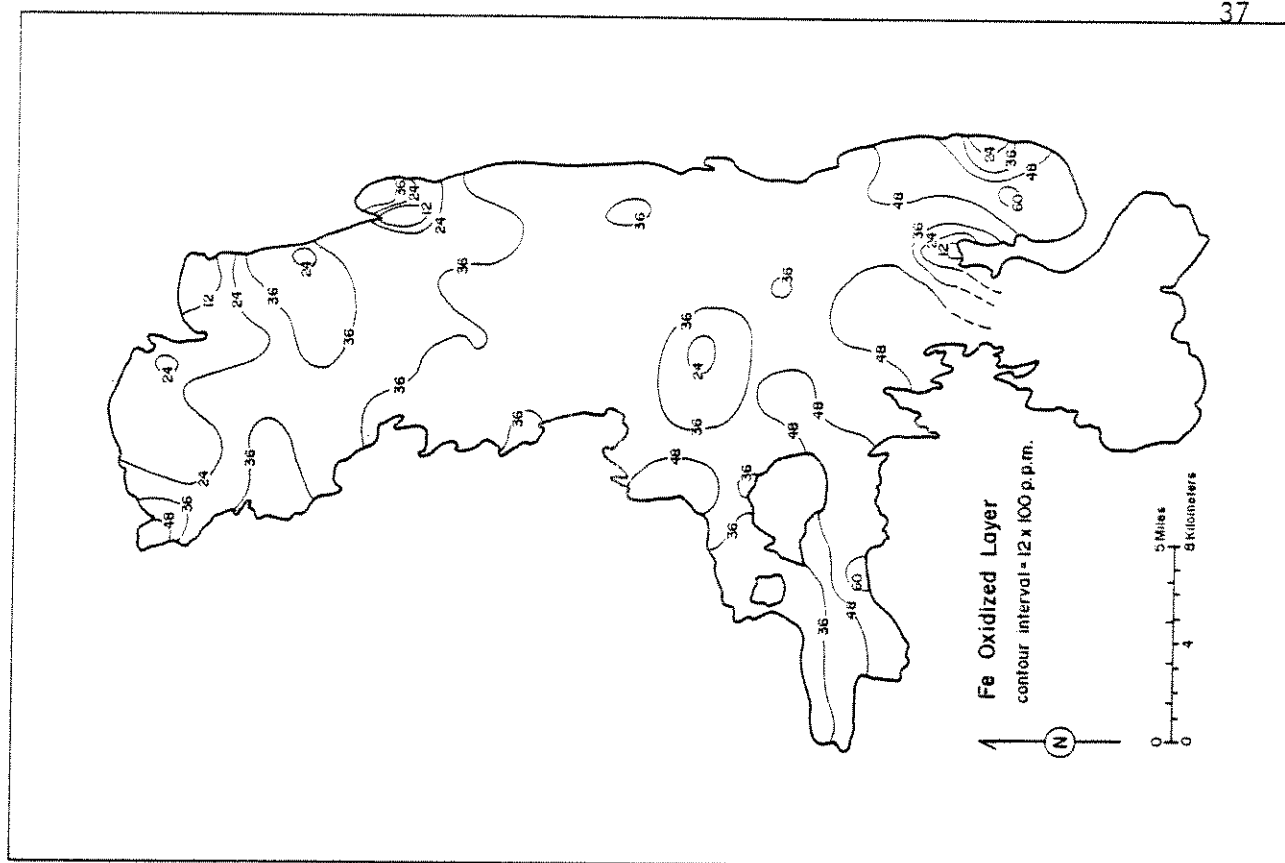
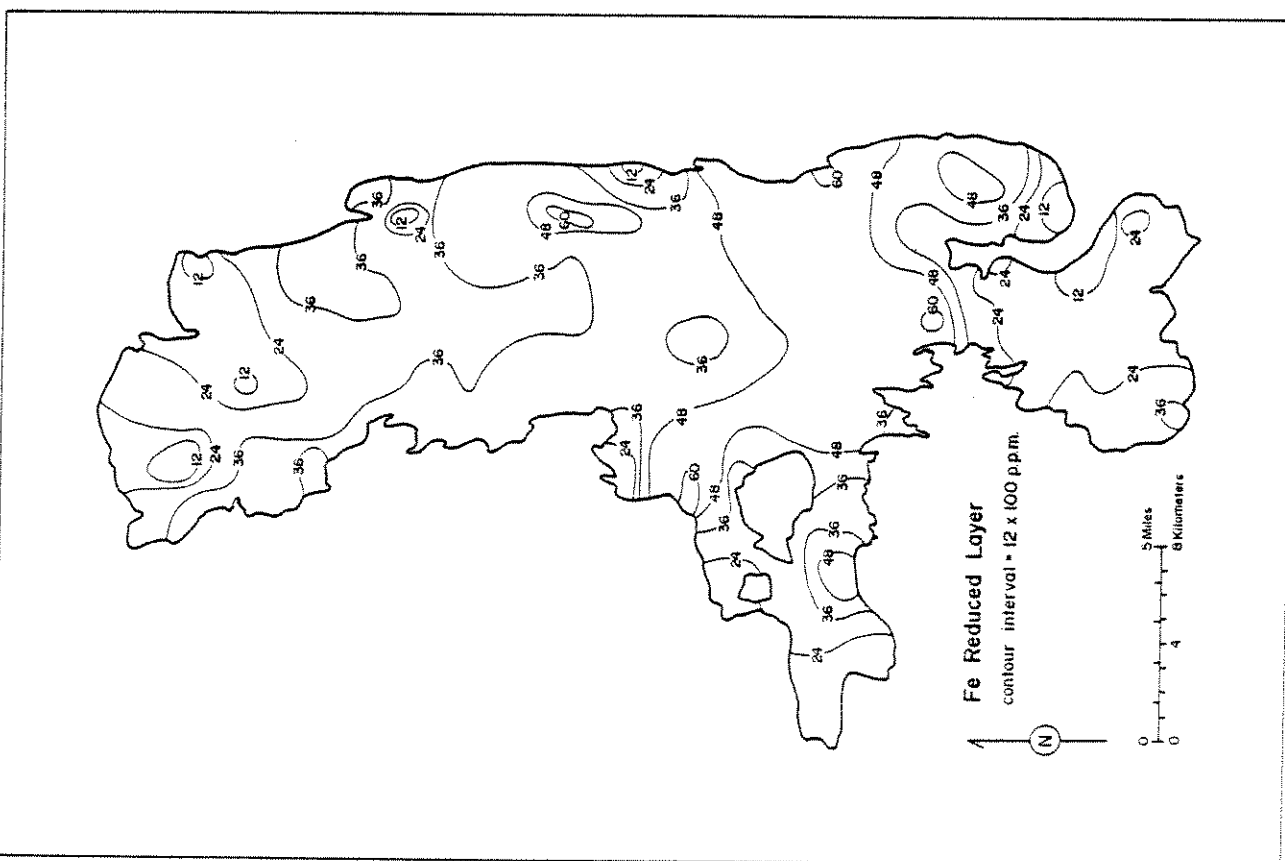


Fig. 4. Contour maps of the distribution of extractable Fe in the reduced (a) and oxidized (b) layers. Contour interval is 1200 ppm.

where smaller discontinuous nodules (down to sand size) are present. Pieces of the crust react violently when treated with hydrogen peroxide, indicating that they may be bound by an organic matrix.

In the other two areas where high Fe concentrations were found (in southeastern Big Arm Bay and the area along the southeast shoreline extending into Skidoo Bay) no Fe nodules or crusts have been located.

#### Manganese

Extractable Mn is enriched in the oxidized layer of the surface sediments (Fig. 5). The average Mn content of the oxidized layer is 1590 ppm (S.D.=1000), while that of the reduced layer is 810 ppm (S.D.=780). A more detailed comparison of the extractable Mn in the oxidized layer versus that in the reduced layer was made on 70 samples for which both oxidized and reduced subsamples were available. In these samples, 83% of the oxidized layers contain at least 10% more extractable Mn than the reduced layers (Fig. 6).

The sequential extraction shows that a much higher proportion of the total Mn is extractable, relative to Fe (Fig. 3). The mean for the oxidized layer is 43.5%, while in the reduced layer an average of 57.3% of the total Mn is extractable.

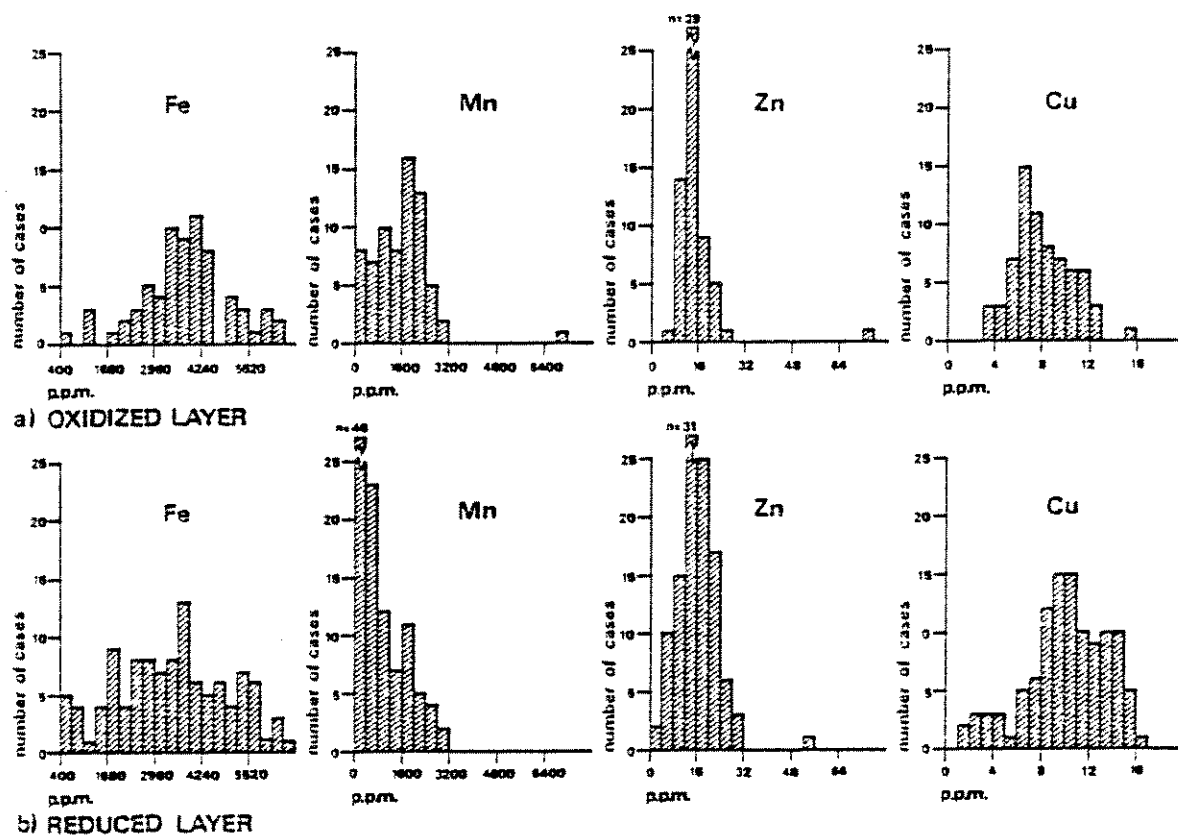


Fig. 5. Histograms of the acetic acid extractable metal concentrations in the oxidized and reduced sediment layers.

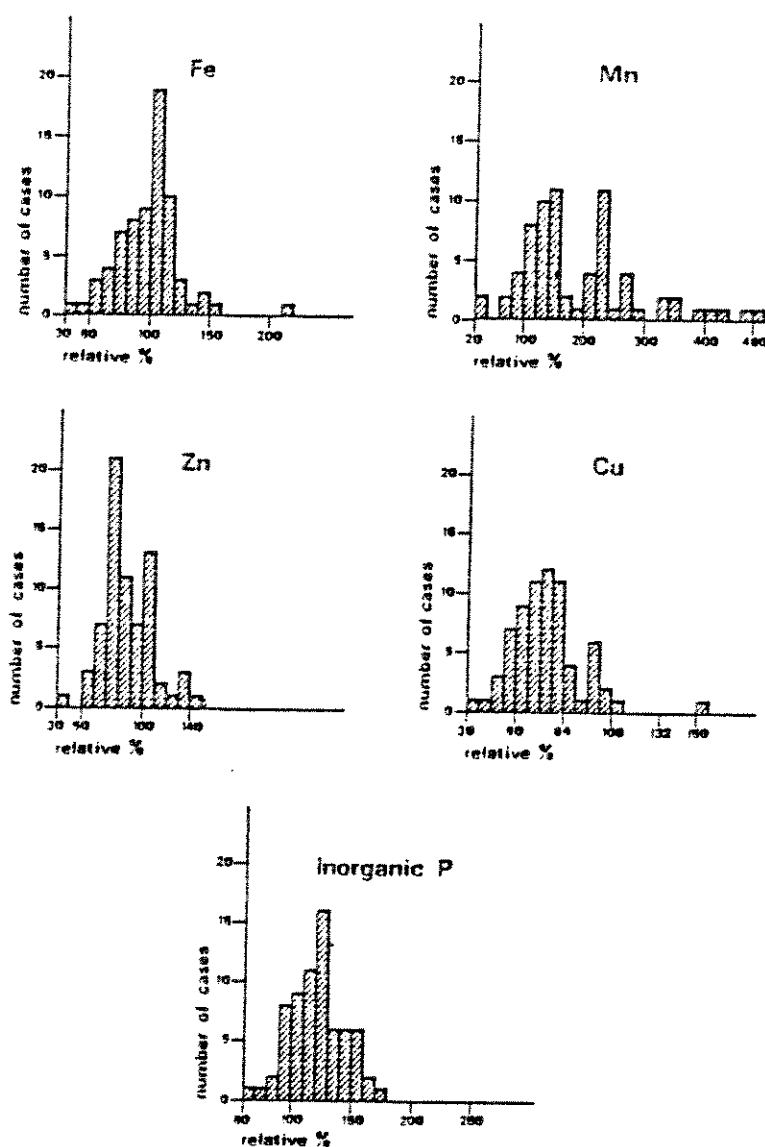


Fig. 6. Histograms portraying comparisons of the amount of extractable material in the oxidized layer to that in the reduced layer, where both subsamples were available at the same sampling site. The relative % was calculated as follows: (Concentration of extractable element in the oxidized layer divided by concentration of extractable element in the reduced layer)  $\times$  100%.

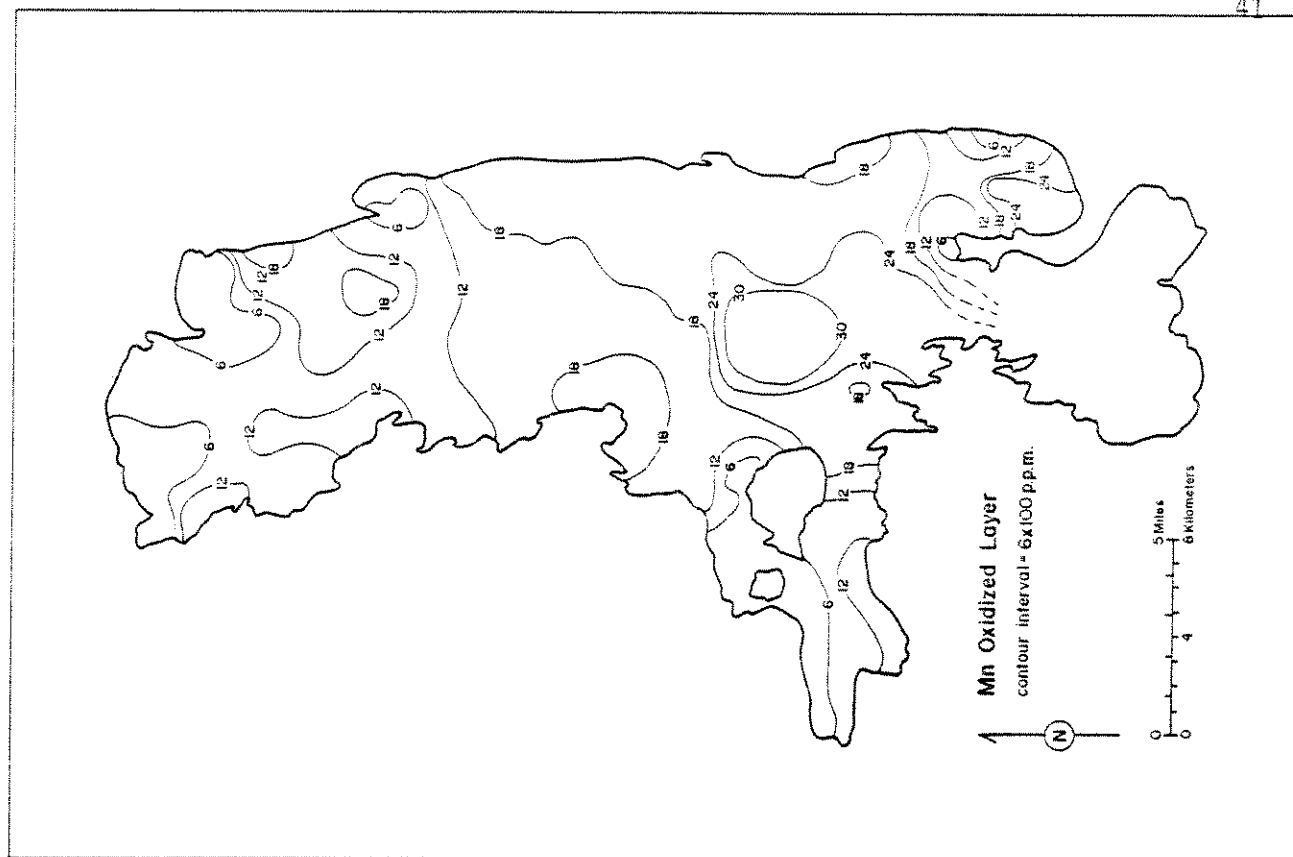
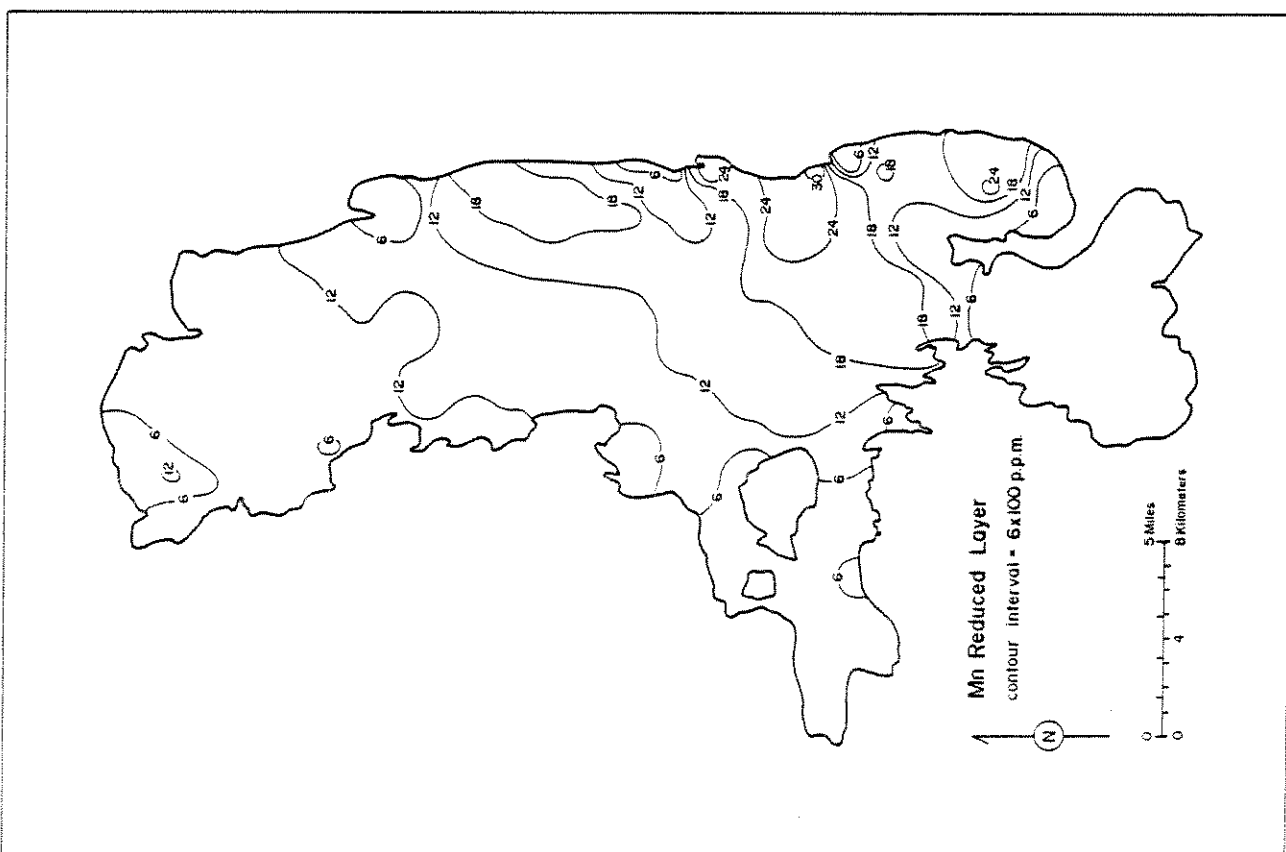


Fig. 7. Contour maps of the distribution of extractable Mn in the reduced (a) and oxidized (b) layers. Contour interval is 600 ppm.

Comparison of the total Mn measured in the sequential extractions (Fig. 3) with other recent lake sediments (Forstner, 1981a) indicates that Mn in Flathead Lake sediments exceeds both the average values (750 ppm) and the range (100-1800 ppm). Forstner (1981a) states, however, that Mn has a wider variation in values than most elements, due to its diagenetic mobility, so high values of Mn are not surprising.

### Zinc

Extractable Zn in the oxidized layer averages 15.1 ppm (S.D.=7.7). In the reduced layer, the mean is 15.9 ppm (S.D.=6.9). A detailed comparison of oxidized and reduced layers from the same samples reveals a systematic enrichment of Zn in the reduced layer. 61.4% of the samples contain at least 10% less extractable Zn in the oxidized layer than in the reduced layer.

The extractable portion of the total Zn present was low (Fig. 3), averaging 10.1% in the oxidized layer, and 9.6% in the reduced layer. The total Zn recoverable in the sequential extraction fell within the range of 87 recent lake values reported by Forstner (1981a).

The area with the highest concentration of Zn is in Somers Bay (Fig. 8), where the concentrations of extractable Zn are 3-5 times higher than the average concentrations. Most of the other locations containing higher than average Zn values are also near developed sec-

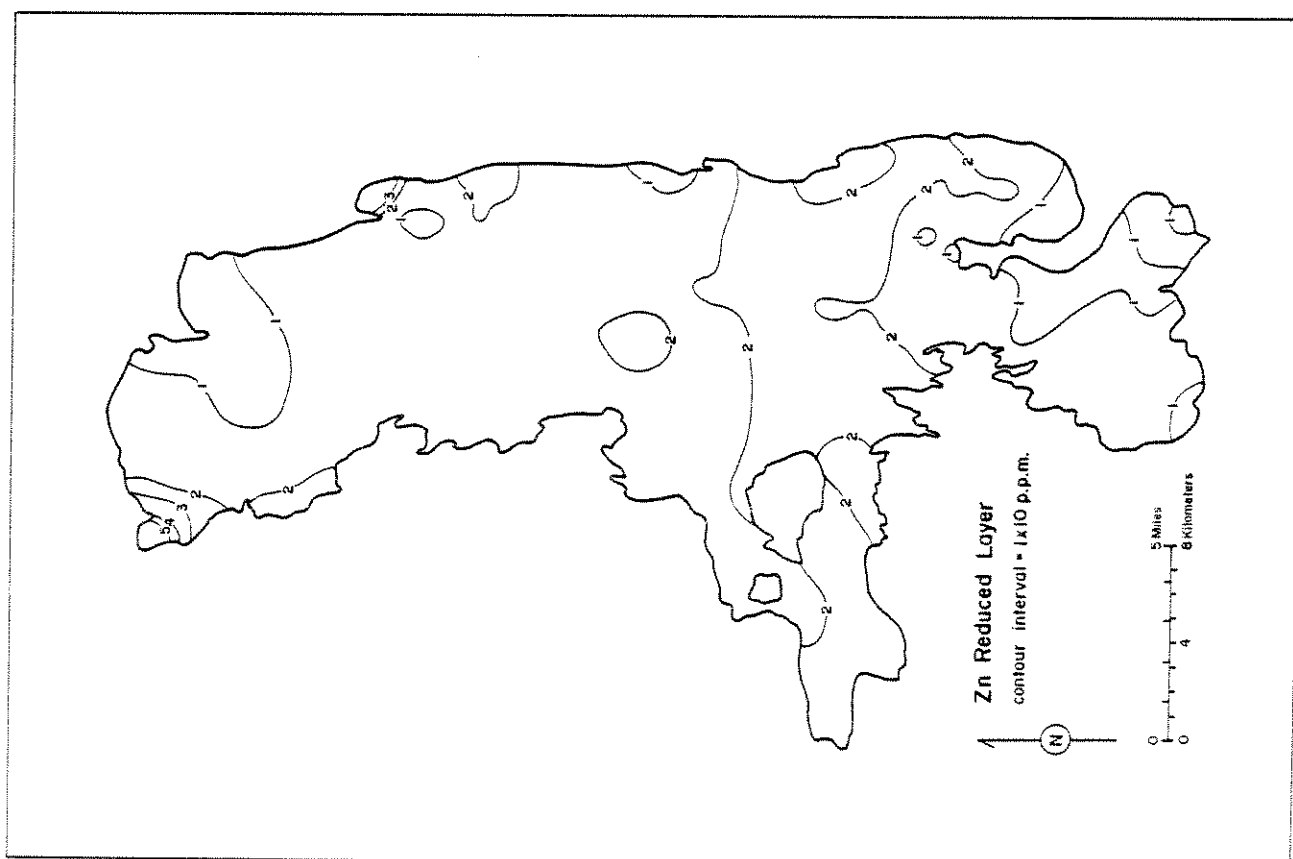
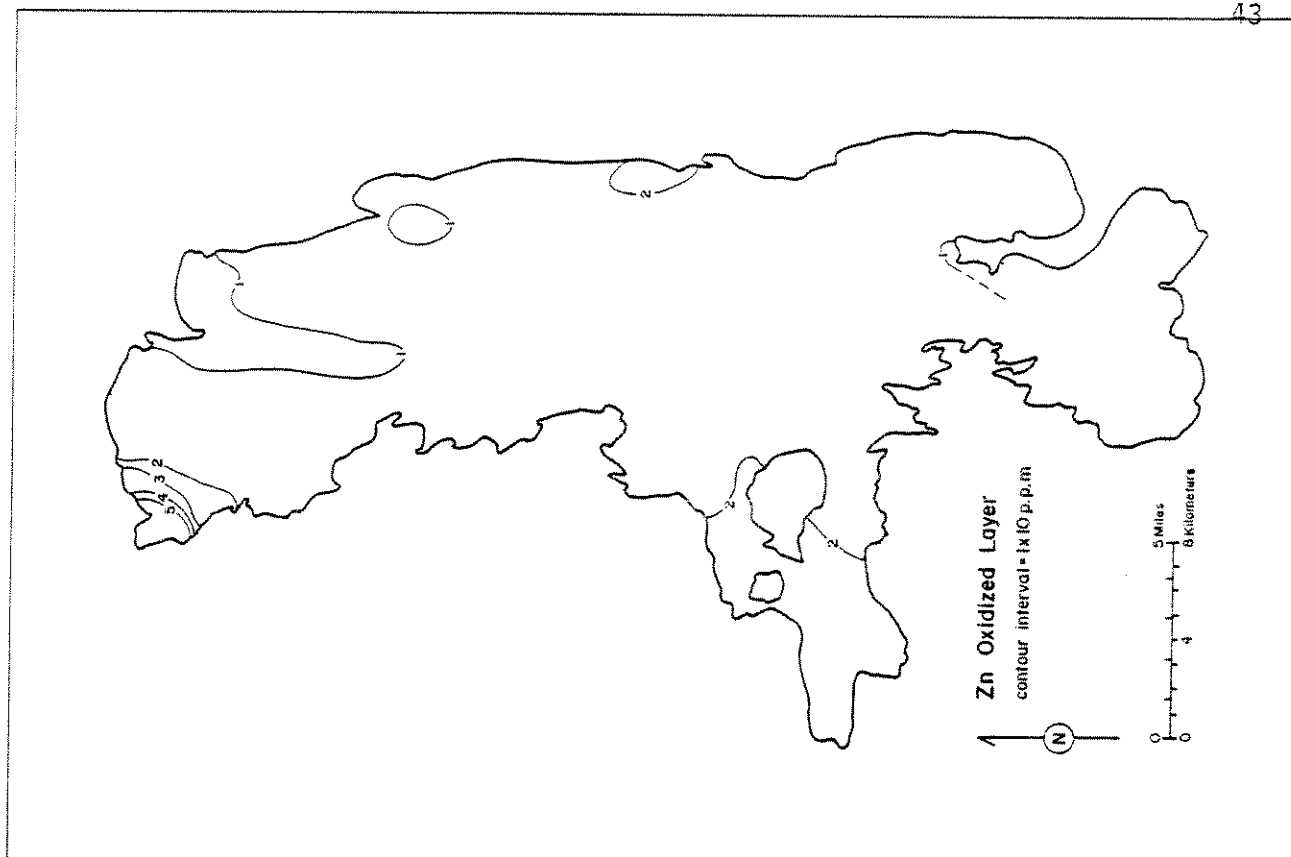


Fig. 8. Contour maps of the distribution of extractable Zn in the reduced (a) and oxidized (b) layers. Contour interval is 10 ppm.



tions of the shoreline. The exception is the deep southern area of the lake, west of Blue Bay, which also has higher than average Zn concentrations in the reduced layer.

### Copper

Extractable Cu in the oxidized layer has a mean of 3.0 ppm (S.D.=3.4). Comparisons of oxidized and reduced layers from the same samples show that 84% of the reduced subsamples contain at least 10% more extractable Zn than the oxidized layer (Fig. 6).

In the sequential extraction, only 4.1% of the total Cu is extractable in the oxidized layer, and 5.8% in the reduced layer (Fig. 3). The total amount of Cu in the sediments is high relative to the mean and high values for 87 recent lakes (Forstner, 1981a), which clustered around a mean of 45 ppm. The total Cu in the samples from Flathead Lake averages 238.0 ppm in the oxidized layer, and ranges from a low of 85.4 to a high of 833.0 ppm. In the reduced layer, the mean is 176.0 ppm, with the total concentrations varying from 67.2 to 428.0 ppm.

The areal distribution of extractable Cu in the reduced layer closely mimics the distribution of Fe in the reduced layer (see Figs. 4a and 9a), but this close correlation is not found in the oxidized layer. However, two of the areas which have high Cu values in the reduced layer also have high values in the oxidized layer: the south-

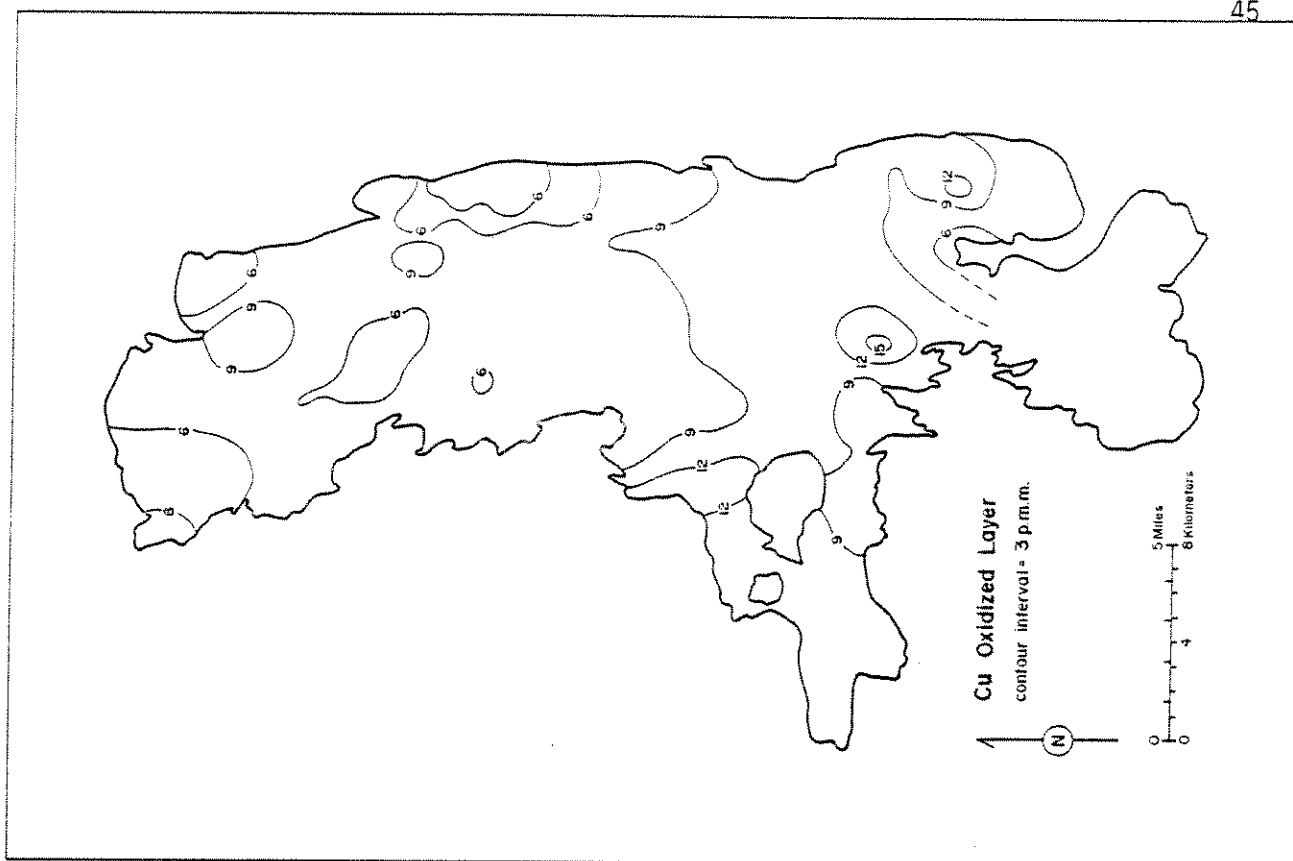
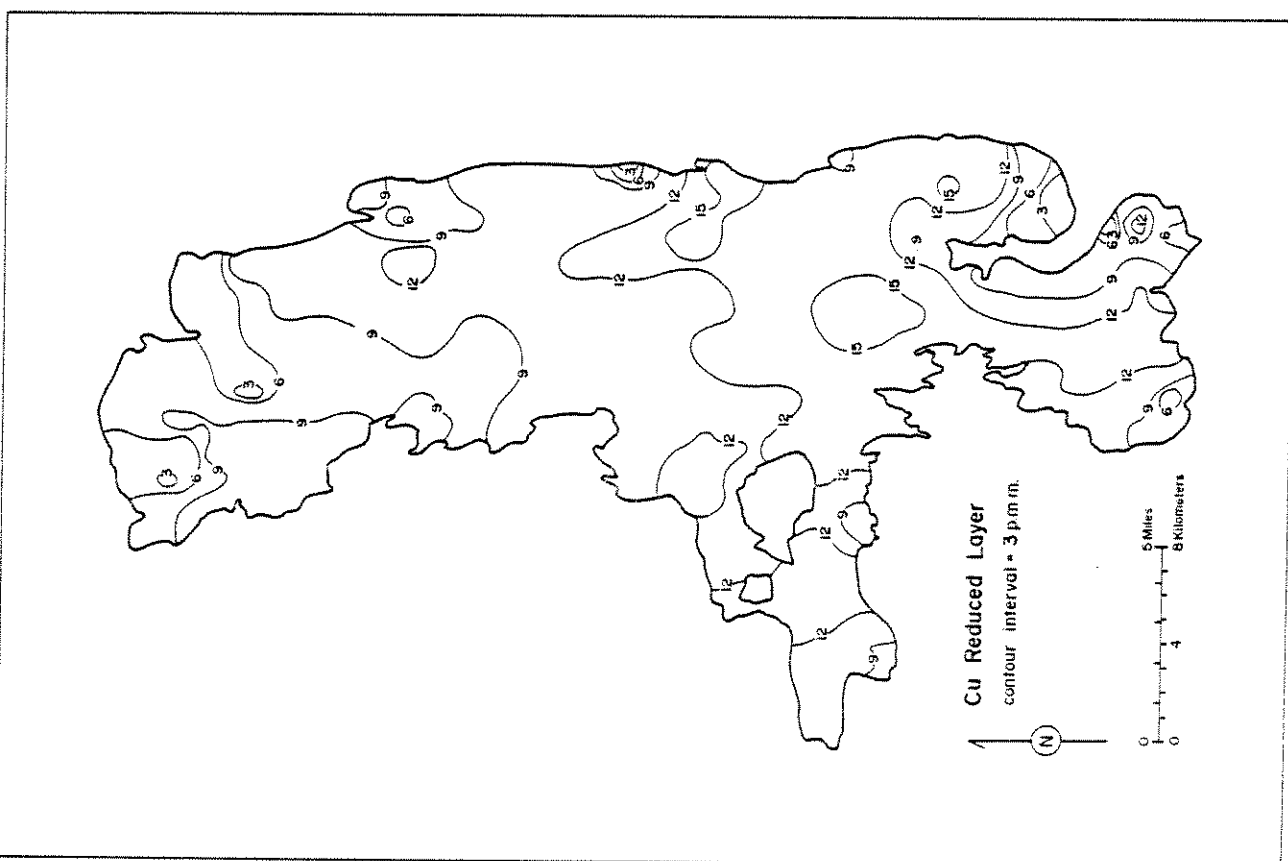


Fig. 9. Contour maps of the distribution of extractable Cu in the reduced (a) and oxidized layers. Contour interval is 3 ppm.

eastern area of Big Arm Bay, and the northeast part of Big Arm Bay, where the nodular Fe crusts were located.

## DISCUSSION

Tables IIa and IIb show the correlation coefficients of the measured variables for the oxidized and reduced layers. Tables III and IV contain the multiple linear regression statistics for the oxidized and reduced layers.

### Manganese Diagenesis

The distribution of extractable Mn in the oxidized layer correlates best with the distribution of extractable Fe (Table IIa), indicating that Fe oxides and hydroxides may adsorb and coprecipitate some of the extractable Mn. Probably some extractable Mn is also leached from discrete Mn oxides (Forstner, 1981b; Hem, 1981). In the reduced layer, the major factors correlating with the distribution of extractable Mn are extractable inorganic phosphorus and extractable Fe (Tables IIb and IV).

As previously mentioned, extractable Mn shows a distinct enrichment in the oxidized layer, averaging 90%. This suggests that Mn may be moving as the result of diagenetic processes in the sediment column, a phenomenon frequently cited in the literature (Lynn and Bonatti, 1965; Robbins and Callender, 1975; and Klinkhammer, 1980).

Klinkhammer (1980) mentions that the simplest way to oxidize  $Mn^{++}$  is by the reaction:

Sample	Layer	Ext. Fe	Res. Fe	Ext. Mn	Res. Mn	Ext. Zn	Res. Zn	Ext. Cu	Res. Cu
34	Red.	1040	27500	37.6	170	14.6	215	12.2	416
60	Ox.	1900	25100	115	172	15.5	208	5.8	283
60	Red.	1860	30300	54.4	173	10.2	246	9.8	123
75	Ox.	1610	36700	1060	493	7.6	214	3.4	82
75	Red.	4540	33900	932	328	8.4	148	8.2	139
86	Ox.	4540	34700	1370	4410	10.9	226	7.4	190
86	Red.	5030	31500	1600	359	14.3	268	11.8	98
94	Ox.	3400	49200	87.1	9280	9.3	226	4.2	829
94	Red.	4590	52000	1690	486	17.3	108	9.4	348
123	Ox.	4540	46800	2080	3380	10.0	62.1	11.0	78
123	Red.	2790	47600	1960	624	10.7	110	7.4	110
136	Ox.	3200	54000	1040	1680	8.0	131	5.0	145
136	Red.	3400	46400	683	298	14.1	85.0	8.2	59
145	Ox.	3690	41900	1900	677	8.7	102	6.2	167
145	Red.	3570	60800	679	323	8.8	113	7.8	120
154	Red.	1330	35100	111	168	2.0	65.5	1.8	129
160	Ox.	4060	38300	442	242	54.7	105	3.0	84
160	Red.	3240	37500	148	182	42.6	106	4.6	142

Table I. Results of the sequential extractions, in ppm. Results given for oxidized and reduced subsamples, where available. Two figures given for each element - extractable and residual. Extractable Zn, e.g., was leached from the sediment sample by 20% acetic acid. Residual Zn was only released from the sediment by complete dissolution.

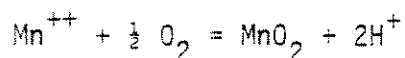
Mn	-.051								
Fe	.294	.514							
Cu	.119	.347	.406						
Inor. P	-.032	.409	.652	.406					
Carbon	.546	-.107	.359	.308	.359				
Sand	.018	-.250	-.234	-.233	-.265	.050			
Silt	-.499	-.182	-.256	-.402	-.167	.094	-.274		
Clay	.414	.356	.407	.532	.355	-.094	-.563	-.640	
	Zn	Mn	Fe	Cu	Inor.P	Carbon	Sand	Silt	

## a) Oxidized layer

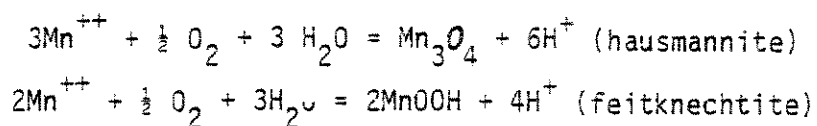
Mn	.327								
Fe	.531	.743							
Cu	.465	.525	.696						
Inor. P	.377	.771	.738	.396					
Carbon	-.029	-.350	-.280	.038	-.417				
Sand	-.526	-.345	-.650	-.712	-.376	.218			
Silt	-.098	-.395	-.227	.089	-.285	.581	-.355		
Clay	.580	.641	.807	.637	.586	-.293	-.702	-.413	
	Zn	Mn	Fe	Cu	Inor.P	Carbon	Sand	Silt	

## b) Reduced layer

Table II. Correlation coefficients between measured parameters in the oxidized (a) and reduced (b) layers..



However, he states that there is the possibility, shown by Morgan (1967) and Klinkhammer and Bender (1980), that hausmannite ( $\text{Mn}_3\text{O}_4$ ), a less oxidized Mn(III) phase, actually forms during oxidation and precipitation. This suggestion has recently been corroborated by Hem (1981), who determined experimentally that, at temperatures between  $0.5^\circ \text{C}$ . and  $37.4^\circ \text{C}$ ., oxidation of  $\text{Mn}^{++}$  leads to the formation of mixtures of hausmannite and feitknechtite by the following reactions:



With aging and further oxidation the hausmannite and feitknechtite may recrystallize to various forms of  $\text{MnO}_2$ , including birnessite and todorokite (Klinkhammer, 1980).

Below the oxidized zone is a neutral zone, in which Mn compounds are neither dissolved nor precipitated. In this zone,  $\text{Mn}^{++}$  moves by diffusion (Robbins and Callender, 1975). A zone of dissolution underlies the neutral zone. In that zone, the Mn oxides and hydroxides formed at the sediment-water interface dissolve by oxidation-reduction reactions (Robbins and Callender, 1975). The metabolic reactions of bacteria probably control the reduction of Mn compounds by the generalized reaction (Berner, 1980):

DEPENDENT: FEEX 2 VARIABLES IN. LAST IN: CLAY

MULTIPLE R = .56720 R SQUARE = .32172 R SQUARE CHG = .05765  
 F CHG = 1.10497 SIGNIF F CHG = .31233 F = 3.08302  
 SIGNIF F = .08020

IN EQUATION VARIABLE	B	BETA	F	SIGF	CORR	PART	PRTL
MNEX	.51038	.42237	2.986	.108	.514	.395	.432
* CLAY	23.46219	.25695	1.105	.312	.407	.240	.280
(CONSTANT)	1603.90607		1.579	.231			

DEPENDENT: CUEX 2 VARIABLES IN. LAST IN: FEEX

MULTIPLE R = .60250 R SQUARE = .36301 R SQUARE CHG = .08041  
 F CHG = 1.64096 SIGNIF F CHG = .22257 F = 3.70425  
 SIGNIF F = .05332

IN EQUATION VARIABLE	B	BETA	F	SIGF	CORR	PART	PRTL
CLAY	.07552	.40512	2.794	.119	.532	.370	.421
* FEEX	6.339-04	.31049	1.641	.223	.476	.284	.335
(CONSTANT)	1.02901		.151	.704			

Table III. Results of multiple linear regression analysis for the oxidized layer. FEEX stands for extractable Fe, INPEX for extractable inorganic phosphorus, etc.



DEPENDENT: FEEX 2 VARIABLES IN. LAST IN: INPEX

MULTIPLE R =	.37059	R SQUARE =	.75792	R SQUARE CHG =	.10733
F CHG =	19.50910	SIGNIF F CHG =	.00006	F	= 68.38006
SIGNIF F =	.00000				

IN EQUATION

VARIABLE	B	BETA	F	SIGF	CORR	PART	PRTL
CLAY	34.43183	.56939	38.662	.000	.307	.481	.684
*INPEX	1.17435	.40447	19.509	.000	.738	.328	.554
(CONSTANT)	87.59280		.069	.793			

DEPENDENT: MNEX 2 VARIABLES IN. LAST IN: FEEX

MULTIPLE R =	.31301	R SQUARE =	.66098	R SQUARE CHG =	.06635
F CHG =	9.61109	SIGNIF F CHG =	.00523	F	= 42.39253
SIGNIF F =	.00000				

IN EQUATION

VARIABLE	B	BETA	F	SIGF	CORR	PART	PRTL
INPEX	.72527	.48909	14.119	.001	.771	.230	.493
*FEEX	.19508	.38195	8.611	.005	.743	.258	.405
(CONSTANT)	-305.27896		20.332	.000			

DEPENDENT: CUEX 3 VARIABLES IN. LAST IN: CLAY

MULTIPLE R =	.78224	R SQUARE =	.61190	R SQUARE CHG =	.06242
F CHG =	6.91572	SIGNIF F CHG =	.01181	F	= 22.59891
SIGNIF F =	.00000				

IN EQUATION

VARIABLE	B	BETA	F	SIGF	CORR	PART	PRTL
*FEEX	9.223-04	.40908	6.227	.016	.696	.237	.356
SILT	.06623	.37235	12.252	.001	.089	.333	.471
CLAY	.06284	.46093	6.916	.012	.637	.250	.372
(CONSTANT)	1.38940		1.217	.276			

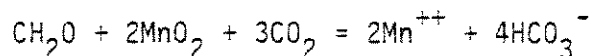
DEPENDENT: INPEX 2 VARIABLES IN. LAST IN: FEEX

MULTIPLE R =	.30975	R SQUARE =	.65570	R SQUARE CHG =	.06107
F CHG =	7.80409	SIGNIF F CHG =	.00769	F	= 41.89714
SIGNIF F =	.00000				

IN EQUATION

VARIABLE	B	BETA	F	SIGF	CORR	PART	PRTL
MNEX	.33496	.49671	14.119	.001	.771	.232	.493
*FEEX	.12719	.36928	7.804	.008	.723	.247	.388
(CONSTANT)	734.31666		36.037	.000			

Table IV. Results of multiple linear regression analysis for the reduced layer.



Below the zone of dissolution  $\text{Mn}^{++}$  equilibrates with authigenic Mn phases (Robbins and Callender, 1975). According to Berner (1980), the most common reduced phase is rhodochrosite ( $\text{MnCO}_3$ ), but other possible phases include reddingite [ $\text{Mn}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ ], and several forms of Mn sulfide.

The reduced sediment layer of Flathead Lake may contain some rhodochrosite, but in view of the small amount of carbonate in the sediment (Decker, 1968) the amount of rhodochrosite is probably low. The Mn phosphate reddingite may form a more important reduced Mn phase, based on the high concentrations of extractable phosphorus, which suggest that phosphates may be stable. Statistical analysis of the data for the reduced layer indicates that extractable inorganic phosphorus correlates with both extractable Mn and extractable Fe (Table IIb). An examination of the partial correlation coefficients seems to show that the correlation of extractable Mn and phosphorus remains independent of the correlation of extractable Fe and phosphorus (Table V). The presence of a second phase containing Mn and phosphorus probably causes the correlation of extractable Mn and phosphorus, which may be the Mn phosphate, reddingite.

One difficulty in this, and other studies, has been the identification of postulated mineral species (Emerson and Widmer, 1978; Klink-

## First Order Partial

Control: Fe

Mn	-.119						
Cu	.156	.016					
Inor. P	-.026	.493	-.245				
Carbon	.147	-.222	.338	-.325			
Sand	-.281	.271	-.476	.203	-.549		
Silt	.028	-.348	.354	-.179	.553	-.679	
Clay	.303	.104	.178	-.023	-.119	-.395	-.399
	Zn	Mn	Cu	Inor.P	Carbon	Sand	Silt

## First Order Partial

Control: Mn

Fe	.455						
Cu	.364	.537					
Inor. P	.208	.388	-.017				
Carbon	.097	-.031	.279	-.246			
Sand	-.466	-.627	-.665	-.184	-.386		
Silt	.037	.109	.380	.514	-.570		
Clay	.511	.643	.460	.189	-.096	-.667	-.226
	Zn	Fe	Cu	Inor.P	Carbon	Sand	Silt

## First Order Partial

Control: Clay

Mn	-.071						
Fe	.131	.499					
Cu	.151	.198	.400				
Inor. P	.056	.636	.554	.035			
Carbon	.182	-.222	-.076	.305	-.316		
Sand	-.205	.191	-.200	-.483	.062	-.623	
Silt	.191	-.187	.197	.502	-.058	.528	-.993
	Zn	Mn	Fe	Cu	Inor.P	Carbon	Sand

Table V. First-order partial correlation coefficients for the reduced layer.

hammer, 1975), particularly by x-ray diffraction methods. One reason for this difficulty is the relatively low volumetric importance of the phases being sought, which makes them difficult to separate and concentrate. Also, since x-ray diffraction cannot identify amorphous phases, the amorphous nature of many authigenic compounds may constitute the most important reason for the difficulty encountered in identification of these authigenic minerals (Emerson and Widmer, 1978).

#### Iron and Phosphorus Diagenesis

Extractable Mn content and the percent clay size fraction correlate best with the distribution of extractable Fe in the oxidized layer (Tables IIa and III). The extractable Fe probably exists in three forms: as hematite; adsorbed and coprecipitated by the Mn oxides mentioned above; and adsorbed by clay minerals. Hematite occurs in the surface sediments of Flathead Lake as films that coat clay grains and other minerals, and as discrete grains (Decker, 1968). Mn oxides readily adsorb and/or coprecipitate Fe, because of the chemical similarity between Fe and Mn (Krauskopf, 1979). Clay minerals efficiently adsorb Fe, especially in the form of  $\text{Fe}(\text{OH})_3$  colloids (Forstner, 1981b). Extractable inorganic phosphorus in the oxidized layer correlates with extractable Fe, and to a lesser extent, with extractable Mn (Tables IIa and III). Fe and Mn oxides and hydroxides efficiently adsorb aqueous phosphorus (Wetzel, 1975). Multiple linear regression and partial correlation coefficients revealed no appreci-

able correlation of inorganic phosphorus with grain size, independent of Fe and Mn content (Tables III and V). This may indicate that the Fe and Mn oxides adsorb phosphorus so efficiently that adsorption by clay minerals plays a minor role in controlling the distribution of phosphorus.

In the reduced layer, grain size and extractable inorganic phosphorus correlate with the distribution of extractable Fe (Tables IIb and IV). As indicated above in the section on Mn diagenesis, both extractable Mn and extractable Fe correlate with the distribution of inorganic phosphorus, seemingly independent of one another.

A diagenetic model for the behavior of extractable Fe proposed for Flathead Lake is similar to the model proposed for Mn diagenesis. The apparent immobility of Fe in the surface sediments (Figs. 5 and 6) constitutes the major difference between the two models. Krauskopf (1979) and Mortimer (1971) have previously dealt with sediment systems undergoing oxidation-reduction and found that Mn often becomes mobile before Fe, because of Mn's greater sensitivity to changes in redox conditions. Inorganic phosphorus may be mobile in the sediments, since the oxidized layer does contain an average of 23% more extractable phosphorus than the reduced layer, with 54% of the samples having an enrichment of more than 10% in the oxidized layer (Figs. 6 and 10). In view of the agricultural activity and increased population in the Kalispell valley, input of cultural phosphorus probably occurs, which may enhance the enrichment of phosphorus in the oxidized layer.

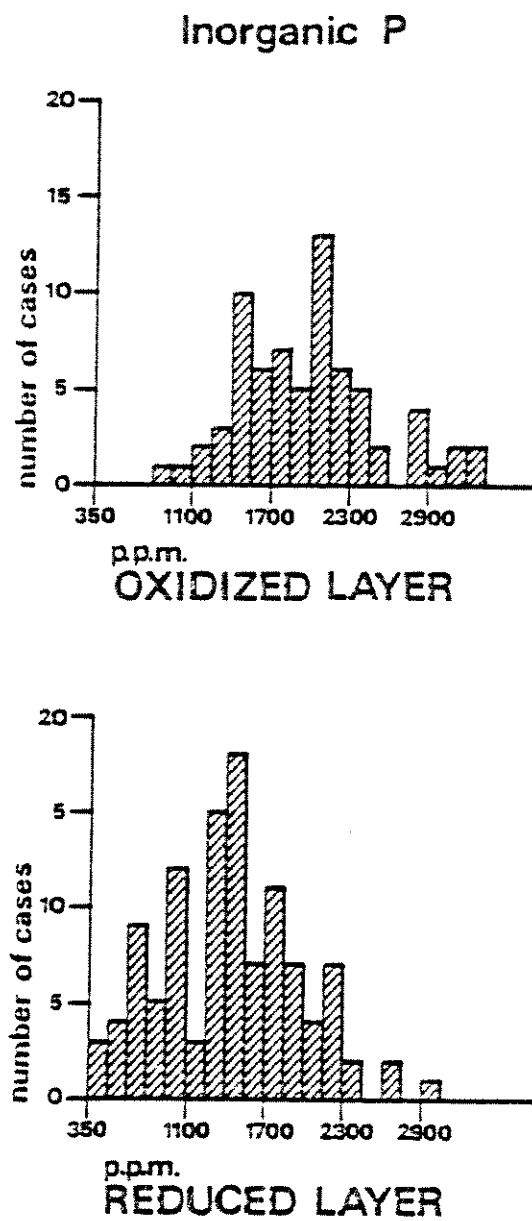
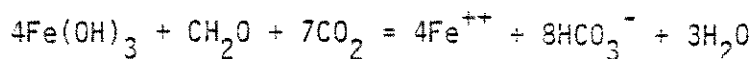


Fig. 10. Histograms of the extractable inorganic phosphorus in the oxidized and reduced sediment layers.

A possible diagenetic model for explaining the distribution of extractable Fe in the sediments of Flathead Lake involves the burial of initially oxidized sediments containing hematite and ferric hydroxides, together with adsorbed inorganic phosphorus. Decomposition of organic matter by bacteria causes the sediments to become reducing. After the bacteria have utilized other, more energy efficient oxidants, such as oxygen, nitrate, and Mn oxides (Berner, 1980), the reduction of Fe begins. The metabolic reactions are of the form (Berner, 1980):



This reaction would release  $\text{Fe}^{++}$  and phosphorus into the pore water. Eventually, as the activity of  $\text{Fe}^{++}$  increased, the ion activity product would exceed the solubility product of one of the reduced authigenic Fe minerals, and precipitation would ensue. Based on the low sulfate content of fresh water, the small amount of organic material and carbonate in the sediments of Flathead Lake, and the large amounts of extractable inorganic phosphorus present, the Fe phase that precipitates probably consists of an Fe phosphate, vivianite ( $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ). Small nodules of vivianite which have been discovered in two previous studies of Flathead Lake sediments (Joyce, 1980; Potter, 1978) support this hypothesis. Emerson and Widmer (1978) in a study of the Greifensee, a Swiss lake, reported similar results.

### Geochemical Classification of Flathead Lake Sediments

Recently, Berner (1981) proposed a geochemical classification of sediments based on the concentrations of  $O_2$ ,  $H_2S$ , and more importantly, on the identification of the Mn and Fe mineral phases that are present. Based on the Fe minerals that are known to be present, hematite and vivianite, on the suspected presence of Mn oxides, hydroxides, and phosphates, and, especially, on the lack of any sulfide minerals, the sediments in Flathead Lake appear to fit into the non-sulfidic continuum of Berner's (1981) classification scheme.

Specifically, this involves the presence of an oxic layer, demonstrated by the presence of hematite, and the assumed presence of Mn oxides. Below this oxic layer, the sediments enter the post-oxic (non-sulfidic) phase, identified by the presence of vivianite, and the assumed presence of reddingite and other reduced Mn phases, and by the lack of sulfide minerals. Because of the small amount of organic matter deposited in the sediments and the presence of a year round oxidizing environment at the sediment water interface, only a small amount of decomposable organic matter is present in the sediments upon burial. The lack of sufficient organic matter probably prevents the sediments from attaining the strongly reducing conditions necessary for the formation of the methanic phase, Berner's (1981) designation for the most reducing non-sulfidic environment.

### Sources of Zinc

The distribution of Zn in the oxidized layer correlates with the amount of carbon present and with grain size (Table IIa). In the



reduced layer, the major correlation is with grain size (Table IIB). Partial correlation coefficients and multiple linear regression statistics indicate that the correlation of Zn with Fe in the reduced layer (Tables IV and V) results from the correlation of Zn with clay size fraction and of Fe with clay size fraction, and that no direct link between extractable Zn and extractable Fe actually exists. The lack of correlation between carbon and Zn in the reduced layer probably arises because of the destruction of organic matter by microorganisms.

Another factor that seems to control the distribution of extractable Zn in the sediments is geographic location. As shown in Fig. 8, the highest Zn values are found in Somers Bay, in both the oxidized and reduced layers. This location has extractable Zn that is 3-5 times higher than average extractable concentrations. In addition, the amount of extractable Zn as a percent of total Zn is 2 times higher than the mean, indicating that more of the Zn in that location is readily available in aqueous form.

The high amount of Zn near a populated area suggests cultural input of Zn to the lake sediments. The long history of industrial activity in Somers, as well as its continuation as a population center for over 80 years, lend support to that idea. Over the years, Somers has had a steamship port, a sawmill, a mill pond, scrap metal yards, a railroad tie factory, a tannery, and other industry. In Somers, as in most small towns, septic systems dispose of household sewage. Domestic

effluents are a common source of Zn in aquatic systems (Wittmann, 1981). A study by Konizeski and others (1968), found that during the months of August through March, when the water level of Flathead Lake is lowered, ground water flows through the sandy floodplain aquifer of the Flathead River directly beneath the town of Somers and into Flathead Lake. This ground water flow may transport Zn into the lake, and ultimately, into the sediments in Somers Bay.

The majority of the other areas that show high extractable Zn values also occur near populated sections of the shoreline. The possibility that ground water flow from communities surrounding the lake contributes Zn to the lake, together with the fact that some of the areas of highest extractable Fe and Cu concentrations are near the shoreline, all point to the need for greater study of the groundwater and sediment porewater chemistry.

The southern portion of the lake comprises the main area of high Zn concentrations not located near the shoreline (Fig. 8). This area also tends to have high percentages of clay size material, because of the great distance from the Flathead River delta. The Flathead River contributes most of the sediment to Flathead Lake. Considering the good correlation of extractable Zn with the clay size fraction (Table II), higher than average values of Zn in this area are not surprising.

#### Sources of Copper

Grain size, and to a lesser extent, extractable Fe, correlate with the distribution of extractable Cu in the oxidized layer (Table

IIa). In the oxidized layer, clay minerals probably adsorb Cu, while Fe oxides and hydroxides both adsorb and coprecipitate it (Forstner, 1981b). Examination of the correlation coefficients and of the multiple linear regression statistics for the reduced layer (Tables IIb and IV) indicates that extractable Fe and grain size correlate with the distribution of extractable Cu. Comparison of the contour maps of Fe and Cu in the reduced layer also shows the correlation between the two elements (Figs. 4a and 9a). However, while Cu correlates with percent clay in the reduced layer (Table IIb), multiple linear regression reveals that extractable Cu also correlates with percent silt (Table IV). This is the only case where a positive correlation of any of the extractable metals appears with coarser grained sediments. As a general rule, extractable metals usually correlate with finer grained sediments, because of surface area effects (Forstner, 1981b).

The positive correlation of extractable Cu with the silt size fraction in the reduced layer, taken together with the extremely high values of total Cu, almost all of which resides in the residual fraction, suggests two sources for the extractable Cu. One source consists of Cu bound loosely by extractable Fe compounds and by clay minerals. The other source consists of detrital Cu minerals.

The presence of detrital Cu minerals would explain the high concentrations of residual Cu in the sediments. Because it is tightly bound to the sediment, the large amounts of Cu should not be available

to the biota, under normal conditions. Any detrital Cu minerals present in the sediment have presumably been altered from their original sulfide mineralogy, due to weathering at the outcrop, during transport, and in the oxidized layer of the sediments. Possible Cu phases now present may include tenorite, cuprite, malachite, and azurite.

Rocks of the Belt Supergroup are a likely source for detrital Cu minerals. They contain ore-grade Cu mineralization, with Cu contents varying from background levels of 20 ppm to highs of at least 20,000 ppm (Harrison, 1972; Harrison and Grimes, 1970). Cu minerals include chalcopyrite, chalcocite, digenite, bornite, and covellite (Harrison, 1972). Several types of Cu deposits are known, and are found in almost every stratigraphic unit, and every geographic area of the Belt basin (Harrison, 1972). Mineral companies are actively exploring the Belt basin for these Cu deposits. Besides Cu, the deposits also provide sources of Pb, Ag, and Hb (Clark, 1971; Lange and Moore, 1981).

#### Remobilization of Extractable Material

The concentrations of extractable metals and nutrients measured in the surface sediments exceed the levels in the waters of Flathead Lake by at least an order of magnitude (Stuart and Stanford, 1981). This reservoir of extractable material may be released if the chemical environment of the sediments changes sufficiently. The release of phosphorus to the lake waters would be particularly important because of the role of phosphorus as the limiting nutrient in the Flathead Lake ecosystem (Stuart and Stanford, 1981).

The distribution of extractable Zn indicates that some pollution of the lake may be occurring near populated areas. Stanford (personal comm., 1982) recently discovered higher levels of primary productivity in the waters of some of the bays with populated shorelines, which tends to support that idea. Increased pollution levels could lead to a situation in which the bottom waters of Flathead Lake are no longer oxidizing. If that occurred, the sediments of Flathead Lake might become a source of both nutrients and metals (Wetzel, 1975; Leland et al., 1973), which would tend to aggravate any developing pollution problem. The high economic, recreational, and ecological value placed on the lake by its many users suggest the need for continued monitoring of the waters and sediments of Flathead Lake.

## Chapter Three

### PHOSPHORUS

Jaswant Singh Jiwan  
Johnnie N. Moore

#### Introduction

In all parts of the world, increasing industrial and domestic waste discharge, agricultural runoff and input from catchment basins subject lakes to pollution. These effluents usually contain an abundance of nutrients which can cause unrestricted growth of aquatic vegetation (Hwang et al., 1975). In recent years, the environmental challenge has been to protect unpolluted lakes and restore those already in various stages of eutrophication. Among the growth promoting nutrients, phosphorus has been implicated as a major factor in the deleterious fertilization of lakes (Hwang et al., 1975). Increasing population density, the intensive use of fertilizers in agriculture and the widespread application of domestic and industrial detergents has raised the concentrations of phosphate and nitrate in many lakes resulting in eutrophication.

In more than 80% of the 200 north temperate lakes studied in the International Eutrophication Programme of the Organization for Economic Cooperation and Development, the availability of phosphorus controlled the process of eutrophication. Phosphorus concentration is considered the most important factor affecting

primary productivity, algal standing crops, fish population and water clarity and quality (Vollenweider, 1971; Ostrofsky and Duthie, 1975, 1980; Wetzel, 1975; Oglesby, 1977; Schindler, 1977; Kalff and Knochel, 1978; Lee, Jones and Rast, 1980).

Limnological investigations of Flathead Lake began towards the end of the nineteenth century (Forbes, 1893), but this early work only established the structure of the ecosystem and did not address aquatic chemistry or productivity. More recent work (Stanford et al., 1981) is establishing the aquatic chemistry and biology of the entire drainage system. All previous limnological work alluded to the oligotrophic status of Flathead Lake (Seastedt and Tibbs, 1974; Tibbs, Gaufin and Prescott, 1976; Potter, 1978). Stanford and Potter (1976) suggested that the nutrient balance in the lake is maintained by interaction of sediment from the spring turbidity plume and other ecological factors. In their hypothesis, clay particles introduced by spring runoff causes flocculation of phytoplankton and organic detritus and concomittant adsorption of inorganic phosphorus. These clay-detritus flocs then settle to the lake bottom. The sediment both supplies and removes phosphorus from the water column and thus aids or inhibits primary productivity. The most recent work on the trophic system of the lake has modified this hypothesis (Stanford, et al., 1981) but phosphorus concentration is still assumed to control the trophic state of the lake, and originates mostly from sediment input.

In most northern-temperate oligotrophic lakes, wind and rivers supply the majority of phosphorus. Once phosphorus reaches the lake, a variety of dynamic interactions occur between

sediment, biota and nutrients. Syers et al., (1973) summarized work on phosphorus in lake sediments and discussed the relationship between amounts and forms of phosphorus and composition and textural properties of sediment. He also discussed chemical mobility and availability of phosphorus to the biota from sediments. In general, lake sediments store phosphorus under certain chemical conditions and release it under others.

Phosphorus cycling, in relation to the input of phosphorus from external sources, governs the biological productivity of a great number of lakes (Wetzel, 1975). Therefore, it has become very important to understand the characteristics of sediments that affect the overlying water quality through chemical, biological and mechanical exchanges. The exchange of phosphorus between the sediments and overlying water is a major component of the phosphorus cycle in natural waters (Drever, 1982). Its importance rests in an apparent net accumulation and upward migration of phosphorus in lake sediments.

Because phosphorus migrates and concentrates at the surface after deposition (Berner, 1978), there is little correlation between the amount of phosphorus in lake sediments and the overlying water (Wetzel, 1975). Phosphorus content in lake sediment can be several orders of magnitude greater than that in overlying water. The ability of the sediment to concentrate and return phosphorus depends on the pH, Eh and major ion concentrations of the sediment and the lake bottom water. Both inorganic and biologic processes alter exchange equilibria and affect



phosphorus migration from sediment into the water.

Because phosphorus concentration controls the trophic state of Flathead Lake, previous workers have attempted to calculate the phosphorus budget (Seastedt and Tibbs, 1974; Tibbs, Gaufin and Stanford, 1975; Nunallee, 1976; E.P.A., 1976). However, none of these studies have considered the contribution or the potential contribution of the sediments filling the lake. The data and interpretation presented here discusses the physical and chemical framework of Flathead Lake sediment that control phosphorus distribution and migration and thus may affect the water quality of the lake.

### Distribution

Extractable total-, inorganic- and organic- phosphorus as <sup>3-</sup>PO<sub>4</sub> was determined for oxidized and reduced sediment recovered by grab sampling (App. I). Values in the oxidized layer range from 1137 to 3617 ppm (mean=2311 ppm, S.D.=484, N=70), 800 to 3225 ppm (mean=1983ppm, S.D.=531) and 53 to 594 ppm (mean=327 ppm, S.D.= 163) respectively (Fig. 1). Concentrations in the reduced sediment range from 617 to 3346 ppm (mean=1765 ppm, S.D.=583, N=110), 387 to 2990 ppm (mean=1441 ppm, S.D.=527) and 27 to 813 ppm (mean=315 ppm, S.D.=171) respectively (Fig. 1). In both the oxidized and reduced sediment, inorganic phosphorus dominates extractable phosphorus and organic phosphorus never exceeds inorganic concentrations.

Inorganic and total phosphorus, in both the oxidized and reduced layers, have very similar lateral distributions (Figs. 2 and 3). Values higher than the mean concentrate in the southern portions of the main lake with isolated higher values along the east shore north of Yellow Bay, in Woods Bay, in Blue Bay and along the southwestern edge of Big Arm Bay. Although the mean values of both total- and inorganic-extractable phosphorus increase from the reduced layer to the oxidized layer, both types of sediment and both types of phosphorus show the same distribution patterns. Organic-extractable phosphorus shows a completely different distribution, unrelated to that of total or inorganic phosphorus.

Organic phosphorus has accumulated in the sediments in concentrations greater than the mean throughout the southern half

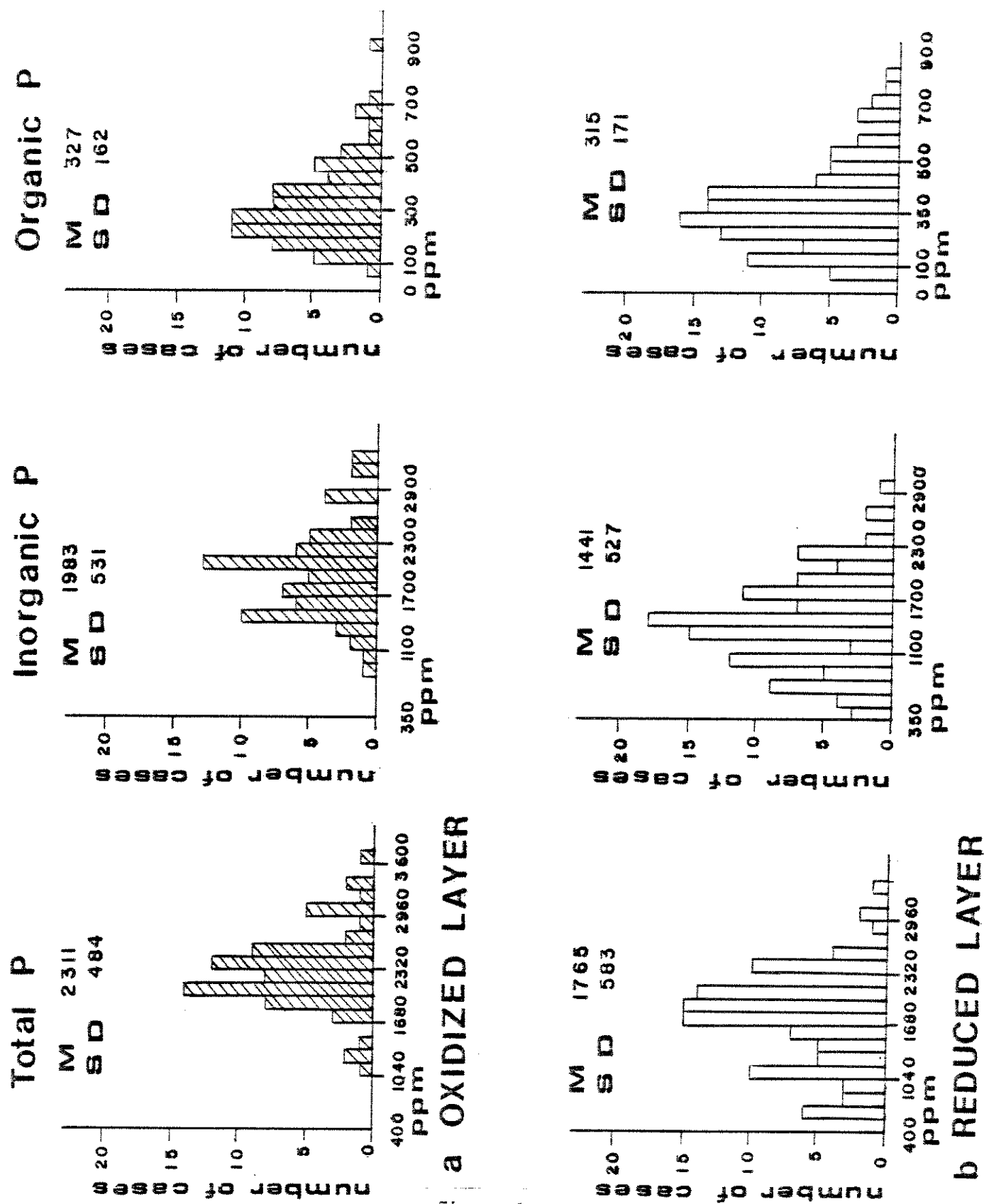


Figure 1

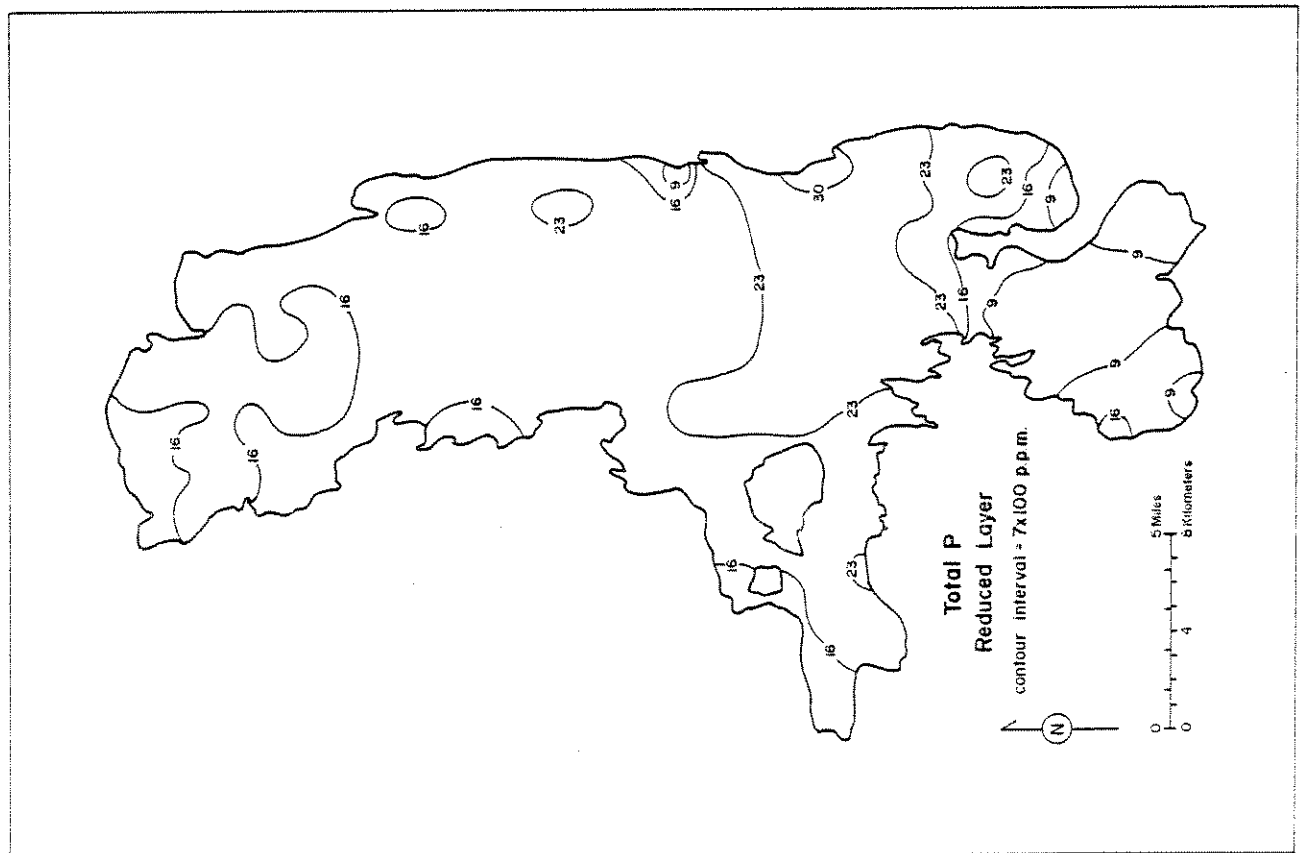
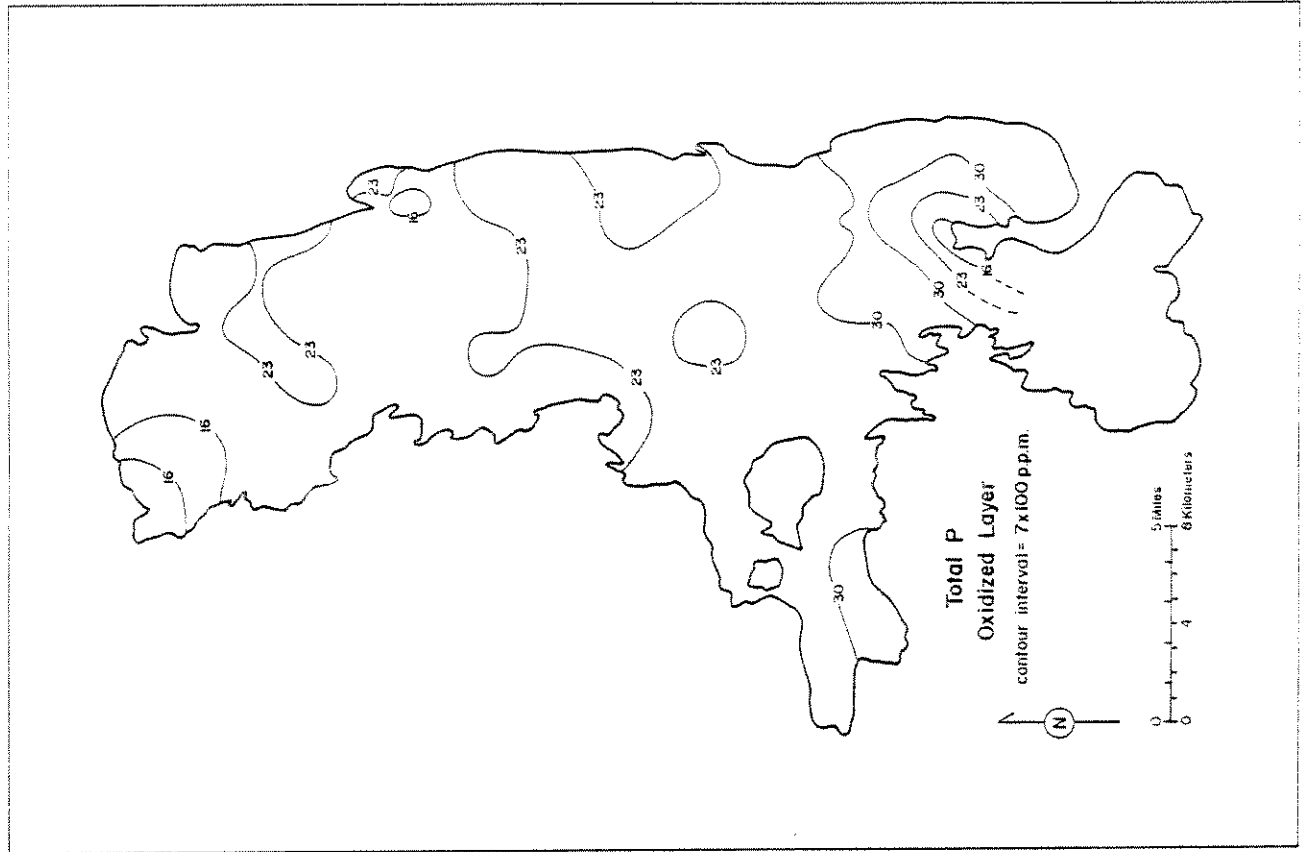


Figure 2

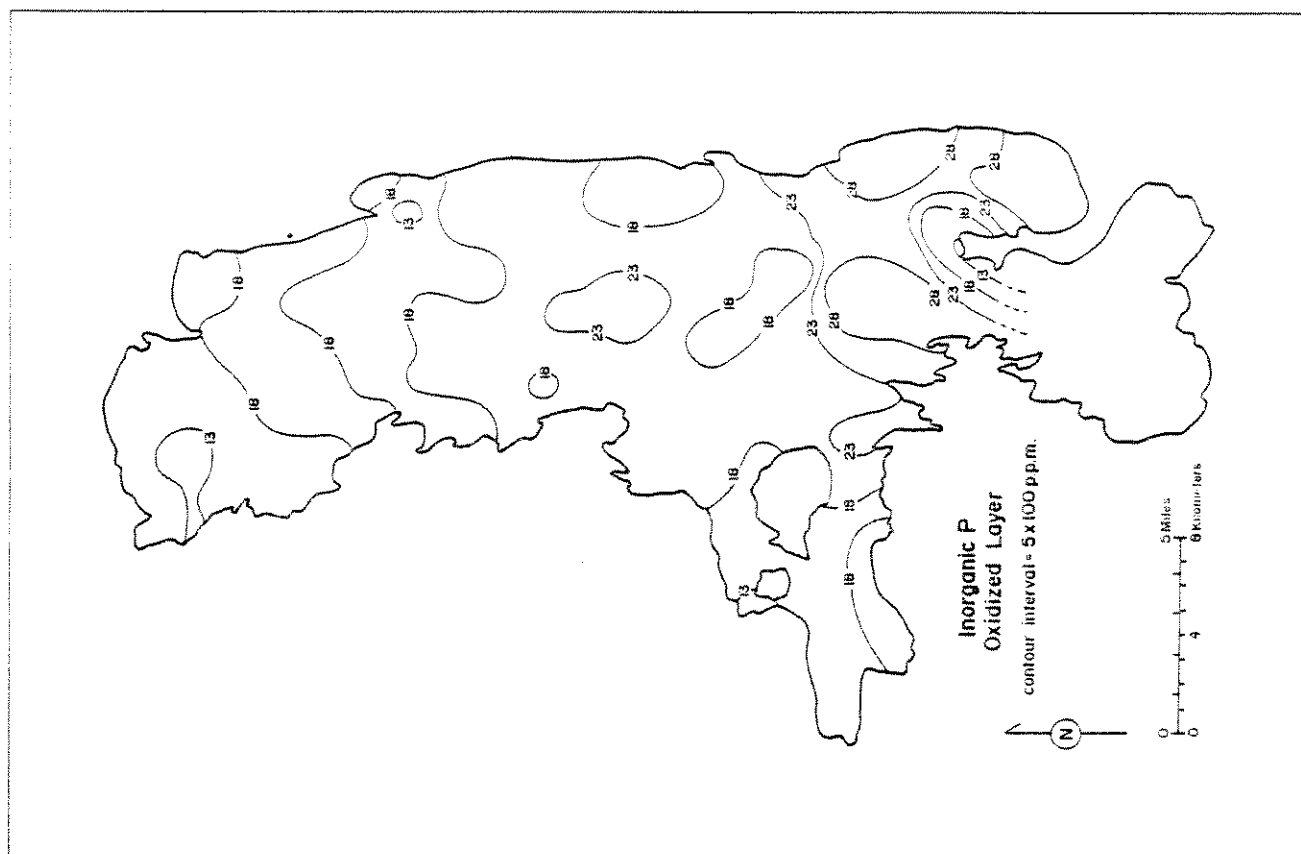
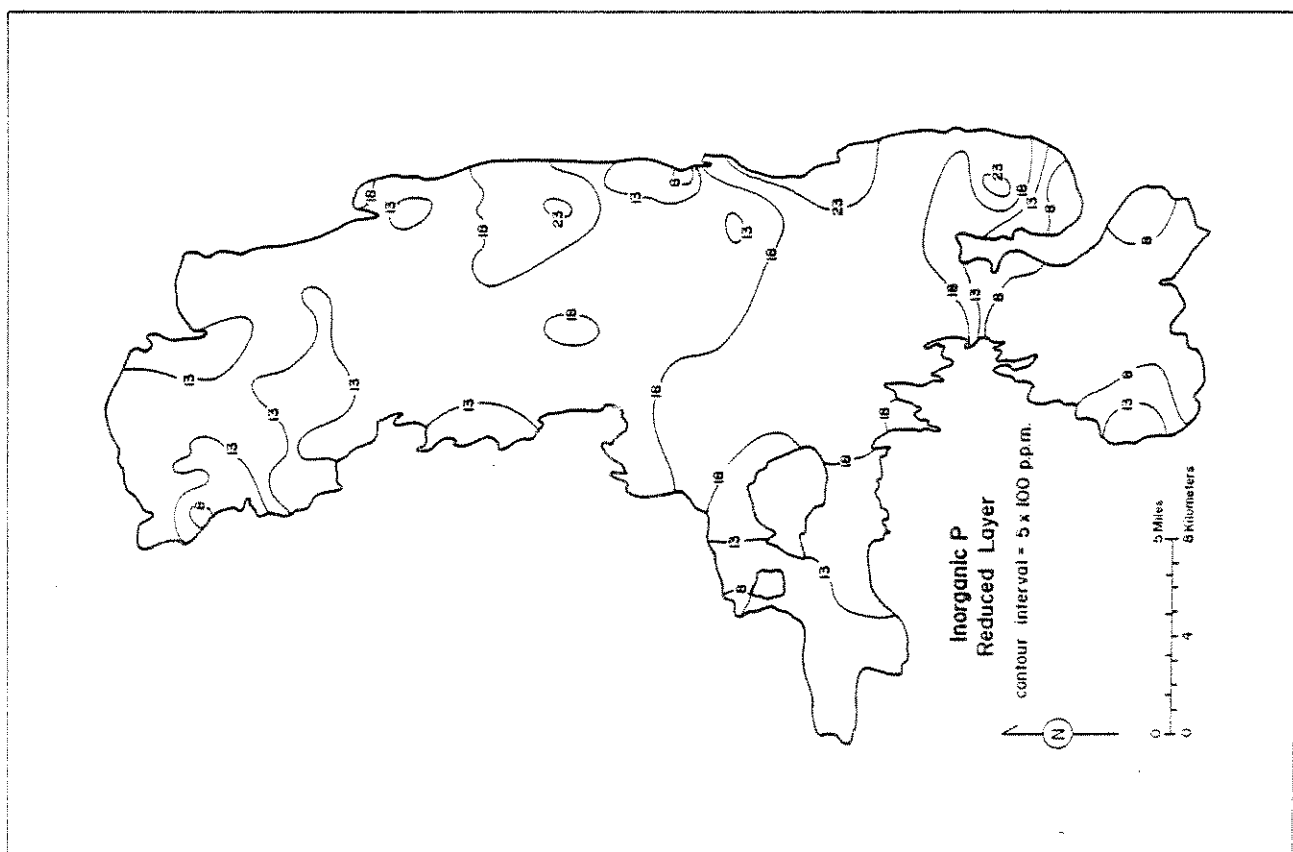


Figure 3

of the lake including Big Arm Bay(Fig 4). Isolated higher values occur in eastern Big Arm Bay, Indian Bay and in the open lake near Yellow Bay. Although the general pattern is similar to total phosphorus, none of the isolated high areas are similarly located, suggesting that organic-extractable phosphorus is unrelated to the distribution of total- and inorganic-extractable phosphorus.

The mean concentration of both total- and inorganic-extractable phosphorus is greater in the sediments of the upper oxidized layer than in the underlying reduced sediments. The mean total-extractable phosphorus increases by 30% and inorganic-extractable phosphorus by 38%. Organic-extractable phosphorus means are nearly identicle showing no average incease from the reduced to the oxidized sediment. These average increases may not mean that at any particular site there is an increase upwards in the concentration of phosphorus. However, the percent change from the reduced to the oxidized layer at individual sites show a mean increase of 18% of total-extactable phosphorus and 23% for inorganic-extractable phosphorus (Table 1) suggesting that there is a net increase. Organic phosphorus shows no significant change, with values ranging from large decreases to large increases.

In summary, the distribution of extractable phosphorus in the surface sediments show that total phsophorus and inorganic phosphorus follow simlar trends and organic phosphorus is unrelated to either. Distributions in the reduced and oxidized sediment is similar but there is a net increase in both total and

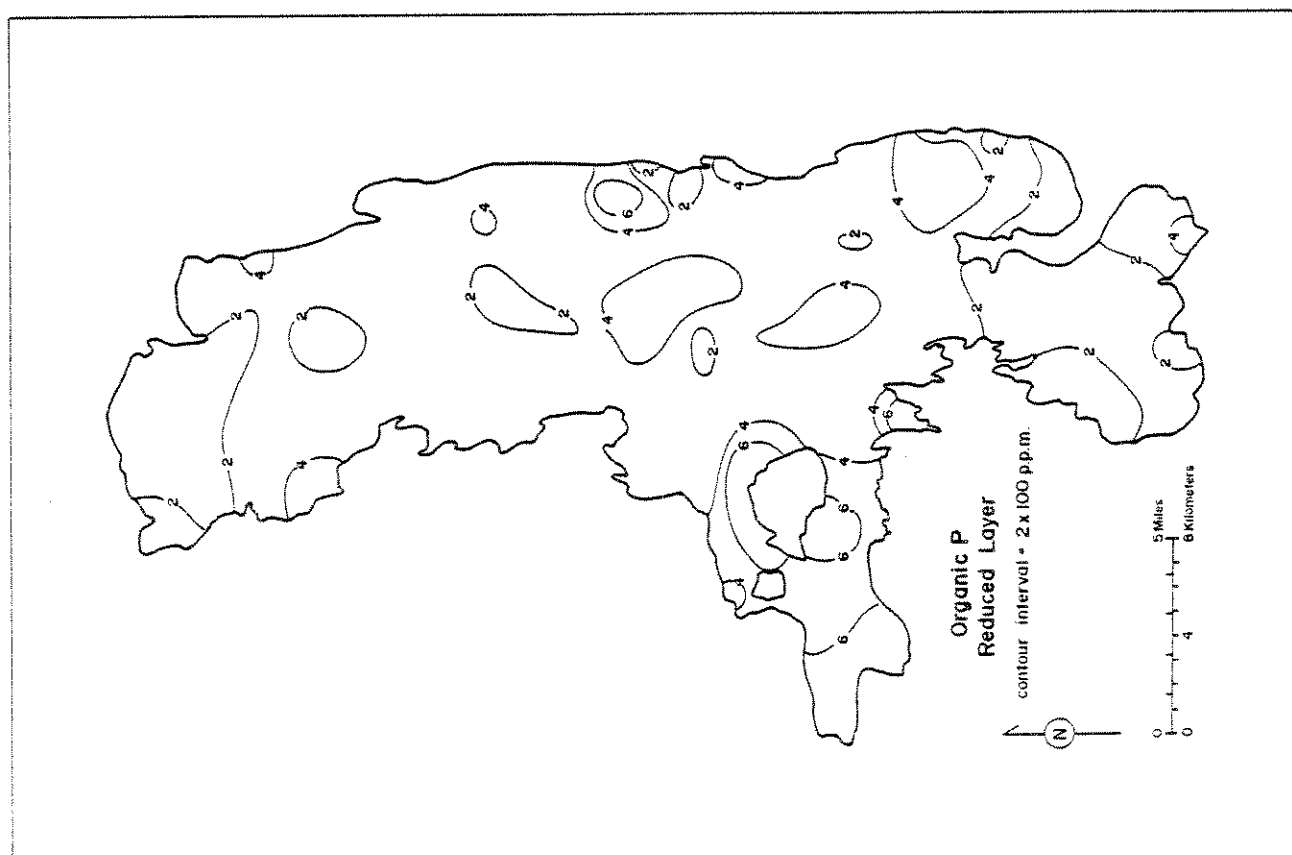
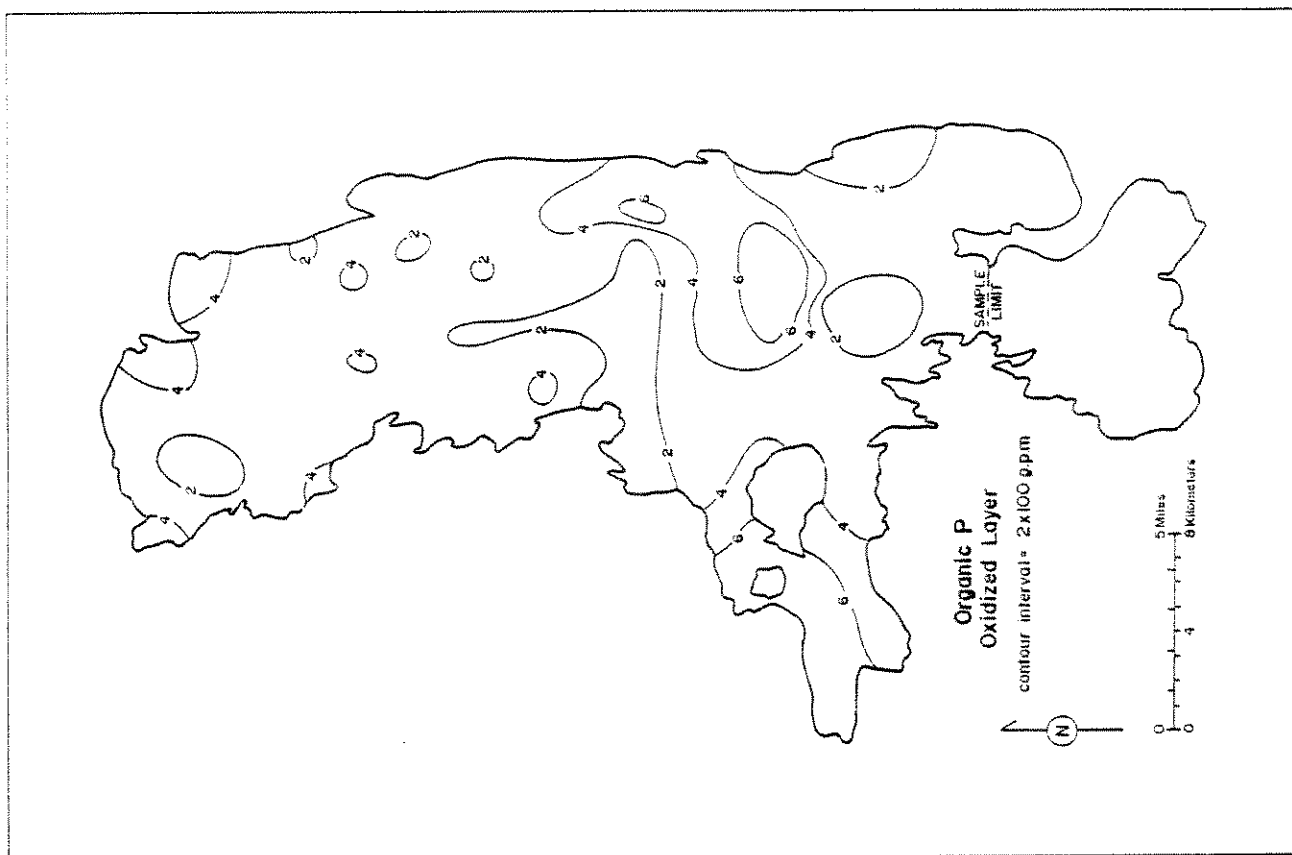


Figure 4

inorganic phosphorus upwards. Organic phosphorus shows a wide range of change and neither average increase or decrease can be documented. Sediments in the southern lake contain more than the average concentration of phosphorus throughout the lake, with total- and inorganic-extractable phosphorus concentrated in higher amounts in areas on the east side and in southwestern Big Arm Bay and organic concentrated in Big Arm Bay and in the southern open lake. Anomolously high concentrations of total- and inorganic-extractable phosphorus occurs near highly developed shoreline and cherry orchards along the east shore. Very high values occur in isolated bays (Woods, Yellow and Blue Bays) suggesting that these concentrations associate with proximity to developed areas. Concentrations of organic phosphorus appears to be related to areas of high productivity where sedimentation rate is slow in Big Arm Bay and central lake.



VARIATIONS FROM REDUCED LAYER TO OXIDIZED LAYER

(DATA IN PPM)

	ZnEX	MnEX	FeEX	CuEX	TOPEX	INPEX	OPEX	
OXIDIZED	Min	7	164	675	3	1137	800	53
	Mean	15	1592	3820	8	2311	1983	327
	Max	72	7030	6335	16	3617	3225	934
	SD	8	997	1205	2.4	484	531	163
REDUCED	Min	3	26	408	1	417	387	27
	Mean	16	808	3427	10	1765	1441	315
	Max	52	3172	6752	16	3346	2990	813
	SD	7	781	1530	3.4	583	527	171

Table 1

### Correlations With Other Variables

Phosphorus in sediments is commonly associated with clays, metal oxide-hydroxides and organic compounds (Forstner and Wittman, 1981; Drever, 1982). Because of these associations the correlations between metal concentration, grain size and organic content often identifies modes of occurrence of phosphorus in sediments. We have used this statistical technique of correlation of variables (Drever, 1982) to analyze data collected on Flathead Lake sediment to determine the mechanisms controlling phosphorus fixation. Correlation coefficients are presented in Tables 2 and 3 and partial correlation coefficients in Table 4. The associations detailed in these tables establish a model of phosphorus fixation and migration that is consistent with theoretical and experimental models developed to explain sediment-water interactions (Drever, 1982; Forstner and Wittman, 1981).

The most striking correlation is between total-extractable phosphorus and inorganic-extractable phosphorus (Tables 2, 3, and 4). In both the oxidized and reduced sediment the correlation coefficient is greater than 0.95 and even with controls the partial correlation coefficient never falls below 0.88. When considered with the similar distribution (Distribution section), these statistics suggest that inorganic phosphorus dominates extractable phosphorus. Poor correlation between organic-extractable phosphorus and total-extractable phosphorus shows that there is no distinguishable relationship between these two types of phosphorus, as is suggested in the distribution maps (Figs. 1, 2 and 3). Inorganic phosphorus dominates the extractable

		CORRELATION COEFFICIENTS						<u>Reduced Layer</u>	
MNEX	.327								
ORPEX	.448	.101							
INPEX	.377	.771	.161						
FEEX	.531	.743	.231	.738					
TOPEX	.491	.741	.435	.950	.748				
CUPEX	.465	.525	.227	.396	.696	.437			
CARTO	-.029	-.350	.021	-.417	-.280	-.372	.038		
SAND	-.526	-.345	-.363	-.376	-.650	-.444	-.712	-.218	
SILT	-.098	-.395	-.138	-.285	-.227	-.307	.089	.581	-.355
CLAY	.580	.641	.454	.586	.807	.668	.637	-.293	-.702
	ZNEX	MNEX	ORPEX	INPEX	FEEX	TOPEX	CUPEX	CARTO	SAND
									SILT

Table 2

[illegible]

79

# PARTIAL CORRELATION CO-EFFICIENTS

## REDUCED LAYER

Control  
Correlation  
Between

CLAY

CLAY

FeEX

MnEX

## OXIDIZED LAYER

CLAY

FeEX

MnEX

TOPEX MnEX	.547 (.741)	.416		.351 (.461)	.193	
TOPEX FeEX	.476 (.748)		.439	.568 (.652)		.545
TOPEX INPEX	.926 (.950)	.889	.886	.956 (.952)	.920	.943
TOPEX CLAY		.164 (.668)	.375		.328 (.493)	.396
INPEX MnEX	.636 (.771)	.439		.323 (.409)	.129	
INPEX FeEX	.554 (.738)		.388	.566 (.628)		.534
INPEX CLAY		-.023 (.586)	.189		.139 (.355)	.245
FeEX MnEX	.499 (.743)			.432 (.514)		
FeEX CLAY			.643 (.807)			.280 (.407)
CuEX SAND	-.483 -.712	-.476	-.665	-.094 (-.233)	-.143	-.162
CuEX SILT	-.502 (.089)	.354	.460	-.094 (-.402)	-.329	-.362

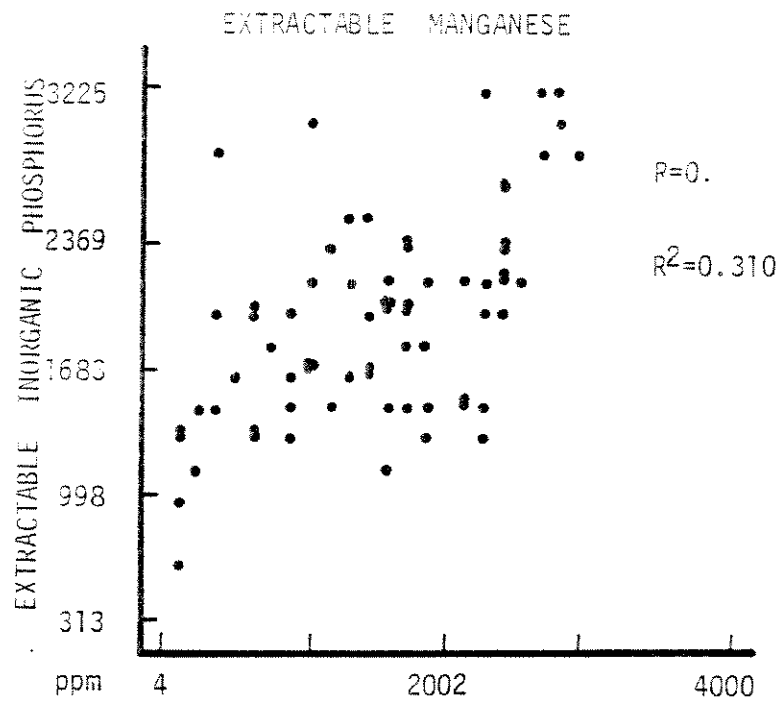
Table 4

phosphorus in the sediment and so correlations with other variables will show only slight modifications by organic phosphorus.

Correlations between phosphorus and other variables differ in the oxidized layer and the reduced sediment below. All correlation coefficients decrease, some only slightly others dramatically, from reduced to oxidized sediment (Table 4). In the oxidized layer, total- and inorganic-extractable phosphorus show good correlation with extractable manganese and iron and clay (Tables 2 and 3; Figs. 5,6 and 7). These correlation coefficients decrease in the oxidized layer, especially with manganese and clay. Likewise, in the reduced layer extractable iron and manganese in the reduced layer correlate strongly with clay but weaken in the oxidized layer. Using iron manganese and clay as controls illuminates these associations (Table 4).

In reduced sediment, the correlation of total- and inorganic-extractable phosphorus with clay decreases significantly when iron and manganese are used as controls (Table 4). These relationships suggest that phosphorus is associated with iron and/or manganese and not with clays. The good correlation with clay is controlled by the correlations of clay with iron and manganese. This association is supported by the correlation between iron and phosphorus staying strong when manganese and clays are used as controls (Table 4). Because the correlations decrease slightly with both, it appears they have some association. Similarly, correlation with manganese decreases when iron is used as the control and only very slightly when clay

OXIDIZED



REDUCED

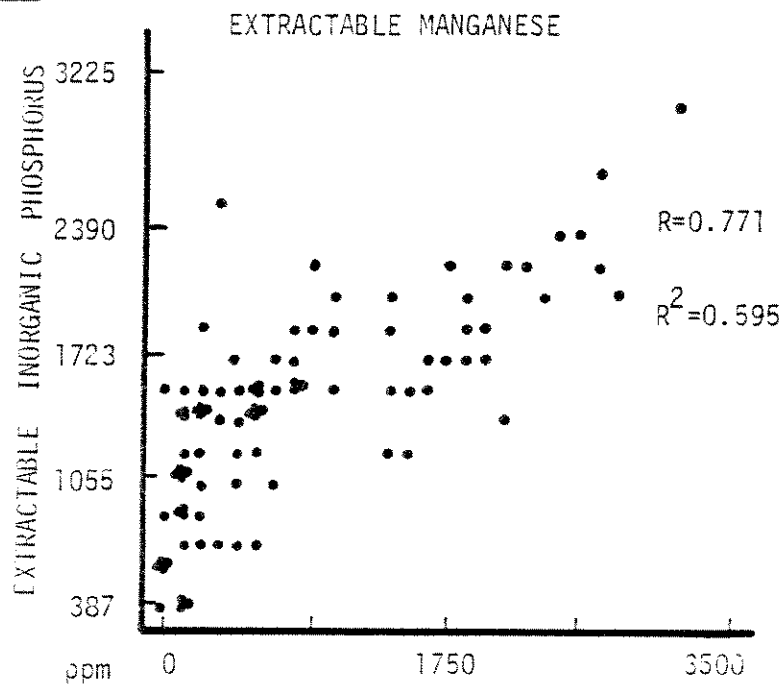


Figure 5

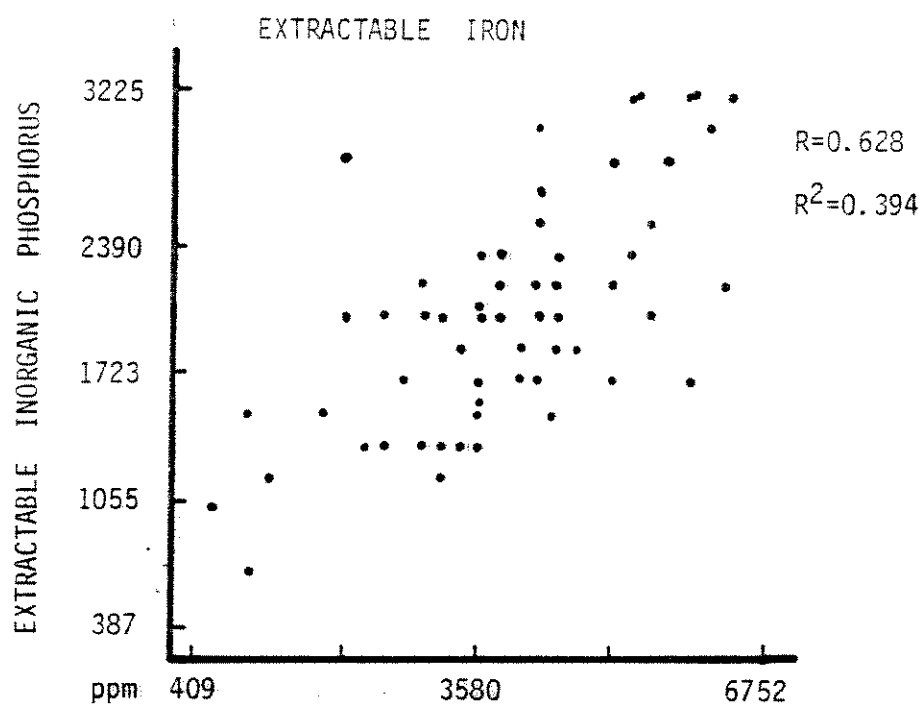
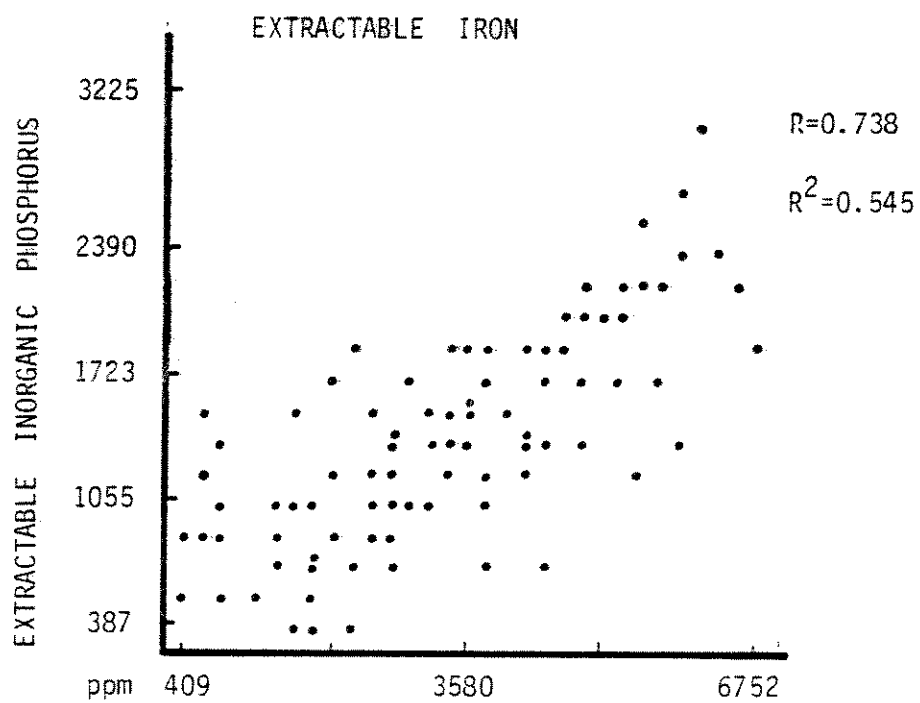
OXIDIZEDREDUCED

Figure 5



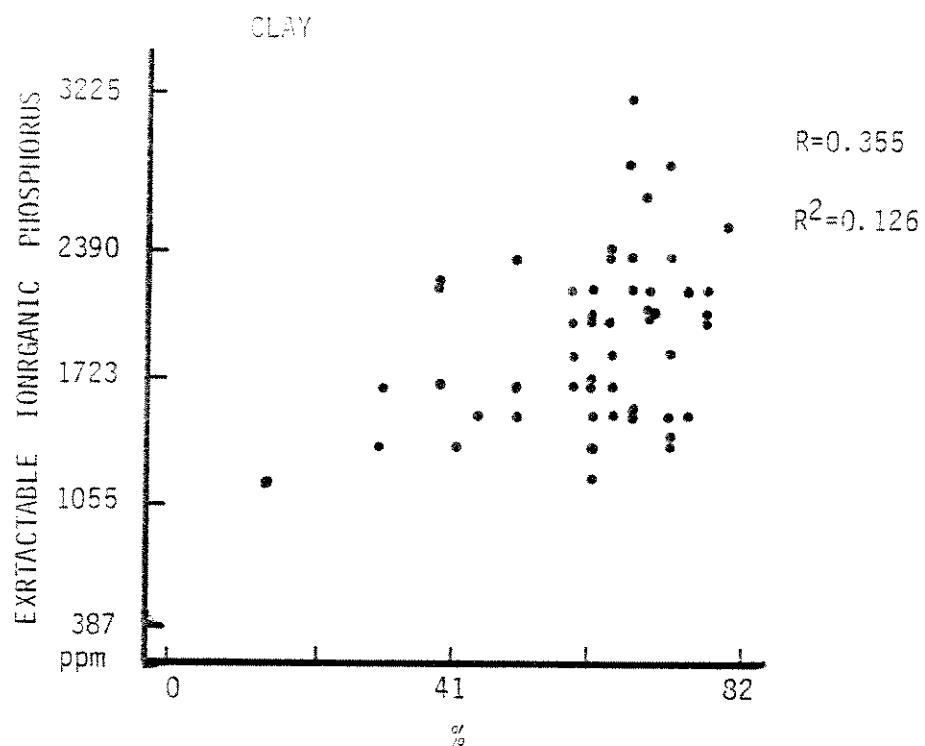
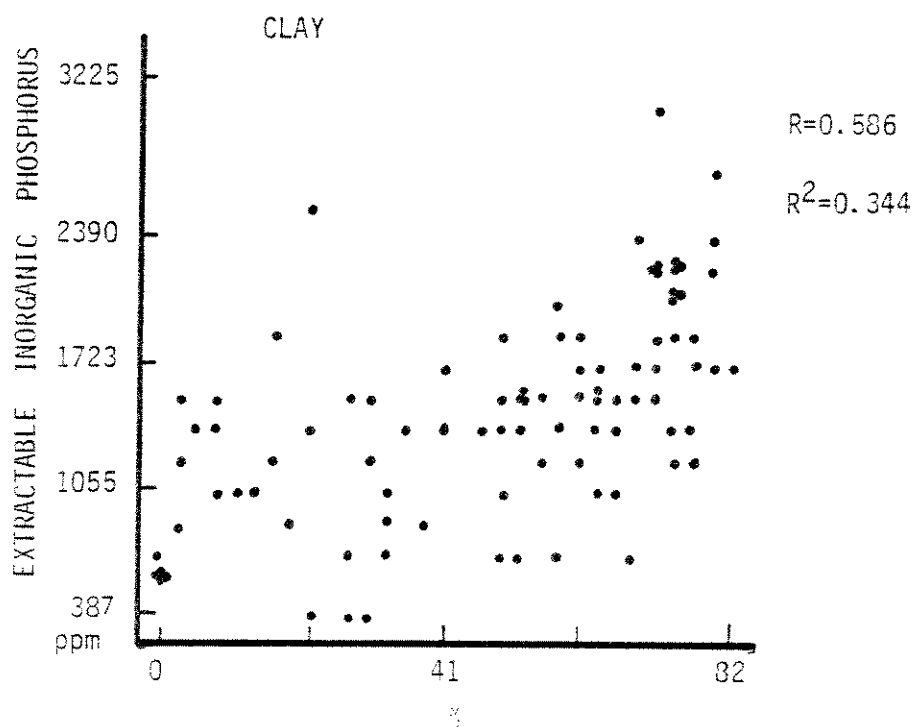
OXIDIZEDREDUCED

Figure 7

is used. These partial correlation coefficients suggest that total- and inorganic-extractable phosphorus is controlled by extractable iron and manganese, both of which are associated with clay (see Chapter Two).

The same variables in the oxidized layer show different associations than those in the reduced sediment. In the oxidized layer the same correlations exist but they are weaker. With clay, manganese and iron as controls the only correlation that remains strong is phosphorus with iron (Table 4). This suggests that total- and inorganic-extractable phosphorus are associated with iron alone in the oxidized layer and not with both iron and manganese as in the reduced sediment.

Organic-extractable phosphorus does not show any strong correlation with any other variables in either the oxidized layer or reduced sediment. However the correlation coefficients differ for each type of sediment (Tables 2 and 3). In the reduced sediment organic phosphorus shows a very weak association with clay and a negative correlation with sand. This suggests that there is some, but probably minor, control by grain size, with organic phosphorus correlated with finer-grained sediment. Total-extractable phosphorus also shows a very weak correlation with organic-extractable phosphorus. All these poor associations change in the oxidized layer.

Organic-extractable phosphorus in the oxidized layer shows no correlation to grain size. All the correlation coefficients are insignificant except for (possibly) a negative correlation with inorganic-extractable phosphorus. The change from a poor correlation with total phosphorus and clay in the reduced

sediment to poor negative correlation with inorganic phosphorus in the oxidized zone may suggest that clay-sized organic phosphorus is altering to inorganic phosphorus in the oxidized zone. This would explain the relative decrease in the relative percentage of organic phosphorus in the oxidized layer compared to reduced sediment (Table 5).

Correlation coefficients and partial-correlation coefficients show several general relationships between extractable phosphorus and metals and grain size. The most striking of these is the dominance of phosphorus by inorganic forms. Phosphorus is strongly associated with manganese and iron in reduced sediment and iron in the oxidized layer. Organic phosphorus is unrelated to those variables controlling total and inorganic phosphorus but is slightly controlled by grain size and inorganic phosphorus.

MIGRATION STATUS

(Change in oxidized layer as % of Reduced layer)

	ZnEX	MnEX	FeEX	CuEX	TOPEX	INPEX	OPEX
Mean	88	192	99	75	118	123	112
Minimum	40	26	35	39	90	68	20
Maximum	144	481	218	151	231	265	415
Range	104	455	183	112	141	197	395
S.D.	20.8	99.2	26.8	17.85	20.4	28.1	72.96

Table 5

### Migration and Concentration

The increase in extractable phosphorus from reduced sediments to the oxidized zone at the sediment-water interface can be explained by migration of phosphorus upwards, or increased input in recent times. The vertical distribution of metals in Flathead Lake sediments suggest that differences in phosphorus concentration result from migration associated with iron and manganese compounds.

Suspension sediments in most lakes contain phosphorus complexed with and attached to many different types of material (Hesse, 1973). Tipping, Woof and Cooke (1981) found amorphous iron-oxide particles that contained from 1.1 to 2.8% phosphorus in a seasonally anoxic lake in Great Britain and many workers have established that humic complexes of iron and aluminium bind phosphorus. Jackson (1975) demonstrated the ability of humic chelate complexes of iron and aluminum to bind orthophosphorus. Clays adsorb phosphorus (Van Olphen, 1963; Stumm and Morgan, 1970) and iron and manganese oxides, hydroxides, phosphates, sulfides and carbonates incorporate phosphorus during their formation in lake and marine sediments (Forstner and Wittman, 1981; Drever, 1982). Phosphorus also complexes with metal ions, specifically iron and manganese oxides and hydroxides (Forstner and Wittman, 1981). The extent of complexing between various phosphates and metal ions depends on the relative concentration of phosphate and metal ions, pH, Eh and the presence of other ligands such as sulfate, carbonate, fluoride and organic species (Emsley and Hall, 1976).

Phosphorus used by organisms as a nutrient accumulates on the lake bottom as algae bloom and die (Halman and Stiller, 1974; Lean, 1973). In many lakes (eg., Flathead Lake) productivity is limited by phosphorus (Halmann, 1972; Stanford, et al., 1981) and lake water contains very small amounts of phosphorus compared to that in lake sediments. Even in oligotrophic lakes phosphorus accumulates in the sediment as iron, manganese and organic compounds settle to the bottom. Under oxidizing conditions these compounds are stable, but when reduced, phosphorus migrates along with other elements (Williams et al., 1976; Drever, 1982). Because Flathead Lake sediments are dominated by clay, poor in carbonate, and show no evidence of sulfides or fluorides, we assume that phosphorus may be associated with such oxides, hydroxides and/or organic compounds. Such an inorganic dominated system was described by Williams et al., (1976).

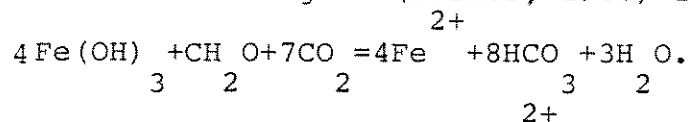
The distribution of extractable phosphorus and extractable iron and manganese, and their correlations to one another (Tables 2, 3 and 4), suggest that iron and manganese constitute the major controls on phosphorus migration and concentration. Because iron and manganese correlates strongly with clay, it seems reasonable to assume phosphorus is controlled by iron and manganese oxides/hydroxides/phosphates attached to clay-sized sediment. In reduced sediment both iron and manganese compounds control phosphorus concentration probably as manganese and iron phosphates adsorbed to clays. Migration from reduced sediment into the oxidized layer concentrates phosphorus along with manganese (Chapter Two), so that through time there is a net accumulation of nutrients and some metals in the surface

sediments. Such processes are well established in the literature (Drever, 1982; Forstner and Wittman, 1981; Jonasson, 1977; Theis and Singer, 1973). These processes are explained by a model involving input of phosphorus adsorbed/complexed with clays and oxides in the oxidizing environment of the lake water and then mobilized by the reducing environment of the sediment (Theis and Singer, 1973; Martens and Goldhaber, 1978; Froelich et al., 1979).

Phosphorus is transported into the lake adsorbed to iron and manganese oxides attached to clays or floating free in the water column with suspension sediments. A smaller amount is introduced by biologic production within the lake. As these sediments settle through the water column dissolved phosphorus may also be added by adsorption to iron and manganese colloids, organics and clays. The phosphorus remains stable in these forms in the oxidizing lake water and accumulates on the bottom along with organic material. As this oxidized sediment accumulates, organics in the sediment decay and bacterial action reduces the sediment just below the surface, out of reach of the oxidizing lake water. Within this reducing environment, phosphate adsorbed to clay and incorporated in more stable organic and iron phosphate compounds, resists breakdown by bacteria (Emsley and Hall, 1976), but organic decay liberates  $\text{CO}_2$  and the sediments become more reducing. Phosphorus is liberated as manganese is reduced by bacterial metabolism (Chapter Two). Krauskopf (1979) and Mortimer (1971) found that in sediments undergoing such Eh-pH changes manganese becomes mobile before iron because of its

greater solubility.

After utilizing the more energy efficient oxygen compounds, reduction of iron begins (Berner, 1980) following the reaction:



This reaction would release  $\text{Fe}^{2+}$  and phosphorus into the pore water. As concentrations increase manganese, iron and phosphorus minerals precipitate when the ionic activation product exceeds the solubility. In Flathead Lake sediments the presence of large amounts of inorganic-extractable phosphorus correlated separately to both iron and manganese concentration, and the low amounts of carbonate and organics (Joyce, 1980; App. I) indicate that phosphorus is tied up in phosphates of iron and manganese. This is supported by the discovery of the iron phosphate vivianite in cores taken by Joyce (1980) and Potter (1978) and the work by Murray (1982, Chapter Two).

As sediment accumulates and compacts, porosity decreases, expelling pore water. The pore water migrates upward into less compacted sediments (more porous) carrying manganese and phosphorus in the reduced state. When they encounter the overlying oxidizing environment, manganese precipitates as oxides (probably attached to clays) and phosphorus coprecipitates/adsorbs to ferric oxides and hydroxides. Ferrous iron released in the reduced sediment always exceeds phosphorus and when oxidized it precipitates much of the phosphorus (Wetzel, 1975; Forstner and Whittman, 1981). Some ferric phosphate may form, but will hydrolyze slowly and return some phosphorus to the pore water (Hutchinson, 1957). If enough organic compounds are present some iron will form humate



complexes at the sediment-water interface. These compounds accumulate as a flocculent and strongly adsorb phosphate (Tipping, Woof and Cooke, 1981). The redox gradient controlling these processes is maintained by bacterial metabolism within the sediment. Changes in oxidation state and upward flow of pore water concentrate phosphorus in the surface oxidized zone (Fig. 8).

In summary, the distribution and migration of phosphorus in Flathead Lake sediments reflects the mobility of iron and manganese. Iron oxides/hydroxides and manganese oxides containing adsorbed and coprecipitated phosphorus accumulate in the oxidizing environment at the sediment-water interface. Burial of sediments and decaying organic matter results in a reducing environment which causes the reduction of iron and manganese oxides/hydroxides releasing iron, manganese and phosphorus to the pore water. Manganese reduces first and migrates to the upper surface powered by pore-water flow. Iron, manganese and phosphorus probably reach equilibrium in the reduced sediment forming manganese and iron phosphates. Phosphorus accumulates in the oxidized layer adsorbed to iron oxides/hydroxides and/or humates/chelates separate from manganese oxides. Because the stability of phosphorus is maintained by oxidizing bottom water, a potentially large source of nutrients exists if the bottom-water chemistry of Flathead lake were to change. Locally, sediments contain over 3000 ppm phosphorus (as  $\text{PO}_4^{3-}$ ) greater than values in much less pristine lakes (eg., Lake Champlain, Hunt, 1971). This phosphorus, in the highly soluble

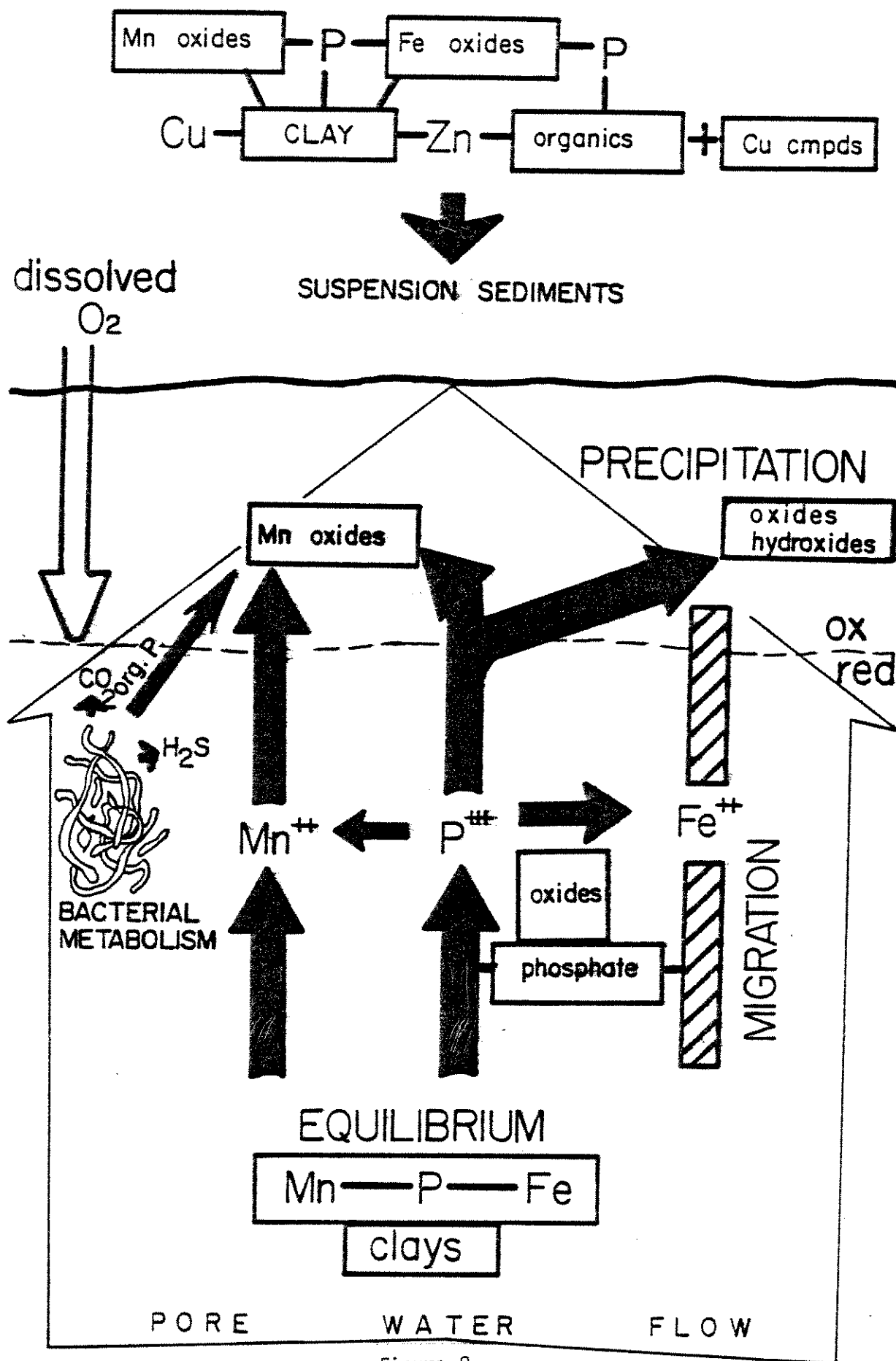


Figure 8

complexes of iron and manganese, would be available if the present oxidation-reduction system of the lake changes in the future.

## Chapter Four

### CONCLUSIONS AND PREDICTIONS

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The present Flathead Lake system has been extant for approximately 12,000 to 14,000 years. During that time sediment has accumulated under conditions very similar to those of today. Suspension sedimentation dominates the lake and nutrients are carried into the lake and deposited along with these sediments. The geochemical framework of sediments concentrates phosphorus in the upper layers of the sediment creating a large potential source which could significantly change the nutrient budget of Flathead Lake. This vast accumulation of nutrients remains securely locked away in iron and manganese compounds as long as the bottom waters remain oxygen-rich. If the bottom water becomes anoxic, even locally, the sediments will release their stores of phosphorus, dramatically changing the nutrient budget of the lake.

In the sediment-water geochemical system acting in the lake (Chapters Two and Three) there are three possibilities for nutrient-sediment interactions (Fig.1). Because the redox gradient that controls nutrient and metals migration is ultimately powered by organic matter in the sediments, it is

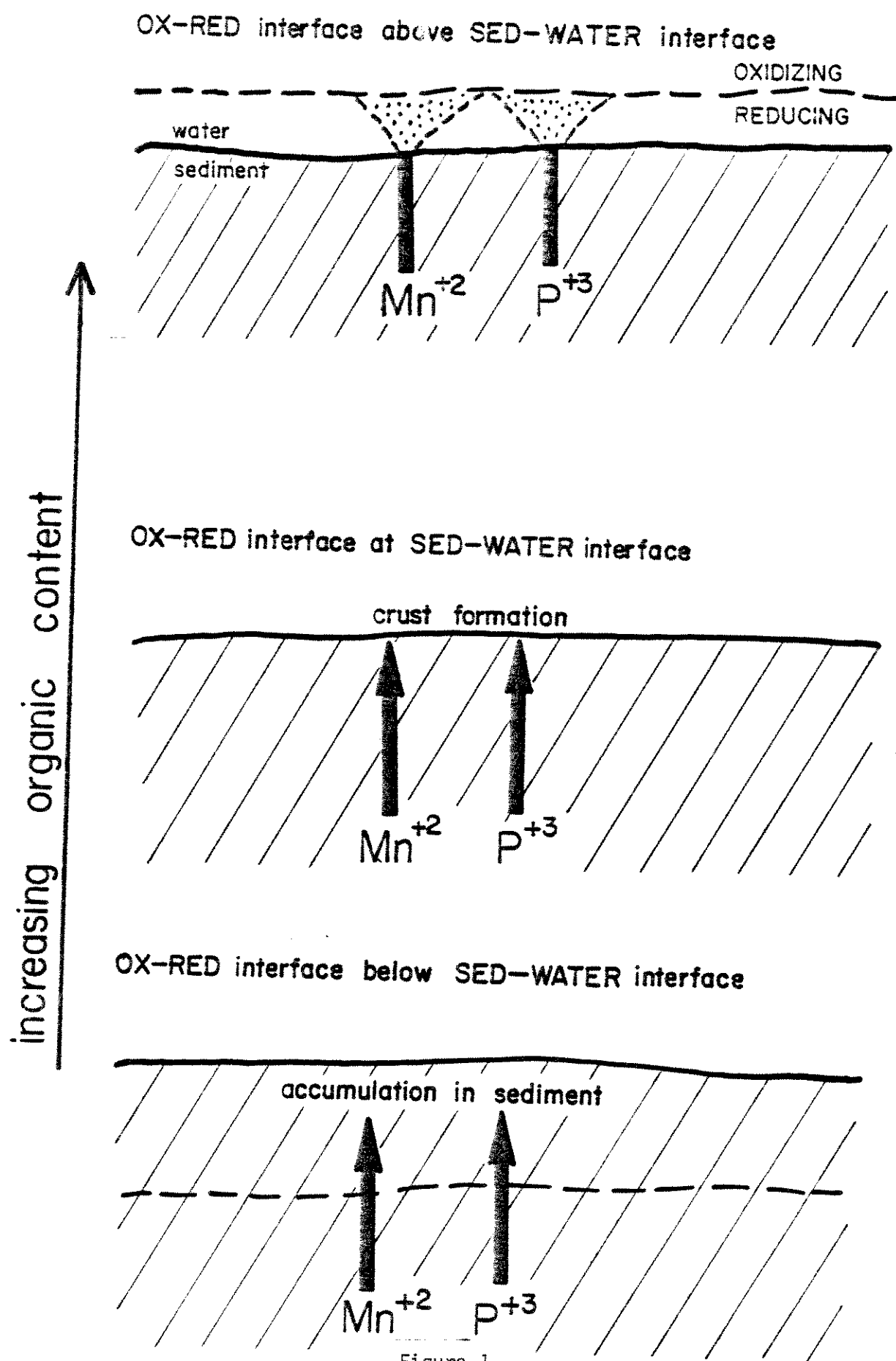


Figure 1

convenient to discuss possible scenarios based on the amount of organic material in the sediment. However, the processes could also be modified if major changes occurred in the concentrations of phosphorus or metals supplied to the lake.

The production of organic matter in lakes is controlled by phosphate and nitrate (Wetzel, 1975; Drever, 1982). Subsequently, productivity determines the amount of organic material collecting in the sediment which controls the oxidation state. Under sediment and bottom water reducing conditions, nutrients and metals are pumped into the lake water; under oxidizing conditions they are trapped at the sediment-water interface. In Flathead Lake, and other large oligotrophic lakes, this system can be described by three possible situations. Each situation is defined by the amount of organic matter accumulating in the sediment.

Situation One:

Small amounts of organics accumulating in sediment would provide limited food for bacterial metabolism. Oxidizing water from the lake would permeate into the sediment forming a discrete layer of oxidized sediment. The thickness of this layer would depend on the amount of reduction, the permeability of the sediments and the oxygen content of the water. This situation exists in oligotrophic lakes forming a distinctive orangish oxidized zone at the sediment-water interface. As manganese and phosphorus migrate upwards in this situation, they accumulate in the oxidized layer of the sediment (Fig.1. lower).

Situation Two:

If under the same lake water conditions organic material were increased so that more accumulated in the sediment, the phosphorus situation would adjust. Higher amounts of organics would lead to more algal metabolism and the reducing pore water could extend farther upward. With just the proper amount of organic material the oxidation-reduction interface would move upwards to the sediment-water interface. Under such conditions iron and manganese crusts would form at the surface, fixing phosphorus in relatively sediment-free oxides and hydroxides (Fig.1, middle).

Situation Three:

If the organic content increased even more, nutrients would not be trapped in the sediments but released to the water column. Very high bacterial production would push the reducing-oxidizing interface into the bottom water. This situation would pump phosphorus into the water column along with iron and manganese (Fig.1, upper). Such a system would be self-feeding. As phosphorus was pumped into the lake water productivity would increase. Higher productivity would supply more organics to the sediment to power the phosphorus pump. Such a cycle would not easily change unless primary productivity was nearly completely eliminated. This cycling process makes it very difficult to reverse lake eutrophication because of the large storehouse of nutrients in the sediments (Drever, 1982; Williams et al., 1976).

Obviously the affect of situation three would depend on the change of nutrient concentration in the lake water. Even with a large amount of phosphorus released, if the total concentration

did not change enough to affect the trophic state of the lake the situation would last only briefly. Because eutrophication rarely, if ever, throughout an entire lake but begins in restricted bays, such affects would probably first occur in isolated areas.

Flathead Lake bays, in general, support higher productivity than the open lake and sediment accumulation in those bays is richer in organics and contains higher concentrations of phosphorus. If we assume all the phosphorus was released from the upper one centimeter of sediment (essentially, the oxidized layer) how would such an input change the trophic state of some particular bays. It turns out, significantly!

Vollenweider (1975, 1976) calculated that phosphorus concentrations of 10 micrograms/liter is the critical value for eutrophication in temperate lakes. Flathead lake lies at the oligotrophic-mesotrophic boundary with average concentrations of 7.5 micrograms/liter of phosphorus. If phosphorus released from sediment under isolated, short-term events increased concentrations above the critical value the affect would be selfsustaining. Specific examples suggest that such a system could easily develop.

Woods Bay, the largest developed bay on the east side of Flathead Lake, contains approximately  $1.7 \times 10^{11}$  liters of water. If all the extractable phosphorus was released from the upper 1 centimeter of sediment,  $6.8 \times 10^{13}$  micrograms of phosphorus would be supplied to the water column. Such an influx would change the concentration to 400 micrograms/liter, forty times the amounts



needed for eutrophication.

Yellow Bay would suffer even worse increases. With a volume of  $3.5 \times 10^9$  liters and  $4.8 \times 10^{12}$  micrograms of phosphorus, the concentration would climb to 1300 micrograms/liter if only the upper 1 centimeter released it's phosphorus. Such a concentration would be 130 times the critical value for eutrophication. Larger bays fare no better. Sommer's Bay, the largest, open bay on the northern shore, would contain 100 times the phosphorus needed for eutrophication.

Even if only 10% of the available phosphorus was released in these senarios the concetrations would be from 4 to 13 times that need for eutrophication. So, the reservoir of phosphorus is very significant and must be considered a potential source for drastic change in the trophic status of Flathead Lkae.

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## APPENDIX I

## Methods

### Sediment Sampling

Sediment samples were collected during the summers of 1980 and 1981, operating out of the University of Montana Biological Station at Yellow Bay. Sampling sites were located on a one-mile grid by sextant resectioning on shoreline topographic features. Grab samples taken at 110 sites were analyzed for grain size, extractable phosphorus and extractable heavy metals.

Originally, the Coulter Counter was used to analyze for grain size. Unfortunately, because of noise generated by the instrument in the finest size material, we feel we cannot trust the data. Also, because the technique involves mixing two data sets, other problems are introduced. Our statistical analysis of the data suggests that the instrument modifies the distribution during analysis. Because of these two problems, we abandoned all data collected on the Coulter Counter and used established methods of grain size analysis using a simple pipette technique developed several decades ago and free of major analytical problems.

In many grab samples, a distinct difference was recognized between an upper, light oxidized layer and a lower, dark reduced layer. Whenever possible, these subsamples were collected and analyzed separately. All grab samples were stored in polyethylene containers, packed in ice on the boat, then transferred to refrigerators where they were kept at 40 °C until analyzed.

Short cores (up to 1m long) of sediment collected at approximately 50 sites in the southern lake were used for establishing a sedimentary framework of the surface sediments.

Long cores (up to 6m long) were collected at 11 sites to determine sedimentation history and elucidate near-surface units in sub-bottom profiles. Extractable phosphorus and heavy metal concentrations were determined for selected samples from the long cores.

### Heavy Metals

The extraction scheme used for heavy metals analysis was a step extraction of the type developed by Chester and Hughes (1967), Gupta and Chen (1975R, and Skei and Paus (1979). The step extraction process used in this study was a simplified version of the scheme devised by Skei and Paul (1979) involving only two steps.

The first step in the process was an extraction using a weak acetic acid solution. A portion of the sample was oven dried at 50-60 C. One-third of a gram of this dried material was then placed in a Nalgene screw-cap test tube, to which was added 25 ml of acetic acid (20%). The test tube was then transferred to a mechanical shaker table and shaken for 12 hours at room temperature. The tube was then centrifuged for 15 minutes at 3000 rpm. The sample was then decanted into a polyethylene vial and stored at or below 4 C. The samples were then analyzed for metals using a Perkin-Elmer 5000 atomic absorption spectrophotometers equipped with hollow cathode lamps. The elements--iron, manganese, zinc, and copper were analyzed in flame mode and/or graphite tube furnace mode.

The second step involved a complete fusion-dissolution of the sediment using a procedure developed by Yule and Swanson



(1969). One-tenth gram of dried sediment was fused with 0.6g of lithium metaborate at 1000 C for 15 minutes in a platinum crucible. The crucible was then quenched in cold, deionized water and the resulting fused glass was then dissolved by adding 10.0 ml of conc HCl and 40.0 ml of hot deionized water in a tall form 100 ml beaker, and stirring with a magnetic stirrer. The solution was then diluted to 200 ml with deionized water, and stored in polyethylene bottles. Metal analysis of the solutions were performed using a varian model AA-6 atomic absorption spectrophotometer in flame mode.

For the analysis of both the extracted solutions and the solutions resulting from total dissolution, re-agent blanks were analyzed and either spikes or duplicates of every third sample were also analyzed. Standard solutions were made up with chemical compositions and concentrations duplicating those of the sample solutions. Re-agent grade materials were used in all cases.

The acetic acid extraction releases only those metal ions that are weakly bound to carbonates, clays, iron and manganese compounds, and organic particles (Loring, 1976). According to Gupta and Chen (1975), those metal ions are the ones that could become available to the biota if the sediments are disturbed, either chemically or physically. The metal released during the fusion-dissolution on the other hand includes all metal present, whether weakly or tightly bound. The difference between the two would be the metal that is tightly bound, for example in crystal lattices, and therefore unavailable to the biota.

### Extractable Phosphorus

Total, inorganic and organic phosphorus were determined in the lake sediments after extraction of the ignited and unignited sediment sample with  $1N\ H_2SO_4$ . A sub-sample was taken, after thoroughly mixing the grab sample, and dried at about  $62^\circ C$ . Two portions of the sample weighing 0.5 gm were taken. One portion was ignited for four hours at  $550^\circ C$  in a muffle furnace. The ignited sample was cooled to room temperature. The ignited and unignited samples were then extracted with  $1N\ H_2SO_4$  for 16 hours on a shaking table. After extraction, these samples were centrifuged for 15 minutes. The phosphorus was measured in both the portions of the decantant by ascorbic acid method.

A solution of 1ml of the decantant from the extraction and about 5 ml of deionized water was neutralized with  $1N\ NaOH$  using phenolphthalein as an indicator. The end point was marked by the appearance of light pink color which persists for at least 20 to 30 seconds after neutralization, the solution was diluted to exactly 25.0 ml. Then, 4 ml of combined re-agent was added, and the solution was allowed to stand for exactly 20 minutes in order to give color an equal time to develop in all samples.

1. 100 ml of combined re-agent was obtained by mixing 50 ml of  $5N\ H_2SO_4$ ; 5 ml potassium antimony tartrate solution having 1.3715 gm of  $K(SbO)_4C_4H_4O_6 \cdot \frac{1}{2}H_2O$  in 500 ml of deionized water; 15 ml of ammonium molybdate solution containing 20 g  $(NH_4)_6Mo_7O_{26} \cdot 2H_2O$  in 500 ml of deionized water; and 30 ml of 0.1 M ascorbic acid.

The color absorbance of each sample was then measured using a spectrophotometer at a wavelength of 880 nm. Standard solutions and blanks were run under similar conditions.

The phosphorus extracted from ignited sediments will be referred herein as inorganic phosphorus and that extracted from unignited portion as total phosphorus. The difference between extractable total and inorganic phosphorus is termed extractable organic phosphorus.

## APPENDIX II

## Raw Data

Metals and phosphorus reported in ppm extractable.

Carbon, sand, silt and clay in weight percent.

Depth in feet, reference lake level is 2893 ft

## METALS

SAMPLE	ZINC		MANGANESE		IRON		COPPER	
	OX	NONOX	OX	NONOX	OX	NONOX	OX	NONOX
80- 1	0.0	12.5	0.0	64.1	0.0	1813.0	0.0	8.9
80- 3	0.0	9.5	0.0	141.2	0.0	1928.6	0.0	13.7
80- 4	0.0	11.2	0.0	130.3	0.0	2385.6	0.0	11.7
80- 5	0.0	10.7	0.0	130.7	0.0	2403.3	0.0	15.0
80- 6	0.0	8.3	0.0	365.1	0.0	3692.3	0.0	6.0
80- 7	0.0	8.6	0.0	235.0	0.0	1854.0	0.0	7.2
80- 8	0.0	9.0	0.0	300.7	0.0	2180.6	0.0	7.0
80- 10	0.0	6.7	0.0	448.1	0.0	2763.1	0.0	11.0
80- 12	0.0	12.0	0.0	1062.2	0.0	3844.7	0.0	16.5
80- 13	0.0	17.6	0.0	48.5	0.0	2009.5	0.0	12.8
80- 15	0.0	5.5	0.0	54.9	0.0	1793.8	0.0	12.2
80- 17	0.0	8.6	0.0	135.4	0.0	1462.3	0.0	3.7
80- 19	0.0	12.8	0.0	64.8	0.0	2440.5	0.0	10.0
80- 20	0.0	8.3	0.0	245.9	0.0	2793.1	0.0	6.3
80- 22	0.0	6.8	0.0	27.0	0.0	895.9	0.0	6.8
80- 26	0.0	13.2	0.0	44.8	0.0	1818.1	0.0	9.6
80- 29	0.0	17.7	0.0	89.9	0.0	2618.9	0.0	11.7
80- 30	0.0	3.0	0.0	251.5	0.0	501.5	0.0	2.8
80- 31	0.0	13.0	0.0	86.6	0.0	2696.7	0.0	9.9
80- 32	0.0	12.7	0.0	87.3	0.0	2715.4	0.0	8.5
80- 34	0.0	19.4	0.0	41.1	0.0	1880.9	0.0	14.2
80- 36	0.0	12.1	0.0	29.4	0.0	1335.8	0.0	11.0
80- 38	14.2	15.4	1124.2	427.3	4207.1	5370.0	10.0	11.9
80- 51	14.2	18.7	2370.4	1065.3	5293.0	4919.1	9.2	14.5
80- 53	18.8	14.9	1028.8	308.0	5850.5	2688.1	7.4	7.6
80- 54	0.0	28.7	0.0	291.5	0.0	3636.6	0.0	12.2
80- 55	20.1	28.5	1641.4	699.2	6255.0	5623.5	9.5	13.8
80- 57	0.0	26.2	0.0	155.6	0.0	1668.8	0.0	8.6
80- 59	0.0	25.7	0.0	74.1	0.0	2025.3	0.0	10.5
80- 60	22.4	15.6	164.8	137.5	2474.1	2765.4	11.5	13.9
80- 62	0.0	20.1	0.0	65.4	0.0	1860.5	0.0	12.1
80- 64	0.0	27.7	0.0	352.1	0.0	4787.3	0.0	12.9
80- 65	0.0	11.3	0.0	26.3	0.0	1795.5	0.0	10.0
80- 67	19.0	19.6	1439.3	1008.4	5393.3	6752.2	12.7	14.1
80- 68	21.0	20.6	380.3	237.5	3507.0	3185.3	12.5	11.6
80- 70	20.5	19.1	223.7	117.8	3031.5	2440.0	10.2	9.3
80- 71	10.1	25.4	1769.3	1429.8	2939.5	5148.3	6.9	12.0
80- 73	14.7	23.9	2490.9	1706.9	5063.4	5410.5	9.6	11.8
80- 75	13.5	13.9	1625.3	981.5	2577.0	4875.2	7.2	11.0
80- 78	15.3	21.9	2664.5	2712.9	6335.0	5902.3	8.1	13.4
80- 79	15.5	23.3	2327.6	1827.8	5879.1	4573.5	8.7	14.4
80- 81	8.1	7.4	218.2	673.5	1094.4	3158.8	3.8	9.9
80- 82	0.0	4.5	0.0	70.9	0.0	1404.0	0.0	3.4
80- 83	0.0	3.8	0.0	44.3	0.0	408.5	0.0	1.6
80- 85	9.7	16.3	472.9	1844.1	2098.3	4417.8	7.3	12.9
80- 86	16.5	21.3	1387.9	1817.1	5515.6	5346.5	12.2	15.4
80- 87	0.0	9.8	0.0	477.8	0.0	2172.0	0.0	7.4
80- 88	0.0	16.3	0.0	3173.0	0.0	6166.6	0.0	13.9
80- 91	0.0	17.6	0.0	1771.7	0.0	6458.5	0.0	14.3
80- 92	15.0	18.3	2896.4	2175.5	5703.6	5592.2	11.0	14.8
80- 93	14.9	16.3	2727.4	2641.8	5972.5	5680.2	10.5	16.0
80- 94	15.6	26.2	2453.8	2125.7	4199.7	5291.7	9.6	14.4
80- 96	15.7	21.0	2612.0	2304.8	5068.4	5337.0	15.9	15.6
80- 98	15.7	19.6	2797.5	1946.9	5181.0	5599.4	11.4	15.9
80- 99	15.7	20.9	2396.2	2830.3	4326.8	5072.0	11.2	13.5

## METALS

SAMPLE	ZINC		MANGANESE		IRON		COPPER	
	OX	NONOX	OX	NONOX	OX	NONOX	OX	NONOX
80-101	0.0	29.1	0.0	1536.9	0.0	5392.3	0.0	14.7
80-102	0.0	19.5	0.0	2404.7	0.0	5793.2	0.0	15.9
80-105	15.6	23.4	7030.8	1462.8	4522.0	4271.4	11.2	13.3
80-106	15.0	22.5	2235.7	2107.5	3569.0	5241.0	10.4	14.5
80-110	16.2	14.8	1642.1	1699.0	1887.8	3001.1	9.9	12.2
80-111	14.2	20.3	2371.9	1529.0	4316.7	4051.0	10.0	9.3
81-112	0.0	6.2	0.0	125.2	0.0	808.5	0.0	1.4
81-114	13.1	13.2	2260.0	802.7	4162.0	3862.0	6.7	10.8
81-115	13.1	16.8	1627.0	589.0	3532.0	4213.0	7.1	9.7
81-116	14.5	14.0	1130.0	512.9	3683.0	3707.0	7.0	8.9
81-117	14.0	13.3	999.0	627.8	3868.0	4739.0	6.3	9.3
81-118	12.7	17.6	1756.0	375.8	4447.0	4428.0	6.3	9.3
81-119	11.4	13.0	1515.0	659.8	2806.0	3849.0	6.7	11.2
81-120	14.4	22.5	671.2	290.7	3228.0	2901.0	6.7	8.2
81-122	22.1	15.9	2132.0	1397.0	3853.0	3272.0	8.9	11.9
81-123	14.2	13.3	2280.0	2125.0	3437.0	5792.0	8.6	11.6
81-124	13.9	13.2	2386.0	1510.0	4465.0	3850.0	9.3	13.8
81-125	13.8	19.4	1508.0	1060.0	4145.0	3827.0	6.3	9.3
81-126	13.8	23.5	1781.0	806.1	4356.0	3688.0	6.7	8.9
81-127	13.5	16.6	1877.0	816.2	3838.0	4883.0	7.4	10.1
81-128	13.2	19.4	1197.0	880.4	3780.0	3383.0	6.7	9.3
81-129	12.0	12.6	1678.0	1382.0	3655.0	3541.0	8.2	12.3
81-130	15.4	17.5	2258.0	2517.0	4459.0	6294.0	5.2	10.1
81-131	16.0	14.8	1876.0	1635.0	3986.0	3699.0	5.2	10.4
81-132	16.4	23.1	2381.0	1994.0	4230.0	4575.0	9.7	10.1
81-133	14.6	20.1	2124.0	1752.0	2937.0	4358.0	4.8	8.9
81-134	10.0	13.4	1263.0	1034.0	3728.0	3680.0	8.6	10.1
81-135	13.0	16.2	1651.0	690.8	3583.0	3347.0	6.3	8.2
81-136	13.3	18.1	1382.0	641.1	3839.0	3529.0	5.9	8.2
81-137	11.4	14.3	890.4	621.5	3859.0	3568.0	7.4	8.9
81-138	12.7	17.1	786.3	387.8	3403.0	3108.0	5.9	10.8
81-139	10.2	12.9	931.2	772.3	3568.0	3390.0	10.8	13.8
81-140	6.7	6.0	189.6	105.4	675.8	711.0	3.3	4.8
81-141	19.9	25.6	726.0	524.9	4137.0	4768.0	8.2	10.4
81-143	17.9	17.5	661.7	999.9	3218.0	3721.0	7.4	9.7
81-144	14.9	15.6	1891.0	831.9	3565.0	3569.0	6.3	11.2
81-145	12.8	12.7	2071.0	634.6	3478.0	4183.0	6.3	9.7
81-146	8.8	11.2	907.7	261.8	2949.0	2503.0	4.4	7.4
81-147	10.5	12.0	1044.0	245.2	2946.0	2339.0	5.9	6.7
81-148	9.3	10.4	1510.0	430.4	4000.0	2810.0	7.4	7.4
81-149	12.1	13.6	1767.0	449.5	4471.0	3869.0	8.2	10.8
81-150	13.4	17.7	1740.0	648.2	3511.0	3998.0	7.8	8.2
81-151	12.2	17.5	1884.0	456.1	4154.0	3080.0	5.9	9.7
81-152	9.7	7.2	257.8	124.5	1106.0	972.3	3.3	3.3
81-153	0.0	8.0	0.0	179.4	0.0	1761.0	0.0	4.4
81-154	0.0	6.4	0.0	174.5	0.0	1512.0	0.0	5.2
81-155	9.4	9.2	365.3	304.1	2203.0	2355.0	11.2	7.4
81-156	0.0	7.1	0.0	131.1	0.0	659.8	0.0	2.9
81-157	13.2	12.1	1395.0	577.8	4027.0	4188.0	6.3	13.8
81-158	17.6	20.2	1136.0	493.5	4155.0	4122.0	6.3	10.1
81-159	24.7	21.5	1633.0	587.3	3093.0	4477.0	5.9	10.4
81-160	72.1	52.3	492.0	233.5	5085.0	3385.0	6.3	8.6
81-161	0.0	12.7	0.0	1646.0	0.0	594.4	0.0	2.9
81-162	11.9	13.3	262.6	112.4	1240.0	845.8	4.0	4.0
81-163	10.3	12.9	717.2	455.8	2333.0	3254.0	7.0	9.3

## DEPTH/SEDIMENT GRAIN SIZE

122

SAMPLE	DEPTH	SAND		SILT		CLAY	
		OX	NONOX	OX	NONOX	OX	NONOX
80- 1	53	0.0	33.0	0.0	38.8	0.0	28.2
80- 3	19	0.0	0.0	0.0	76.5	0.0	23.5
80- 4	18	0.0	****	0.0	****	0.0	****
80- 5	19	0.0	1.2	0.0	67.3	0.0	31.5
80- 6	15	0.0	9.0	0.0	40.9	0.0	50.1
80- 7	30	0.0	20.0	0.0	70.2	0.0	9.8
80- 8	80	0.0	2.7	0.0	81.8	0.0	15.5
80- 10	65	0.0	37.6	0.0	11.2	0.0	51.2
80- 12	330	0.0	0.0	0.0	58.6	0.0	61.4
80- 13	20	0.0	****	0.0	****	0.0	****
80- 15	15	0.0	7.0	0.0	66.0	0.0	27.0
80- 17	8	0.0	41.5	0.0	58.5	0.0	0.0
80- 19	17	0.0	12.0	0.0	54.0	0.0	34.0
80- 20	***	0.0	46.6	0.0	16.3	0.0	37.1
80- 22	***	0.0	62.6	0.0	37.4	0.0	0.0
80- 26	***	0.0	10.7	0.0	89.3	0.0	0.0
80- 29	***	0.0	5.9	0.0	62.5	0.0	31.6
80- 30	4	0.0	60.0	0.0	19.6	0.0	20.4
80- 31	16	0.0	6.9	0.0	72.0	0.0	21.1
80- 32	16	0.0	37.1	0.0	53.7	0.0	9.2
80- 34	22	0.0	1.3	0.0	98.7	0.0	0.0
80- 36	20	0.0	13.1	0.0	86.9	0.0	0.0
80- 38	132	****	3.4	****	73.8	****	22.8
80- 51	198	0.0	0.0	30.0	25.8	70.0	74.2
80- 53	90	36.3	27.9	26.2	37.1	37.5	35.0
80- 54	105	0.0	0.9	0.0	23.8	0.0	75.3
80- 55	115	****	0.0	****	31.0	****	69.0
80- 57	75	0.0	1.6	0.0	49.2	0.0	49.2
80- 59	65	0.0	****	0.0	****	0.0	****
80- 60	80	2.4	0.4	27.5	51.2	70.1	48.4
80- 62	36	0.0	2.6	0.0	30.0	0.0	67.4
80- 64	120	0.0	0.4	0.0	27.4	0.0	72.2
80- 65	17	0.0	0.0	0.0	51.4	0.0	48.6
80- 67	140	0.0	0.0	24.8	29.2	75.2	70.8
80- 68	115	0.0	0.0	25.7	58.1	74.3	41.9
80- 70	75	****	****	****	****	****	****
80- 71	240	0.0	0.0	25.2	27.5	74.8	72.5
80- 73	252	0.0	0.0	23.9	30.0	76.1	70.0
80- 75	180	0.0	0.0	31.5	28.7	68.5	71.3
80- 78	300	****	0.5	****	22.2	****	77.3
80- 79	295	****	0.0	****	27.5	****	72.5
80- 81	***	****	69.3	****	17.6	****	13.1
80- 82	***	0.0	54.5	0.0	42.4	0.0	3.1
80- 83	***	0.0	95.5	0.0	0.5	0.0	0.0
80- 85	***	****	0.0	****	51.5	****	48.5
80- 86	***	0.0	0.0	21.8	21.0	78.2	79.0
80- 87	***	0.0	0.0	0.0	18.0	0.0	82.0
80- 88	252	0.0	0.0	0.0	30.0	0.0	70.0
80- 91	205	0.0	0.0	0.0	25.8	0.0	74.2
80- 92	216	0.0	0.7	33.7	29.7	66.3	69.6
80- 93	240	****	0.0	****	20.4	****	79.6
80- 94	258	0.0	0.0	32.1	28.0	67.9	72.0
80- 96	270	0.0	0.0	30.2	41.6	69.8	58.4
80- 98	270	0.0	0.0	33.8	36.4	66.2	63.6
80- 99	270	0.0	0.0	36.6	26.6	63.4	73.4

## DEPTH/SEDIMENT GRAIN SIZE

123

SAMPLE	DEPTH	SAND		SILT		CLAY	
		OX	NONOX	OX	NONOX	OX	NONOX
80-101	348	0.0	0.0	0.0	25.2	0.0	74.8
80-102	180	0.0	4.0	0.0	27.8	0.0	68.2
80-105	264	0.0	0.0	29.1	24.9	70.9	75.1
80-106	258	0.0	0.0	34.3	27.2	65.7	72.8
80-110	155	****	0.0	****	57.7	****	42.3
80-111	160	0.0	0.0	34.0	47.4	66.0	52.6
81-112	40	0.0	87.2	0.0	9.8	0.0	3.0
81-114	180	0.0	0.0	32.6	30.8	67.4	69.2
81-115	110	0.0	0.0	36.2	41.3	63.8	58.7
81-116	115	0.0	0.0	37.3	37.6	62.7	62.4
81-117	140	0.0	0.0	36.1	37.3	63.9	62.7
81-118	70	0.0	0.0	38.2	36.4	61.8	63.6
81-119	100	0.0	0.0	42.4	38.1	57.6	61.9
81-120	55	0.0	0.0	39.1	33.3	60.9	64.3
81-122	250	1.8	1.2	26.9	24.9	71.3	73.9
81-123	300	0.0	0.0	30.7	23.3	69.3	76.7
81-124	300	0.0	0.0	32.4	35.2	67.7	64.8
81-125	180	****	0.0	****	28.8	****	71.2
81-126	145	0.0	0.0	35.4	31.1	64.6	68.9
81-127	160	0.0	0.0	36.7	41.5	63.3	58.5
81-128	135	0.0	0.0	37.4	40.6	62.6	59.4
81-129	320	0.0	0.0	40.9	41.2	59.1	58.8
81-130	250	0.0	0.0	27.4	22.5	72.6	77.5
81-131	155	1.0	0.0	41.4	24.3	57.6	75.7
81-132	200	0.0	0.0	33.4	27.5	66.6	72.5
81-133	185	0.0	0.0	40.0	29.5	60.0	70.5
81-134	200	0.0	0.0	39.5	43.9	60.5	56.1
81-135	140	****	0.0	****	49.2	****	50.8
81-136	100	0.0	0.0	43.3	44.8	56.7	55.2
81-137	125	0.0	0.0	39.9	43.0	60.1	57.0
81-138	90	****	****	****	****	****	****
81-139	200	0.0	0.0	41.0	41.2	59.0	58.8
81-140	95	****	****	****	****	****	****
81-141	190	5.2	****	37.6	****	57.2	****
81-143	110	****	****	****	****	****	****
81-144	210	****	0.0	****	36.9	****	63.1
81-145	290	0.0	0.0	51.6	47.2	48.4	52.7
81-146	75	1.0	2.2	57.0	70.5	42.0	27.3
81-147	70	0.0	1.7	61.3	65.4	38.7	32.9
81-148	185	0.0	0.0	70.4	70.5	29.6	29.5
81-149	235	0.0	1.2	56.0	44.3	44.0	54.5
81-150	155	0.0	0.0	49.9	47.2	50.1	52.4
81-151	120	3.1	3.3	59.1	51.1	37.8	45.6
81-152	12	****	77.7	****	16.5	****	5.8
81-153	20	0.0	42.1	0.0	48.7	0.0	9.2
81-154	10	0.0	65.5	0.0	26.5	0.0	8.0
81-155	45	****	8.5	****	73.4	****	18.1
81-156	12	0.0	86.2	0.0	9.6	0.0	4.2
81-157	85	0.0	****	50.6	****	49.4	****
81-158	65	0.0	0.0	39.3	35.7	60.7	64.3
81-159	70	0.0	0.0	41.0	42.7	59.0	57.3
81-160	40	****	0.9	****	49.7	****	49.4
81-161	10	0.0	86.8	0.0	8.8	0.0	4.4
81-162	20	67.6	72.9	18.8	17.0	13.6	10.1
81-163	55	0.0	0.0	68.7	69.3	31.3	30.7

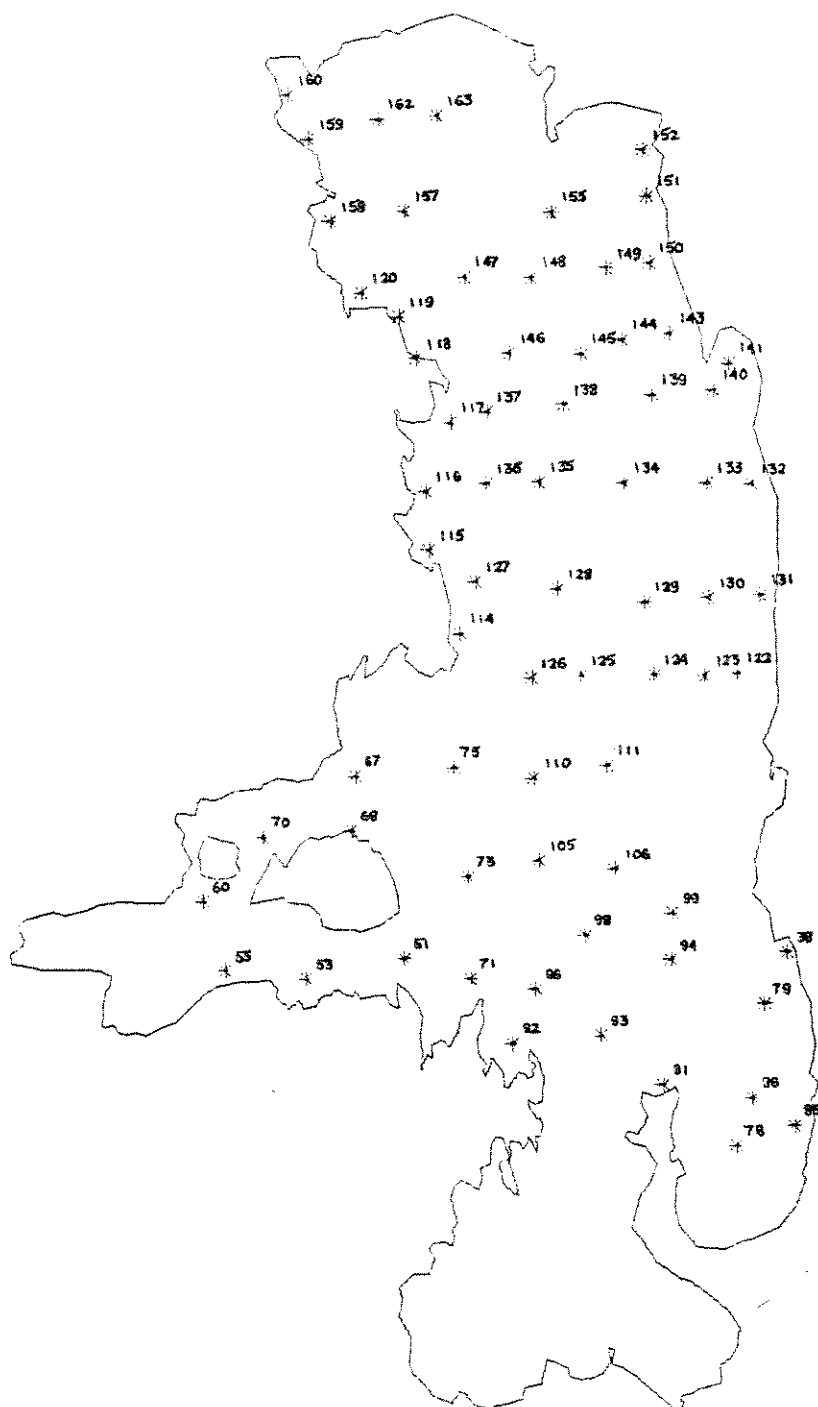


SAMPLE	ORGANIC PHOSPHORUS		INORGANIC PHOSPHORUS		TOTAL PHOSPHORUS		CARBON	
	OX	NONOX	OX	NONOX	OX	NONOX	OX	NONOX
80- 1	0.0	120.0	0.0	762.0	0.0	882.0	0.0	1.5
80- 3	0.0	30.0	0.0	387.0	0.0	417.0	0.0	7.1
80- 4	0.0	218.0	0.0	502.0	0.0	720.0	0.0	3.5
80- 5	0.0	238.0	0.0	446.0	0.0	684.0	0.0	*****
80- 6	0.0	99.0	0.0	772.0	0.0	871.0	0.0	*****
80- 7	0.0	166.0	0.0	1072.0	0.0	1238.0	0.0	1.9
80- 8	0.0	116.0	0.0	1190.0	0.0	1306.0	0.0	2.3
80- 10	0.0	107.0	0.0	692.0	0.0	799.0	0.0	0.3
80- 12	0.0	248.0	0.0	1581.0	0.0	1829.0	0.0	1.0
80- 13	0.0	295.0	0.0	756.0	0.0	1051.0	0.0	4.0
80- 15	0.0	194.0	0.0	444.0	0.0	638.0	0.0	4.7
80- 17	0.0	469.0	0.0	673.0	0.0	1142.0	0.0	5.1
80- 19	0.0	361.0	0.0	1098.0	0.0	1459.0	0.0	2.1
80- 20	0.0	105.0	0.0	959.0	0.0	1064.0	0.0	0.3
80- 22	0.0	114.0	0.0	572.0	0.0	686.0	0.0	1.4
80- 26	0.0	469.0	0.0	781.0	0.0	1250.0	0.0	4.1
80- 29	0.0	323.0	0.0	919.0	0.0	1242.0	0.0	6.6
80- 30	0.0	346.0	0.0	927.0	0.0	1273.0	0.0	0.3
80- 31	0.0	318.0	0.0	1329.0	0.0	1647.0	0.0	2.3
80- 32	0.0	78.0	0.0	1437.0	0.0	1515.0	0.0	2.5
80- 34	0.0	40.0	0.0	670.0	0.0	710.0	0.0	1.2
80- 36	0.0	35.0	0.0	633.0	0.0	668.0	0.0	2.9
80- 38	143.0	361.0	2958.0	2600.0	3101.0	2961.0	2.4	*****
80- 51	252.0	235.0	2425.0	1972.0	2777.0	2207.0	1.5	1.4
80- 53	301.0	549.0	1752.0	1441.0	2053.0	1990.0	1.4	1.6
80- 54	0.0	715.0	0.0	1325.0	0.0	2040.0	0.0	2.0
80- 55	485.0	570.0	2134.0	1757.0	2619.0	2327.0	2.3	1.7
80- 57	0.0	684.0	0.0	1016.0	0.0	1700.0	0.0	2.3
80- 59	0.0	677.0	0.0	877.0	0.0	1554.0	0.0	3.1
80- 60	709.0	493.0	1338.0	1068.0	2047.0	1561.0	2.2	2.1
80- 62	0.0	390.0	0.0	798.0	0.0	1188.0	0.0	2.4
80- 64	0.0	730.0	0.0	1366.0	0.0	2096.0	0.0	*****
80- 65	0.0	280.0	0.0	1542.0	0.0	1822.0	0.0	*****
80- 67	252.0	257.0	2090.0	1917.0	2342.0	2174.0	1.1	1.2
80- 68	575.0	813.0	1541.0	1327.0	2116.0	2140.0	*****	1.2
80- 70	672.0	678.0	1324.0	1274.0	1996.0	1952.0	1.8	*****
80- 71	270.0	295.0	2104.0	2098.0	2374.0	2393.0	1.1	*****
80- 73	191.0	269.0	2157.0	2262.0	2348.0	2531.0	1.1	*****
80- 75	328.0	222.0	2117.0	2251.0	2445.0	2473.0	1.2	*****
80- 78	392.0	344.0	3225.0	2641.0	3617.0	2985.0	*****	1.6
80- 79	135.0	416.0	3205.0	2013.0	3340.0	2429.0	*****	1.2
80- 81	337.0	138.0	800.0	1015.0	1137.0	1153.0	0.8	0.4
80- 82	0.0	56.0	0.0	881.0	0.0	937.0	0.0	0.7
80- 83	0.0	53.0	0.0	540.0	0.0	593.0	0.0	0.0
80- 85	271.0	191.0	2825.0	1846.0	3096.0	2137.0	*****	1.7
80- 86	394.0	510.0	2501.0	1751.0	2895.0	2261.0	1.4	1.6
80- 87	0.0	497.0	0.0	1740.0	0.0	2237.0	0.0	0.4
80- 88	0.0	356.0	0.0	2990.0	0.0	3346.0	0.0	1.2
80- 91	0.0	278.0	0.0	2252.0	0.0	2530.0	0.0	1.2
80- 92	278.0	318.0	2782.0	2276.0	3060.0	2594.0	1.8	1.7
80- 93	200.0	246.0	3103.0	2167.0	3303.0	2413.0	*****	1.4
80- 94	327.0	128.0	2765.0	2253.0	3092.0	2381.0	1.4	1.3
80- 96	108.0	359.0	2889.0	2115.0	2997.0	2474.0	1.4	1.3
80- 98	112.0	555.0	3142.0	1805.0	3254.0	2360.0	1.8	1.3
80- 99	281.0	384.0	2331.0	2079.0	2612.0	2463.0	1.4	1.0

## PHOSPHORUS/CARBON

SAMPLE	ORGANIC PHOSPHORUS		INORGANIC PHOSPHORUS		TOTAL PHOSPHORUS		CARBON	
	OX	NONOX	OX	NONOX	OX	NONOX	OX	NONOX
80-101	0.0	374.0	0.0	1191.0	0.0	2285.0	0.0	1.6
80-102	0.0	425.0	0.0	2384.0	0.0	2809.0	0.0	1.3
80-105	638.0	437.0	1905.0	1878.0	2543.0	2315.0	1.4	1.1
80-106	934.0	225.0	1487.0	2167.0	2421.0	2392.0	1.0	*****
80-110	463.0	163.0	1513.0	1775.0	1976.0	1938.0	1.1	0.8
80-111	426.0	513.0	2193.0	1485.0	2619.0	1898.0	1.2	*****
81-112	0.0	145.0	0.0	967.0	0.0	1112.0	0.0	*****
81-114	162.0	349.0	2003.0	1534.0	2165.0	1883.0	*****	*****
81-115	350.0	348.0	1988.0	1315.0	2238.0	1663.0	*****	*****
81-116	372.0	350.0	1740.0	1070.0	2112.0	1420.0	*****	*****
81-117	252.0	274.0	1588.0	1342.0	1840.0	1616.0	*****	*****
81-118	232.0	417.0	1876.0	1380.0	2108.0	1797.0	*****	*****
81-119	217.0	398.0	1795.0	1537.0	2012.0	1935.0	*****	*****
81-120	493.0	585.0	1404.0	1065.0	1897.0	1650.0	*****	*****
81-122	519.0	784.0	1542.0	1250.0	2061.0	2034.0	*****	*****
81-123	683.0	529.0	1397.0	1463.0	2060.0	1992.0	*****	*****
81-124	161.0	328.0	2028.0	1617.0	2189.0	1945.0	*****	*****
81-125	175.0	538.0	2553.0	1524.0	2728.0	2062.0	*****	*****
81-126	166.0	426.0	2302.0	1548.0	2468.0	1974.0	*****	*****
81-127	525.0	387.0	1619.0	1731.0	2144.0	2118.0	*****	*****
81-128	171.0	178.0	2370.0	1856.0	2541.0	2034.0	*****	*****
81-129	358.0	329.0	2099.0	1587.0	2447.0	1916.0	*****	*****
81-130	458.0	205.0	2181.0	2305.0	2639.0	2510.0	*****	*****
81-131	348.0	346.0	1911.0	1722.0	2259.0	2068.0	*****	*****
81-132	220.0	279.0	2163.0	1876.0	2383.0	2155.0	*****	*****
81-133	275.0	472.0	2248.0	1804.0	2523.0	2276.0	*****	*****
81-134	427.0	157.0	1572.0	1862.0	1999.0	2219.0	*****	*****
81-135	146.0	207.0	2008.0	1545.0	2154.0	1752.0	*****	*****
81-136	262.0	278.0	2137.0	1630.0	2399.0	1908.0	*****	*****
81-137	222.0	398.0	2035.0	1388.0	2257.0	1766.0	*****	*****
81-138	224.0	287.0	1843.0	1483.0	2067.0	1770.0	*****	*****
81-139	192.0	320.0	1794.0	1554.0	1986.0	1874.0	*****	*****
81-140	232.0	219.0	1011.0	979.0	1243.0	1198.0	*****	*****
81-141	312.0	278.0	2077.0	1774.0	2389.0	2052.0	*****	*****
81-143	208.0	208.0	1970.0	1918.0	2178.0	2126.0	*****	*****
81-144	533.0	266.0	1439.0	1515.0	1972.0	1781.0	*****	*****
81-145	227.0	259.0	1524.0	1456.0	1751.0	1715.0	*****	*****
81-146	401.0	269.0	1417.0	1541.0	1818.0	1810.0	*****	*****
81-147	290.0	248.0	2208.0	832.0	2498.0	1080.0	*****	*****
81-148	368.0	120.0	1803.0	1276.0	2171.0	1398.0	*****	*****
81-149	377.0	204.0	1573.0	1244.0	1950.0	1448.0	*****	*****
81-150	182.0	372.0	2324.0	1523.0	2506.0	1895.0	*****	*****
81-151	235.0	428.0	2147.0	1417.0	2382.0	1845.0	*****	*****
81-152	429.0	325.0	1486.0	1390.0	2015.0	1715.0	*****	*****
81-153	0.0	385.0	0.0	1629.0	0.0	2014.0	0.0	*****
81-154	0.0	27.0	0.0	1097.0	0.0	1124.0	0.0	*****
81-155	338.0	294.0	2030.0	1819.0	2368.0	2113.0	*****	*****
81-156	0.0	280.0	0.0	1285.0	0.0	1565.0	0.0	*****
81-157	252.0	316.0	1764.0	1377.0	2016.0	1693.0	*****	*****
81-158	329.0	374.0	1695.0	1339.0	2024.0	1713.0	*****	*****
81-159	232.0	125.0	1237.0	777.0	1469.0	902.0	*****	*****
81-160	496.0	332.0	1695.0	1434.0	2191.0	1766.0	*****	*****
81-161	0.0	124.0	0.0	1618.0	0.0	1842.0	0.0	*****
81-162	53.0	76.0	1181.0	1080.0	1234.0	1156.0	*****	*****
81-163	355.0	166.0	1431.0	1521.0	1787.0	1687.0	*****	*****

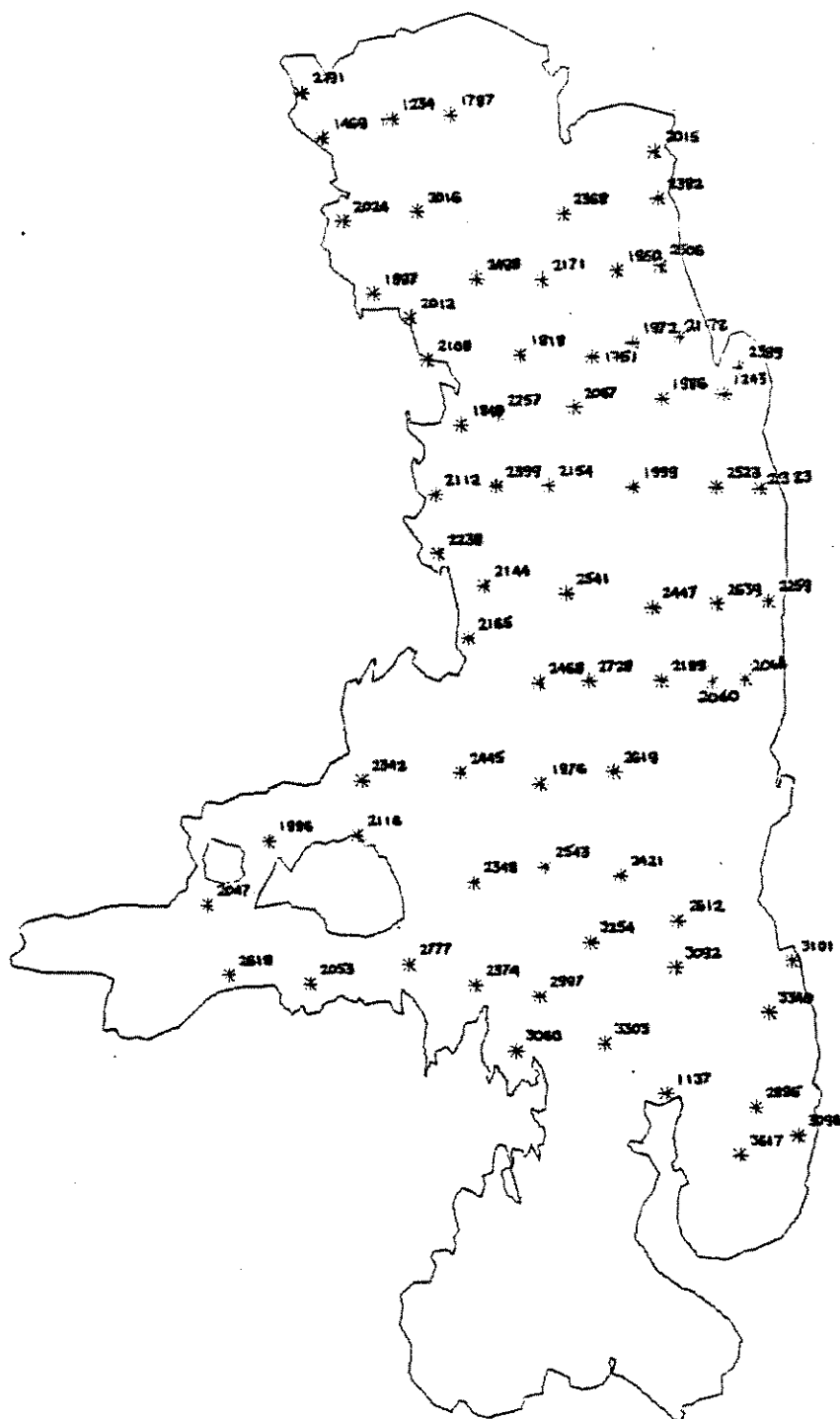
## SAMPLES - OXIDIZED



0 1  
KILOMETERS

0 1  
MILES

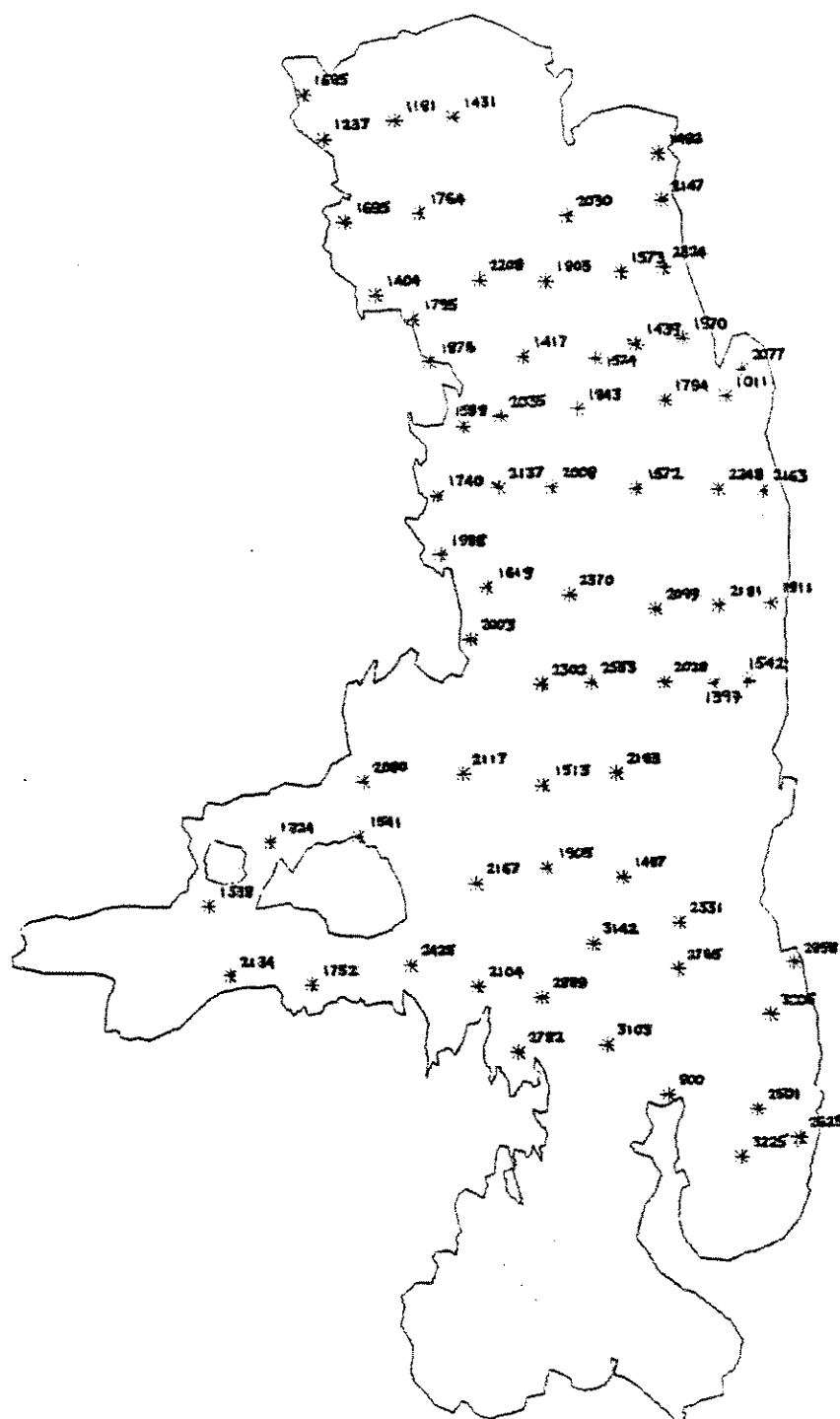
## TOTAL P - OXIDIZED



0 5  
KILOMETERS

0 5  
MILES

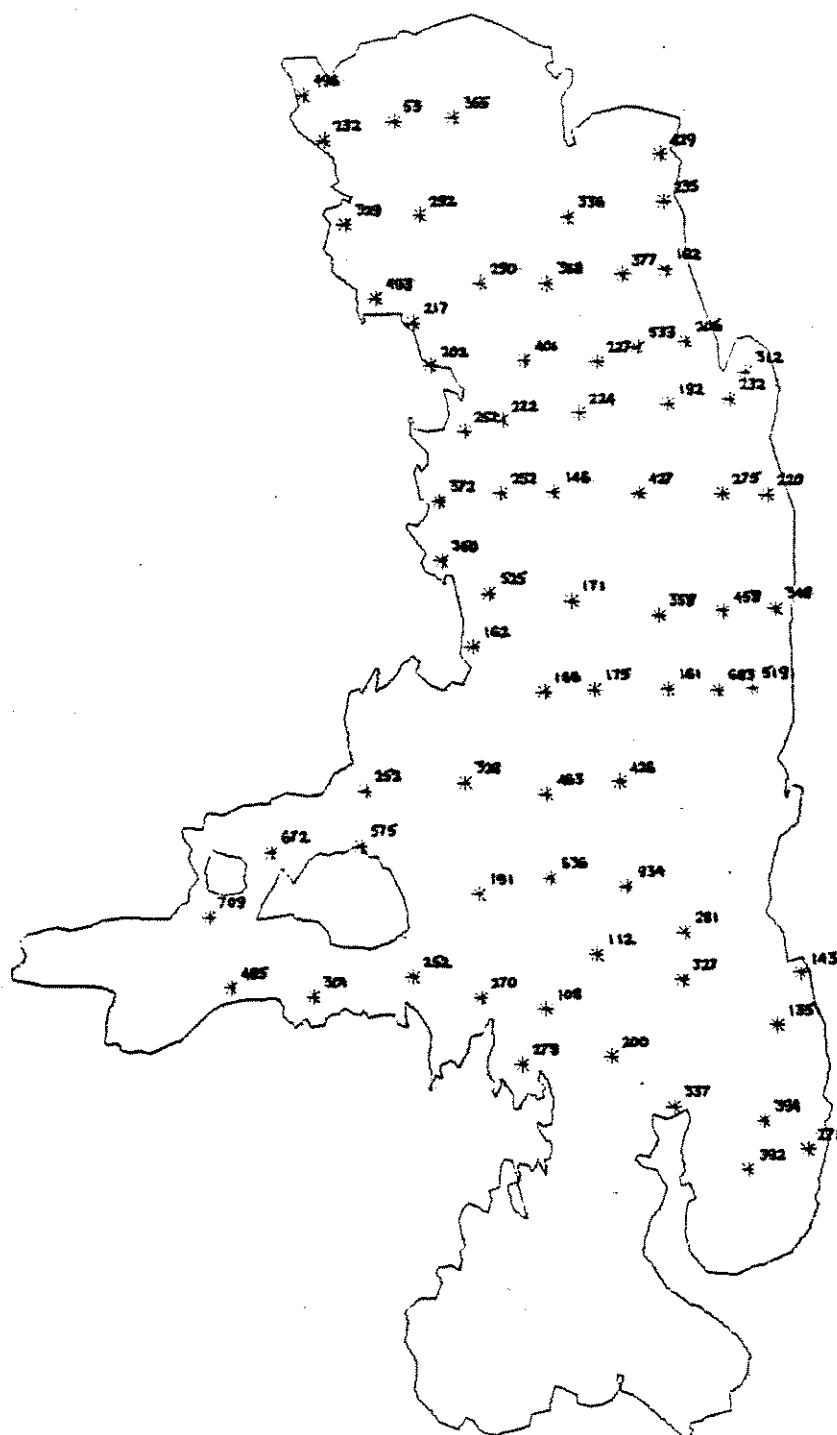
## INORGANIC P - OXIDIZED



Kilometers

Miles

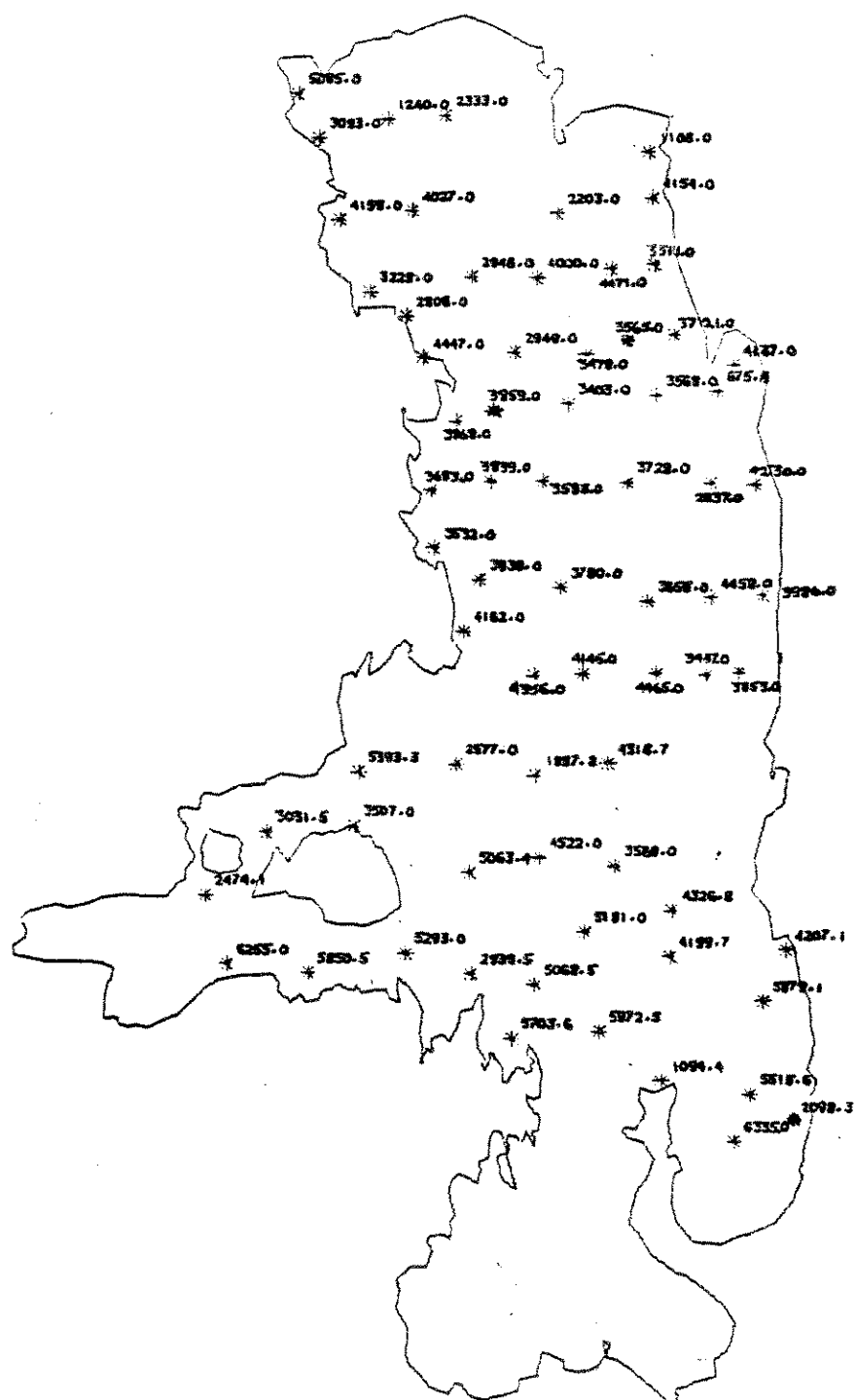
## ORGANIC P - OXIDIZED



0 1 2 3 4  
KILOMETERS

0 1 2 3 4  
MILES

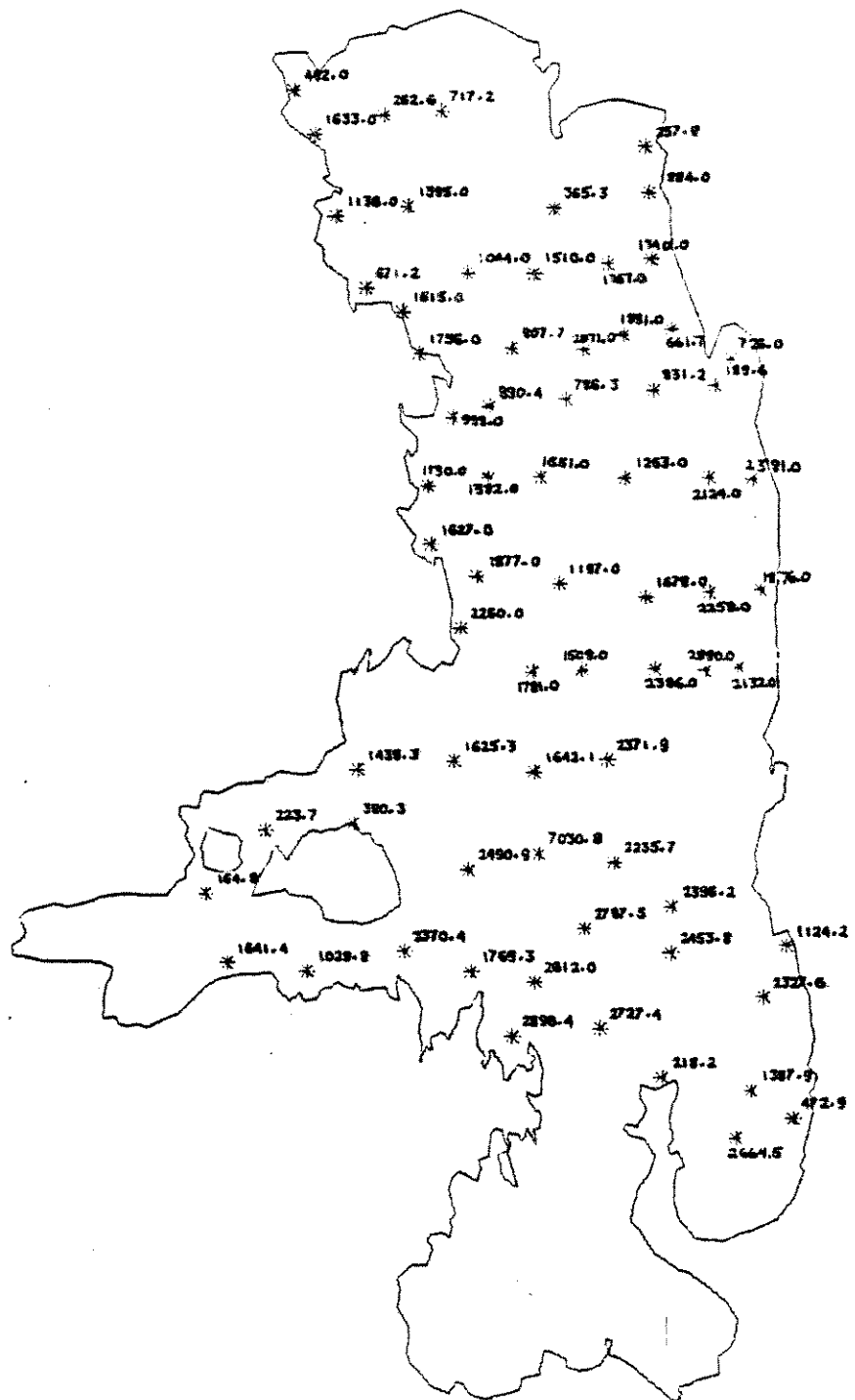
## IRON - OXIDIZED



0 10 KILOMETERS

0 10 MILES

# MANGANESE - OXIDIZED

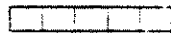
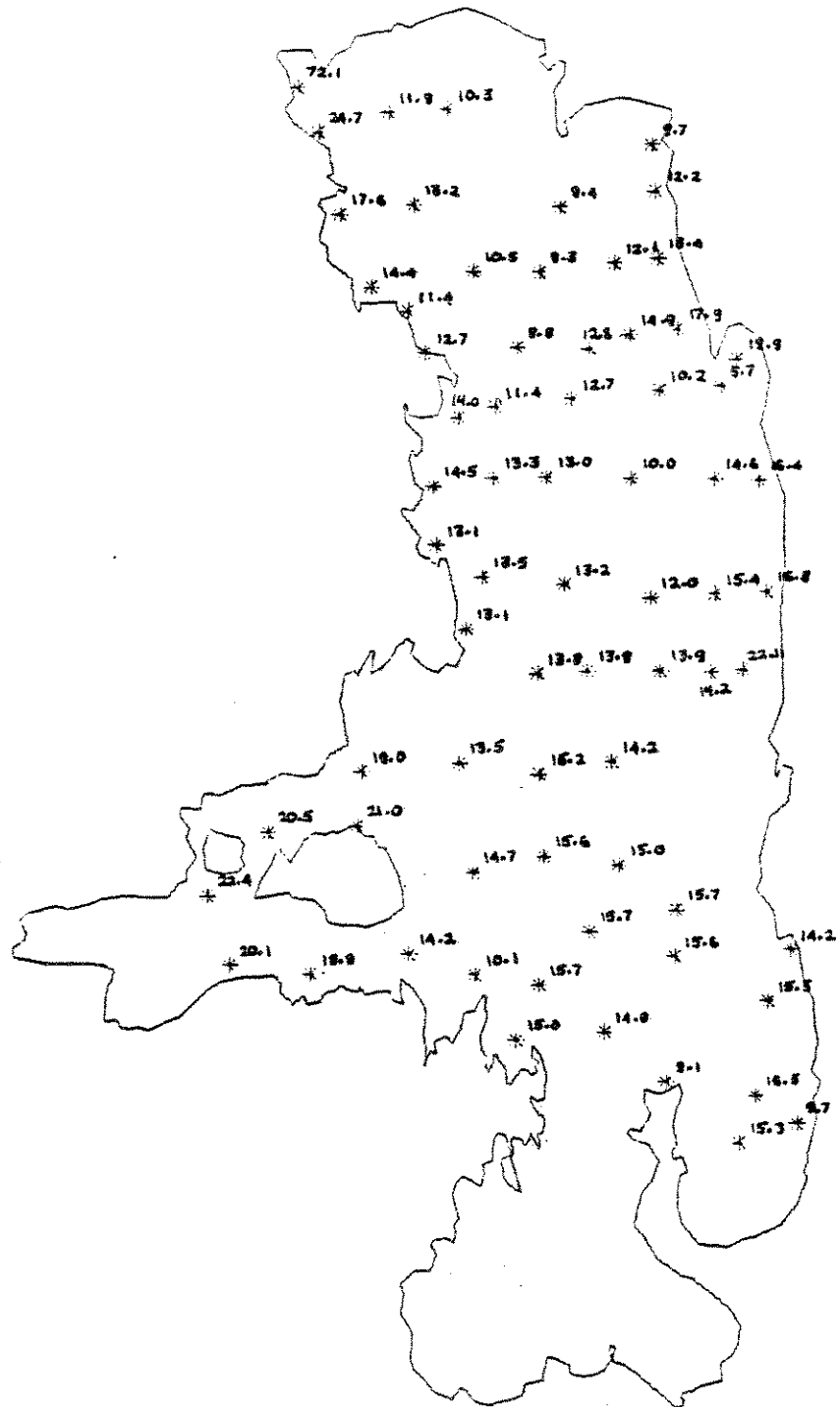


0 1 2 3 4 5  
KILOMETERS

0 1 2 3 4 5  
MILES



## ZINC - OXIDIZED

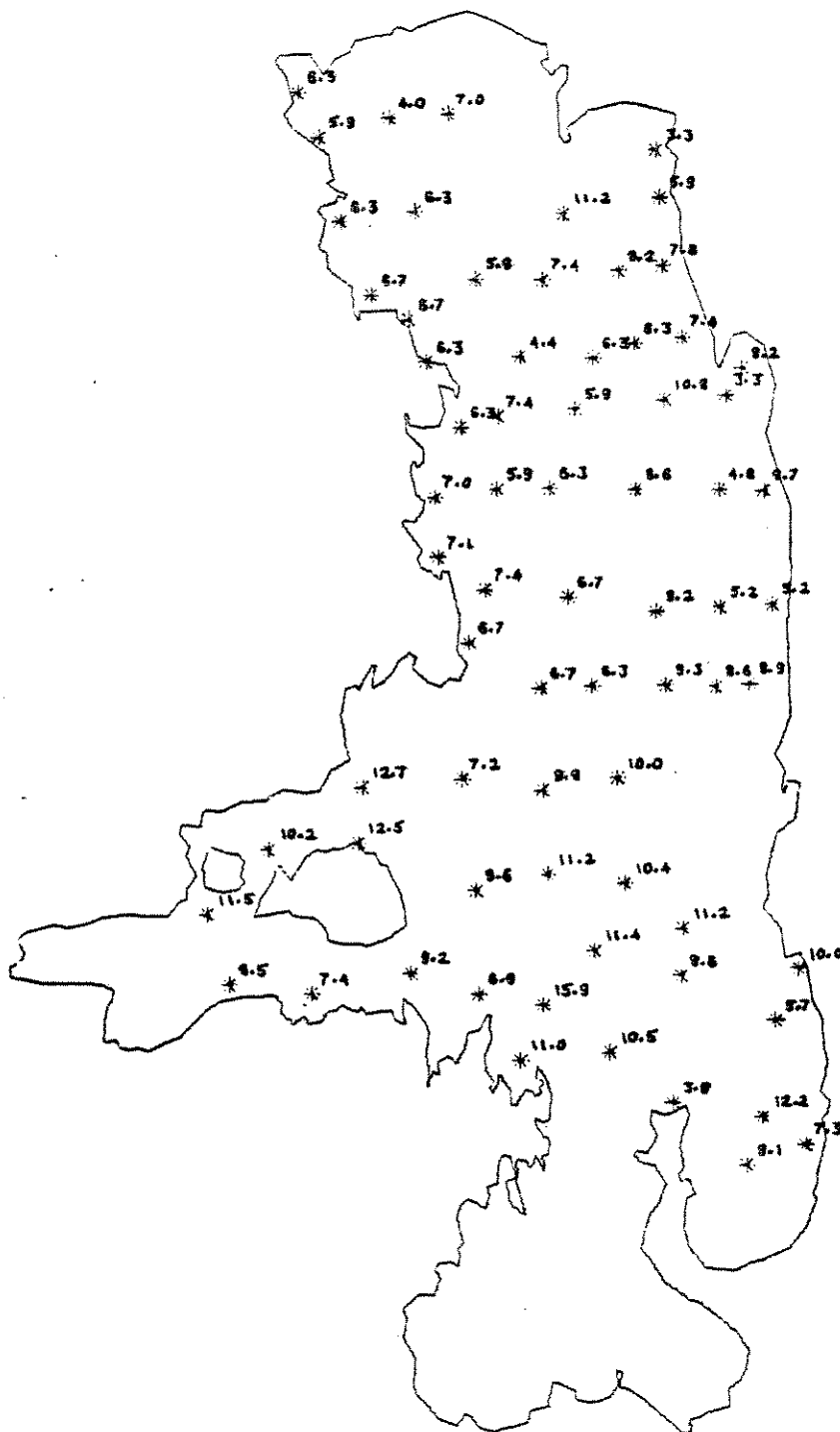


KILOMETERS



MILES

## COPPER - OXIDIZED

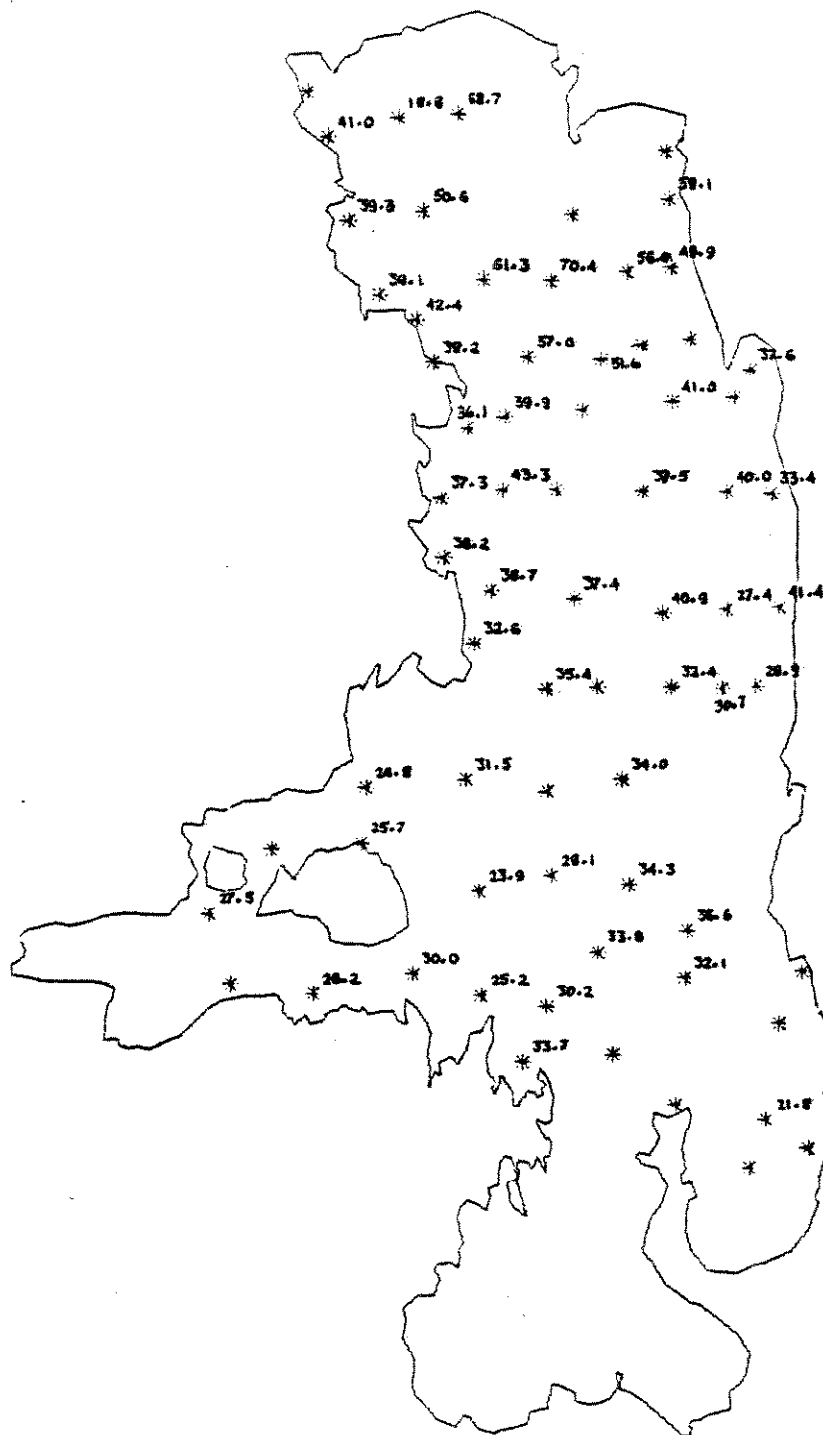


KILOMETERS

MILES



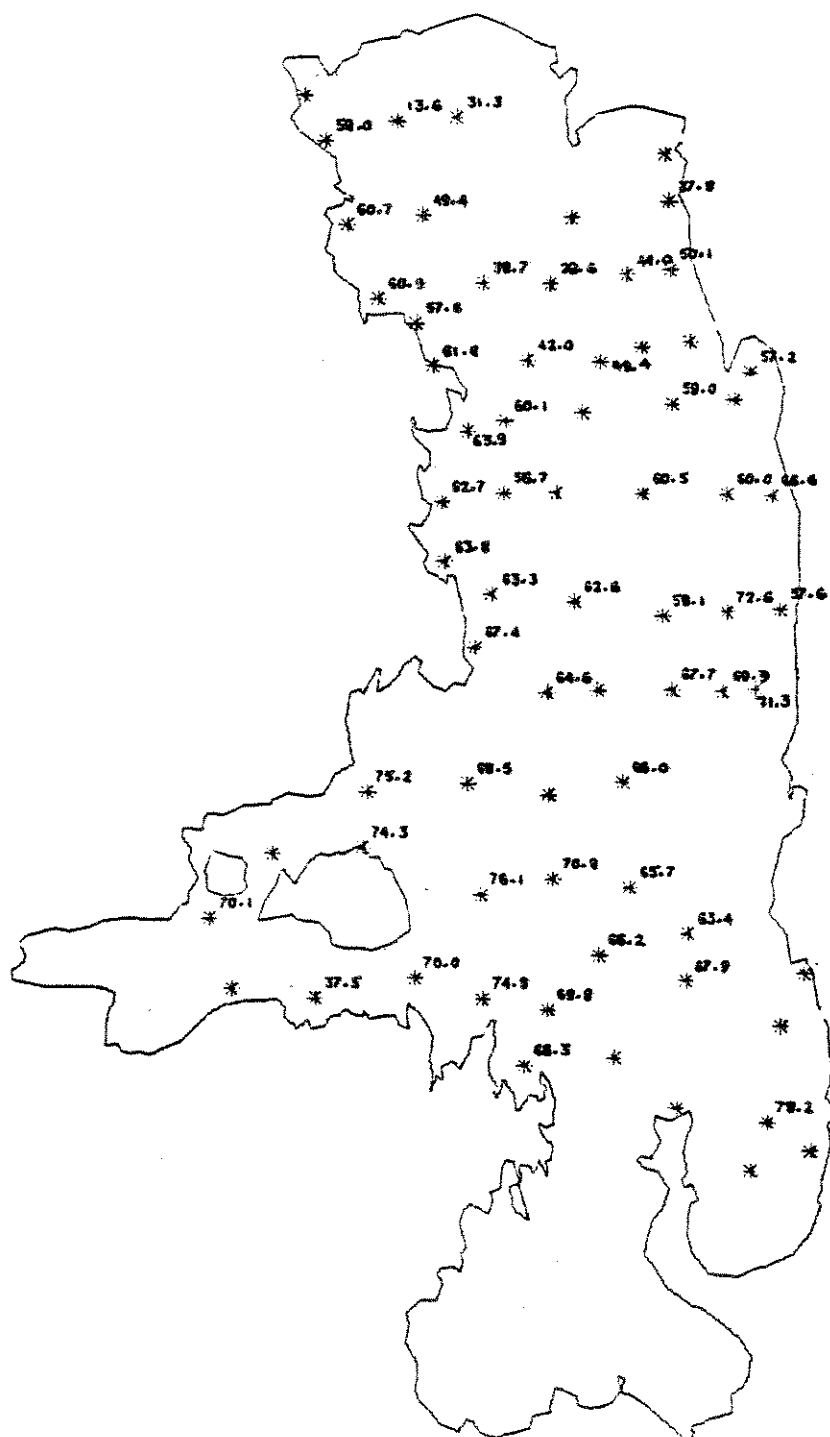
## SILT - OXIDIZED



0 1 Kilometers

0 1 Miles

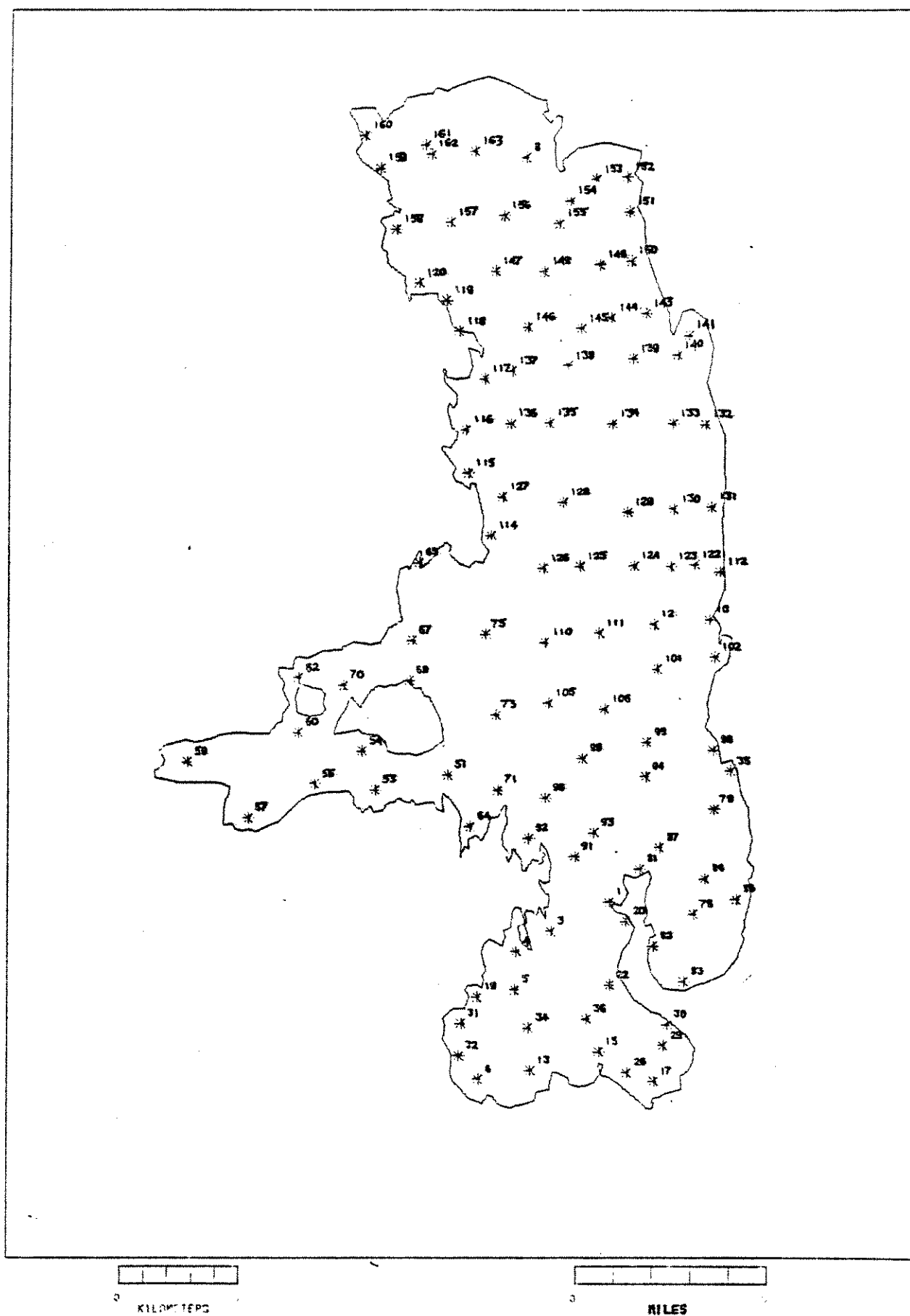
## CLAY - OXIDIZED



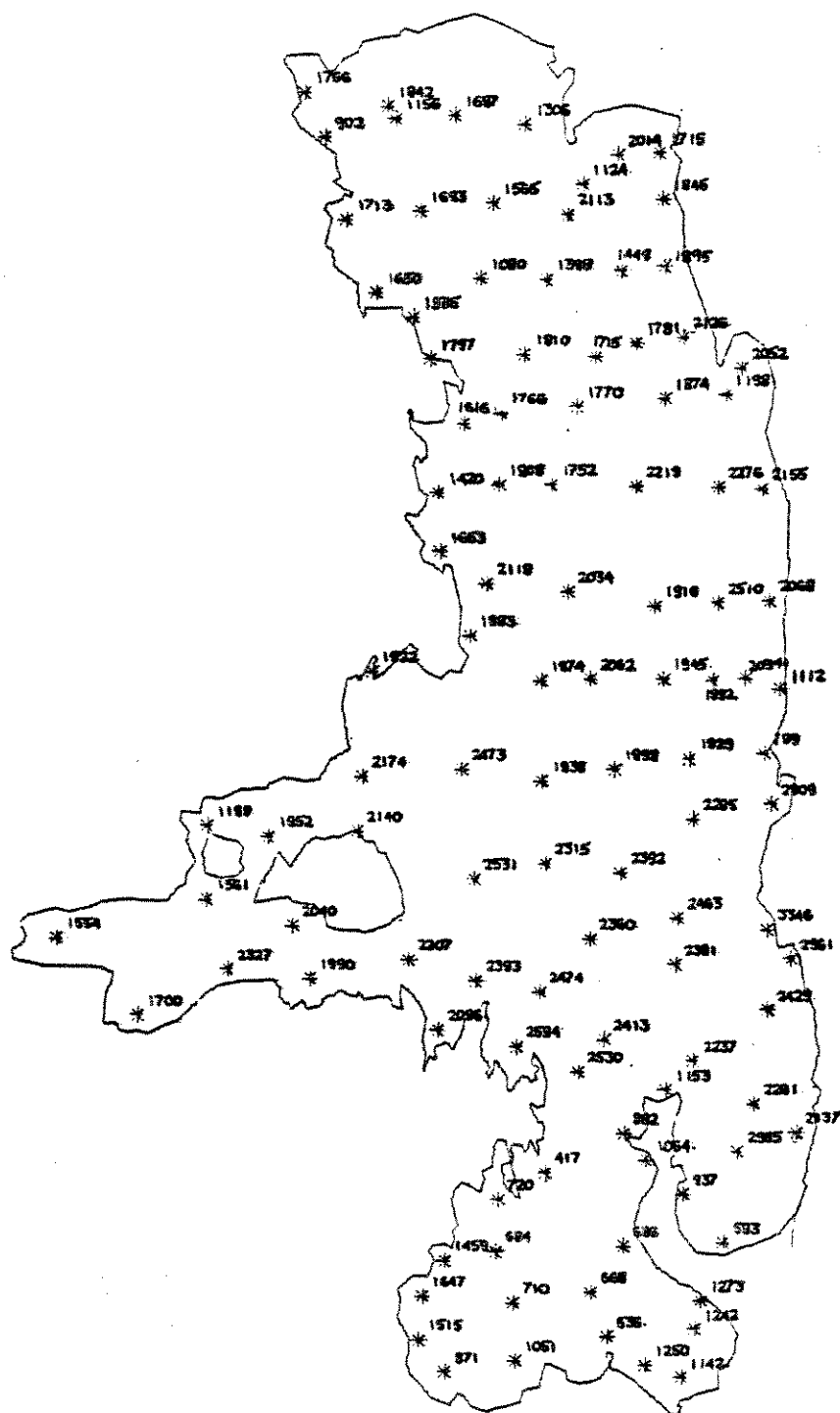
0 10  
KILOMETERS

0 10  
MILES

## SAMPLES - REDUCED



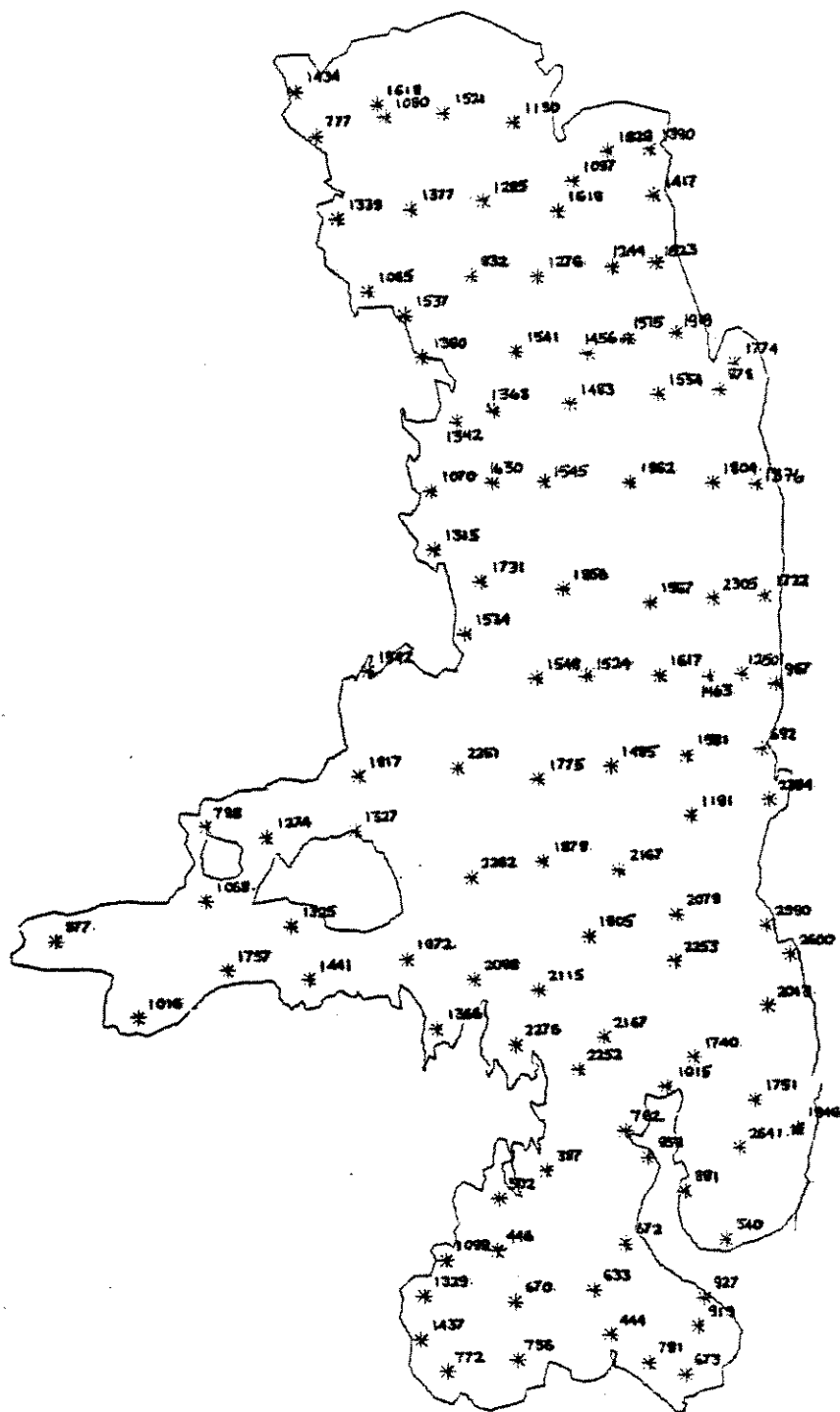
## TOTAL P - REDUCED



0 1 2 3 4 5  
KILOMETERS

0 1 2 3 4 5  
MILES

## INORGANIC P - REDUCED

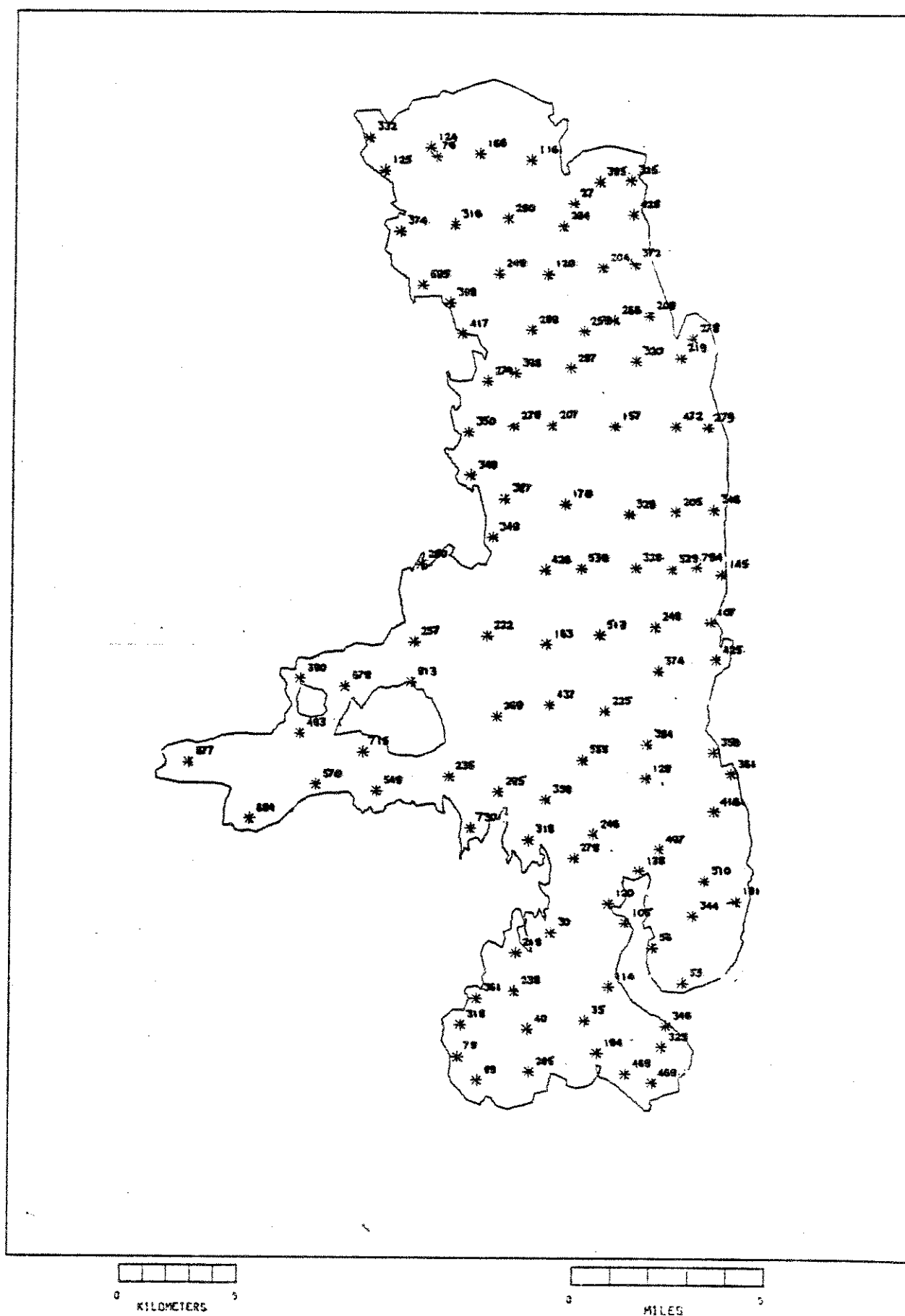


0 1 2 3 4 5  
KILOMETERS

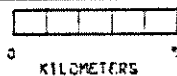
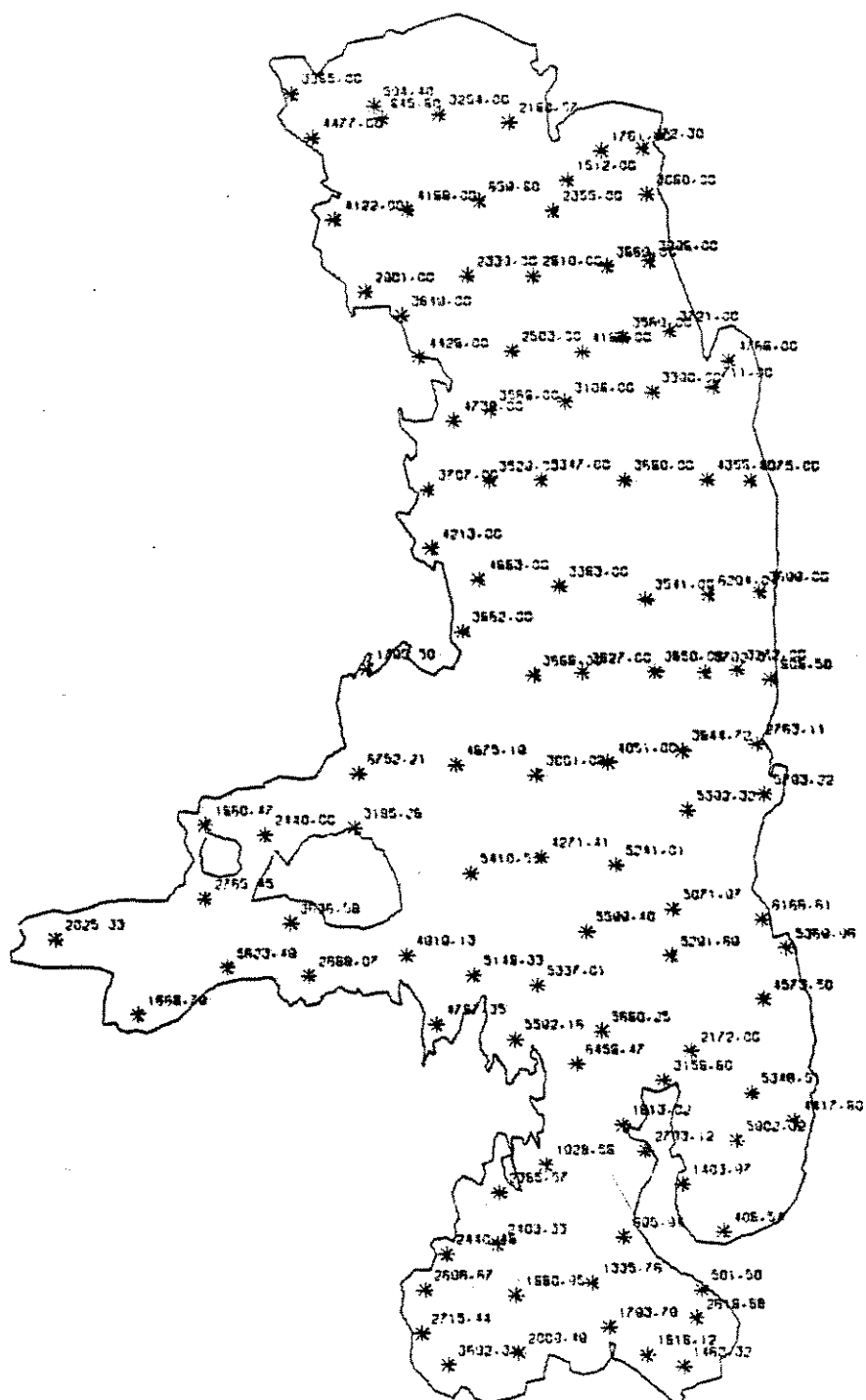
0 1 2 3 4 5  
MILES



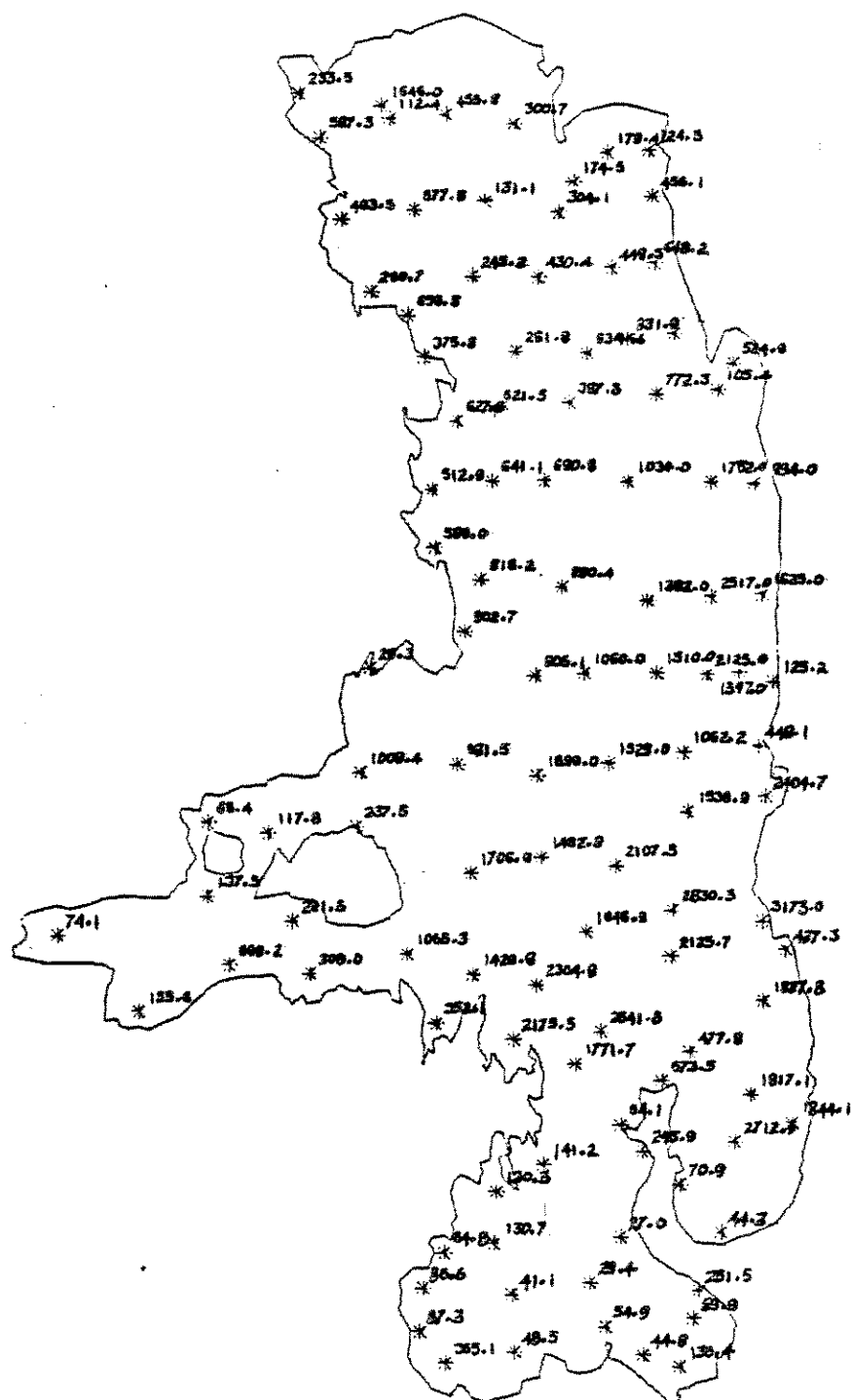
## ORGANIC PHOSPHORUS - REDUCED



IRON - REDUCED



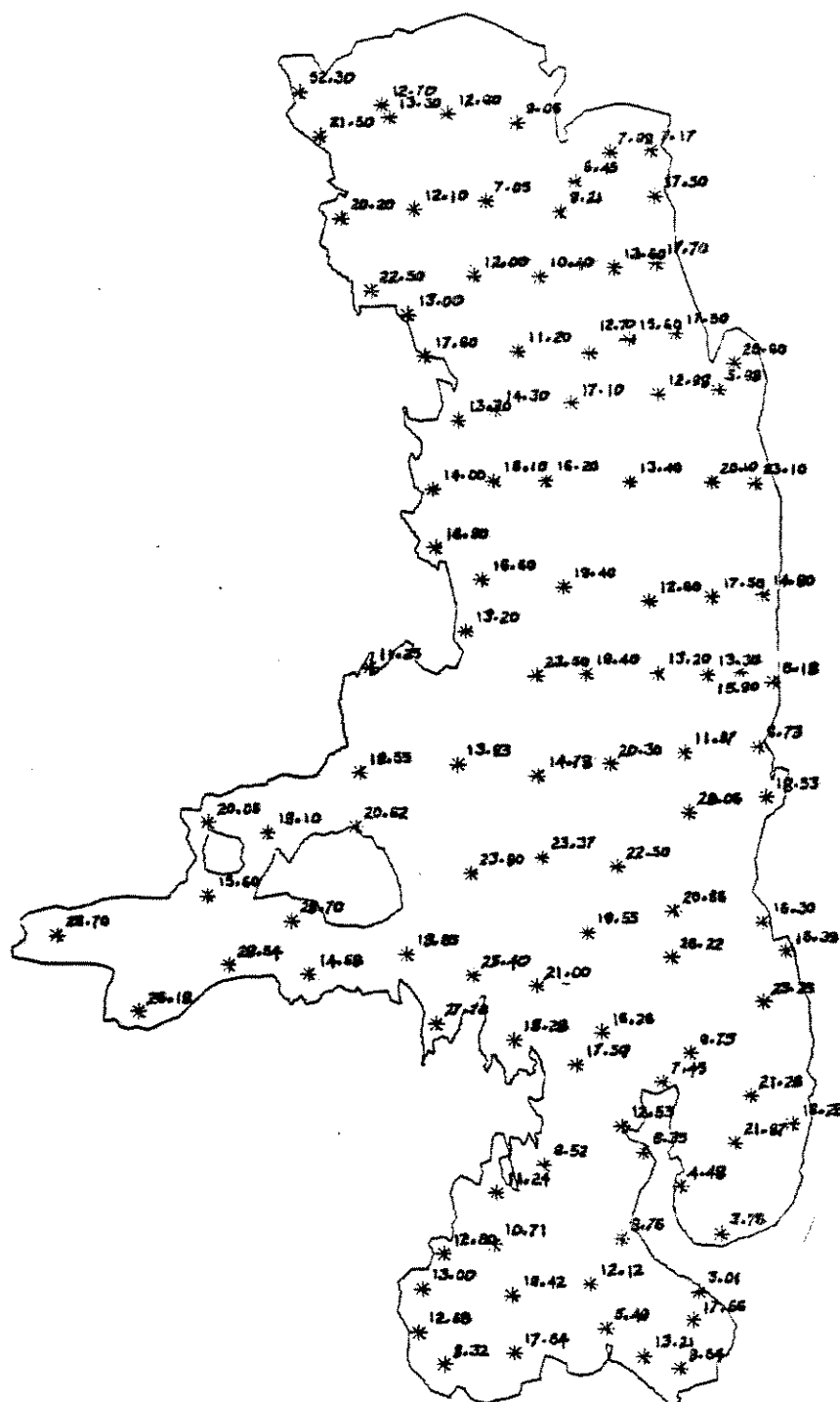
## MANGANESE - REDUCED



0 5 10  
KILOMETERS

0 5 10  
MILES

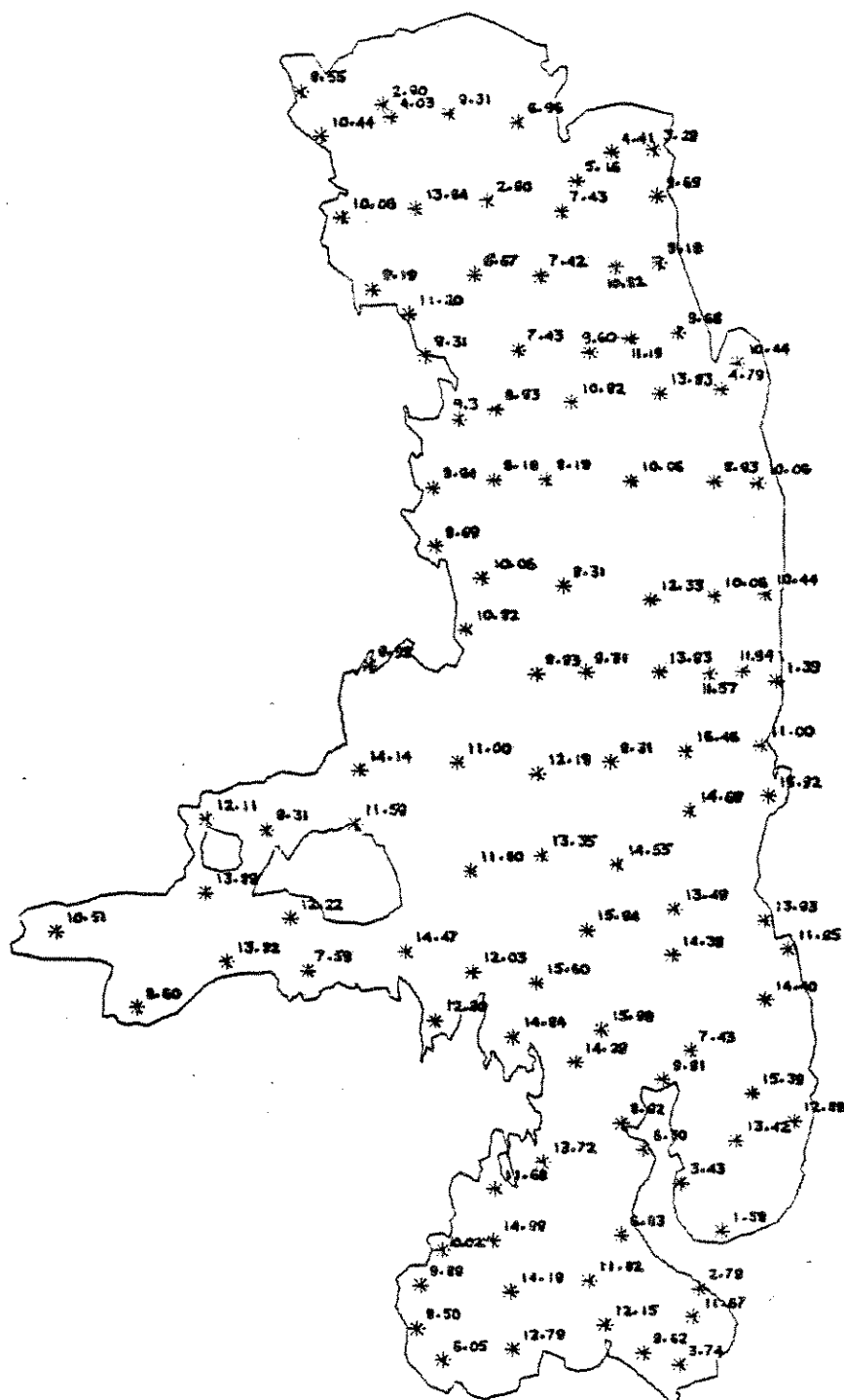
## ZINC - REDUCED



0 5  
KILOMETERS

0 5  
MILES

COPPER - REDUCED

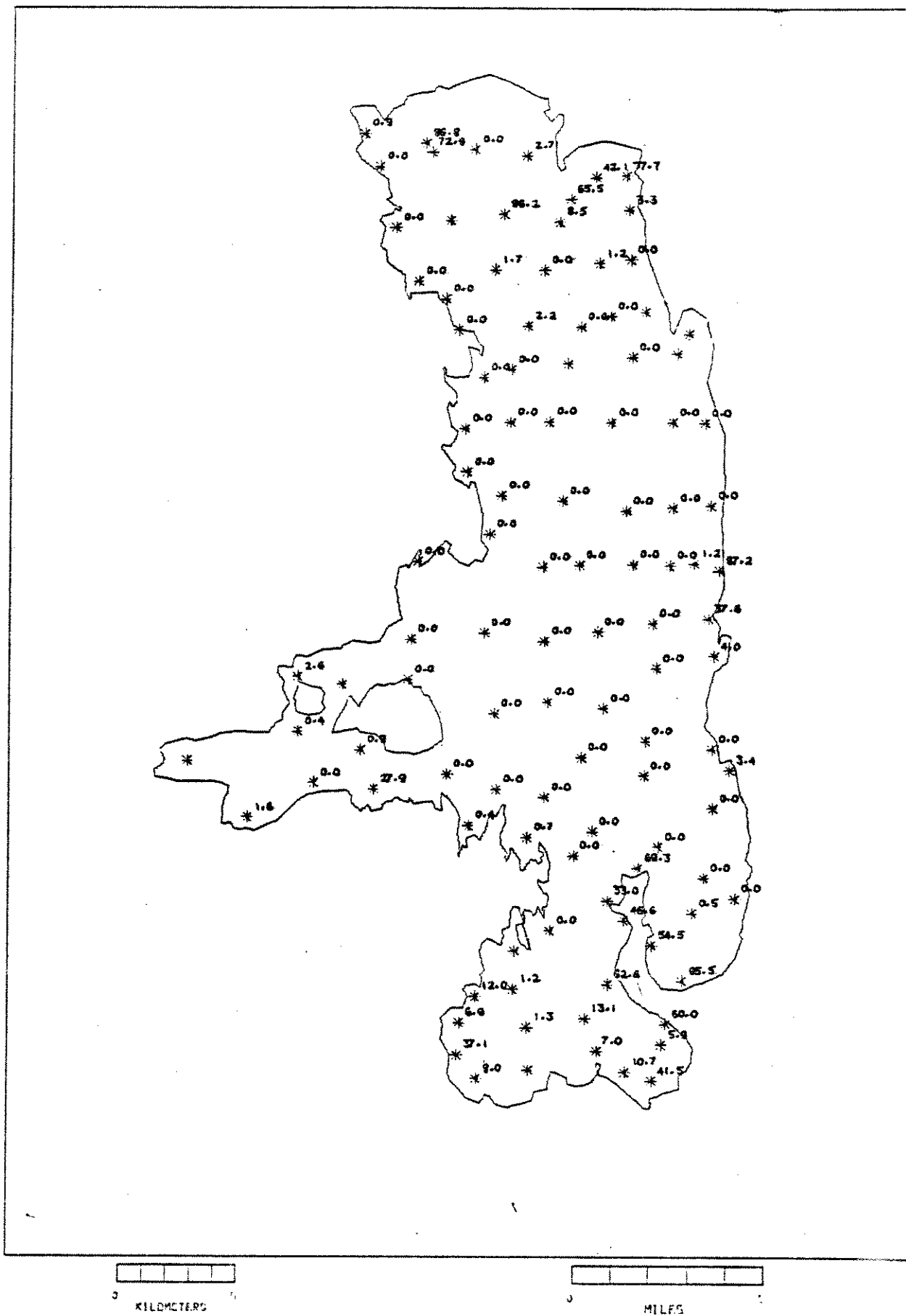


0 KILOMETERS 5

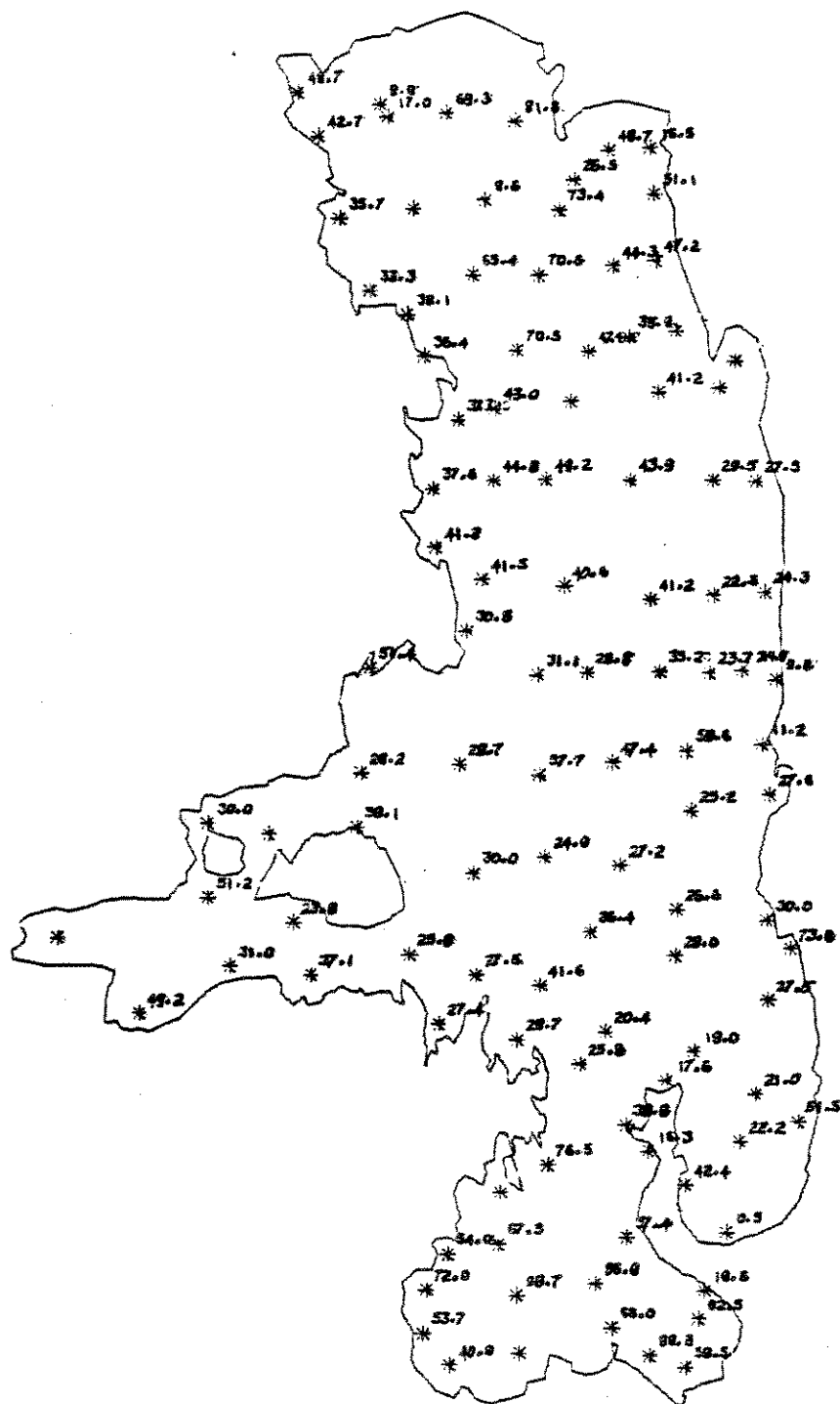
--	--	--	--	--

0 MILES

SAND - REDUCED



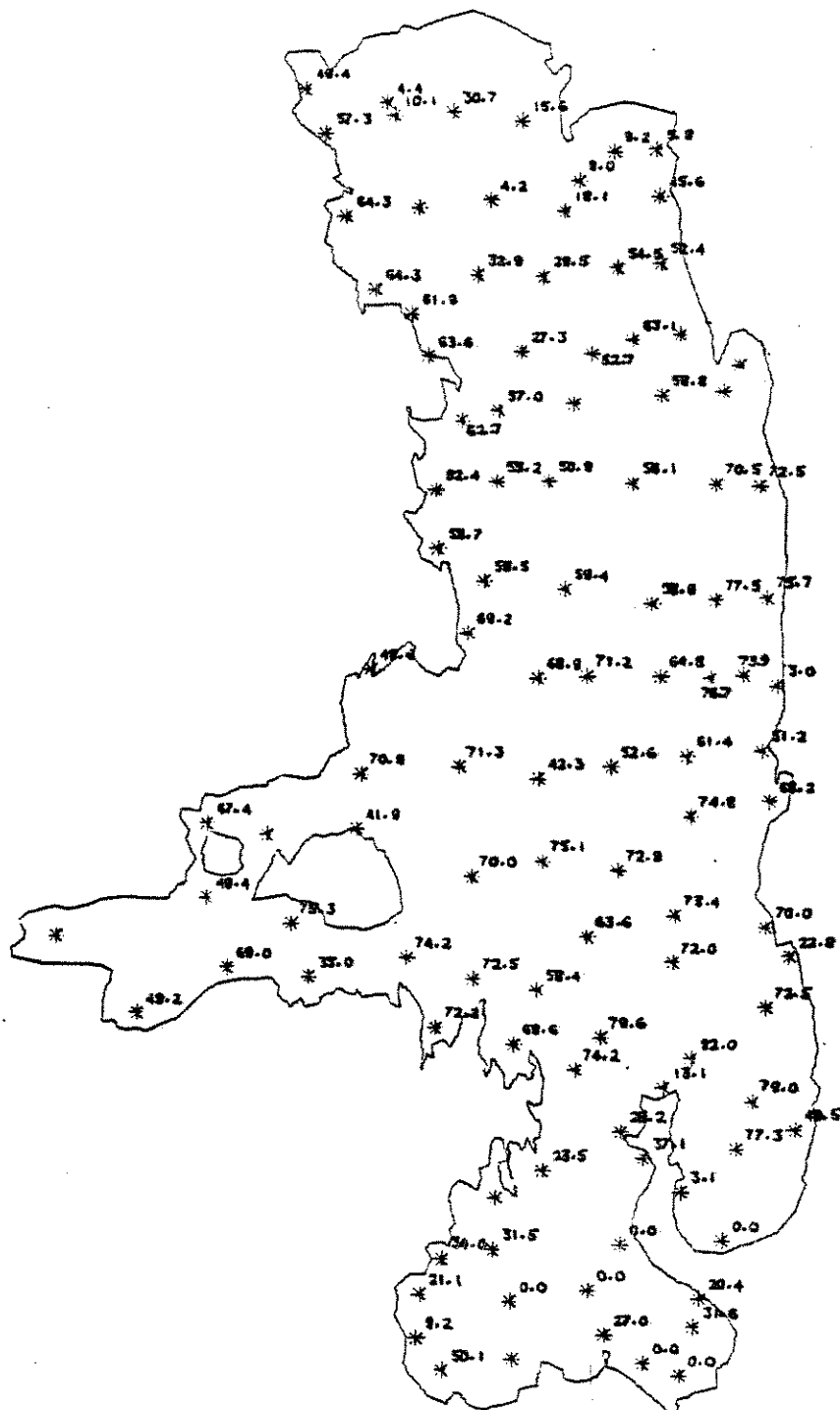
## SILT - REDUCED



0 1 2 3 4 5  
KILOMETERS

0 1 2 3 4 5  
MILES

CLAY - REDUCED



0 KILOMETERS

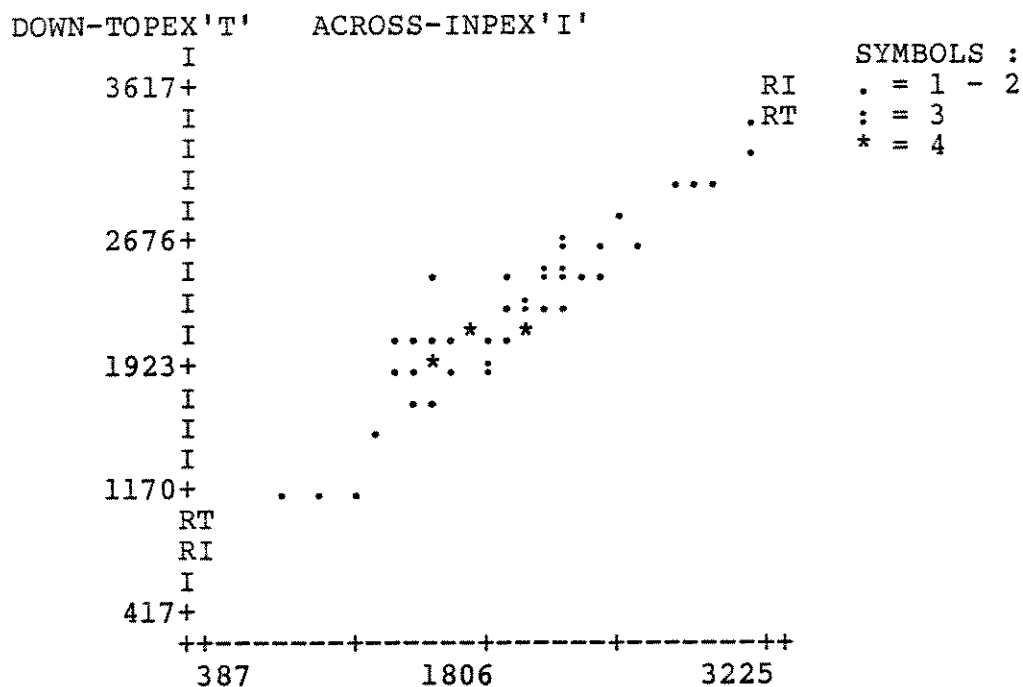
0 1 2 3 4  
MILES



## APPENDIX III

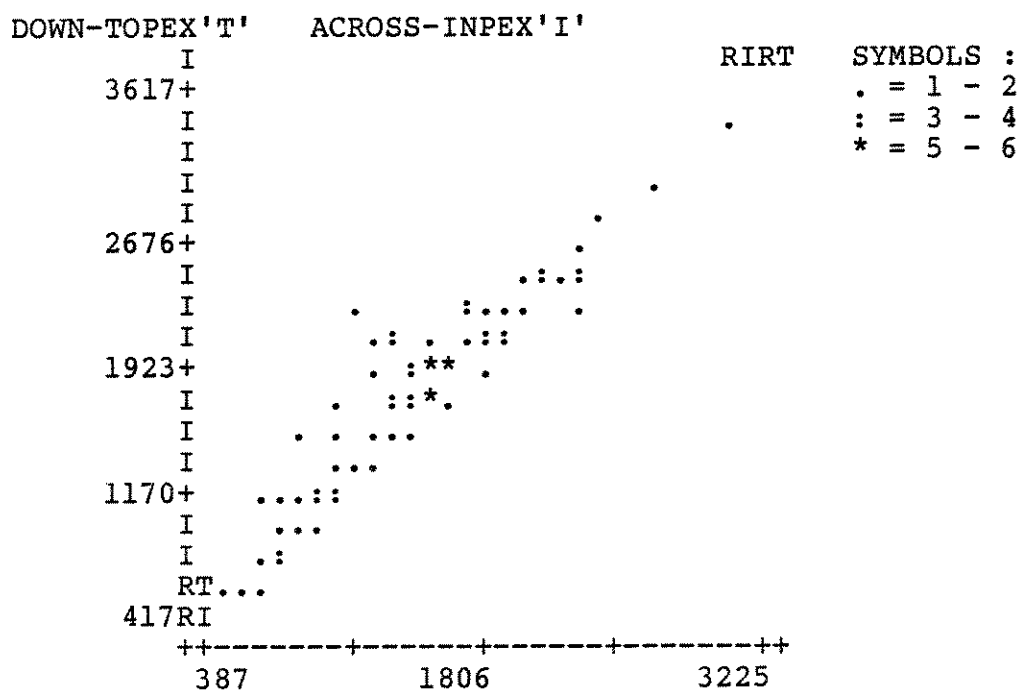
## Scatterplots

## TOTAL PHOSPHORUS VS. INORGANIC PHOSPHORUS OXIDIZED



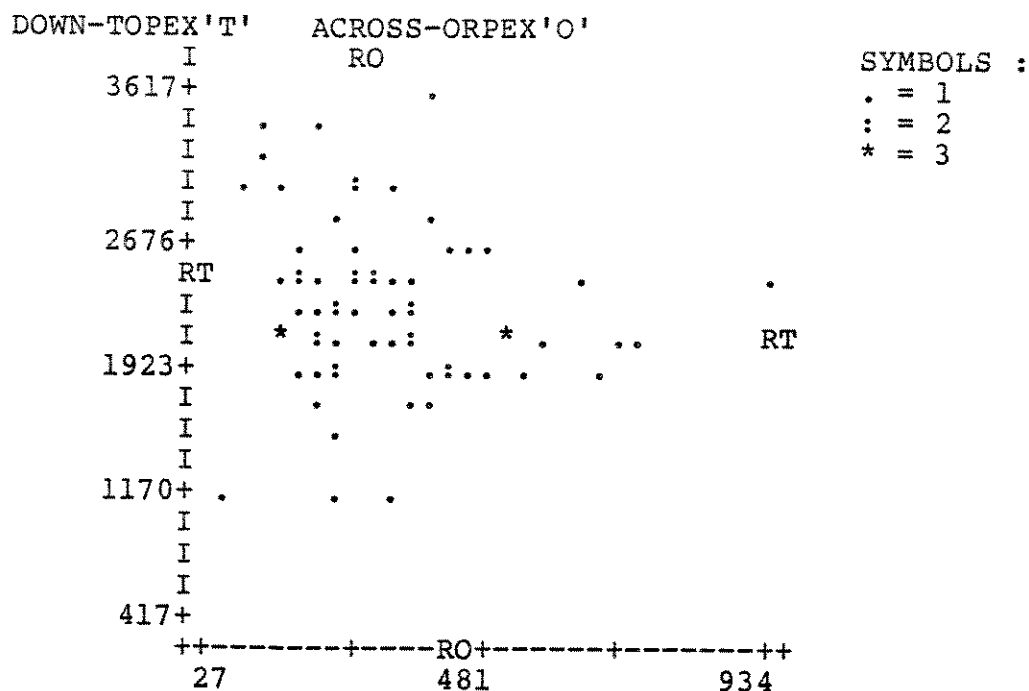
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	2.3+03	484.26	.952	.907	.000	.87	589.82	148.92	70
INPEX	2.0+03	531.09				1.04	-431.16	163.32	70

## TOTAL PHOSPHORUS VS. INORGANIC PHOSPHORUS REDUCED



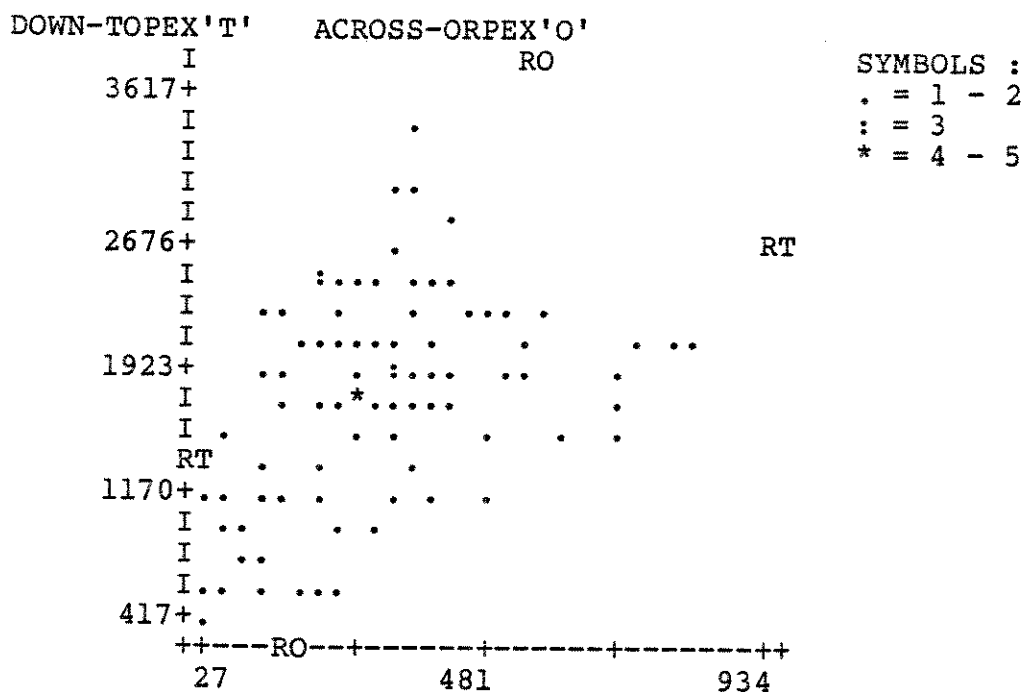
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	1.8+03	583.19	.950	.903	.000	1.05	250.96	182.74	110
INPEX	1.4+03	527.23				.86	-75.35	165.21	110

## TOTAL PHOSPHORUS VS. ORGANIC PHOSPHORUS OXIDIZED



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	2.3+03	484.26	-.137	.019	.129	-.41	2.4+03	483.21	70
ORPEX	327.61	162.83				-4.6-02	434.06	162.47	70

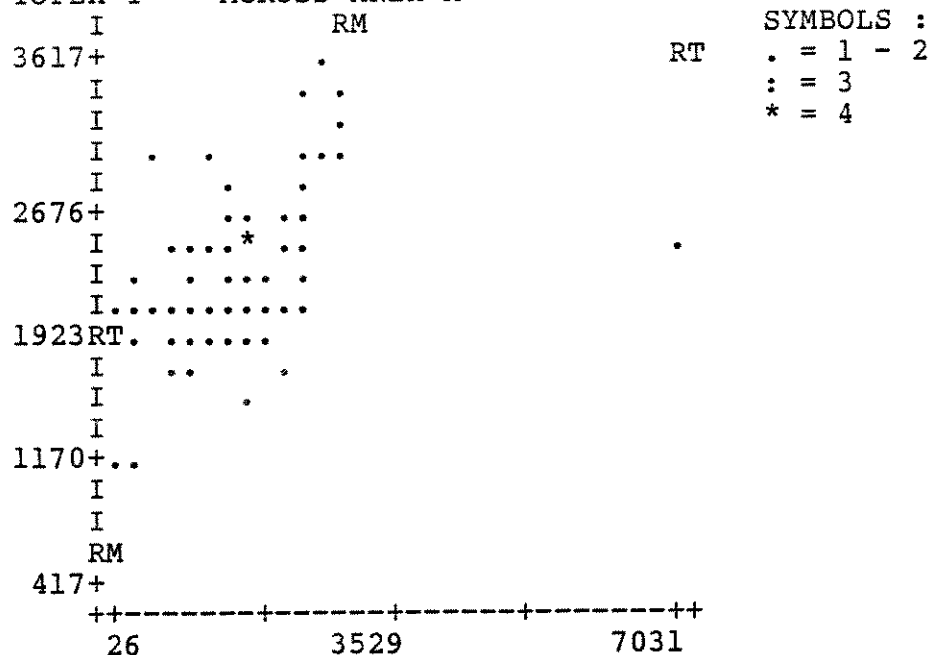
## TOTAL PHOSPHORUS VS. ORGANIC PHOSPHORUS REDUCED



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	1.8+03	583.19	.435	.189	.000	1.48	1.3+03	527.49	110
ORPEX	315.29	171.10				.13	89.84	154.76	110

## TOTAL PHOSPHORUS VS. MANGANESE OXIDIZED

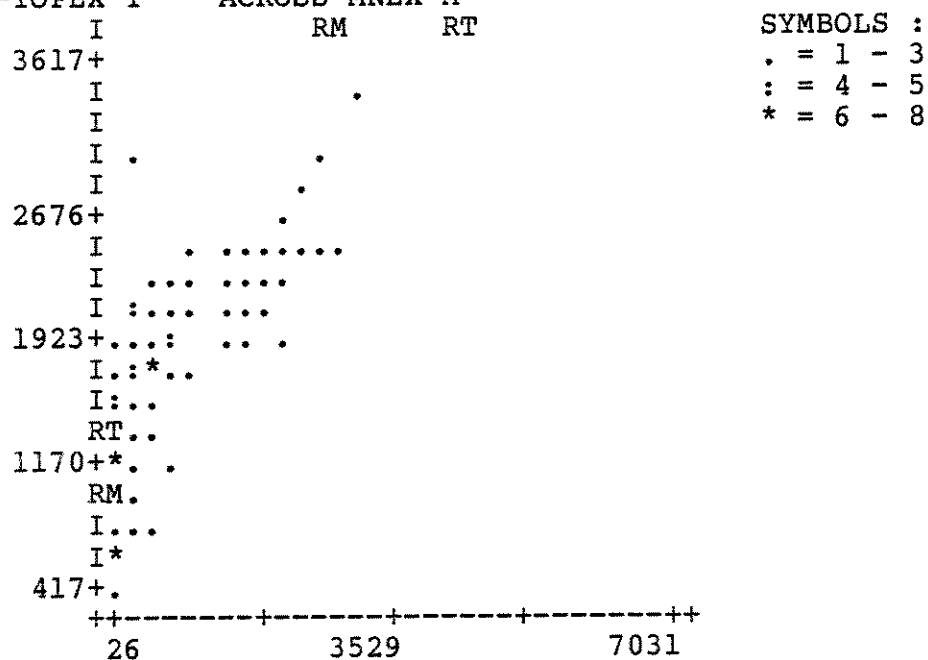
DOWN-TOPEX'T' ACROSS-MNEX'M'



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	2.3+03	484.26	.461	.212	.000	.22	2.0+03	432.94	70
MNEX	1.6+03	996.86				.95	-599.95	891.22	70

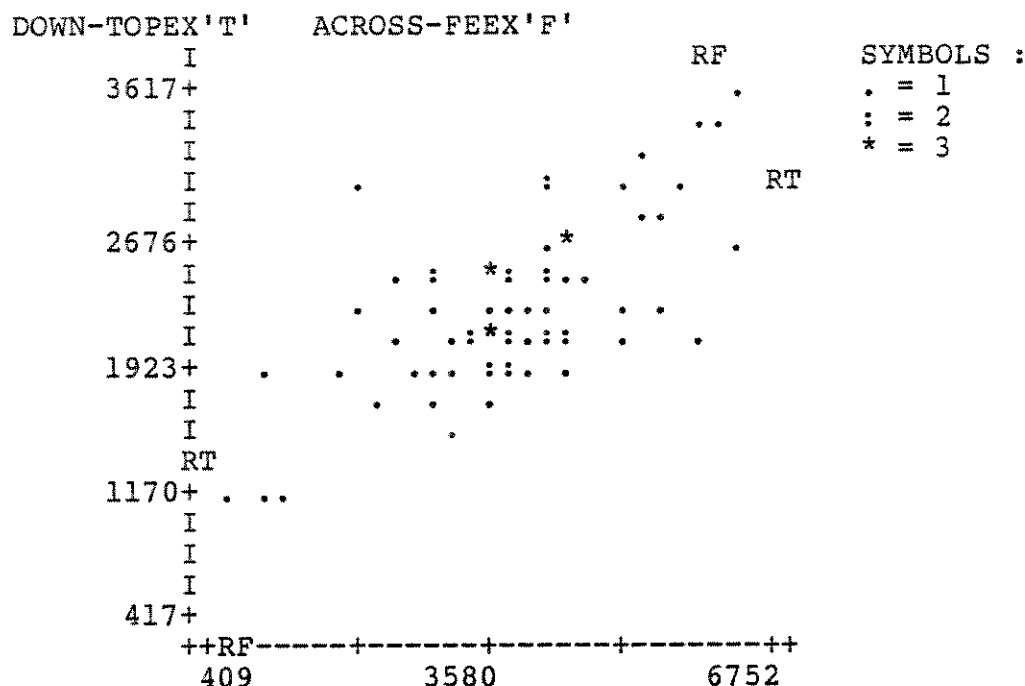
## TOTAL PHOSPHORUS VS. MANGANESE REDUCED

DOWN-TOPEX'T' ACROSS-MNEX'M'



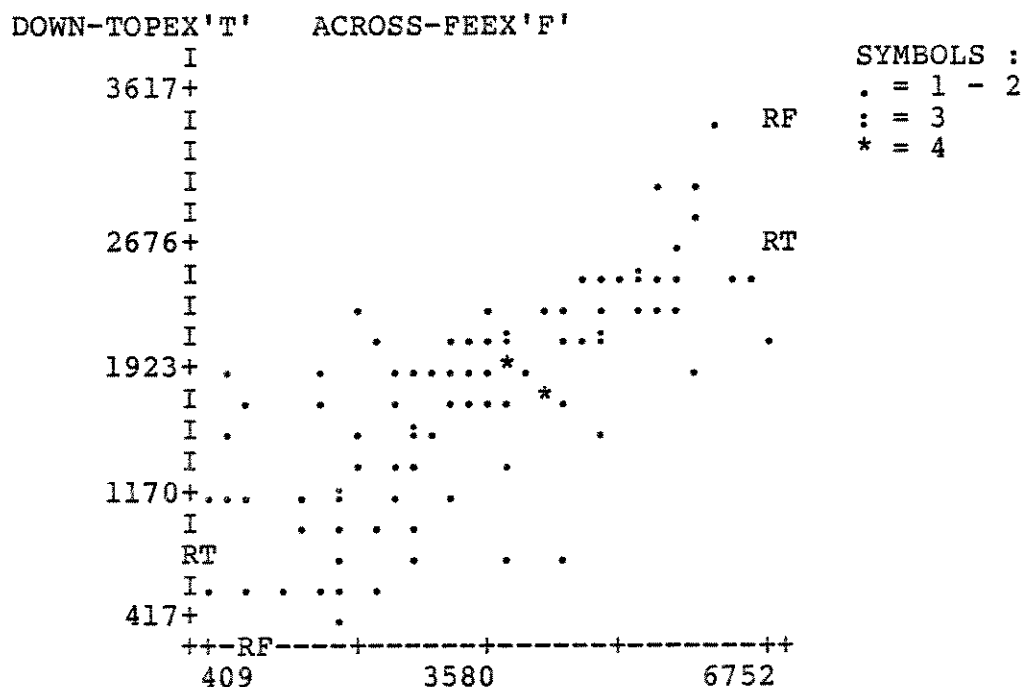
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	1.8+03	583.19	.741	.548	.000	.55	1.3+03	393.71	110
MNEX	808.72	781.83				.99	-944.18	527.80	110

## TOTAL PHOSPHORUS VS. IRON OXIDIZED



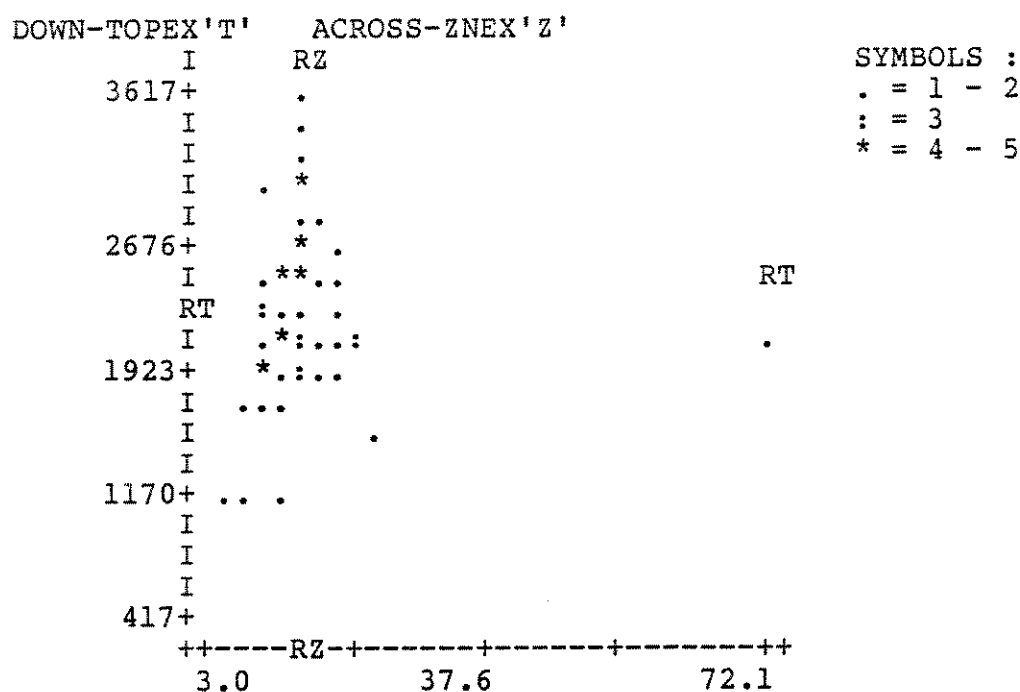
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	2.3+03	484.26	.652	.425	.000	.26	1.3+03	369.96	70
FEEX	3.8+03	1.2+03				1.62	72.90	920.27	70

### TOTAL PHOSPHORUS VS. IRON REDUCED



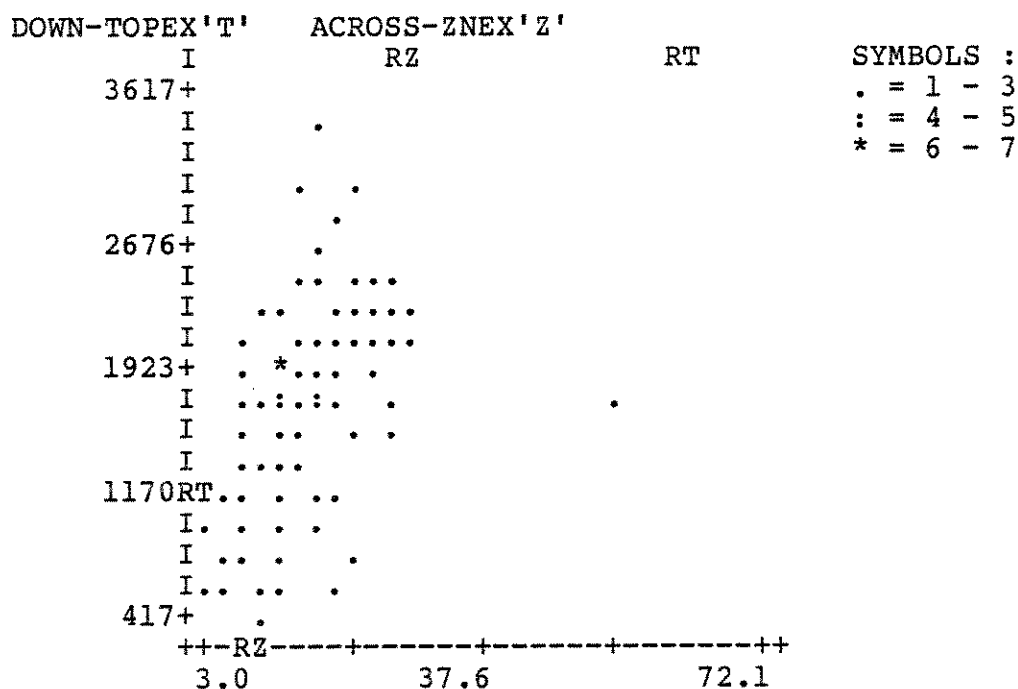
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	1.8+03	583.19	.748	.559	.000	.28	788.92	388.95	110
FEEX	3.4+03	1.5+03				1.96	-37.88	1.0+03	110

## TOTAL PHOSPHORUS VS. ZINC OXIDIZED



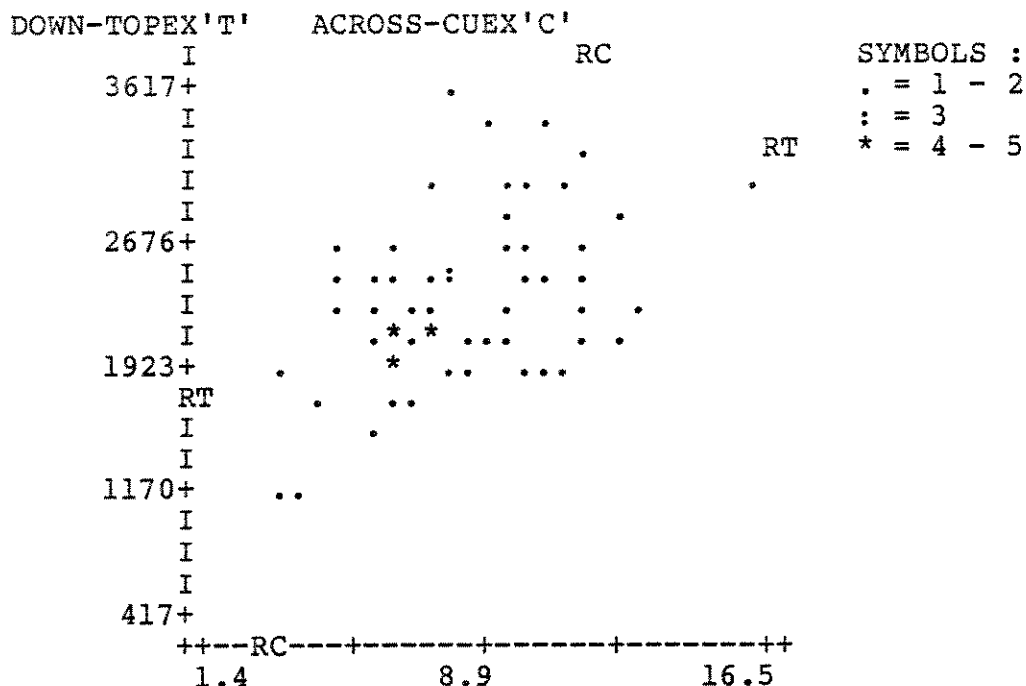
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	2.3+03	484.26	.042	.002	.365	2.63	2.3+03	487.37	70
ZNEX	15.10	7.74				6.7-04	13.55	7.79	70

## TOTAL PHOSPHORUS VS. ZINC REDUCED



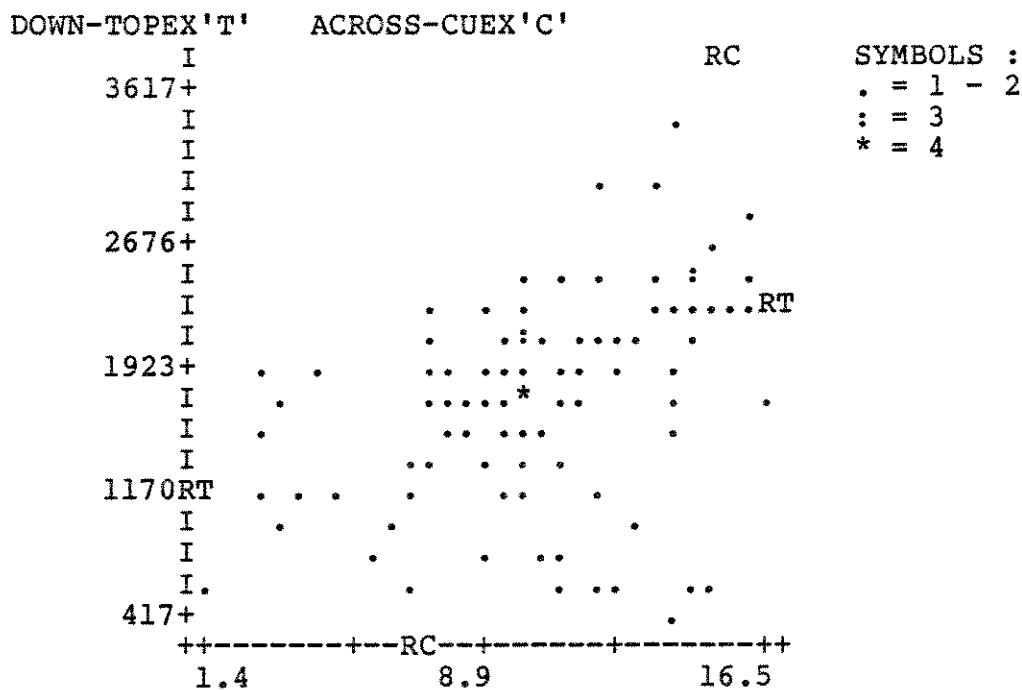
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	1.8+03	583.19	.491	.241	.000	41.37	1.1+03	510.32	110
ZNEX	15.90	6.92				5.8-03	5.60	6.06	110

## TOTAL PHOSPHORUS VS. COPPER OXIDIZED

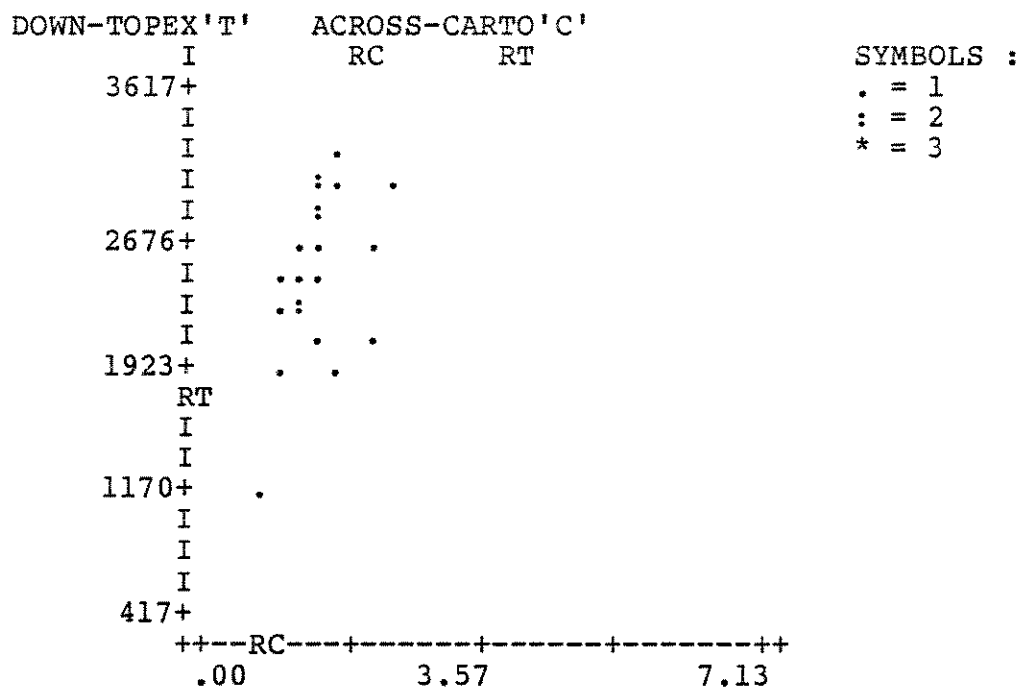


	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	2.3+03	484.26	.497	.247	.000	97.89	1.5+03	423.26	70
CUEX	7.97	2.46				2.5-03	2.13	2.15	70

## TOTAL PHOSPHORUS VS. COPPER REDUCED

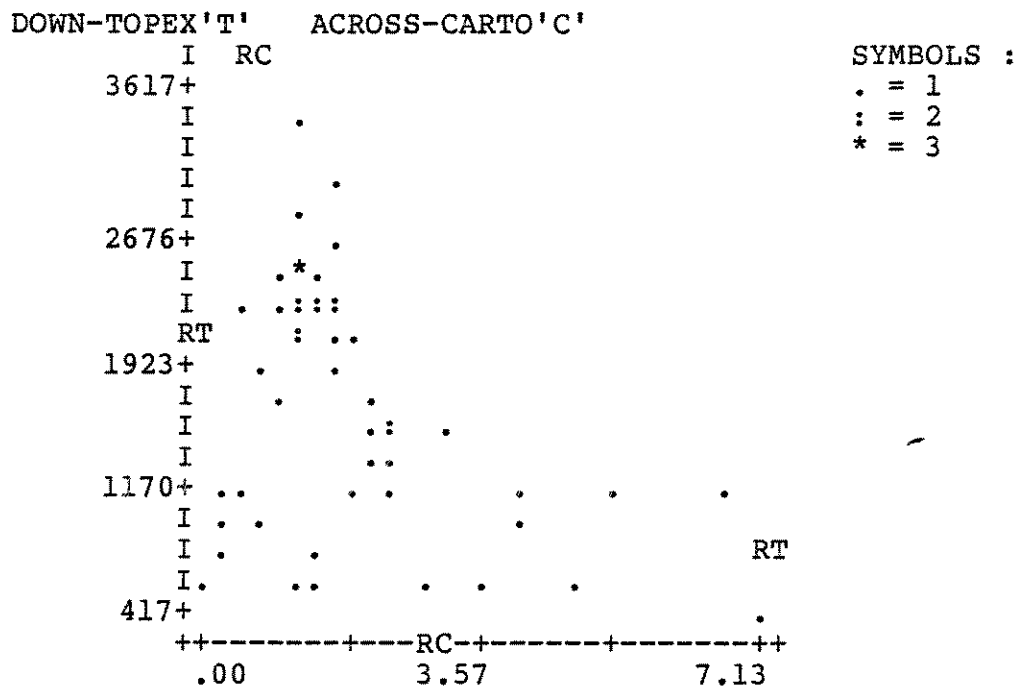


	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	1.8+03	583.19	.437	.191	.000	73.84	1.0+03	526.98	110
CUEX	10.23	3.45				2.6-03	5.66	3.12	110



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	2.5+03	498.94	.424	.180	.028	496.37	1.8+03	463.51	21
CARTO	1.46	.43				3.6-04	.55	.40	21

## TOTAL PHOSPHORUS VS. CARBON REDUCED



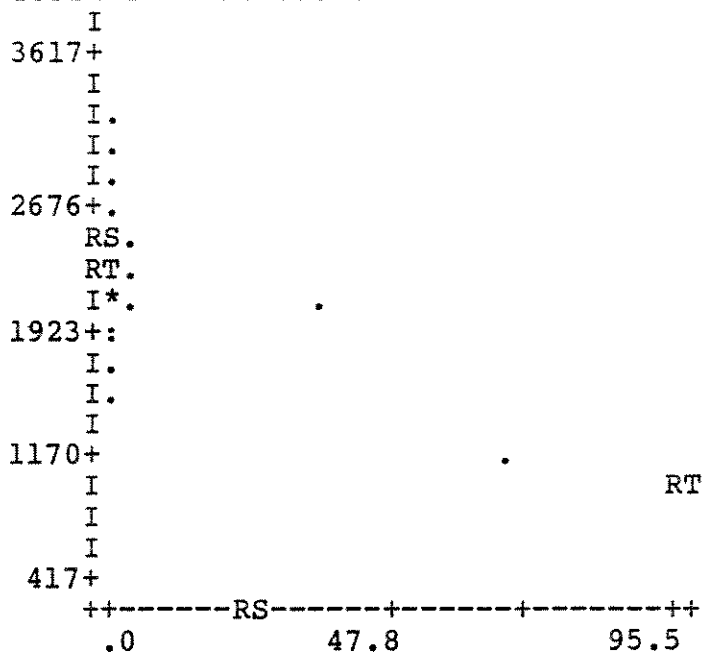
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	1.7+03	727.71	-.372	.138	.004	-181.00	2.1+03	682.56	50
CARTO	1.94	1.49				-7.6-04	3.24	1.40	50



## TOTAL PHOSPHORUS VS. SAND OXIDIZED

156

DOWN-TOPEX'T' ACROSS-SAND'S'

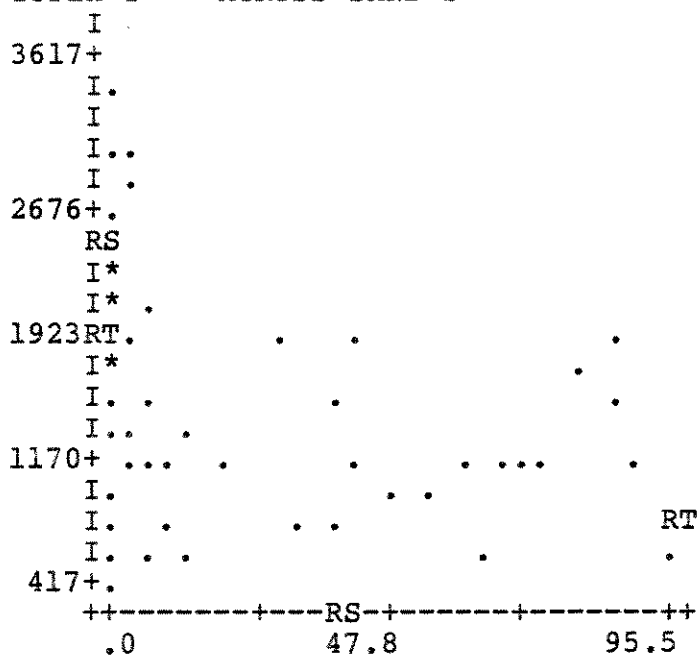


SYMBOLS :  
 . = 1 - 4  
 : = 5 - 7  
 \* = 8 - 11

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	2.3+03	391.83	-.379	.144	.003	-14.10	2.3+03	366.18	52
SAND	2.28	10.54				-1.0-02	25.56	9.85	52

## TOTAL PHOSPHORUS VS. SAND REDUCED

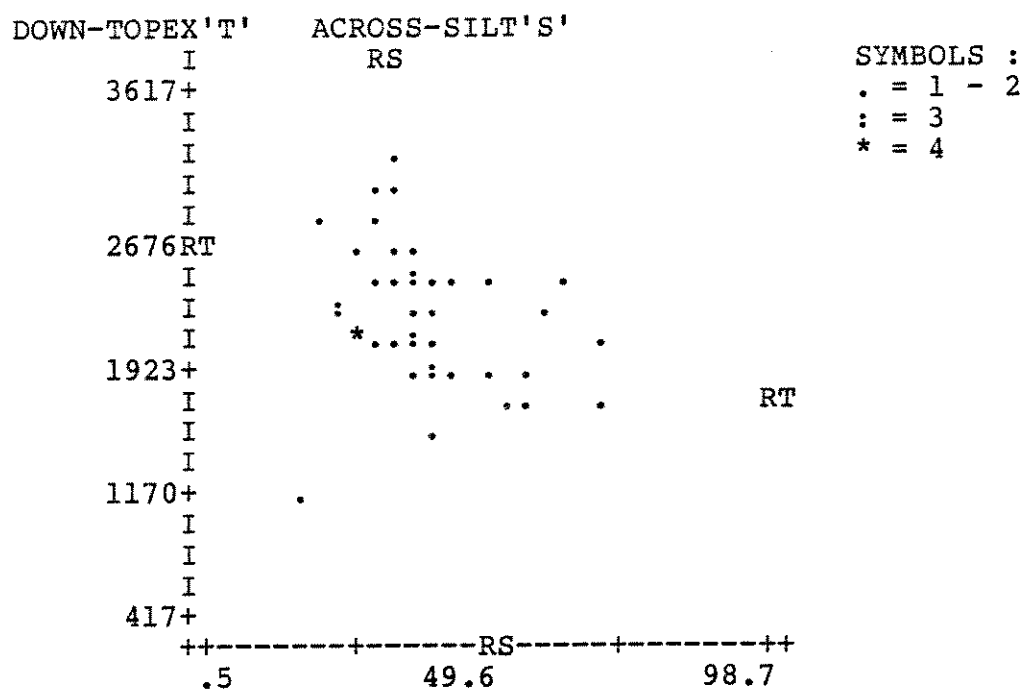
DOWN-TOPEX'T' ACROSS-SAND'S'



SYMBOLS :  
 . = 1 - 5  
 : = 6 - 9  
 \* = 10 - 13

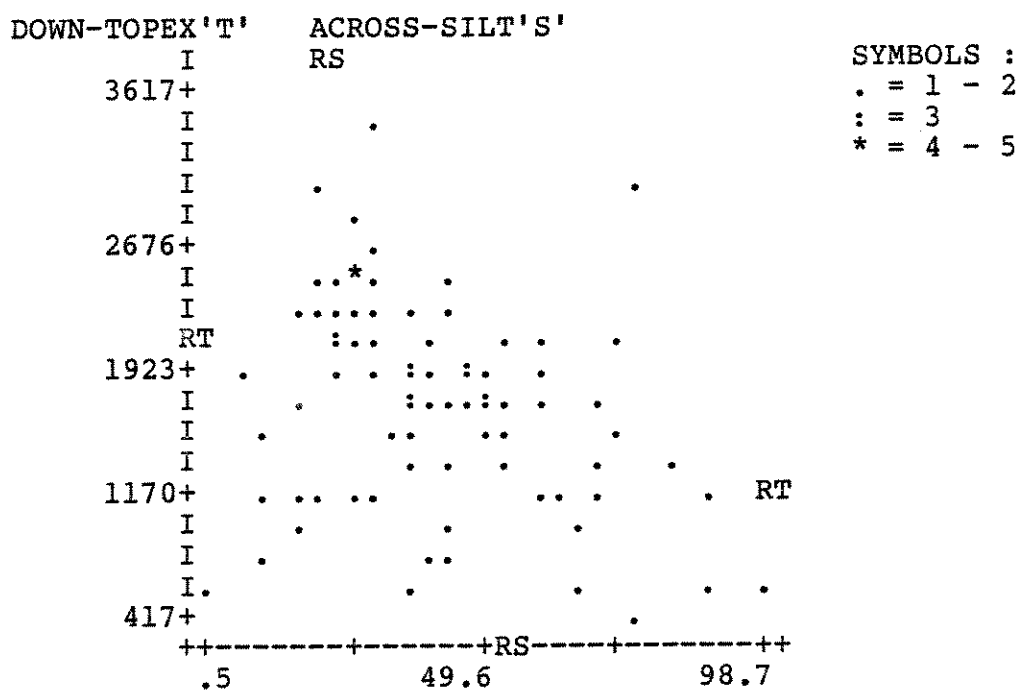
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	1.8+03	590.07	-.444	.197	.000	-10.73	1.9+03	531.34	101
SAND	11.95	24.43				-1.8-02	44.75	22.00	101

## TOTAL PHOSPHORUS VS. SILT OXIDIZED



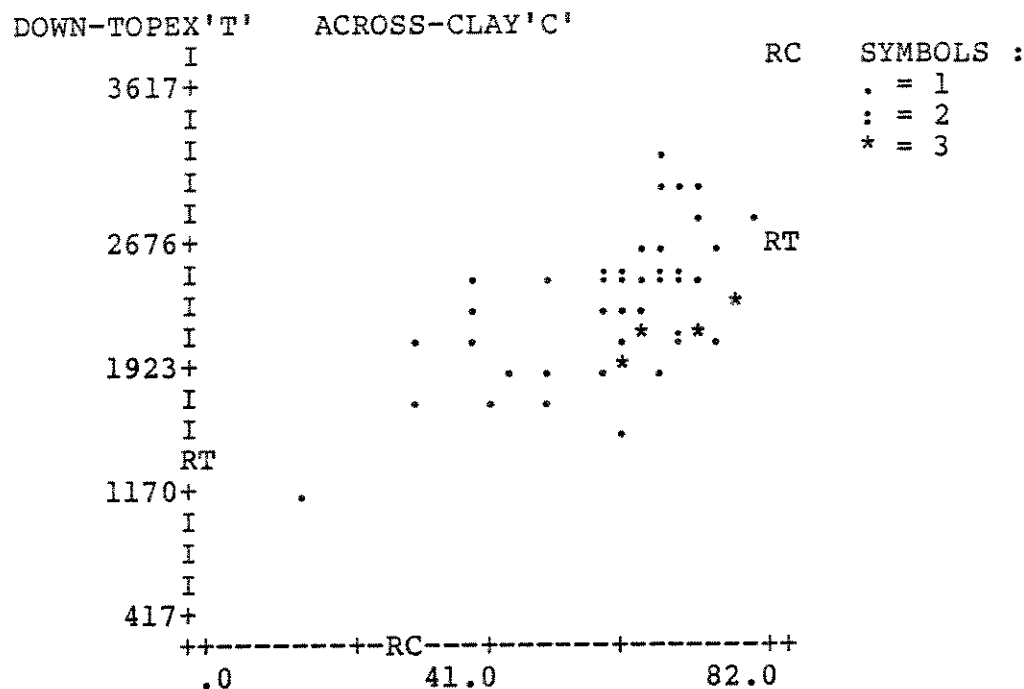
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	2.3+03	391.83	-.221	.049	.058	-7.64	2.6+03	385.95	52
SILT	37.88	11.34				-6.4-03	52.48	11.16	52

## TOTAL PHOSPHORUS VS. SILT REDUCED



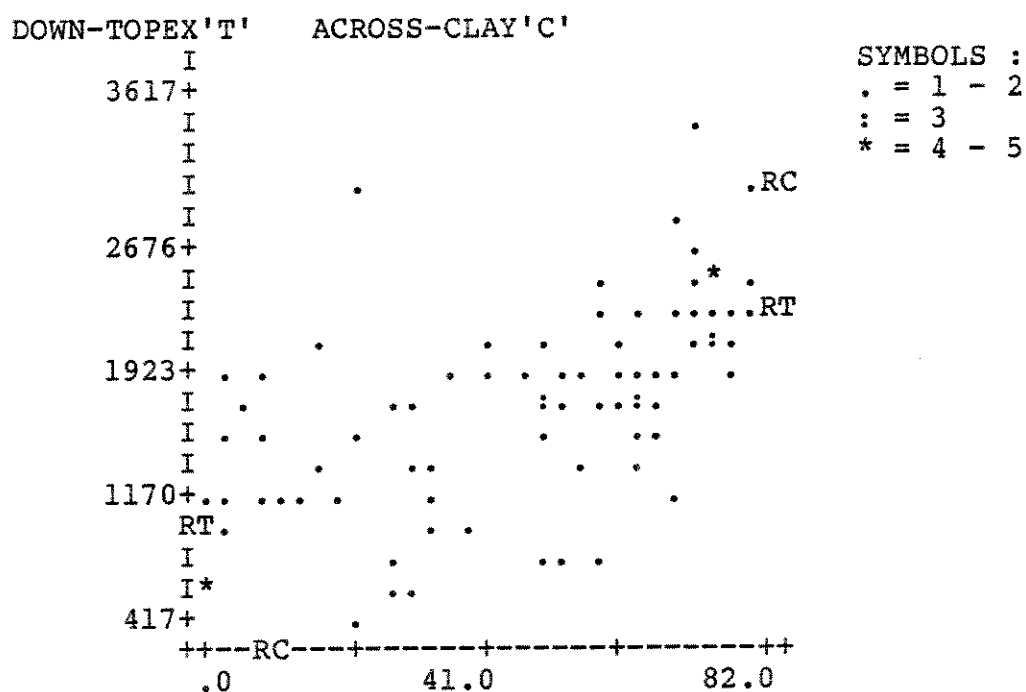
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	1.8+03	590.07	-.307	.094	.001	-9.32	2.2+03	564.49	101
SILT	40.32	19.40				-1.0-02	58.29	18.56	101

## TOTAL PHOSPHORUS VS. CLAY OXIDIZED



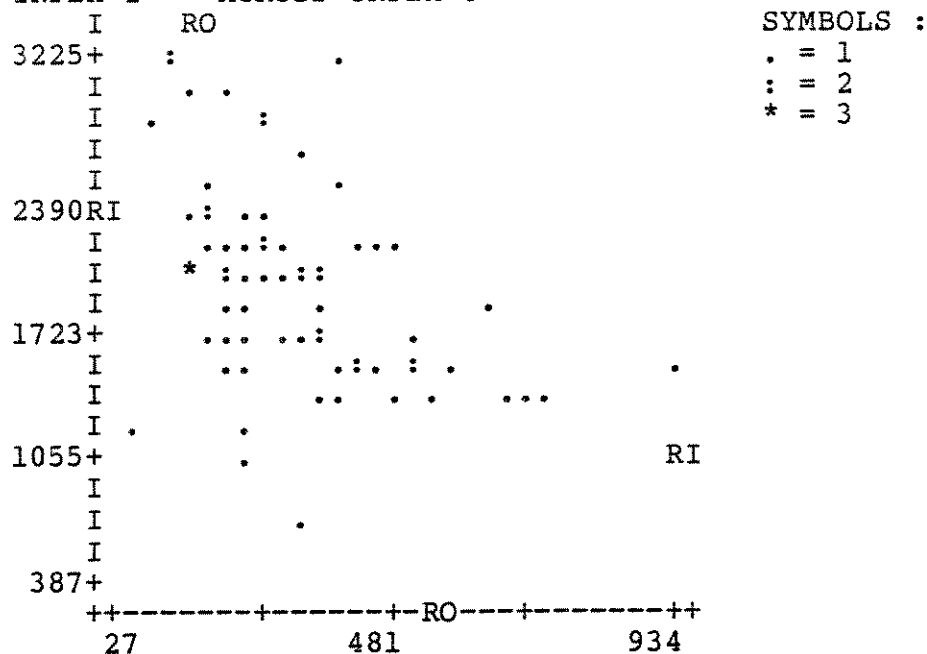
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	2.3+03	391.83	.493	.243	.000	14.64	1.4+03	344.35	52
CLAY	59.84	13.19				1.7-02	21.97	11.59	52

## TOTAL PHOSPHORUS VS. CLAY REDUCED



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
TOPEX	1.8+03	590.07	.668	.446	.000	15.56	1.0+03	441.49	101
CLAY	47.86	25.31				2.9-02	-3.22	18.94	101

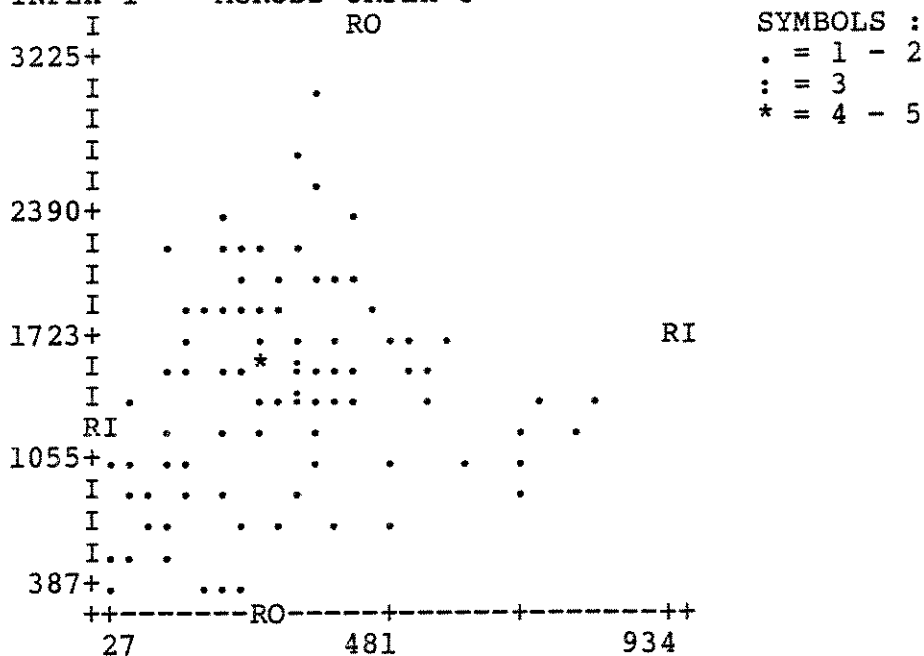
DOWN-INPEX'I' ACROSS-ORPEX'O'



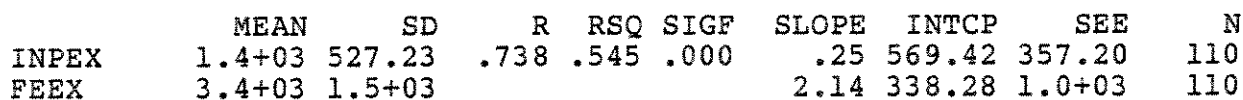
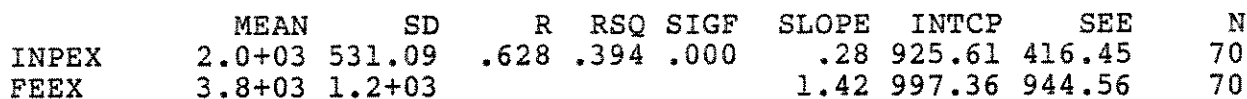
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
INPEX	2.0+03	531.09	-.430	.185	.000	-1.40	2.4+03	482.93	70
ORPEX	327.61	162.83				-.13	589.22	148.06	70

INORGANIC PHOSPHORUS VS. ORGANIC PHOSPHORUS REDUCED

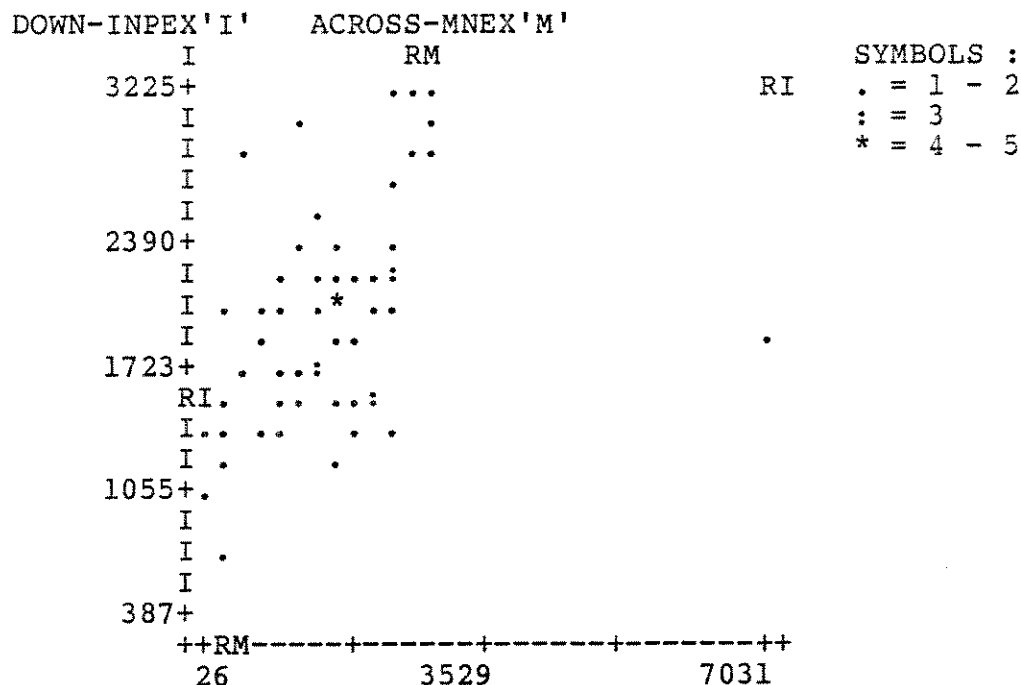
DOWN-INPEX'I' ACROSS-ORPEX'O'



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
INPEX	1.4+03	527.23	.161	.026	.046	.50	1.3+03	522.74	110
ORPEX	315.29	171.10				5.2-02	239.88	169.65	110

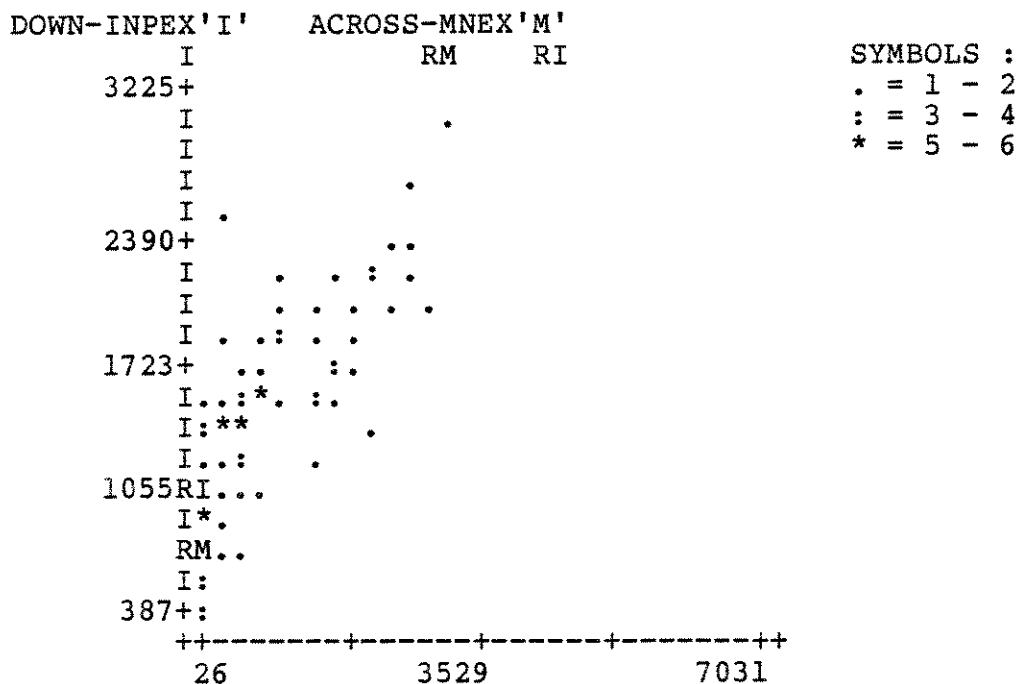


## INORGANIC PHOSPHORUS VS. MANGANESE OXIDIZED



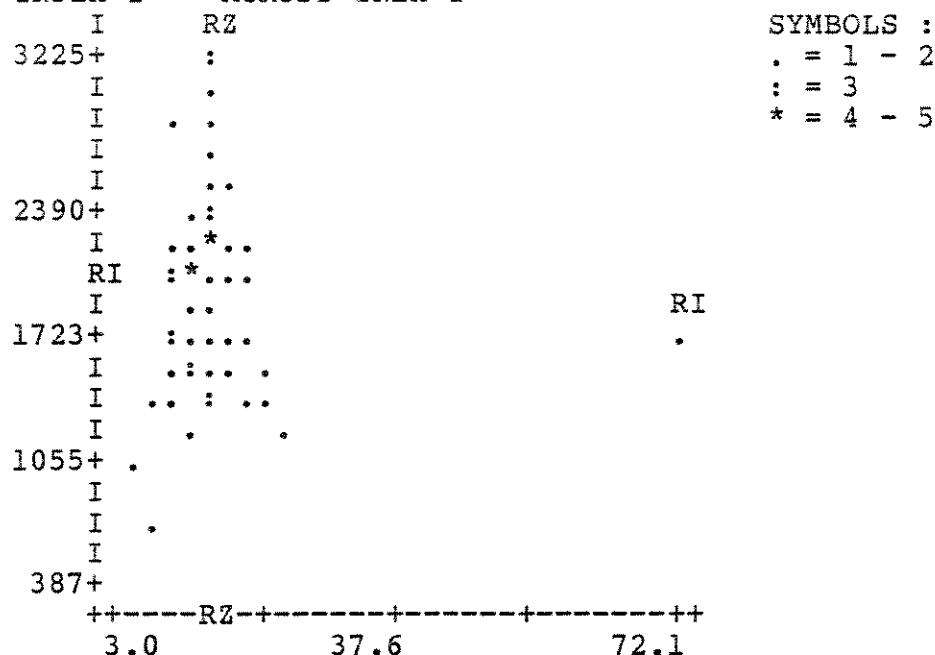
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
INPEX	2.0+03	531.09	.409	.167	.000	.22	1.6+03	488.29	70
MNEX	1.6+03	996.86				.77	71.84	916.52	70

## INORGANIC PHOSPHORUS VS. MANGANESE REDUCED



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
INPEX	1.4+03	527.23	.771	.595	.000	.52	1.0+03	337.23	110
MNEX	808.72	781.83				1.14	-839.29	500.08	110

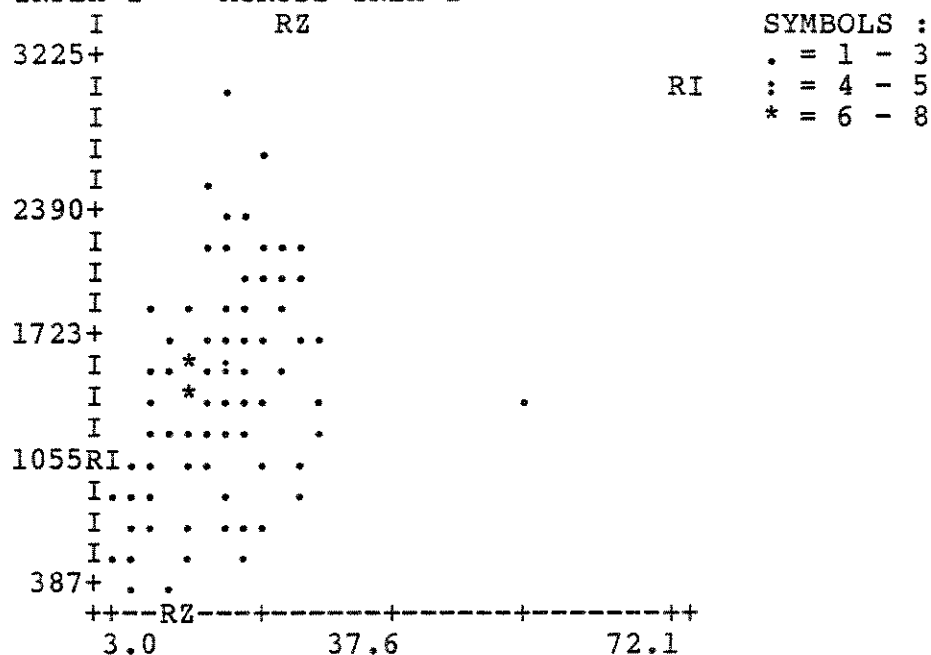
DOWN-INPEX'I' ACROSS-ZNEX'Z'



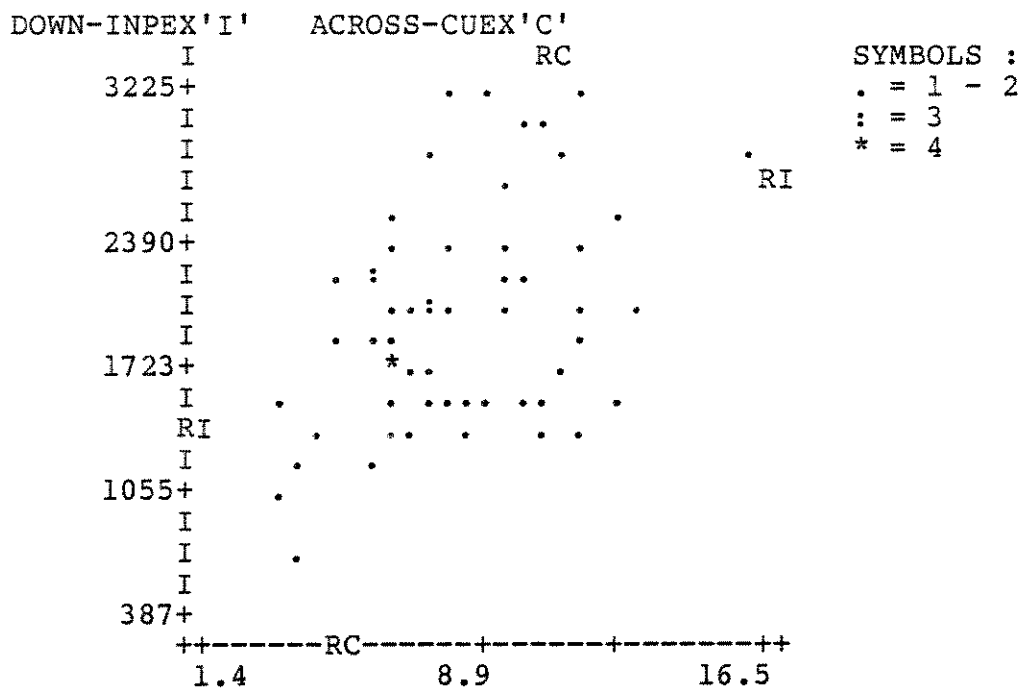
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
INPEX	2.0+03	531.09	-.032	.001	.397	-2.18	2.0+03	534.71	70
ZNEX	15.10	7.74				-4.6-04	16.02	7.79	70

INORGANIC PHOSPHORUS VS. ZINC REDUCED

DOWN-INPEX'I' ACROSS-ZNEX'Z'

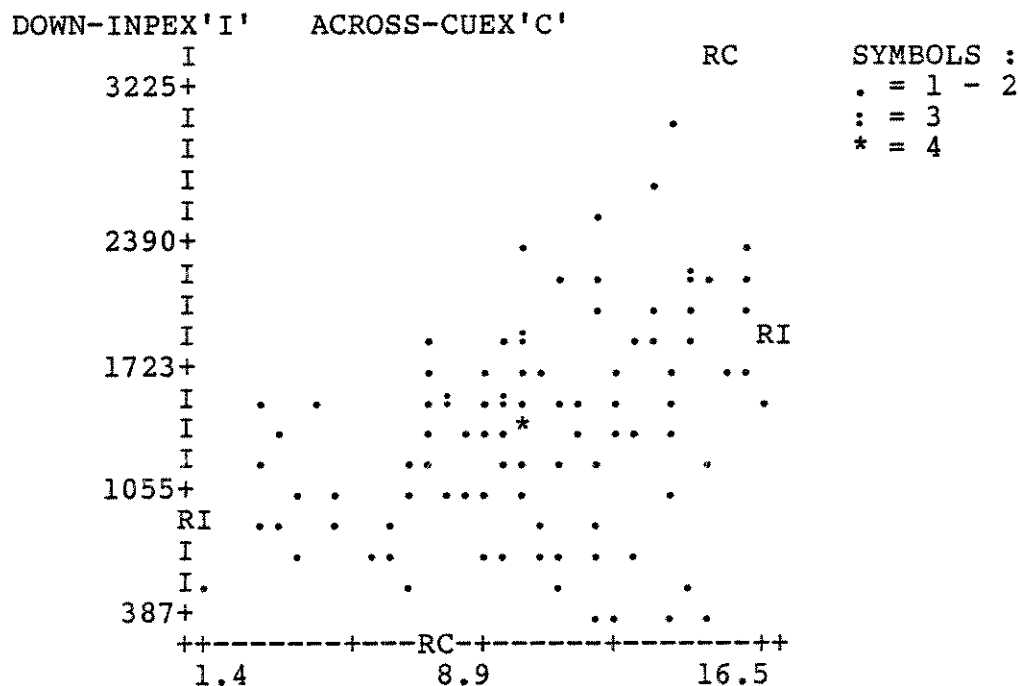


	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
INPEX	1.4+03	527.23	.377	.142	.000	28.73	984.41	490.51	110
ZNEX	15.90	6.92				5.0-03	8.76	6.44	110



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
INPEX	2.0+03	531.09	.406	.165	.000	87.78	1.3+03	488.80	70
CUEX	7.97	2.46				1.9-03	4.24	2.26	70

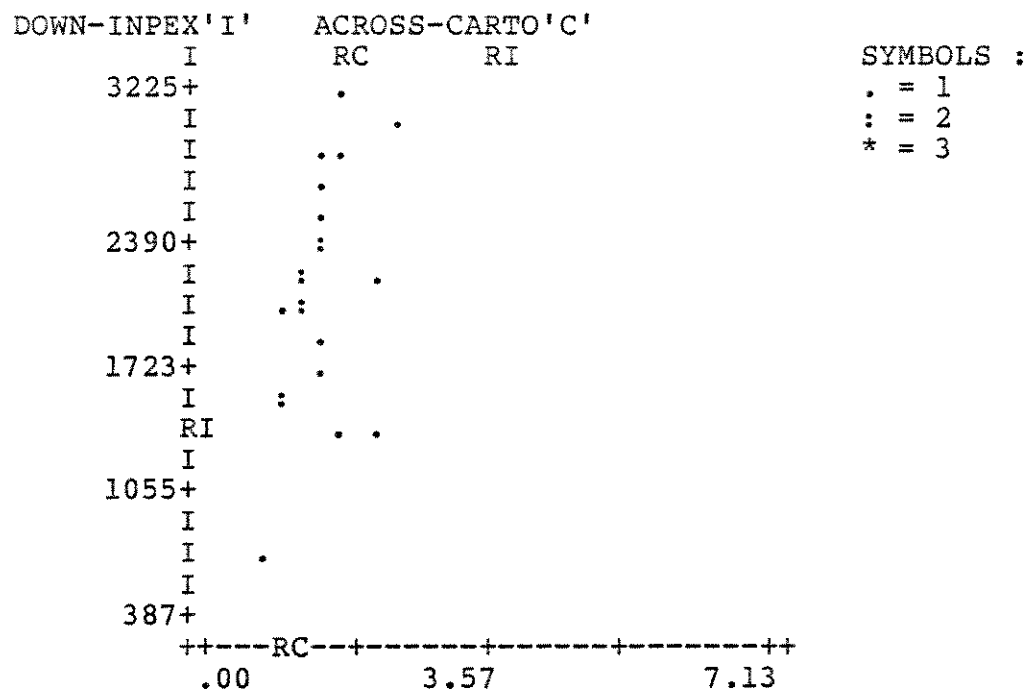
## INORGANIC PHOSPHORUS VS. COPPER REDUCED



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
INPEX	1.4+03	527.23	.396	.157	.000	60.44	822.96	486.44	110
CUEX	10.23	3.45				2.6-03	6.50	3.18	110

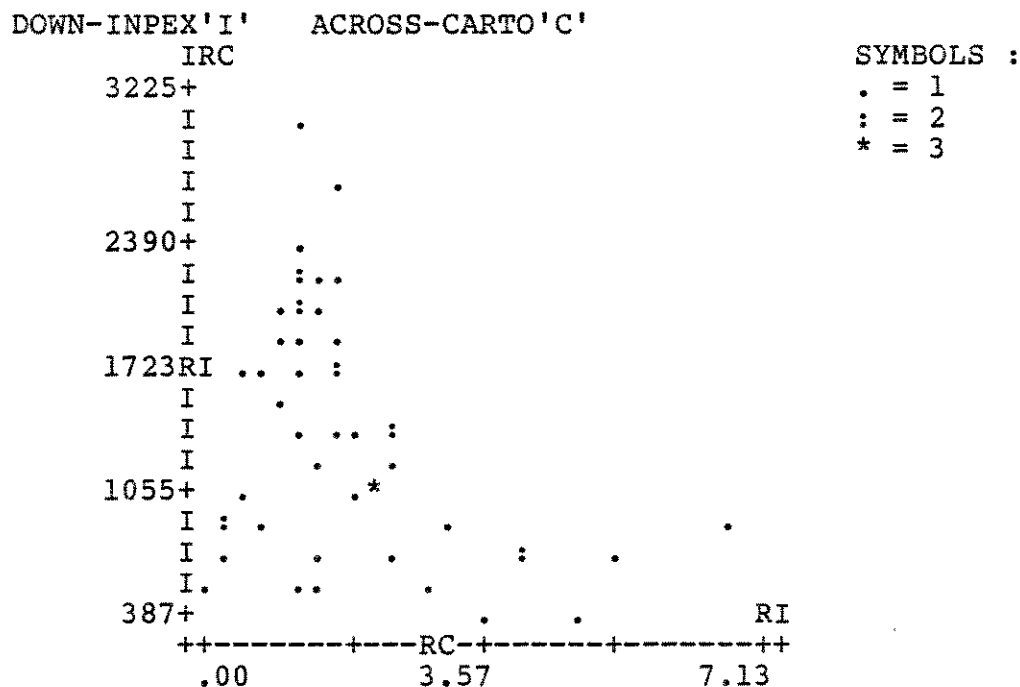


## INORGANIC PHOSPHORUS VS. CARBON OXIDIZED



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
INPEX	2.1+03	609.09	.359	.129	.055	512.54	1.4+03	583.26	21
CARTO	1.46	.43				2.5-04	.92	.41	21

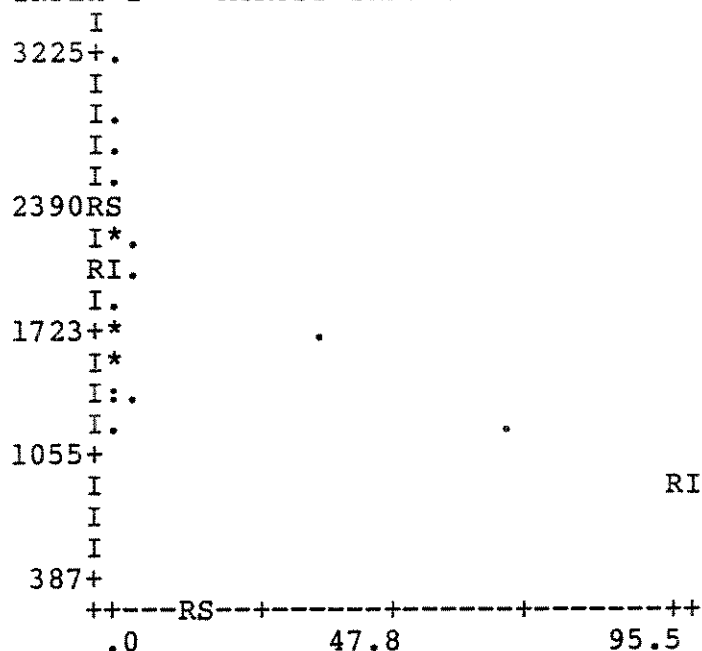
## INORGAINC PHOSPHORUS VS. CARBON REDUCED



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
INPEX	1.4+03	649.44	-.417	.174	.001	-181.14	1.7+03	596.44	50
CARTO	1.94	1.49				-9.6-04	3.26	1.37	50

## INORGANIC PHOSPHORUS VS. SAND OXIDIZED

DOWN-INPEX'I' ACROSS-SAND'S'



SYMBOLS :

. = 1 - 3

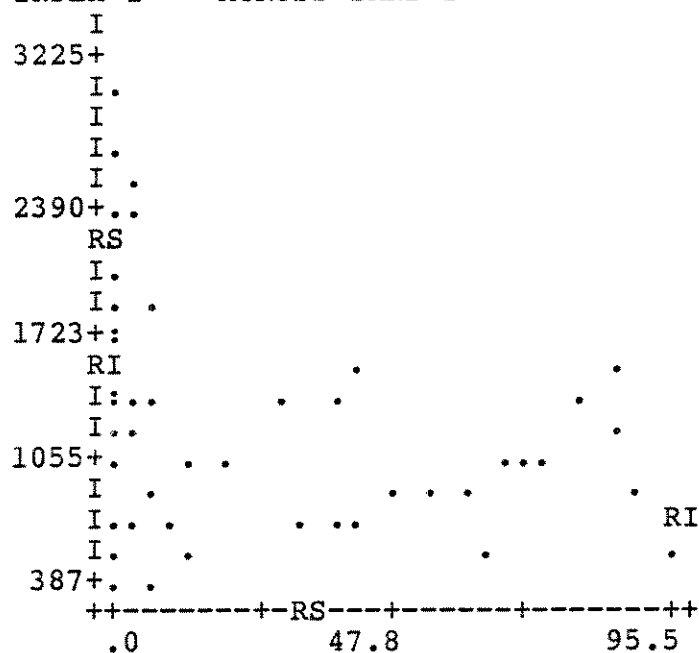
: = 4 - 5

\* = 6 - 8

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
INPEX	2.0+03	431.09	-.265	.070	.029	-10.83	2.0+03	419.84	52
SAND	2.28	10.54				-6.5-03	14.93	10.26	52

## INORGANIC PHOSPHORUS VS. SAND REDUCED

DOWN-INPEX'I' ACROSS-SAND'S'



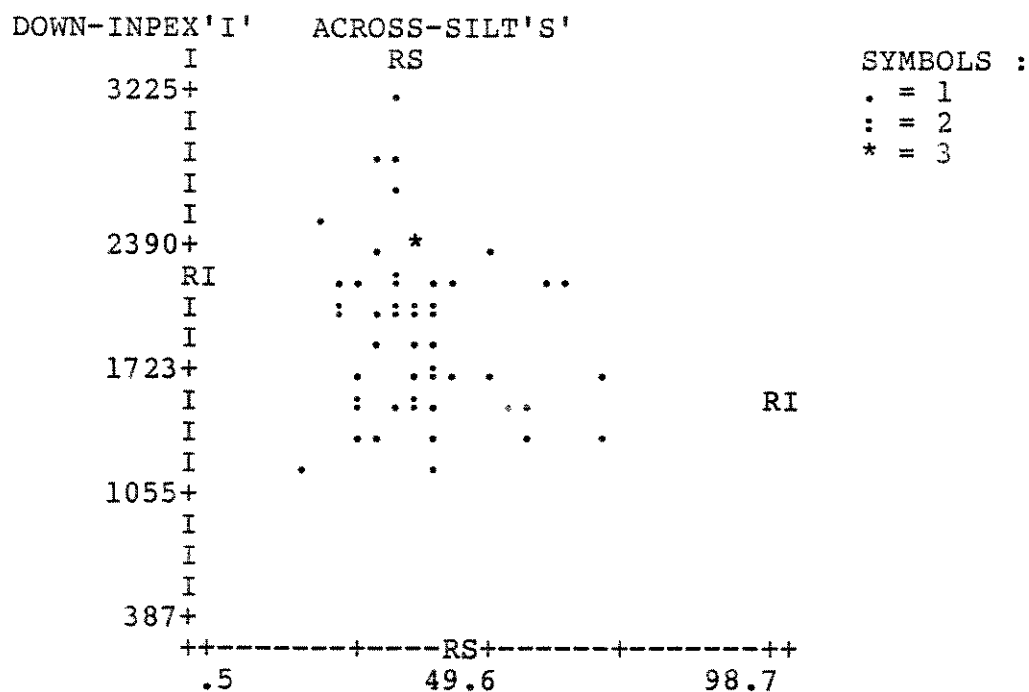
SYMBOLS :

. = 1 - 6

: = 7 - 11

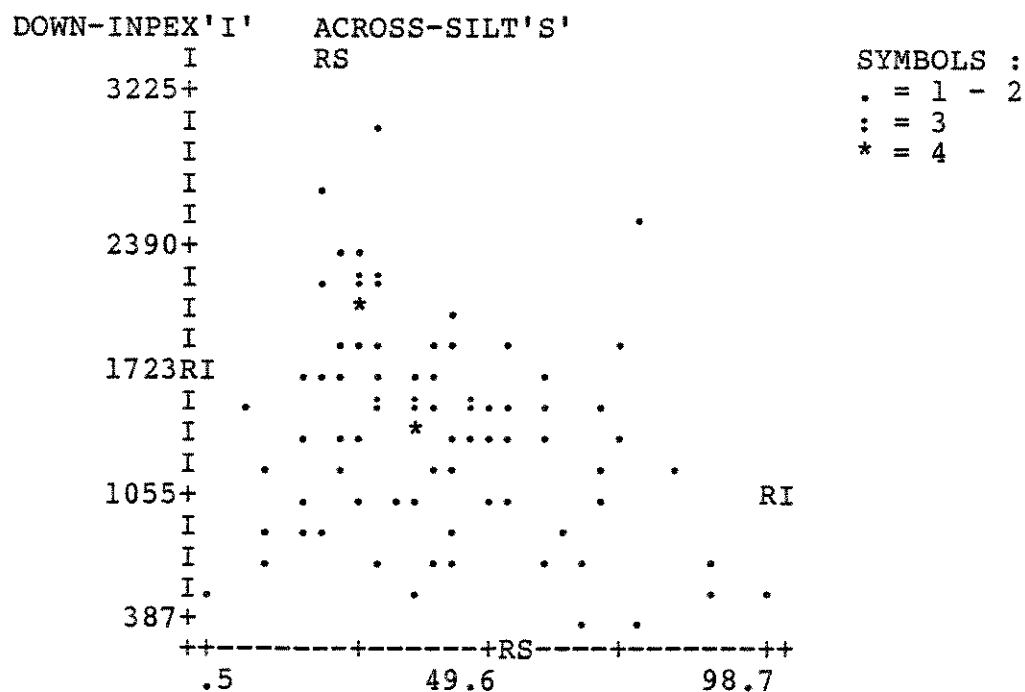
\* = 12 - 16

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
INPEX	1.5+03	529.18	-.376	.141	.000	-8.14	1.6+03	492.84	101
SAND	11.95	24.43				-1.7-02	37.31	22.76	101



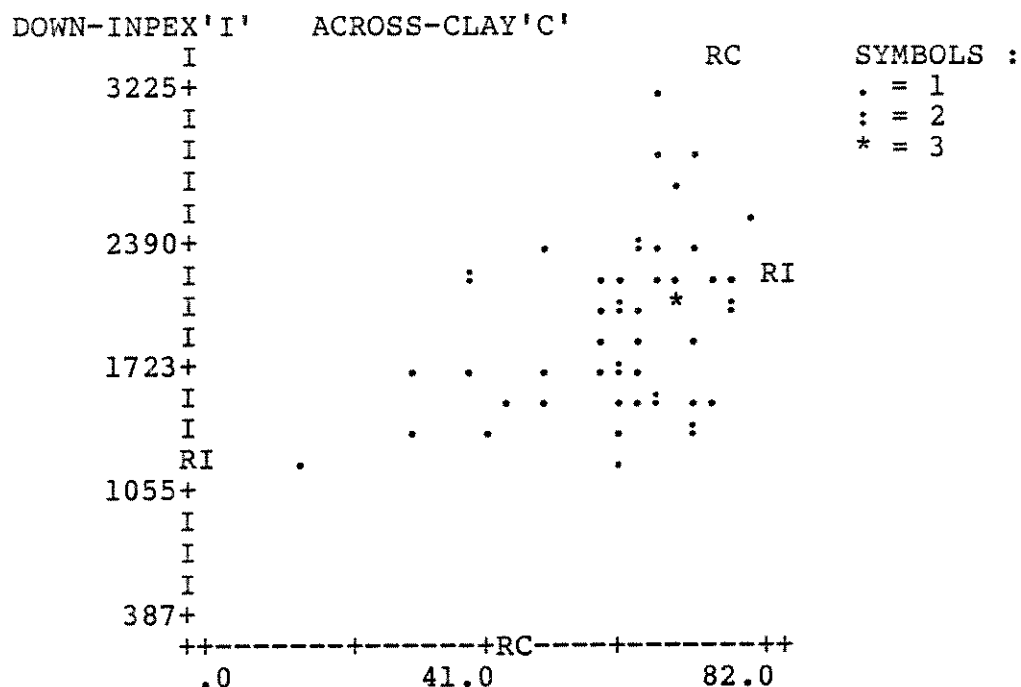
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
INPEX	2.0+03	431.09	-.167	.028	.119	-6.34	2.2+03	429.28	52
SILT	37.88	11.34				-4.4-03	46.46	11.29	52

## INORGANIC PHOSPHORUS VS. SILT REDUCED



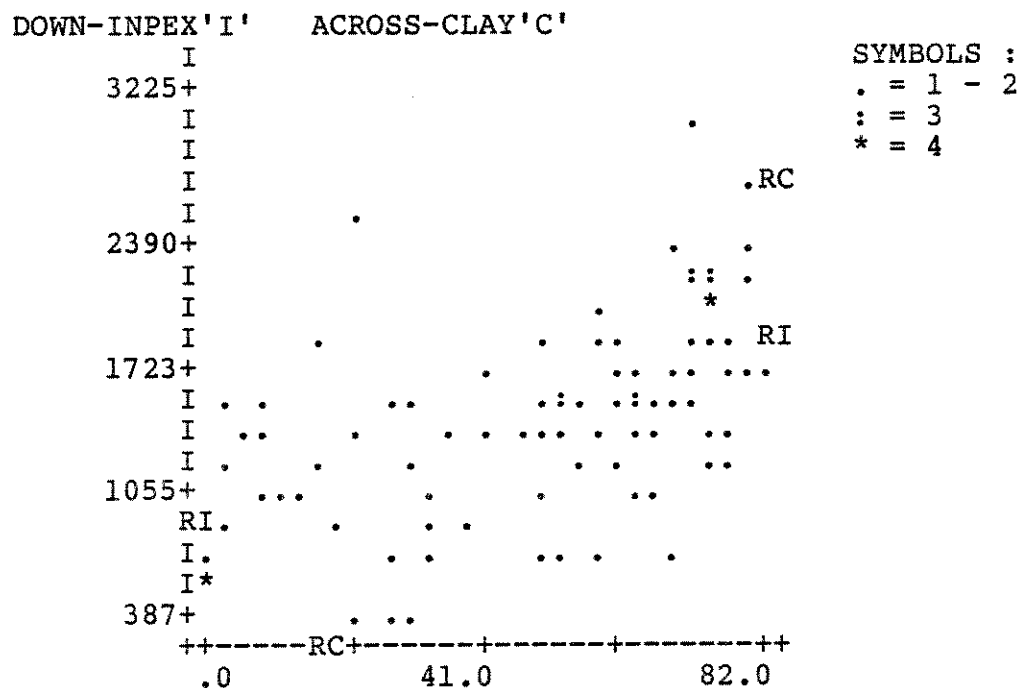
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
INPEX	1.5+03	529.18	-.285	.081	.002	-7.77	1.8+03	509.79	101
SILT	40.32	19.40				-1.0-02	55.58	18.69	101

## INORGANIC PHOSPHORUS VS. CLAY OXIDIZED

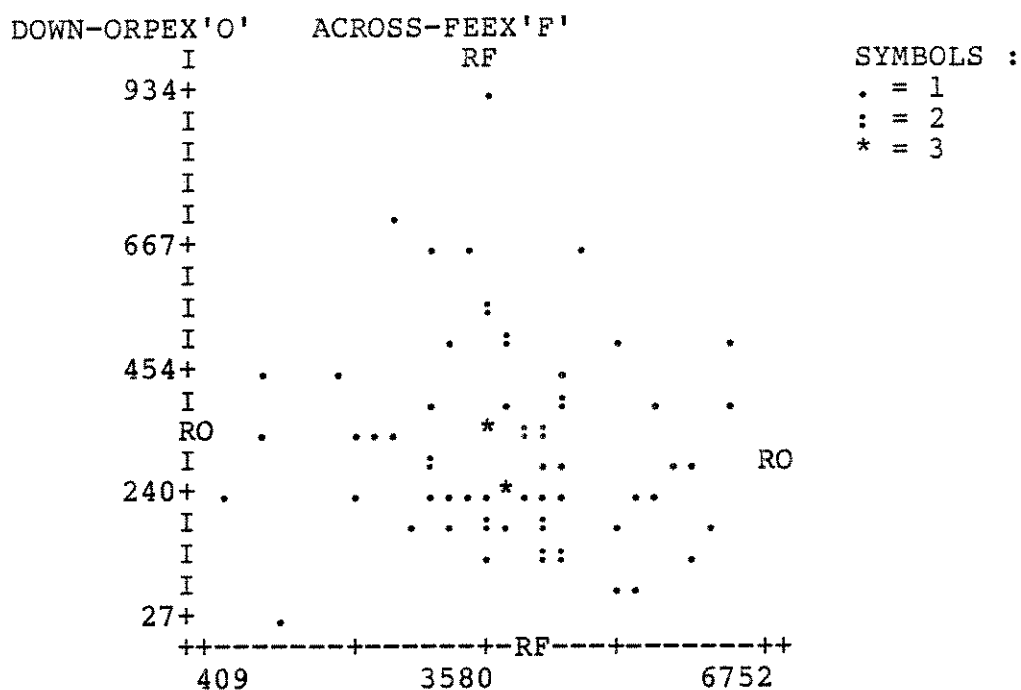


	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
INPEX	2.0+03	431.09	.355	.126	.005	11.59	1.3+03	407.05	52
CLAY	59.84	13.19				1.1-02	38.61	12.46	52

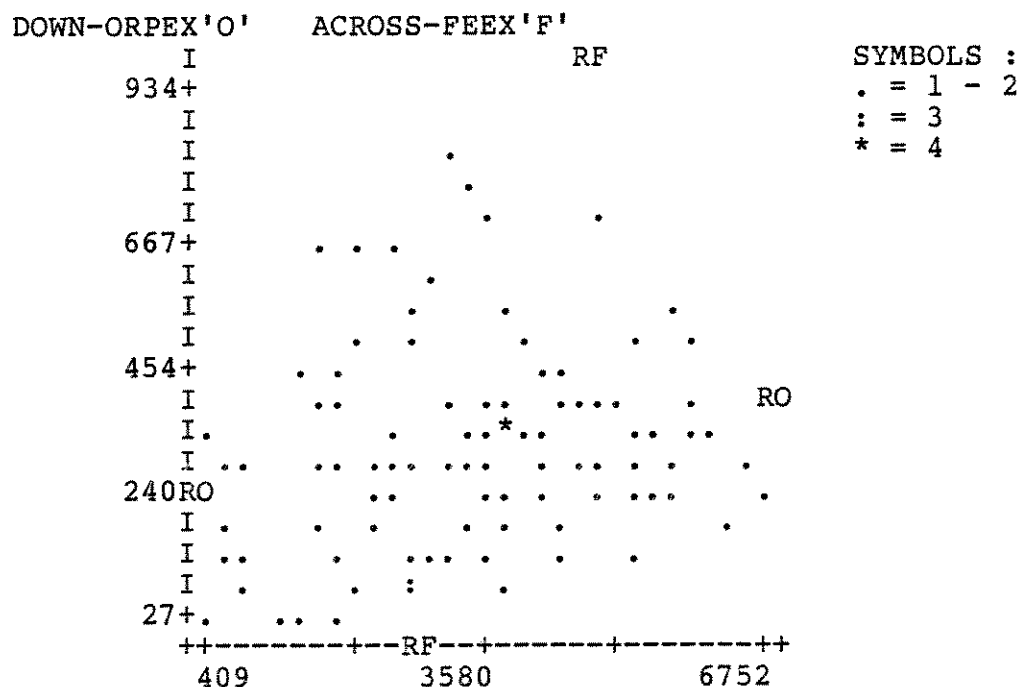
## INORGANIC PHOSPHORUS VS. CLAY REDUCED



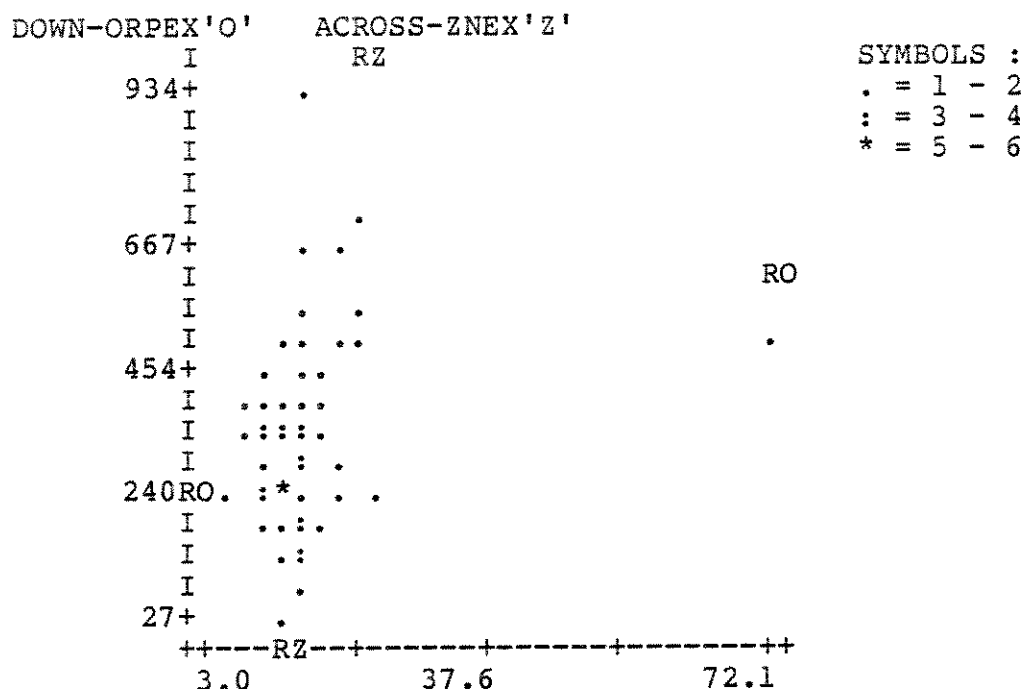
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
INPEX	1.5+03	529.18	.586	.344	.000	12.26	874.59	430.79	101
CLAY	47.86	25.31				2.8-02	6.87	20.61	101



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ORPEX	327.61	162.83	-.103	.011	.199	-1.4-02	380.59	163.15	70
FEEX	3.8+03	1.2+03				-.76	4.1+03	1.2+03	70

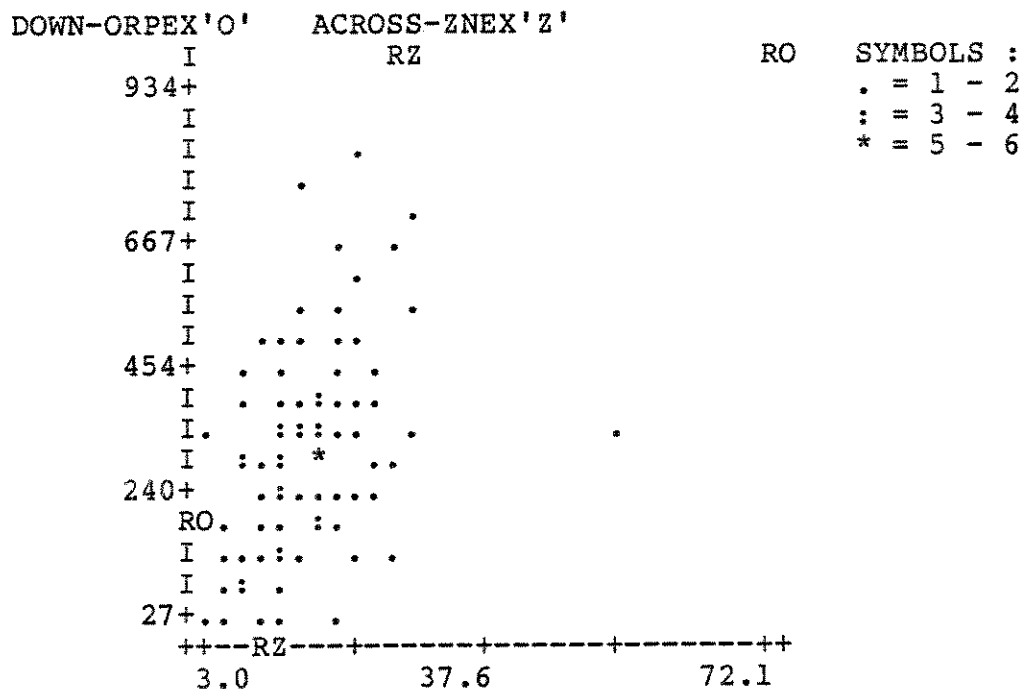


	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ORPEX	315.29	171.10	.231	.053	.008	2.6-02	226.68	167.24	110
FEEX	3.4+03	1.5+03				2.07	2.8+03	1.5+03	110

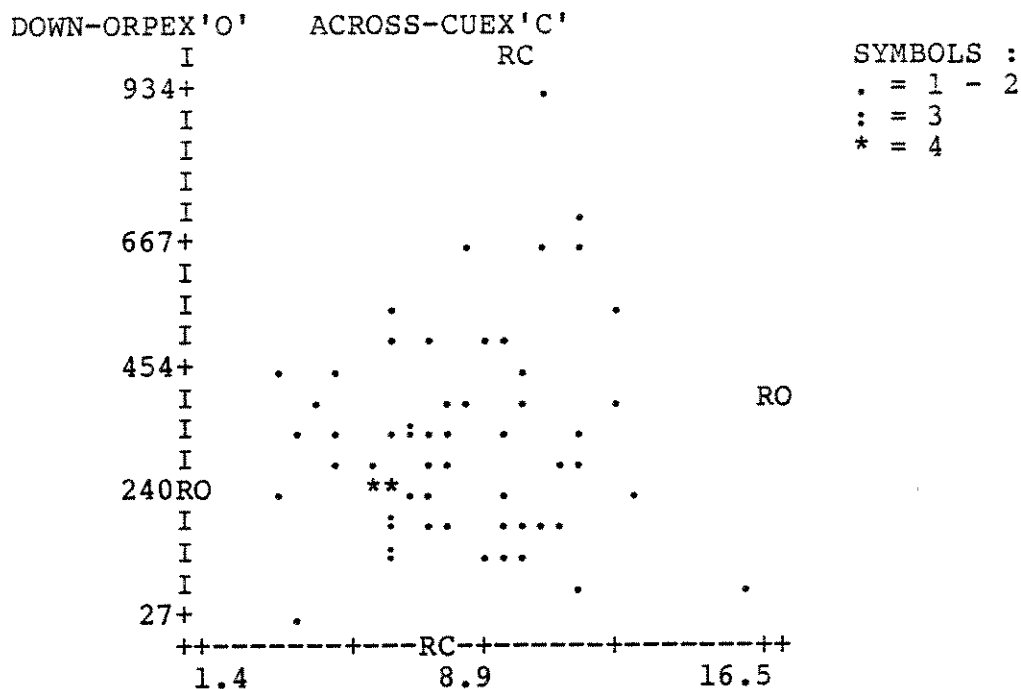


	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ORPEX	327.61	162.83	.233	.054	.026	4.91	253.44	159.49	70
ZNEX	15.10	7.74				1.1-02	11.47	7.58	70

## ORGANIC PHOSPHORUS VS. ZINC REDUCED

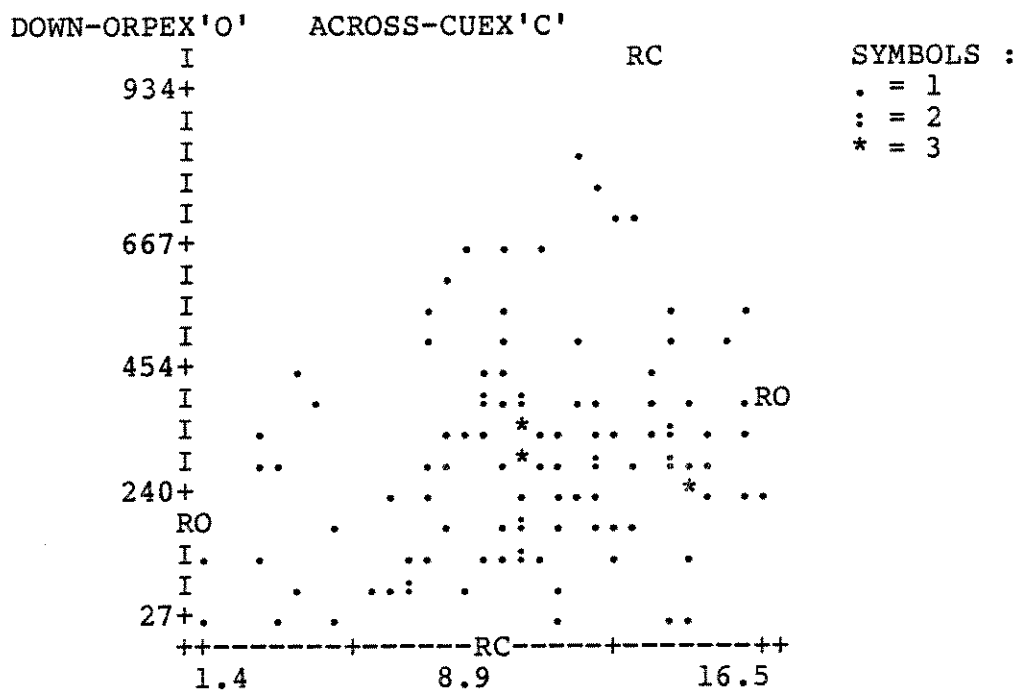


	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ORPEX	315.29	171.10	.448	.200	.000	11.06	139.44	153.71	110
ZNEX	15.90	6.92				1.8-02	10.19	6.22	110



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ORPEX	327.61	162.83	.162	.026	.090	10.76	241.88	161.84	70
CUEX	7.97	2.46				2.5-03	7.17	2.44	70

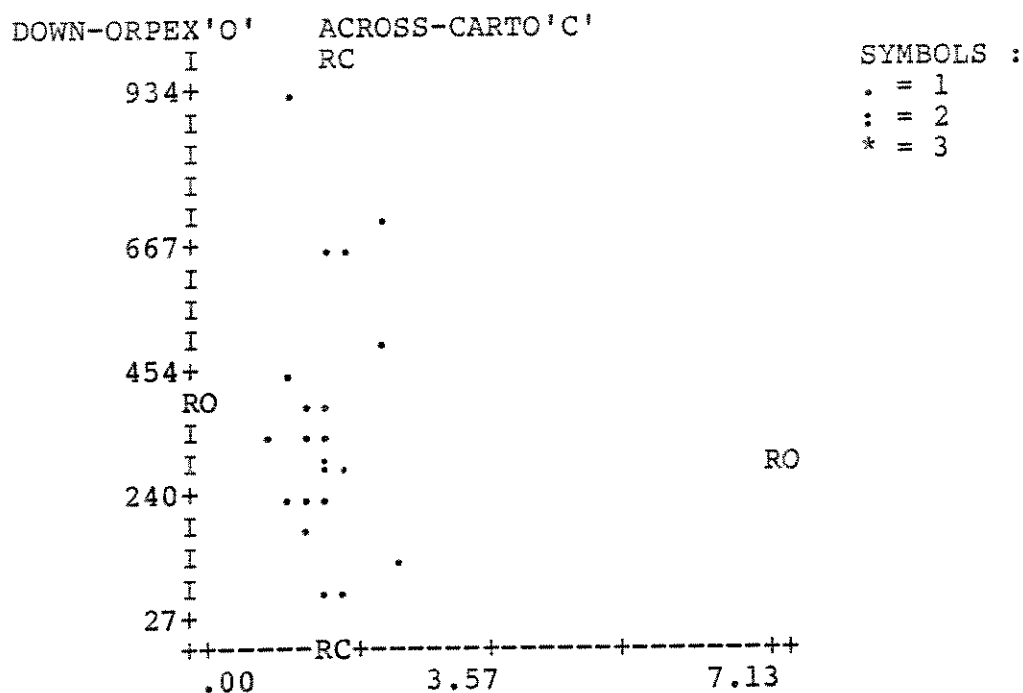
## ORGANIC PHOSPHORUS VS. COPPER REDUCED



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ORPEX	315.29	171.10	.227	.051	.009	11.23	200.41	167.42	110
CUEX	10.23	3.45				4.6-03	8.79	3.38	110

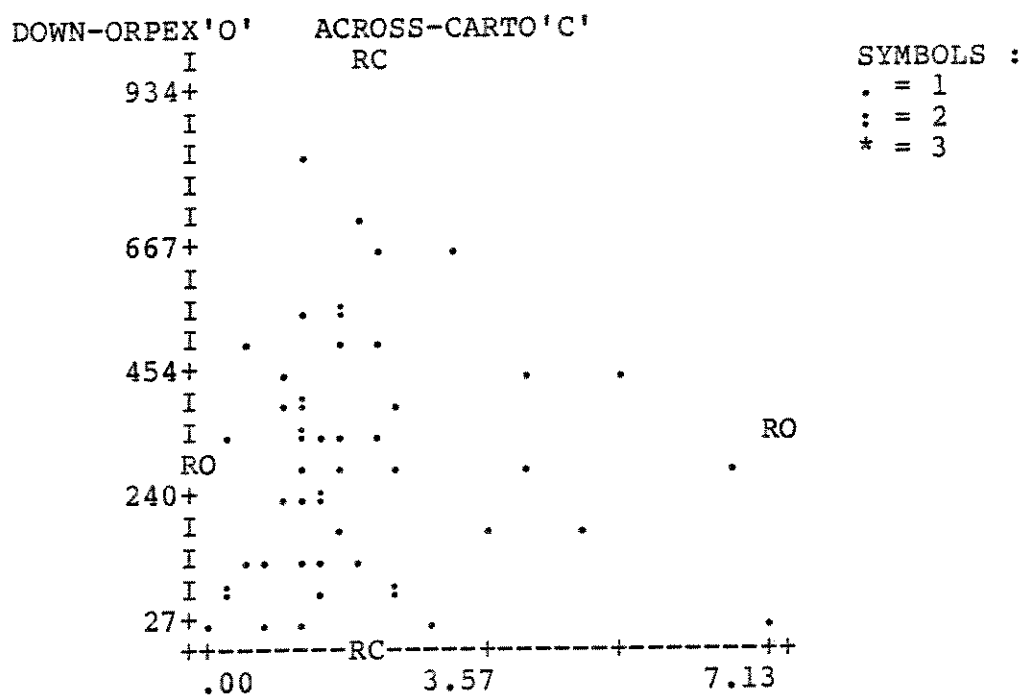
## ORGANIC PHOSPHORUS VS. CARBON OXIDIZED

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	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ORPEX	376.24	212.52	-.035	.001	.441	-17.19	401.33	217.91	21
CARTO	1.46	.43				-6.9-05	1.49	.44	21

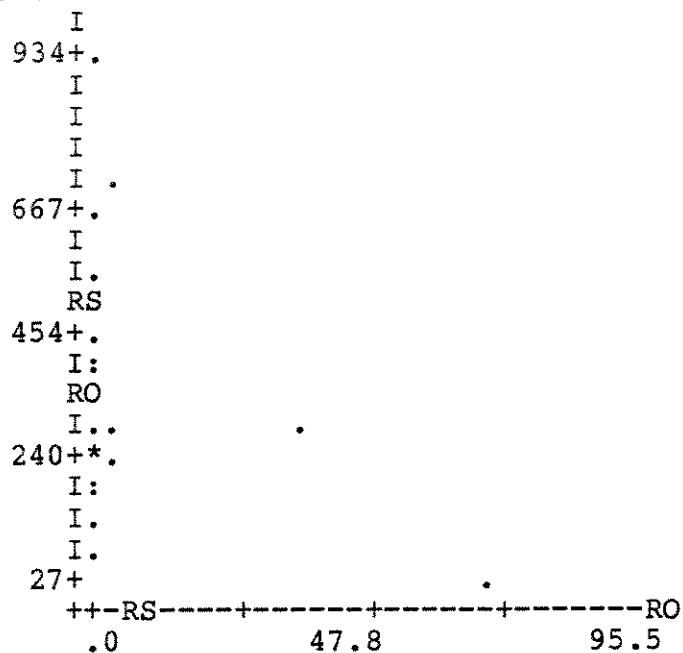
## ORGANIC PHOSPHORUS VS. CARBON REDUCED



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ORPEX	315.26	195.14	.021	.000	.443	2.73	309.95	197.12	50
CARTO	1.94	1.49				1.6-04	1.89	1.51	50



DOWN-ORPEX'O'      ACROSS-SAND'S'

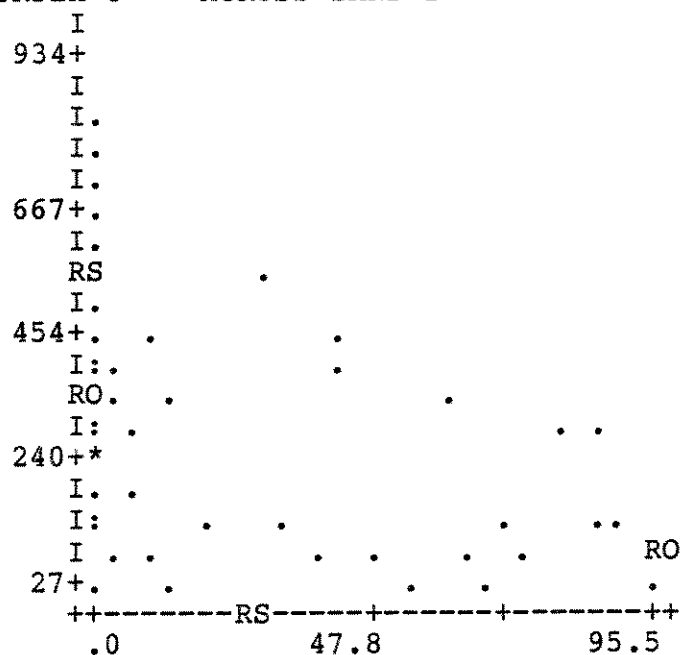


SYMBOLS :  
 . = 1 - 4  
 : = 5 - 7  
 \* = 8 - 10

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ORPEX	327.96	165.76	-.209	.044	.069	-3.28	335.43	163.73	52
SAND	2.28	10.54				-1.3-02	6.63	10.41	52

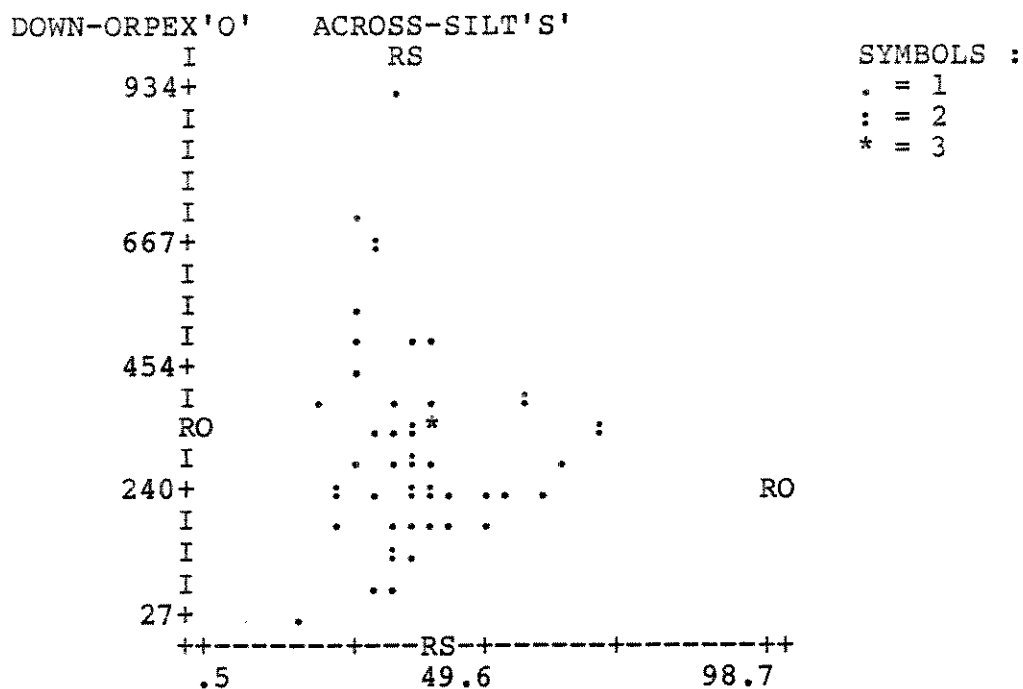
ORGANIC PHOSPHORUS VS. SAND REDUCED

DOWN-ORPEX'O'      ACROSS-SAND'S'



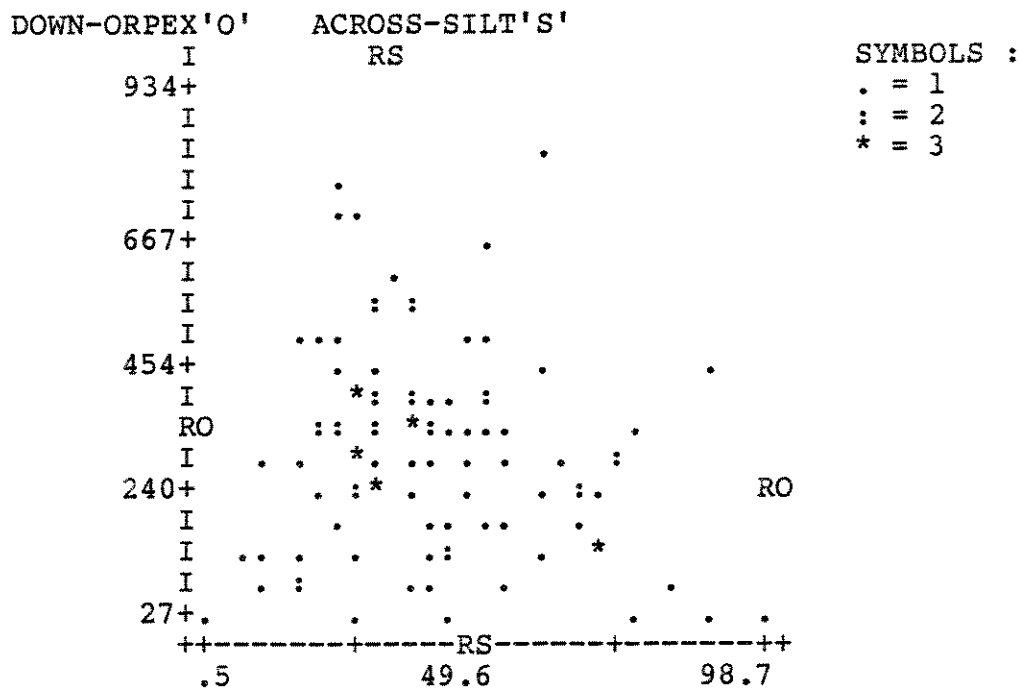
SYMBOLS :  
 . = 1 - 5  
 : = 6 - 9  
 \* = 10 - 13

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ORPEX	311.94	170.14	-.363	.132	.000	-2.53	342.19	159.31	101
SAND	11.95	24.43				-5.2-02	28.23	22.88	101

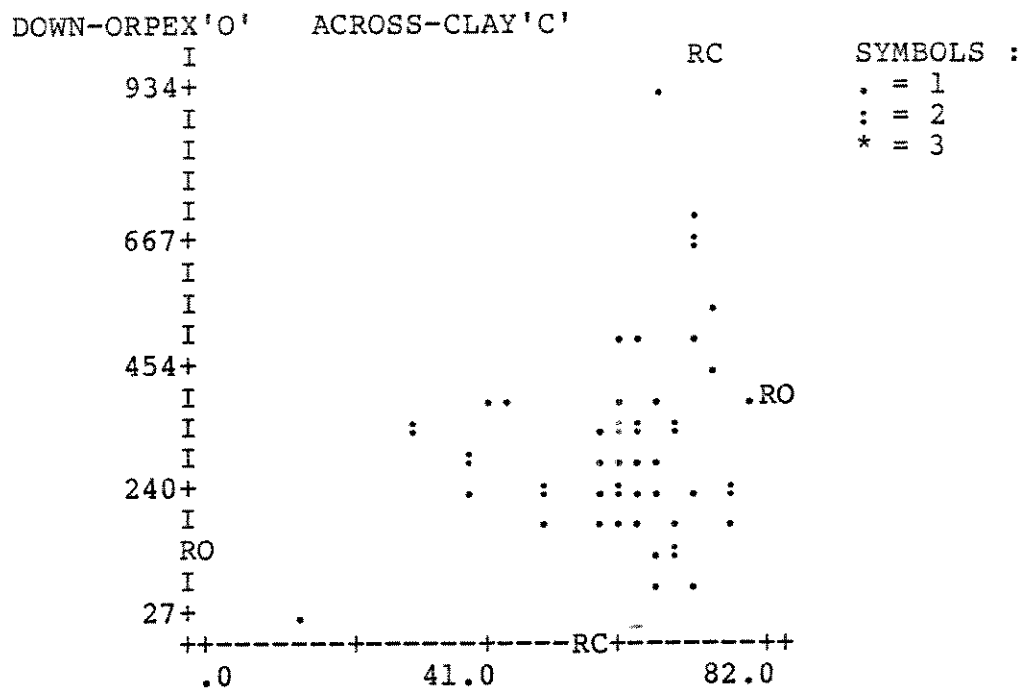


	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ORPEX	327.96	165.76	-.084	.007	.277	-1.22	374.36	166.83	52
SILT	37.88	11.34				-5.7-03	39.76	11.41	52

## ORGANIC PHOSPHORUS VS. SILT REDUCED

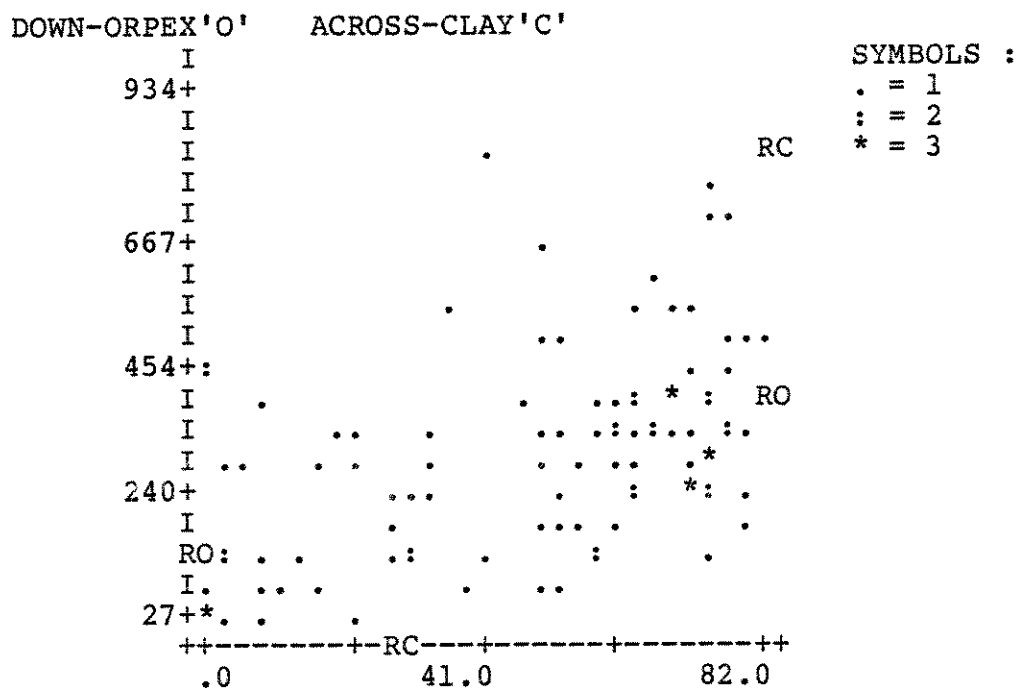


	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ORPEX	311.94	170.14	-.138	.019	.085	-1.21	360.68	169.36	101
SILT	40.32	19.40				-1.6-02	45.22	19.32	101



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ORPEX	327.96	165.76	.238	.057	.044	3.00	148.66	162.58	52
CLAY	59.84	13.19				1.9-02	53.62	12.94	52

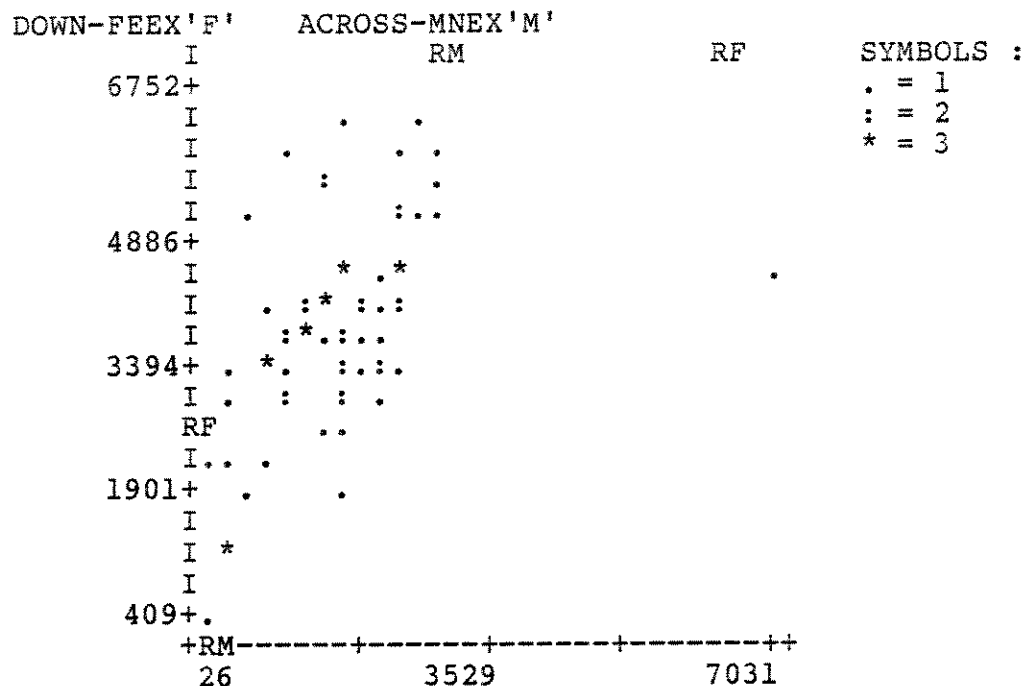
## ORGANIC PHOSPHORUS VS. CLAY REDUCED



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ORPEX	311.94	170.14	.454	.206	.000	3.05	165.80	152.33	101
CLAY	47.86	25.31				6.8-02	26.77	22.66	101

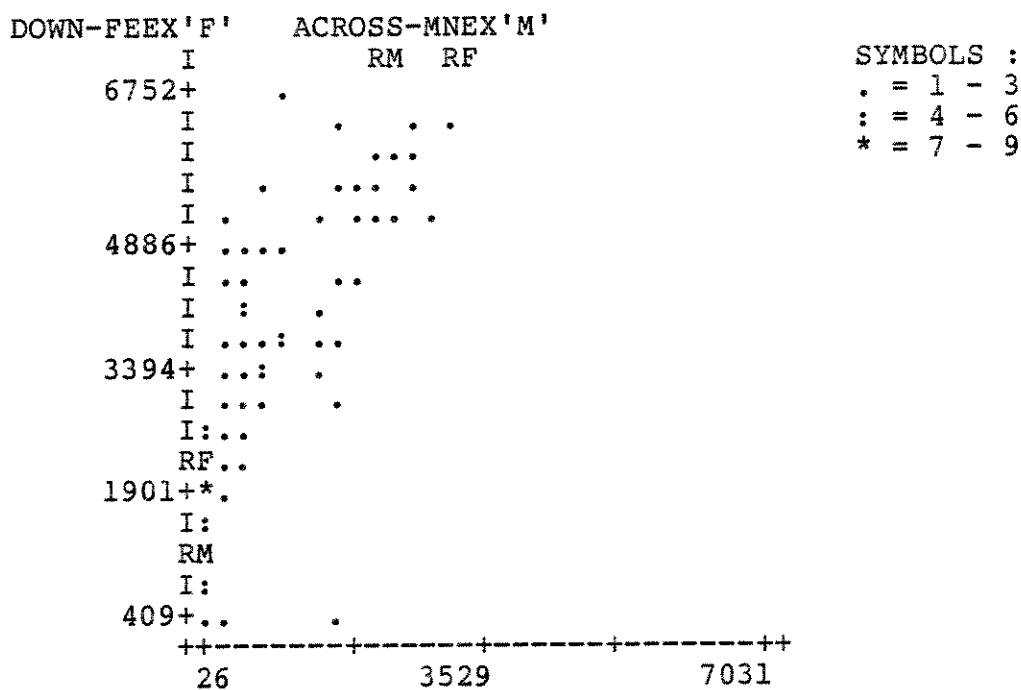
IRON VS. MANGANESE OXIDIZED

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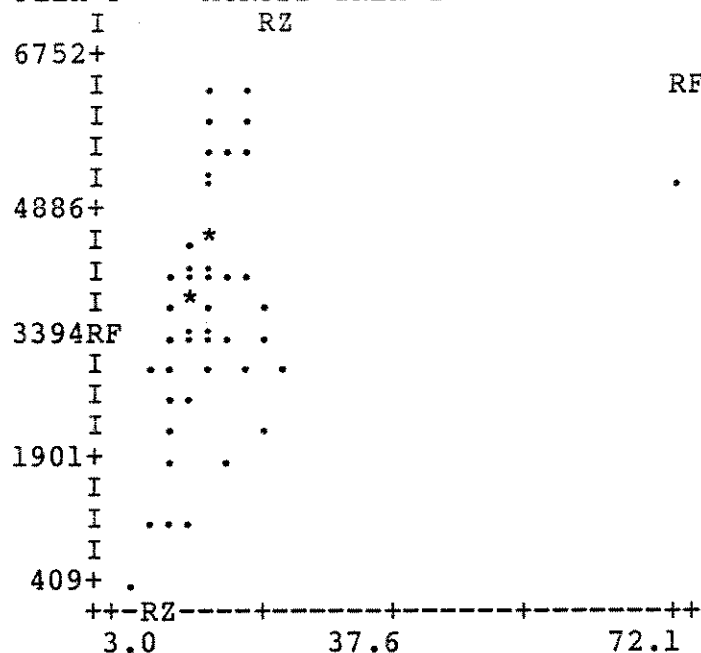
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
FEEX	3.8+03	1.2+03	.514	.264	.000	.62	2.8+03	1.0+03	70
MNEX	1.6+03	996.86				.43	-32.18	861.44	70

IRON VS. MANGANESE REDUCED



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
FEEX	3.4+03	1.5+03	.743	.552	.000	1.45	2.3+03	1.0+03	110
MNEX	808.72	781.83				.38	-492.30	525.61	110

DOWN-FEEX 'F' ACROSS-ZNEX 'Z'



SYMBOLS :

. = 1 - 2

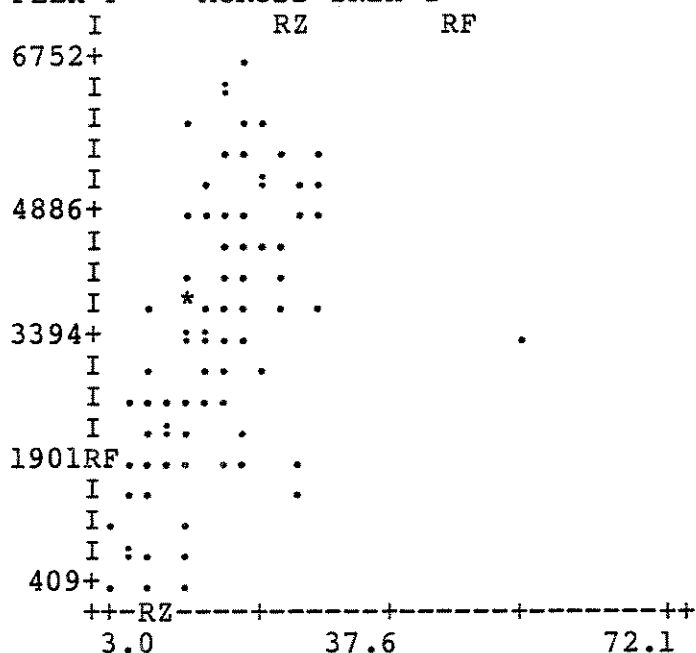
RF : = 3 - 4

\* = 5 - 6

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
FEEX	3.8+03	1.2+03	.294	.086	.007	45.78	3.1+03	1.2+03	70
ZNEX	15.10	7.74				1.9-03	7.89	7.45	70

IRON VS. ZINC REDUCED

DOWN-FEEX 'F' ACROSS-ZNEX 'Z'



SYMBOLS :

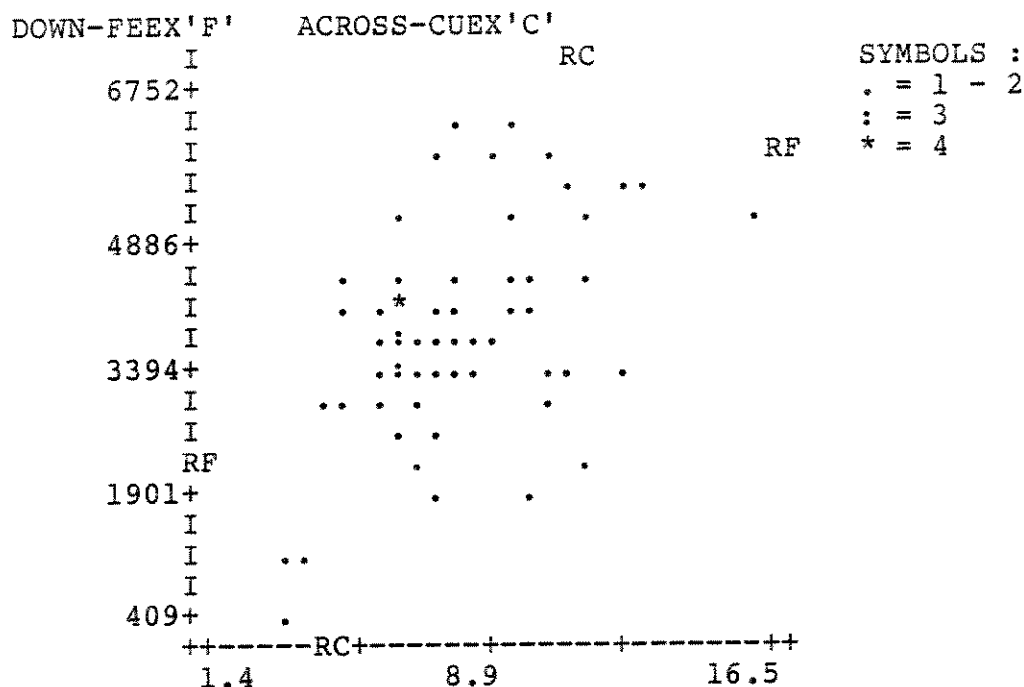
. = 1 - 2

: = 3 - 4

\* = 5 - 6

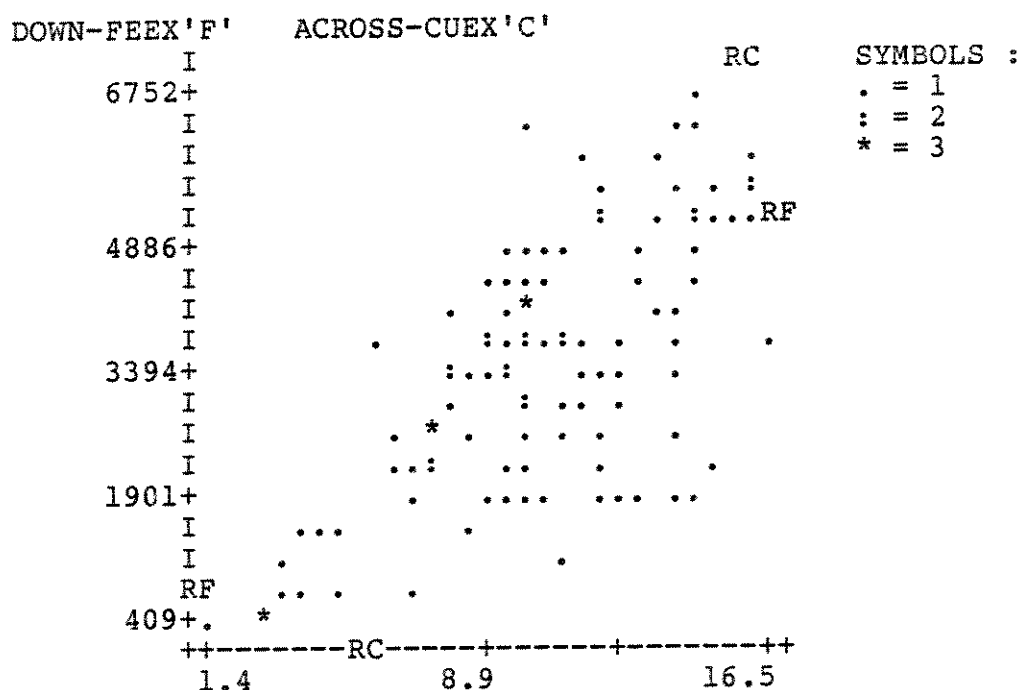
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
FEEX	3.4+03	1.5+03	.531	.282	.000	117.39	1.6+03	1.3+03	110
ZNEX	15.90	6.92				2.4-03	7.66	5.89	110

## IRON VS. COPPER OXIDIZED



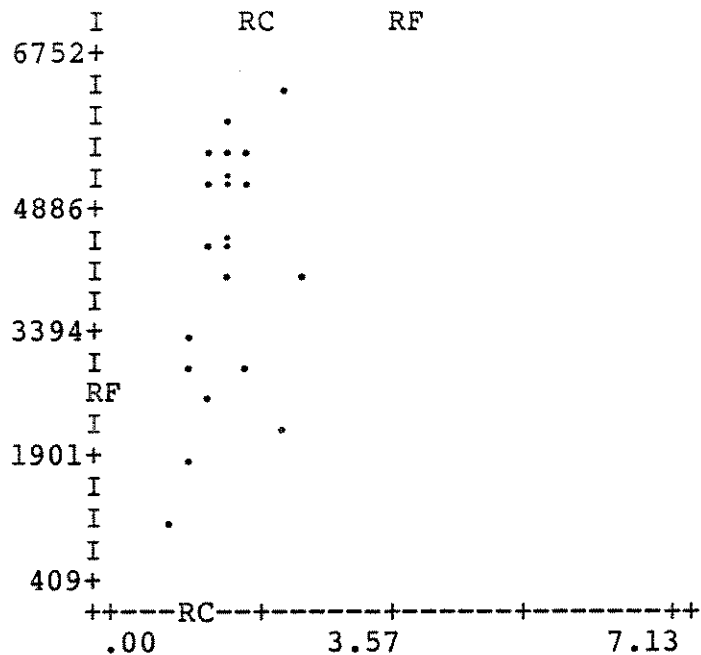
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
FEEX	3.8+03	1.2+03	.476	.226	.000	232.92	2.0+03	1.1+03	70
CUEX	7.97	2.46				9.7-04	4.26	2.18	70

## IRON VS. COPPER REDUCED



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
FEEX	3.4+03	1.5+03	.696	.485	.000	308.89	268.48	1.1+03	110
CUEX	10.23	3.45				1.6-03	4.85	2.49	110

DOWN-FEEX 'F' ACROSS-CARTO 'C'



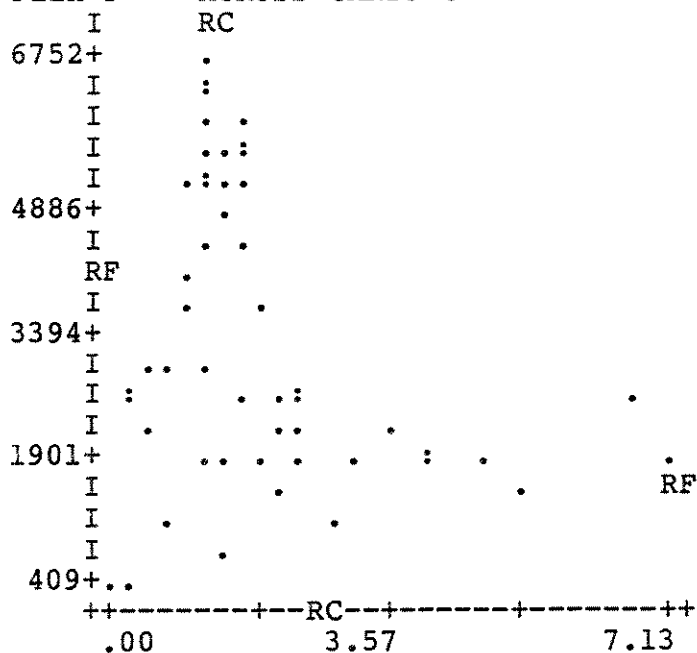
SYMBOLS :

. = 1  
: = 2  
\* = 3

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
FEEX	4.2+03	1.4+03	.350	.122	.060	1.2+03	2.5+03	1.4+03	21
CARTO	1.46	.43				1.1-04	1.02	.41	21

IRON VS. CARBON REDUCED

DOWN-FEEX 'F' ACROSS-CARTO 'C'

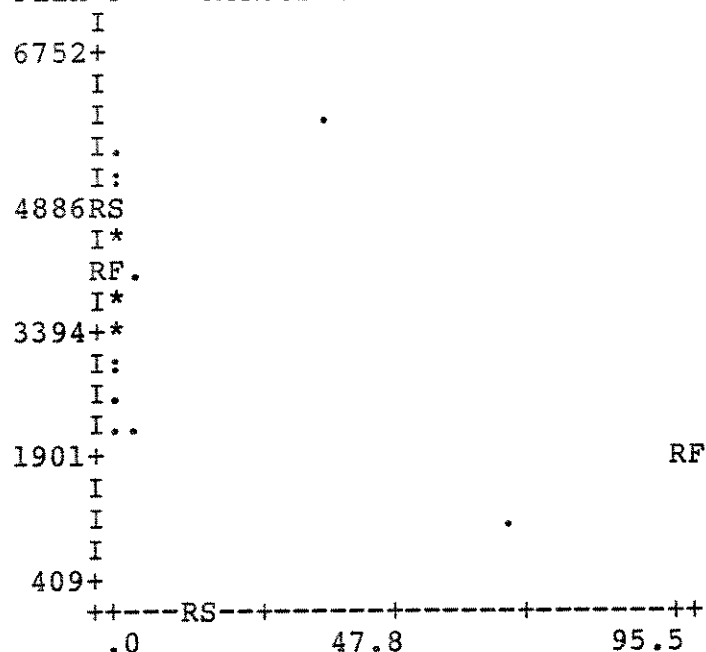


SYMBOLS :

. = 1  
: = 2  
\* = 3

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
FEEX	3.4+03	1.8+03	-.280	.078	.025	-328.84	4.0+03	1.7+03	50
CARTO	1.94	1.49				-2.4-04	2.74	1.45	50

DOWN-FEEX'F' ACROSS-SAND'S'



SYMBOLS :

. = 1 - 3

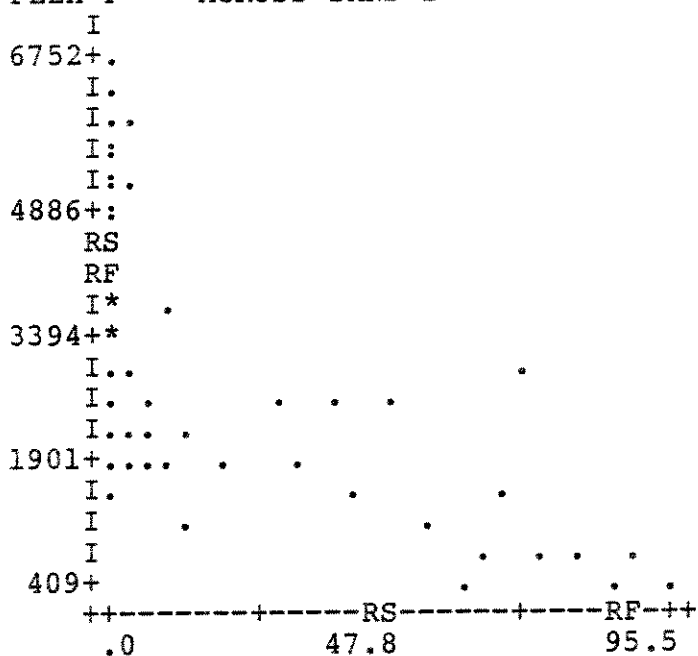
: = 4 - 6

\* = 7 - 9

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
FEEX	3.9+03	900.68	-.234	.055	.047	-20.02	4.0+03	884.32	52
SAND	2.28	10.54				-2.7-03	13.02	10.35	52

IRON VS. SAND REDUCED

DOWN-FEEX'F' ACROSS-SAND'S'



SYMBOLS :

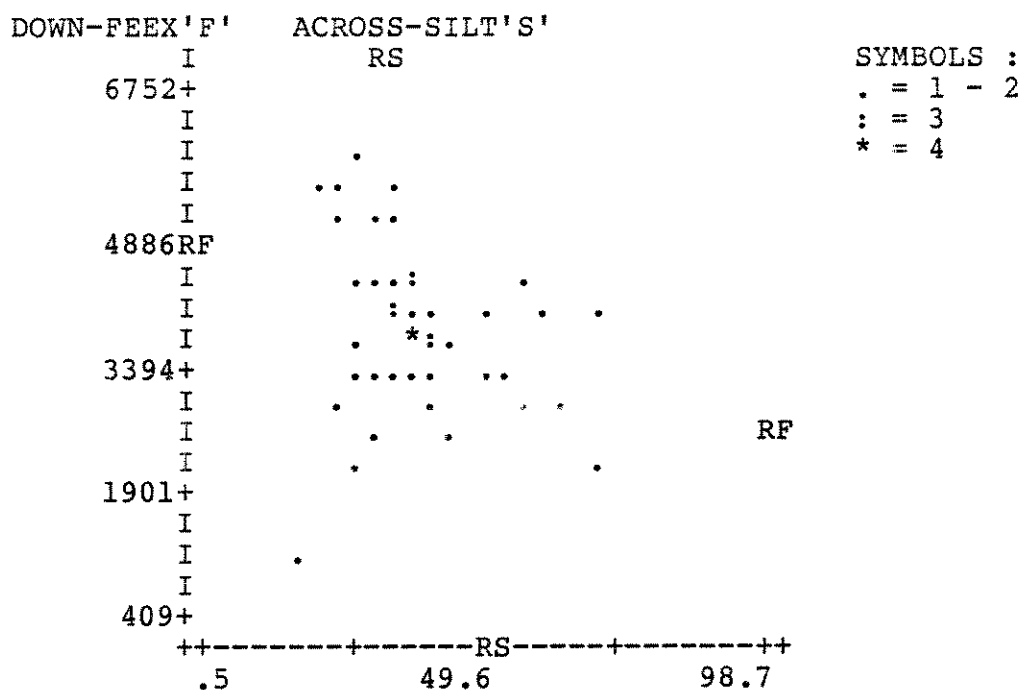
. = 1 - 4

: = 5 - 7

\* = 8 - 11

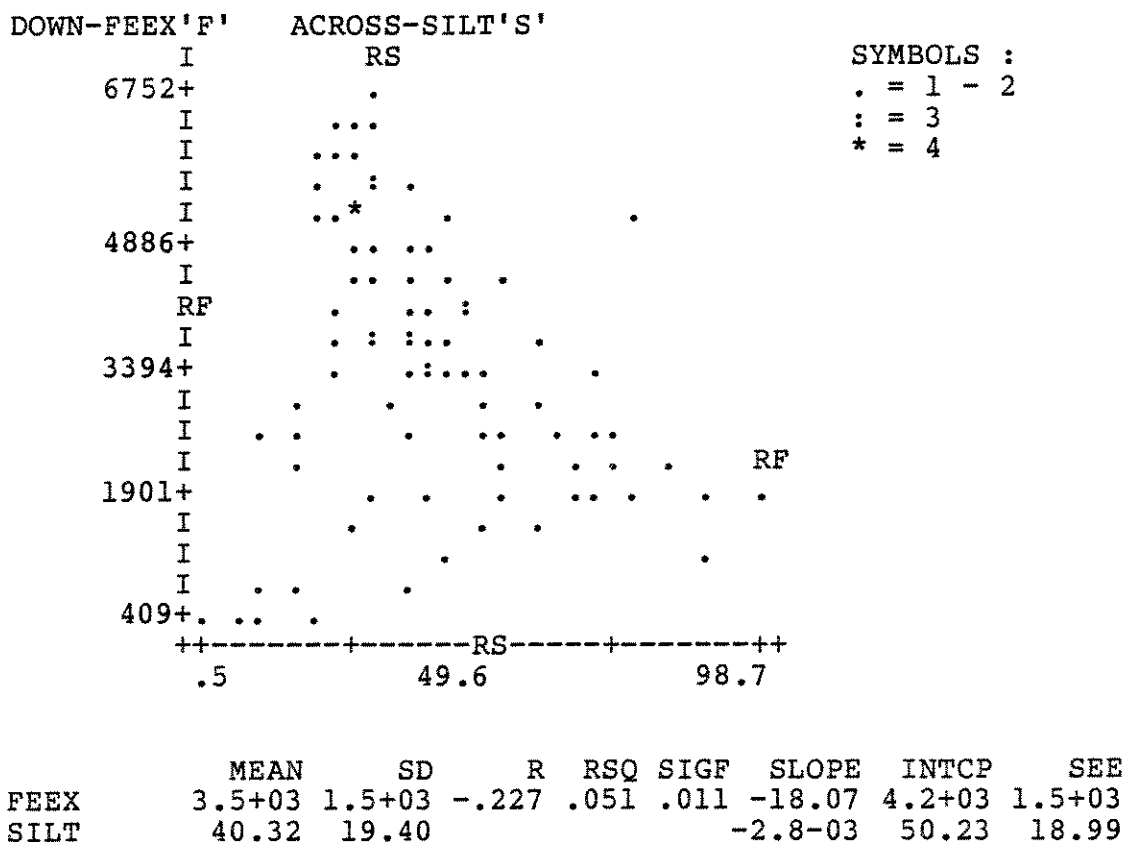
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
FEEX	3.5+03	1.5+03	-.650	.423	.000	-41.14	4.0+03	1.2+03	101
SAND	11.95	24.43				-1.0-02	47.72	18.66	101





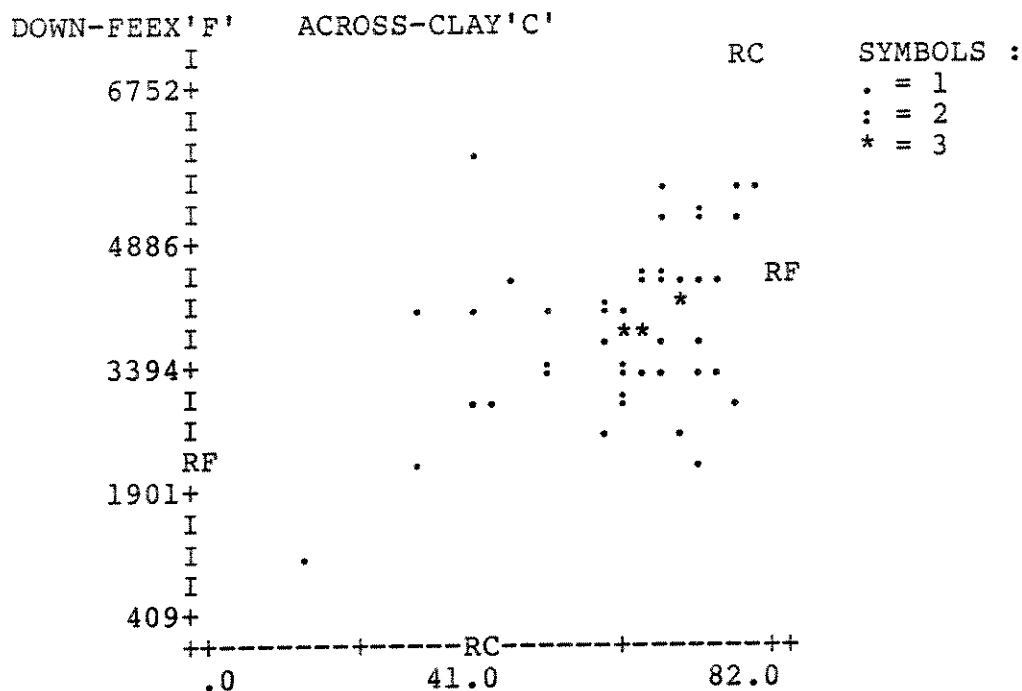
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
FEEX	3.9+03	900.68	-.256	.066	.033	-20.35	4.7+03	879.29	52
SILT	37.88	11.34				-3.2-03	50.51	11.07	52

## IRON VS. SILT REDUCED



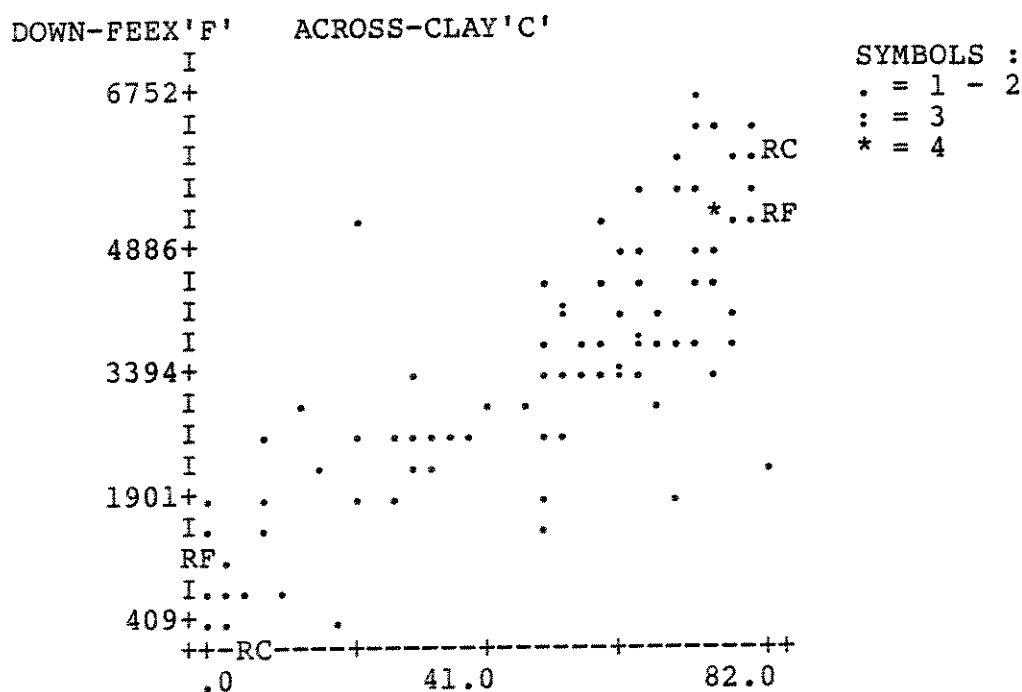
## IRON VS. CLAY OXIDIZED

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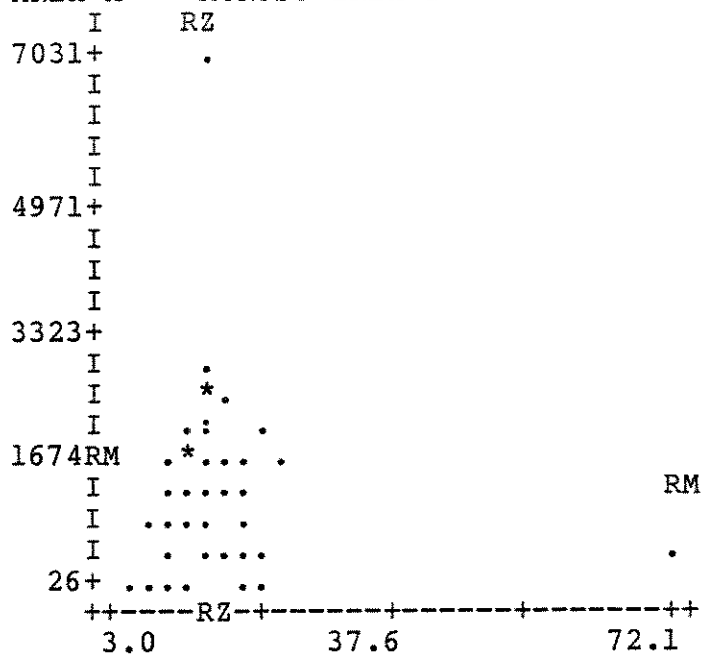
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
FEEX	3.9+03	900.68	.407	.166	.001	27.81	2.3+03	830.74	52
CLAY	59.84	13.19				6.0-03	36.47	12.17	52

## IRON VS. CLAY REDUCED



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
FEEX	3.5+03	1.5+03	.807	.651	.000	49.27	1.1+03	918.69	101
CLAY	47.86	25.31				1.3-02	1.88	15.04	101

DOWN-MNEX'M' ACROSS-ZNEX'Z'



SYMBOLS :

. = 1 - 3

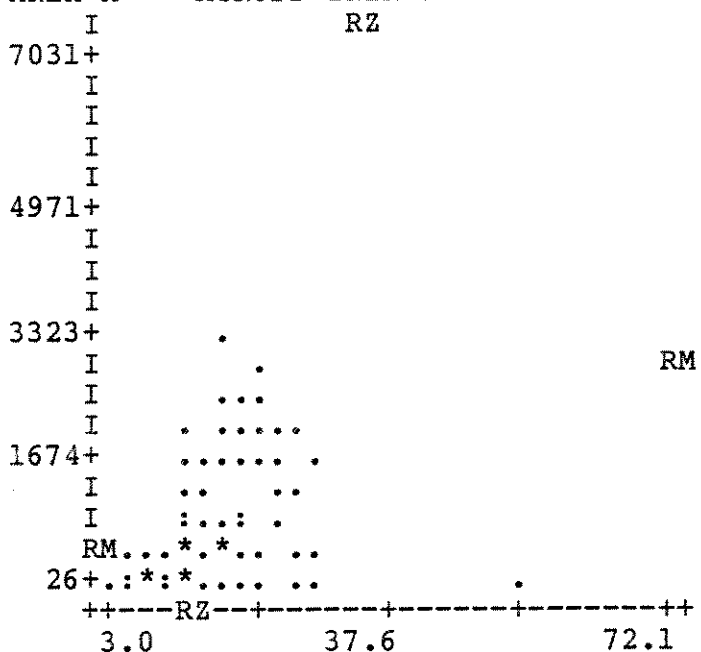
: = 4 - 6

\* = 7 - 9

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
MNEX	1.6+03	996.86	-.051	.003	.338	-6.55	1.7+03	1.0+03	70
ZNEX	15.10	7.74				-3.9-04	15.73	7.78	70

MANGANESE VS. ZINC REDUCED

DOWN-MNEX'M' ACROSS-ZNEX'Z'



SYMBOLS :

. = 1 - 3

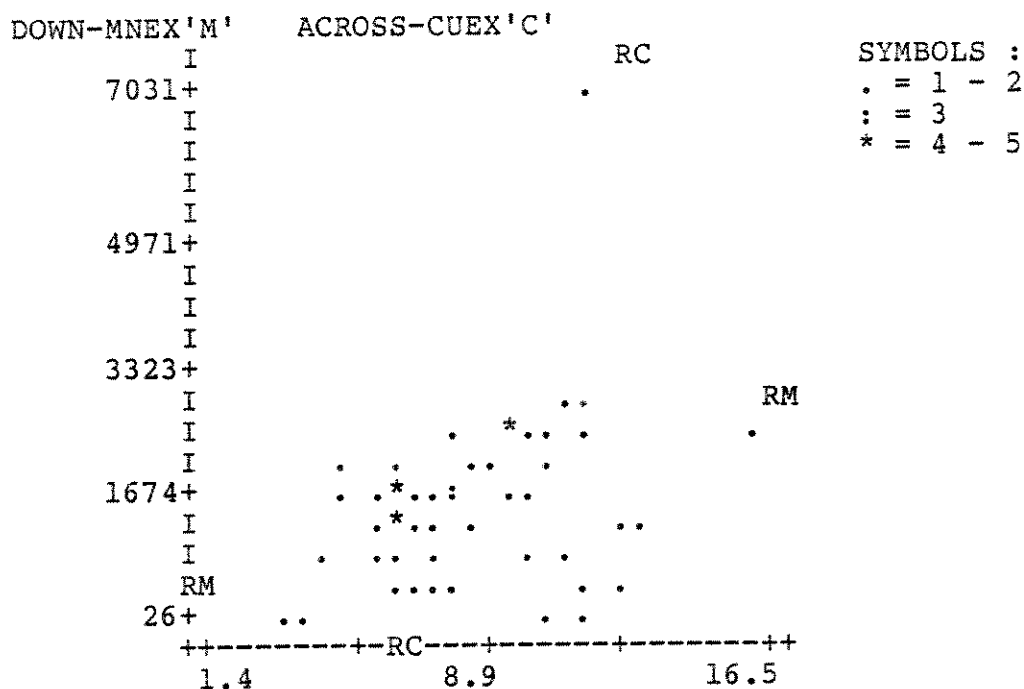
: = 4 - 5

\* = 6 - 8

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
MNEX	808.72	781.83	.327	.107	.000	36.95	221.19	742.18	110
ZNEX	15.90	6.92				2.9-03	13.55	6.57	110

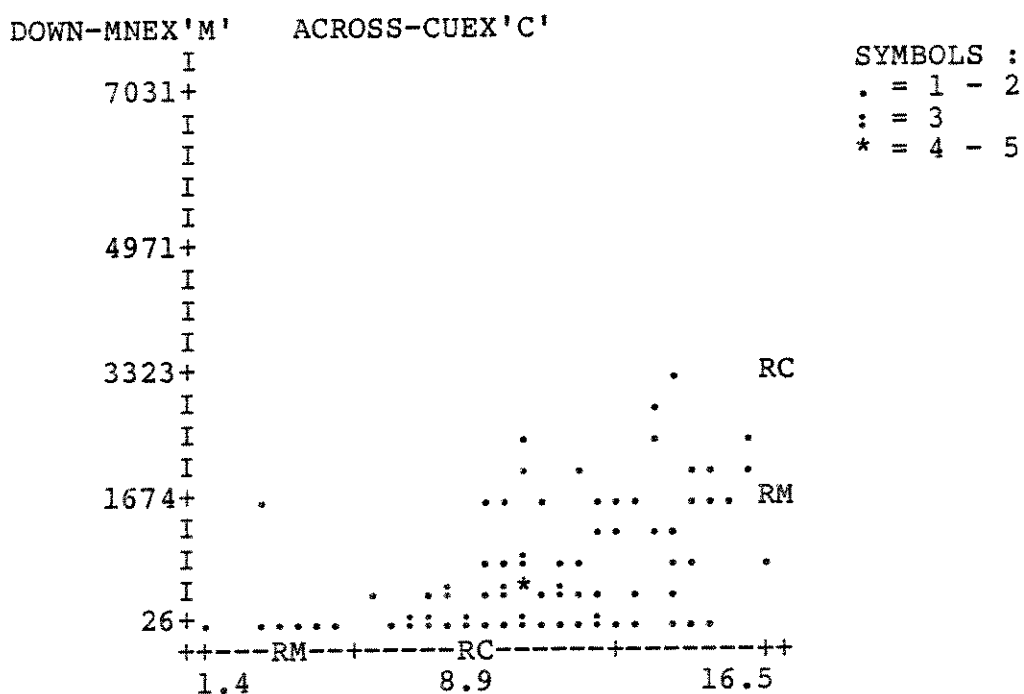
## MANGANESE VS. COPPER OXIDIZED

184



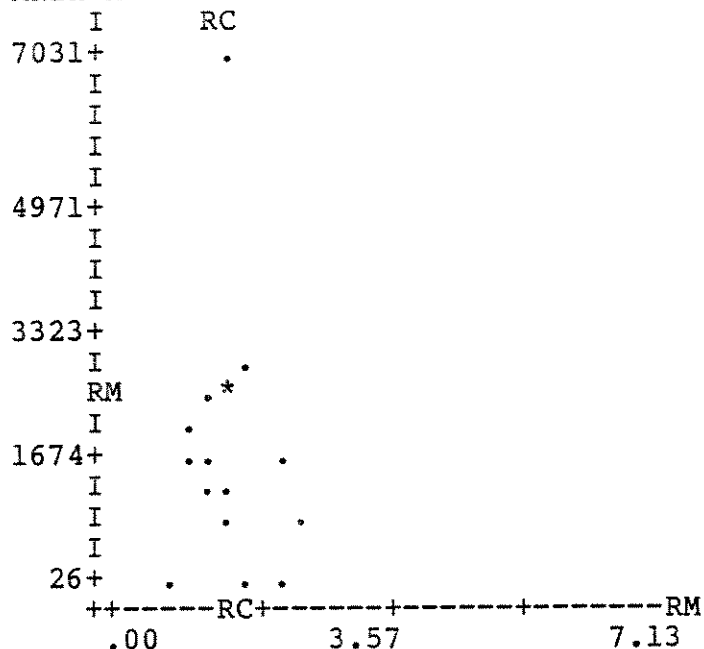
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
MNEX	1.6+03	996.86	.347	.120	.002	140.54	472.48	941.88	70
CUEX	7.97	2.46				8.6-04	6.61	2.32	70

## MANGANESE VS. COPPER REDUCED



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
MNEX	808.72	781.83	.525	.276	.000	119.00	-408.51	668.34	110
CUEX	10.23	3.45				2.3-03	8.35	2.95	110

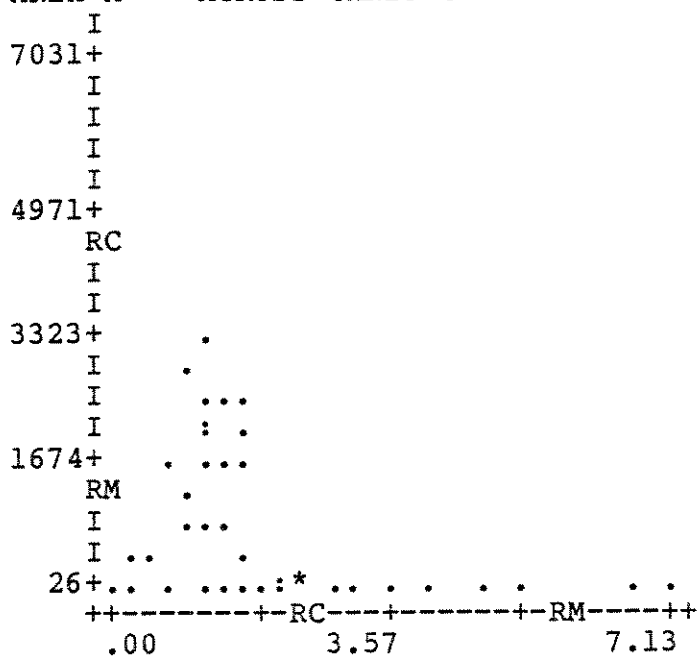
DOWN-MNEX 'M'      ACROSS-CARTO 'C'



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
MNEX	2.0+03	1.4+03	-.107	.011	.323	-355.76	2.5+03	1.5+03	21
CARTO	1.46	.43				-3.2-05	1.52	.44	21

MANGANESE VS. CARBON REDUCED

DOWN-MNEX 'M'      ACROSS-CARTO 'C'

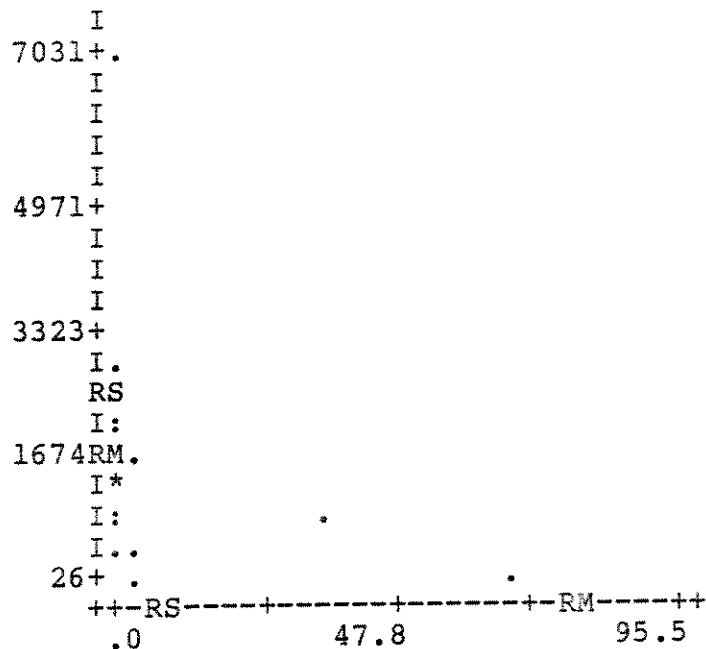


	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
MNEX	863.44	960.03	-.350	.123	.006	-225.10	1.3+03	908.47	50
CARTO	1.94	1.49				-5.5-04	2.41	1.41	50

## MANGANESE VS. SAND OXIDIZED

186

DOWN-MNEX 'M'      ACROSS-SAND 'S'

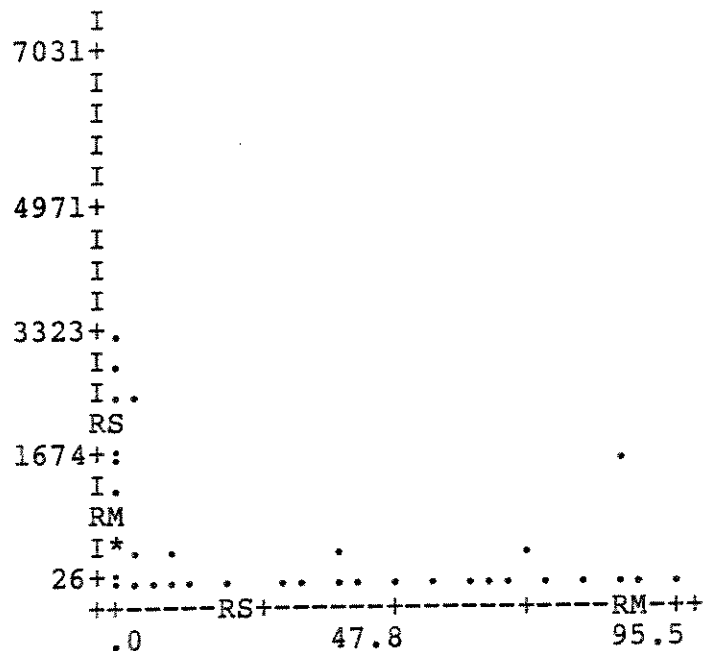


SYMBOLS :  
 . = 1 - 4  
 : = 5 - 7  
 \* = 8 - 11

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
MNEX	1.7+03	1.0+03	-.250	.063	.037	-23.77	1.8+03	978.65	52
SAND	2.28	10.54				-2.6-03	6.87	10.31	52

## MANGANESE VS. SAND REDUCED

DOWN-MNEX 'M'      ACROSS-SAND 'S'

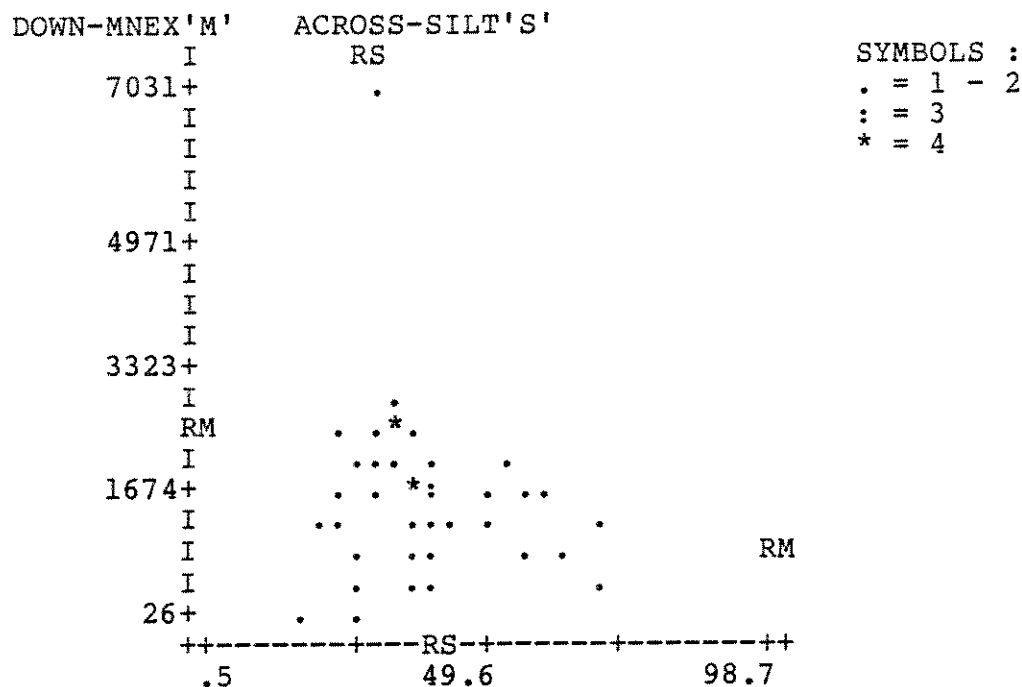


SYMBOLS :  
 . = 1 - 6  
 : = 7 - 12  
 \* = 13 - 18

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
MNEX	851.42	797.15	-.345	.119	.000	-11.26	985.98	751.97	101
SAND	11.95	24.43				-1.1-02	20.96	23.05	101

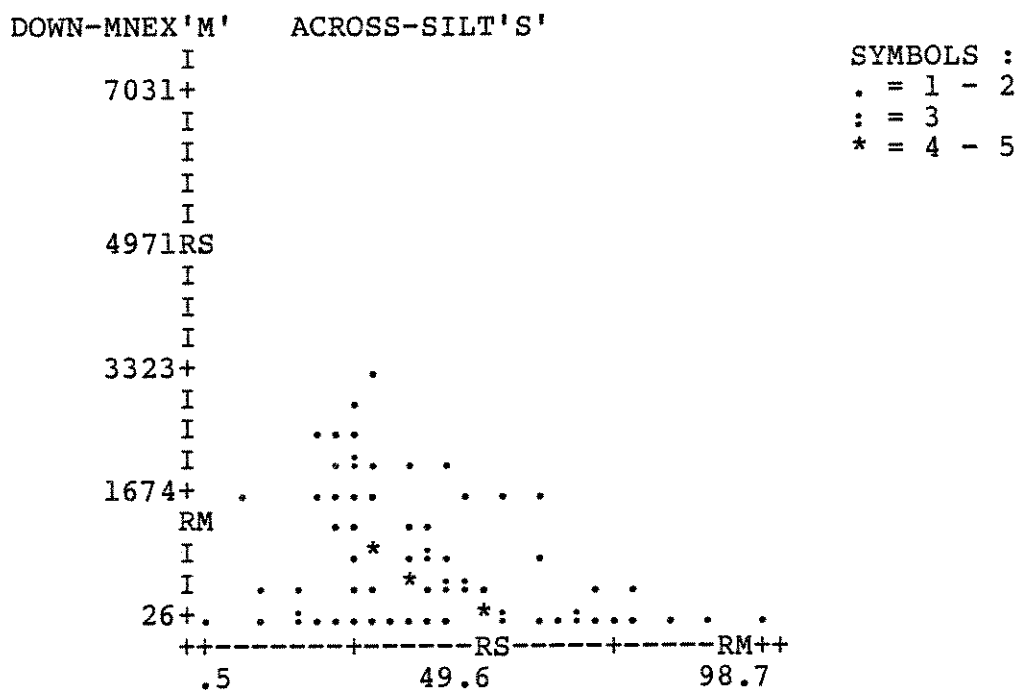
## MANGANESE VS. SILT OXIDIZED

187

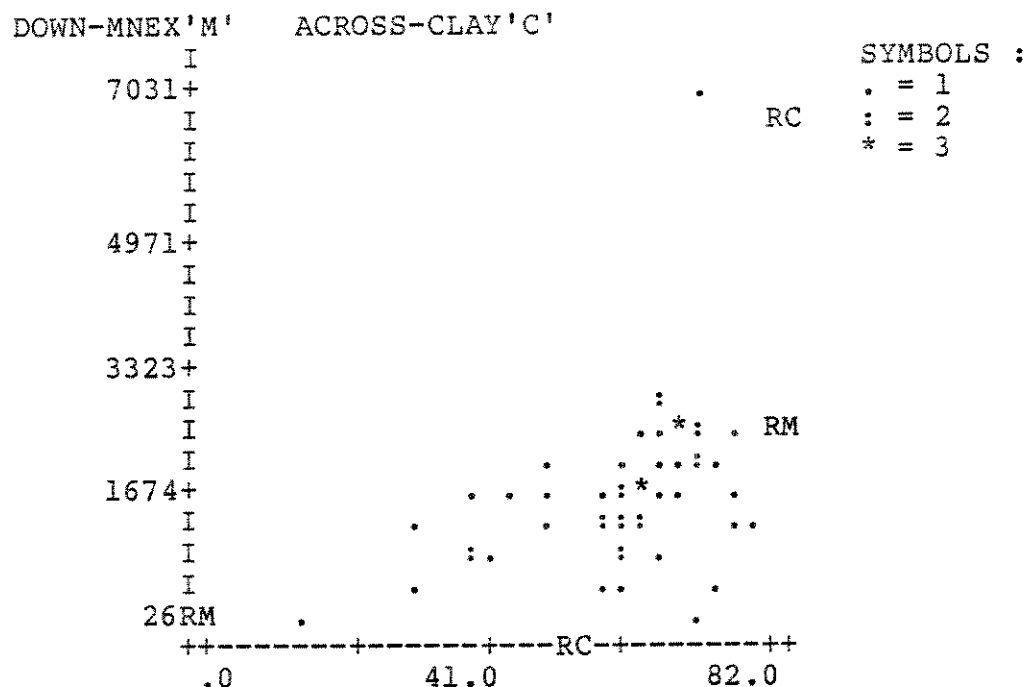


	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
MNEX	1.7+03	1.0+03	-.182	.033	.099	-16.04	2.4+03	994.01	52
SILT	37.88	11.34				-2.1-03	41.47	11.26	52

## MANGANESE VS. SILT REDUCED

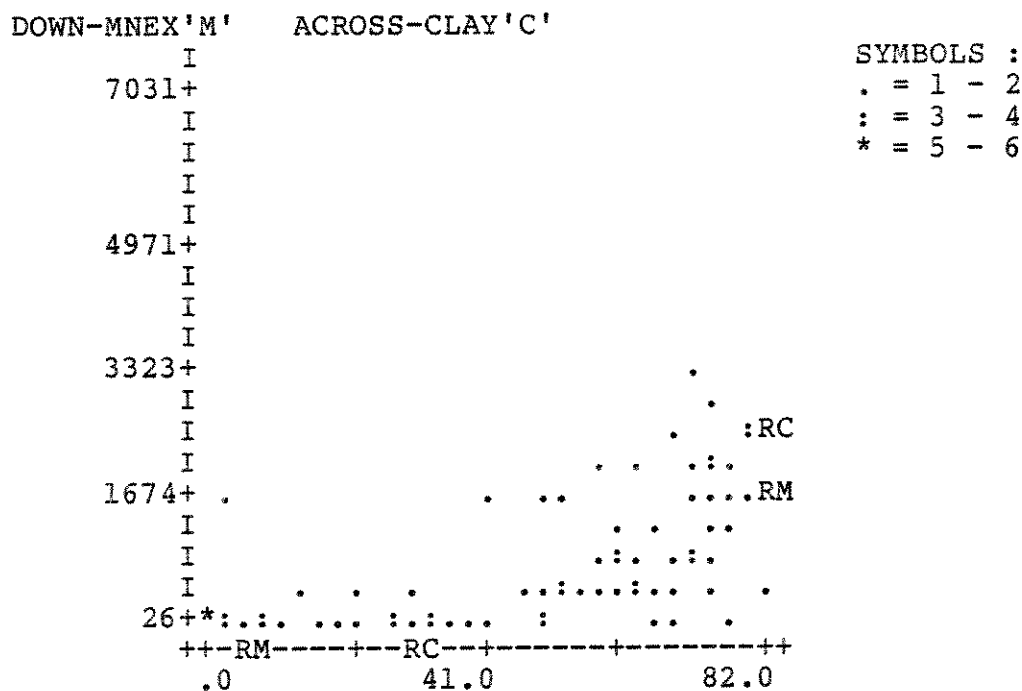


	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
MNEX	851.42	797.15	-.395	.156	.000	-16.25	1.5+03	735.87	101
SILT	40.32	19.40				-9.6-03	48.51	17.91	101



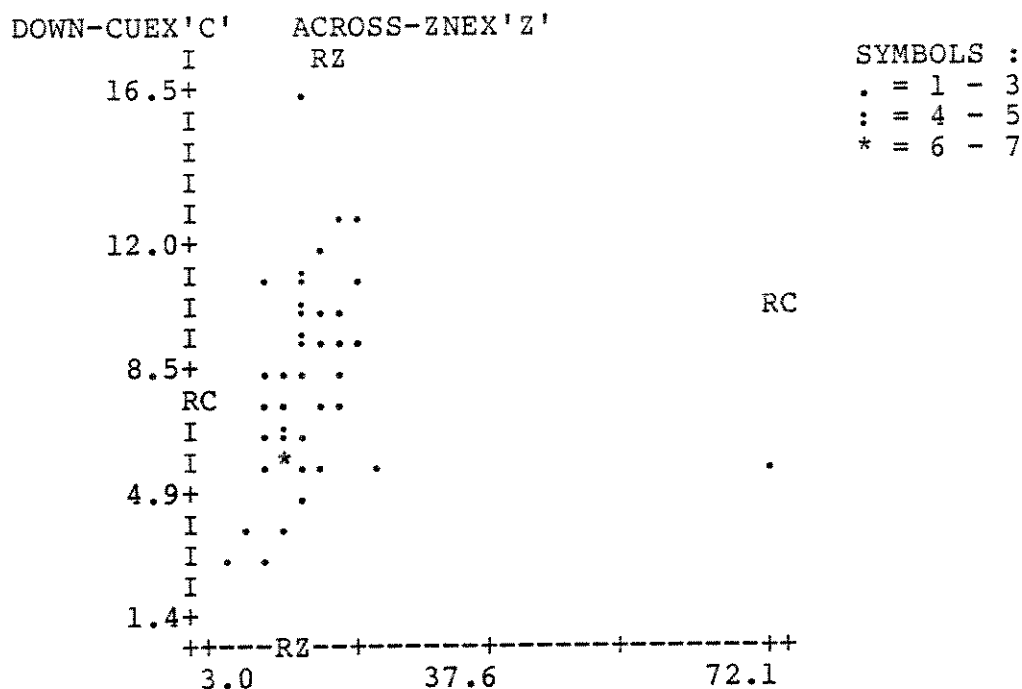
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
MNEX	1.7+03	1.0+03	.356	.127	.005	27.02	126.32	944.56	52
CLAY	59.84	13.19				4.7-03	51.66	12.45	52

## MANGANESE VS. CLAY REDUCED



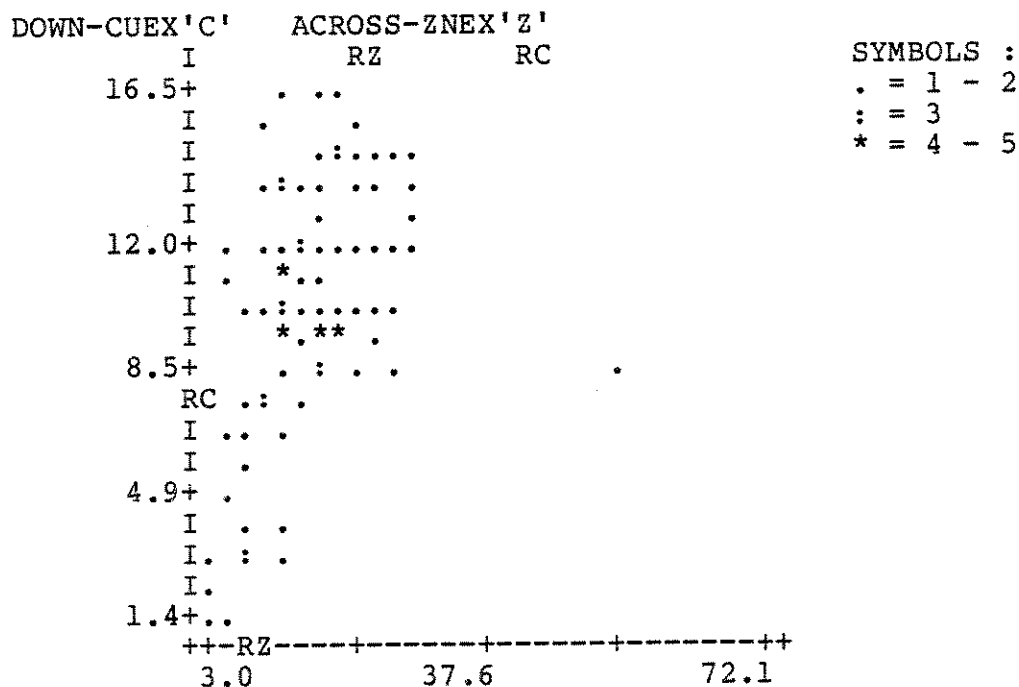
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
MNEX	851.42	797.15	.641	.410	.000	20.17-114.02	615.22		101
CLAY	47.86	25.31				2.0-02	30.54	19.54	101





	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
CUEX	7.97	2.46	.119	.014	.163	3.8-02	7.40	2.46	70
ZNEX	15.10	7.74				.38	12.11	7.74	70

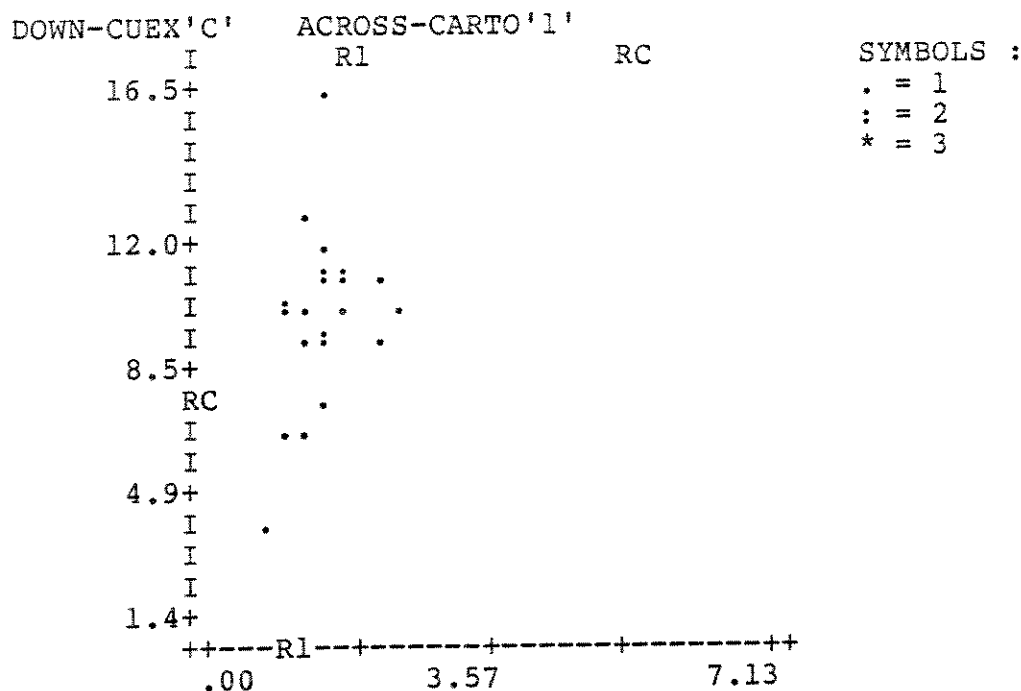
## COPPER VS. ZINC REDUCED



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
CUEX	10.23	3.45	.465	.216	.000	.23	6.55	3.07	110
ZNEX	15.90	6.92				.93	6.36	6.16	110

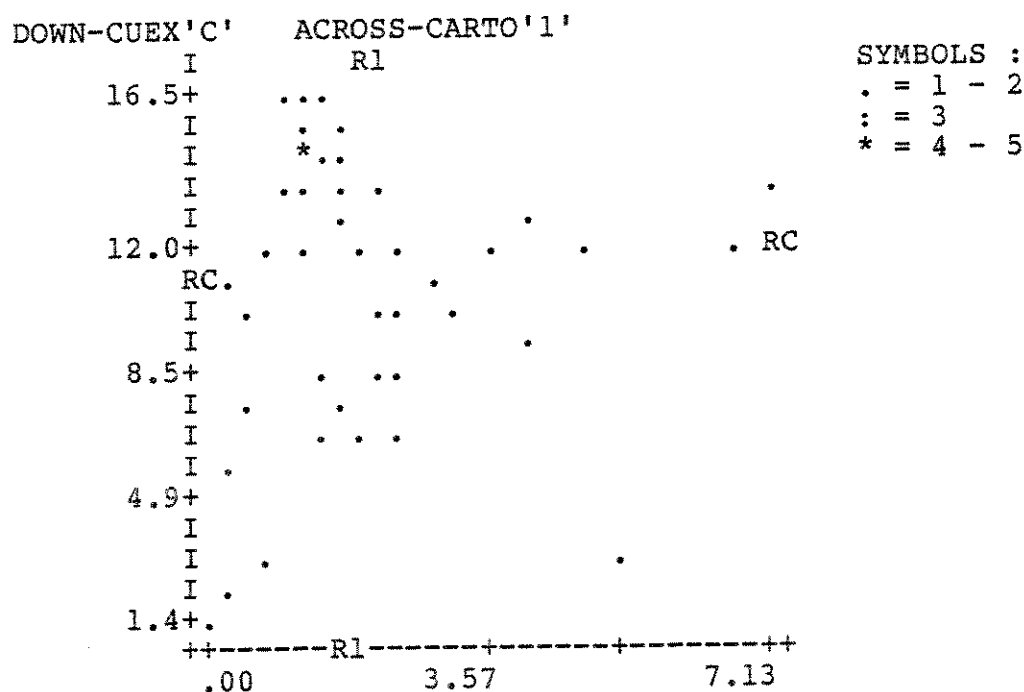
## COPPER VS. CARBON OXIDIZED

190



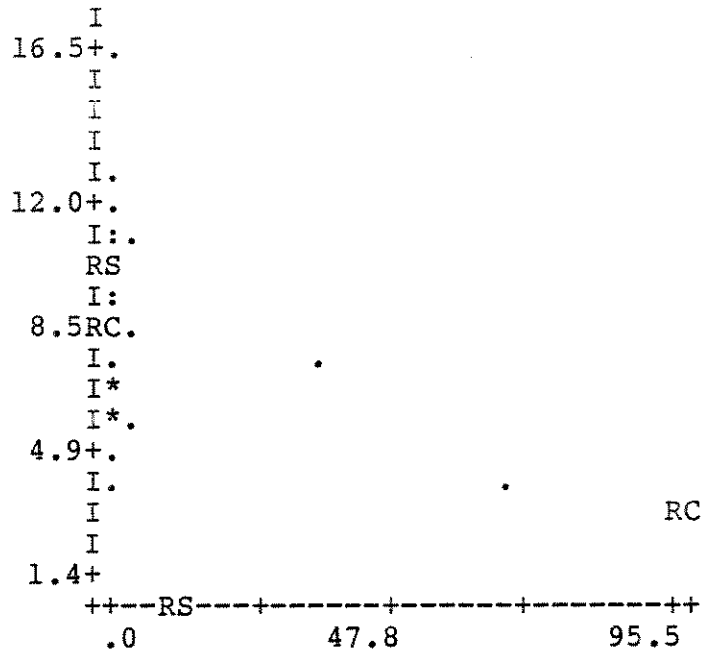
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
CUEX	10.04	2.43	.308	.095	.087	1.75	7.48	2.37	21
CARTO	1.46	.43				5.4-02	.92	.42	21

## COPPER VS. CARBON REDUCED



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
CUEX	11.35	3.72	.038	.001	.396	9.5-02	11.16	3.76	50
CARTO	1.94	1.49				1.5-02	1.77	1.51	50

DOWN-CUEX 'C'      ACROSS-SAND 'S'

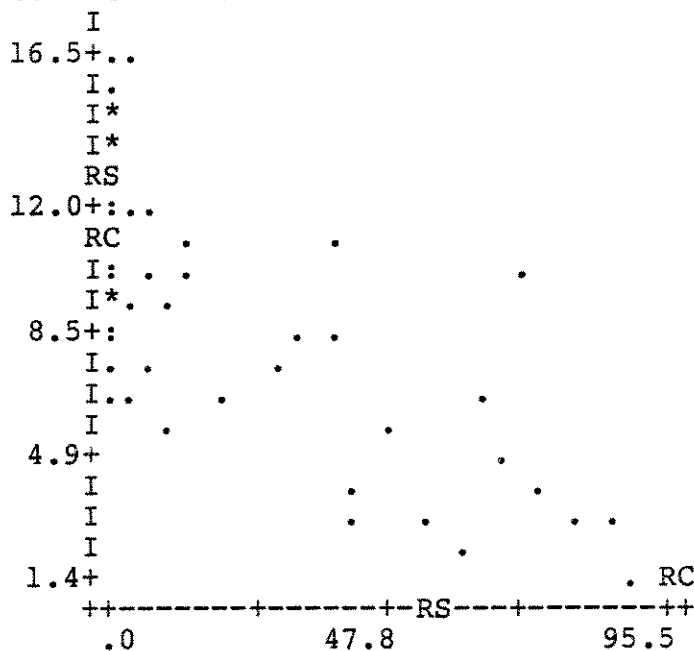


SYMBOLS :  
 . = 1 - 4  
 : = 5 - 7  
 \* = 8 - 10

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
CUEX	8.15	2.45	-.233	.055	.048	-5.4-02	8.27	2.41	52
SAND	2.28	10.54				-1.00	10.46	10.35	52

COPPER VS. SAND REDUCED

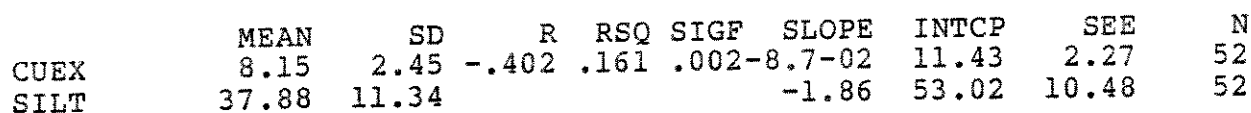
DOWN-CUEX 'C'      ACROSS-SAND 'S'



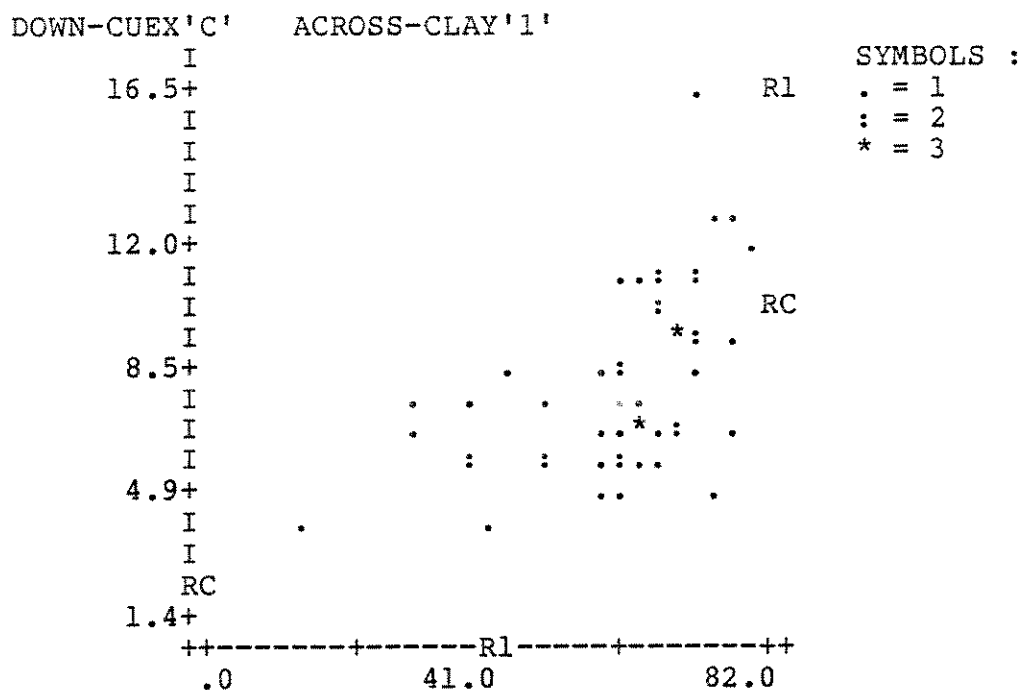
SYMBOLS :  
 . = 1 - 4  
 : = 5 - 8  
 \* = 9 - 12

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
CUEX	10.21	3.53	-.712	.507	.000	-.10	11.44	2.49	101
SAND	11.95	24.43				-4.93	62.29	17.24	101

## 192

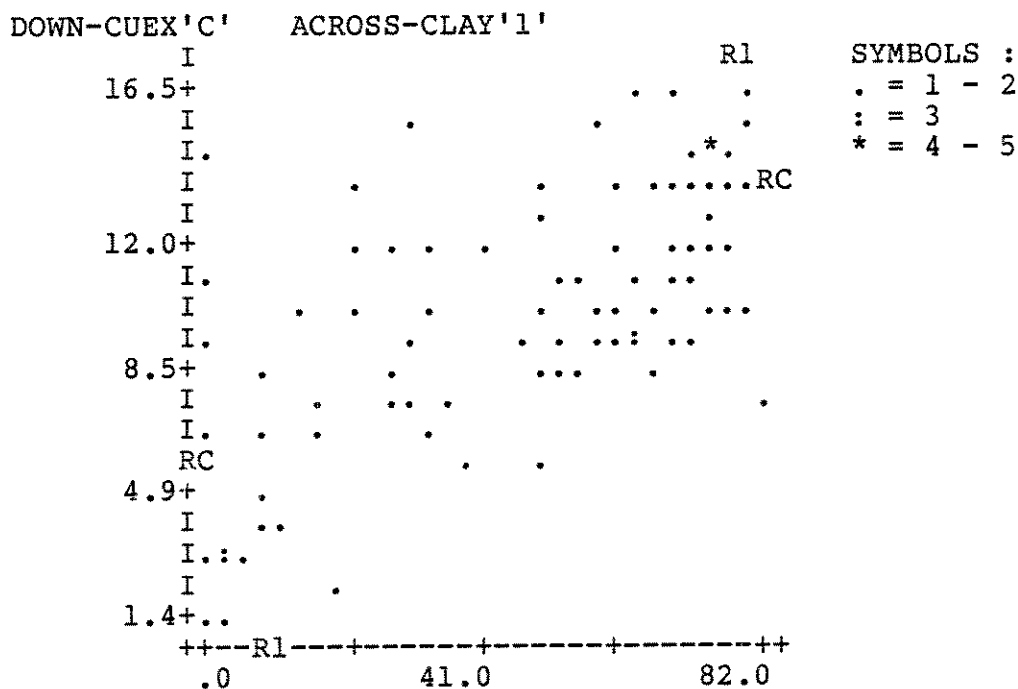


	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
CUEX	10.21	3.53	.089	.008	.187	1.6-02	9.56	3.53	101
SILT	40.32	19.40				.49	35.30	19.42	101



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
CUEX	8.15	2.45	.532	.283	.000	9.9-02	2.24	2.10	52
CLAY	59.84	13.19				2.86	36.52	11.29	52

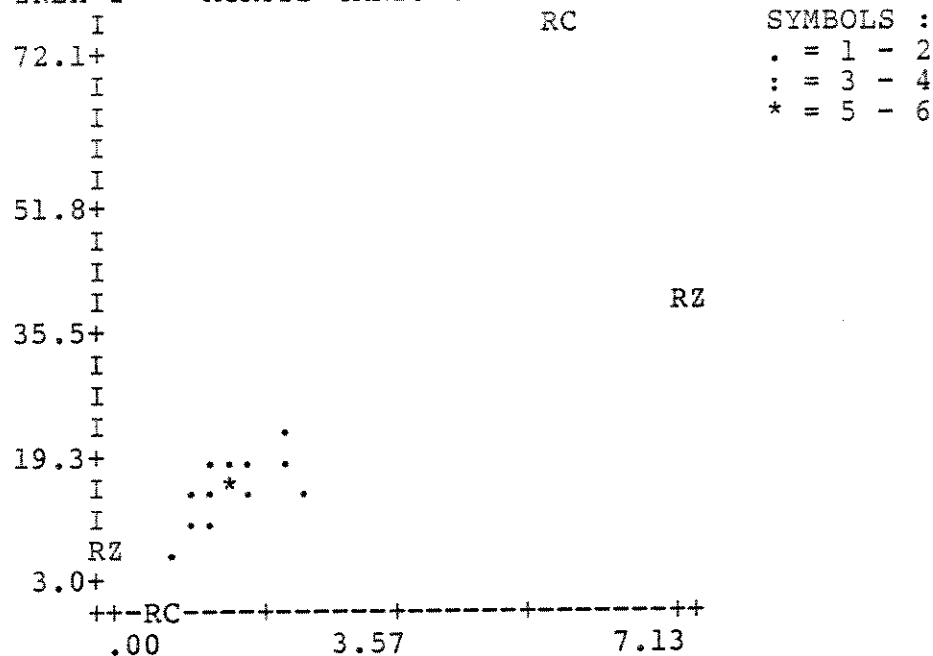
## COPPER VS. CLAY REDUCED



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
CUEX	10.21	3.53	.637	.406	.000	8.9-02	5.96	2.73	101
CLAY	47.86	25.31				4.57	1.19	19.61	101

## ZINC VS. CARBON OXIDIZED

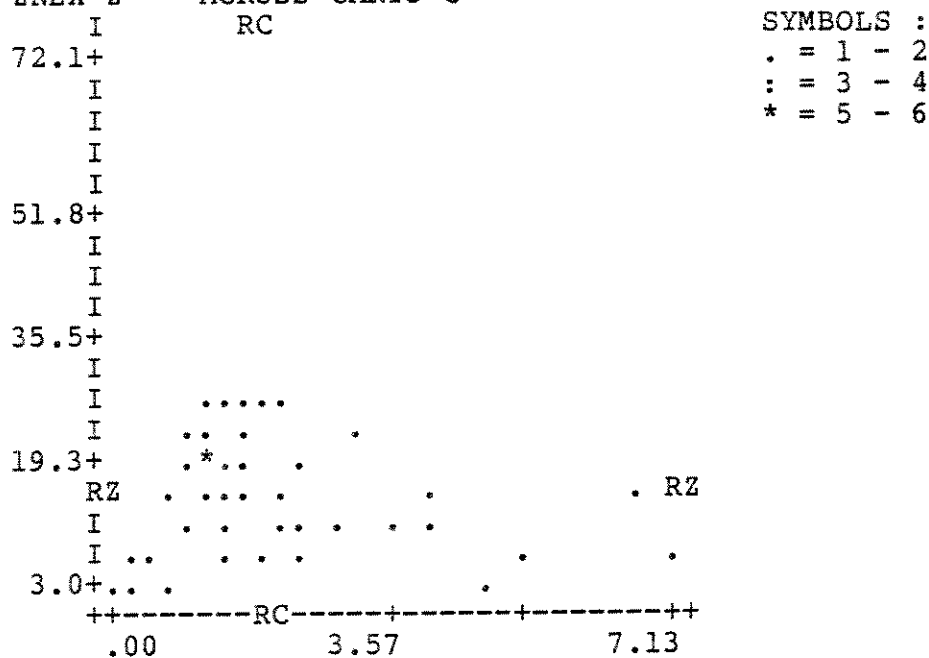
DOWN-ZNEX'Z' ACROSS-CARTO'C'



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ZNEX	15.75	3.25	.546	.299	.005	4.16	9.67	2.79	21
CARTO	1.46	.43				7.2-02	.33	.37	21

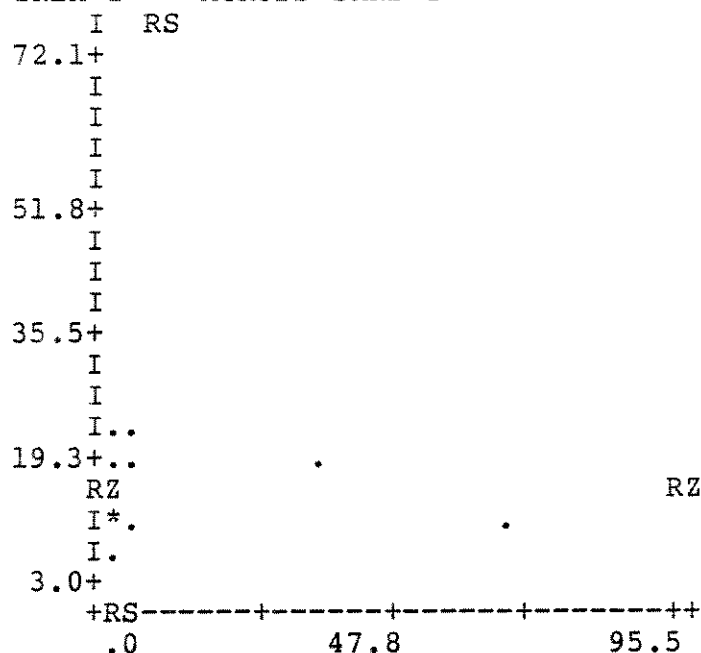
## ZINC VS. CARBON REDUCED

DOWN-ZNEX'Z' ACROSS-CARTO'C'



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ZNEX	15.80	6.89	-.029	.001	.422	-.13	16.05	6.96	50
CARTO	1.94	1.49				-6.2-03	2.04	1.51	50

DOWN-ZNEX 'Z'      ACROSS-SAND 'S'



SYMBOLS :

. = 1 - 7

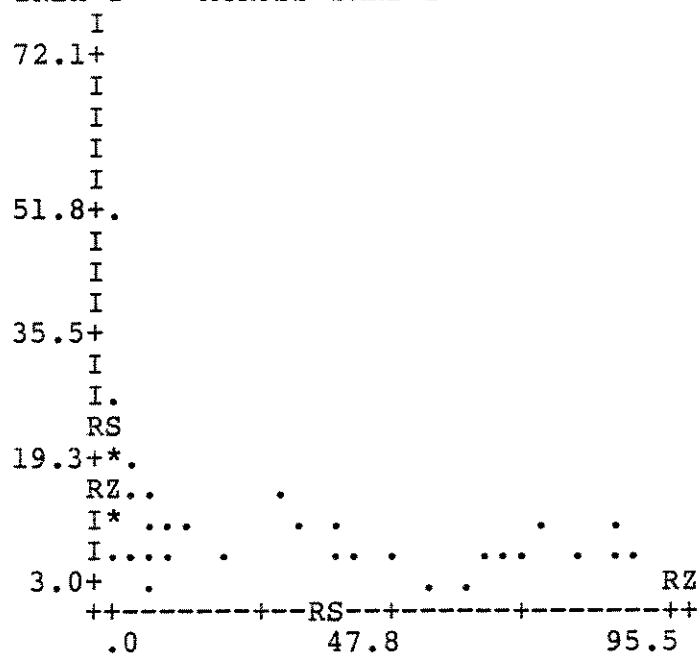
: = 8 - 14

\* = 15 - 21

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ZNEX	14.47	3.36	.018	.000	.449	5.8-03	14.46	3.39	52
SAND	2.28	10.54				5.7-02	1.45	10.64	52

ZINC VS. SAND REDUCED

DOWN-ZNEX 'Z'      ACROSS-SAND 'S'



SYMBOLS :

. = 1 - 6

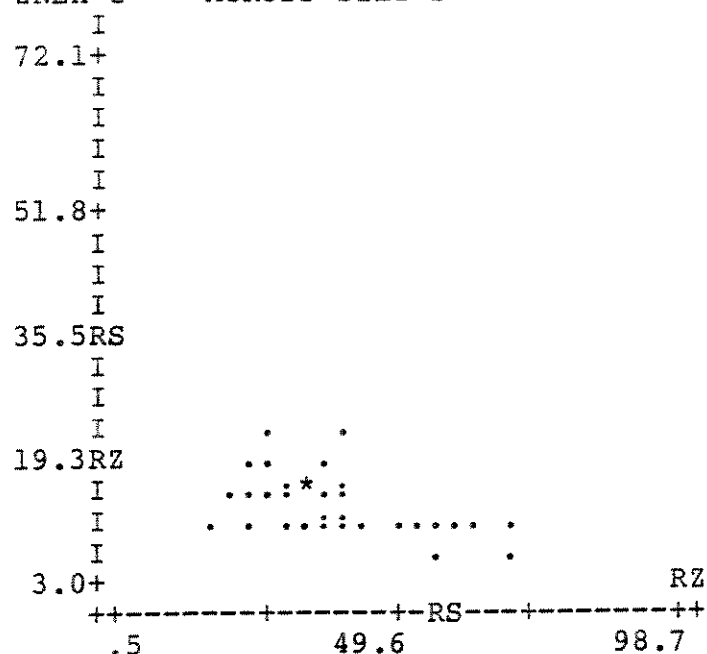
: = 7 - 12

\* = 13 - 18

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ZNEX	15.81	6.99	-.526	.277	.000	-.15	17.61	5.97	101
SAND	11.95	24.43				-1.84	41.04	20.88	101

## ZINC VS. SILT OXIDIZED

DOWN-ZNEX'Z' ACROSS-SILT'S'

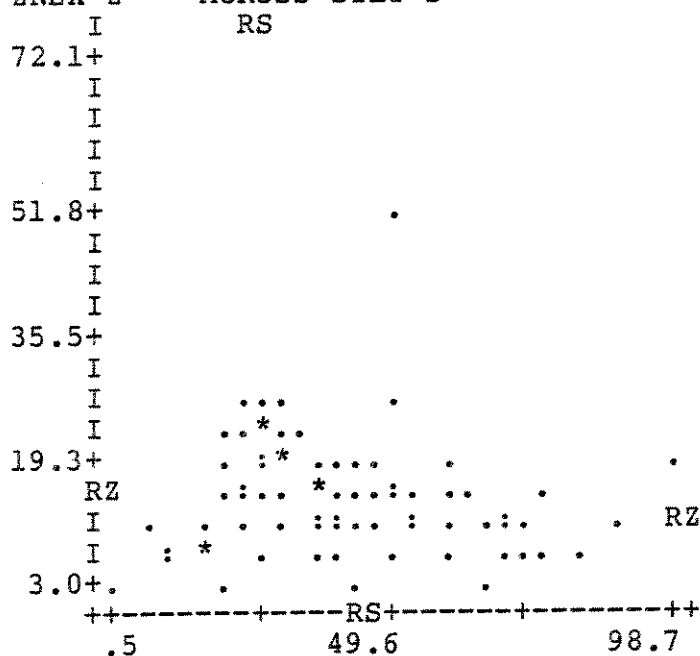


SYMBOLS :  
 . = 1 - 3  
 : = 4 - 5  
 \* = 6 - 7

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ZNEX	14.47	3.36	-.499	.249	.000	-.15	20.08	2.94	52
SILT	37.88	11.34				-1.68	62.24	9.92	52

## ZINC VS. SILT REDUCED

DOWN-ZNEX'Z' ACROSS-SILT'S'

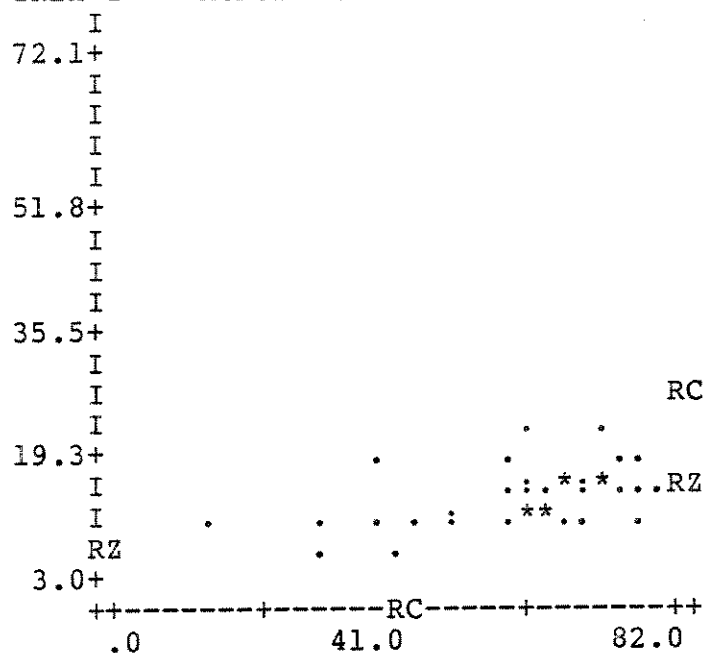


SYMBOLS :  
 . = 1 - 2  
 : = 3  
 \* = 4 - 5

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ZNEX	15.81	6.99	-.098	.010	.166	-3.5-02	17.23	6.99	101
SILT	40.32	19.40				-.27	44.60	19.41	101



DOWN-ZNEX 'Z'      ACROSS-CLAY 'C'

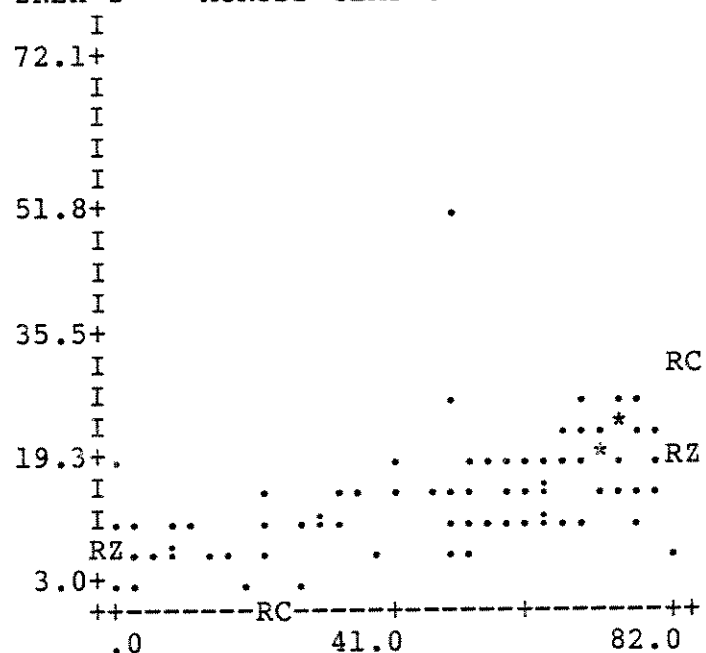


SYMBOLS :  
 . = 1 - 2  
 : = 3  
 \* = 4 - 5

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ZNEX	14.47	3.36	.414	.172	.001	.11	8.15	3.09	52
CLAY	59.84	13.19				1.63	36.32	12.13	52

ZINC VS. CLAY REDUCED

DOWN-ZNEX 'Z'      ACROSS-CLAY 'C'



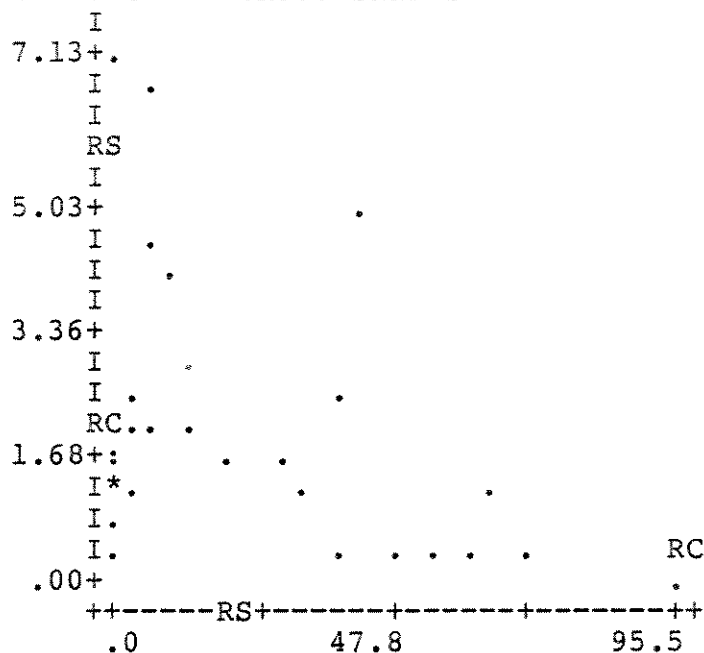
SYMBOLS :  
 . = 1 - 2  
 : = 3  
 \* = 4

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ZNEX	15.81	6.99	.580	.337	.000	.16	8.15	5.72	101
CLAY	47.86	25.31				2.10	14.63	20.72	101

## CARBON VS. SAND OXIDIZED

198

DOWN-CARTO 'C' ACROSS-SAND 'S'

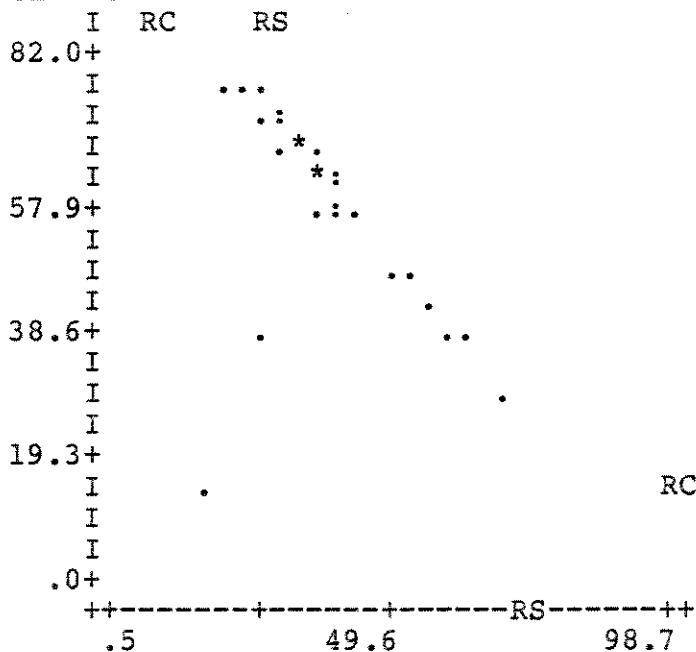


SYMBOLS :  
 . = 1 - 4  
 : = 5 - 7  
 \* = 8 - 11

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
CARTO	1.84	1.48	-.218	.048	.070	-1.4-02	2.03	1.46	47
SAND	13.96	23.22				-3.42	20.25	22.91	47
SAND	11.95	24.43							101

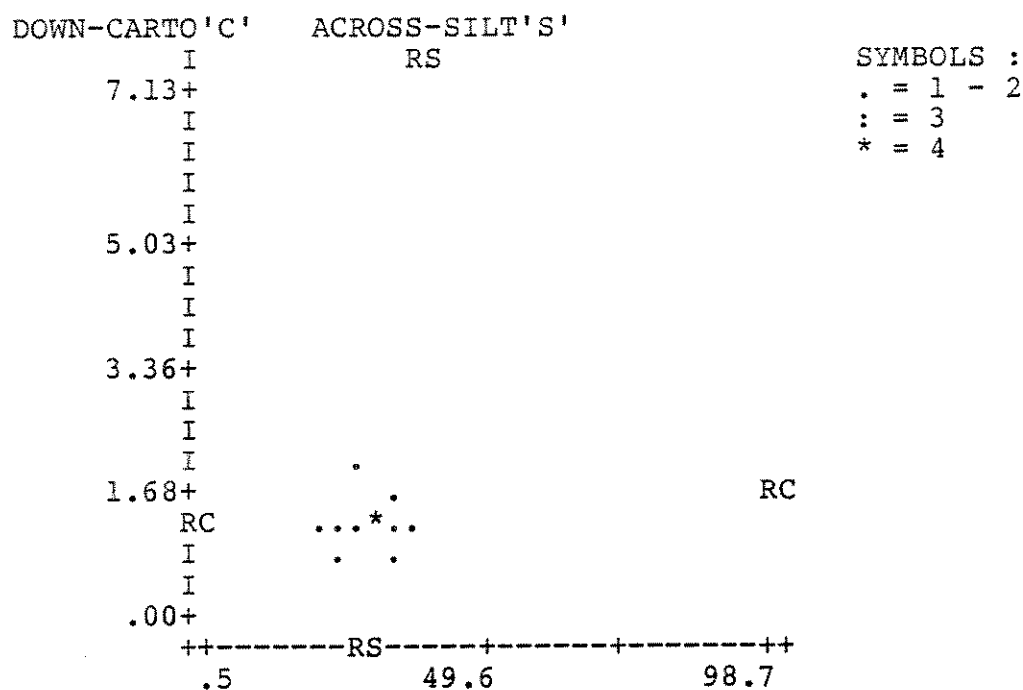
## CARBON VS. SAND REDUCED

DOWN-CLAY 'C' ACROSS-SILT 'S'



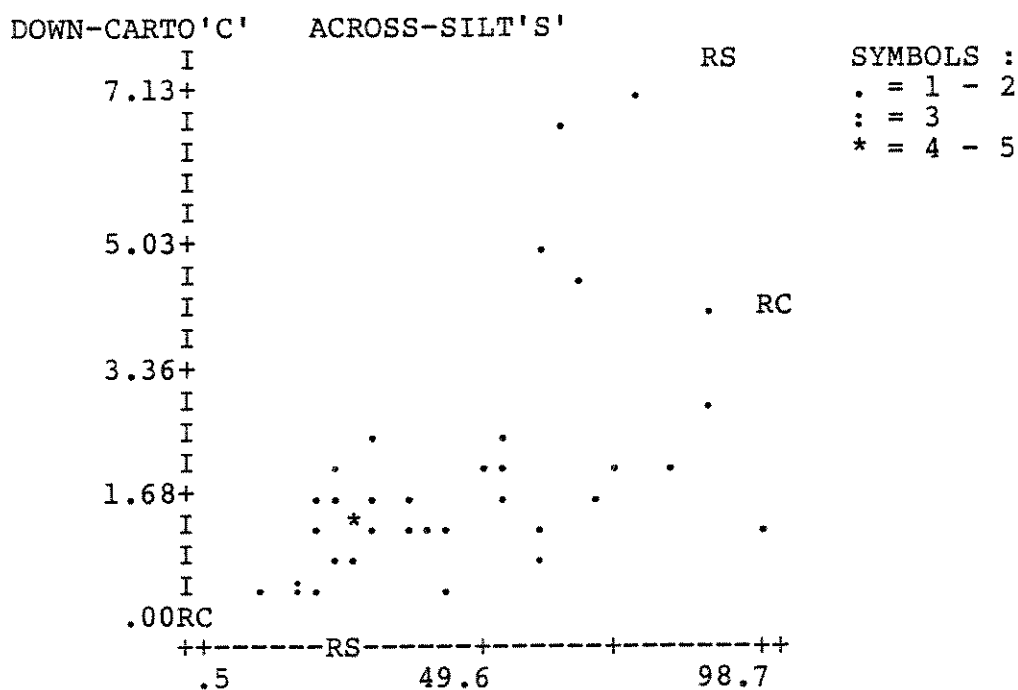
SYMBOLS :  
 . = 1 - 3  
 : = 4 - 5  
 \* = 6 - 8

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
CLAY	59.84	13.19	-.640	.410	.000	-.74	88.06	10.24	52
SILT	37.88	11.34				-.55	70.79	8.80	52

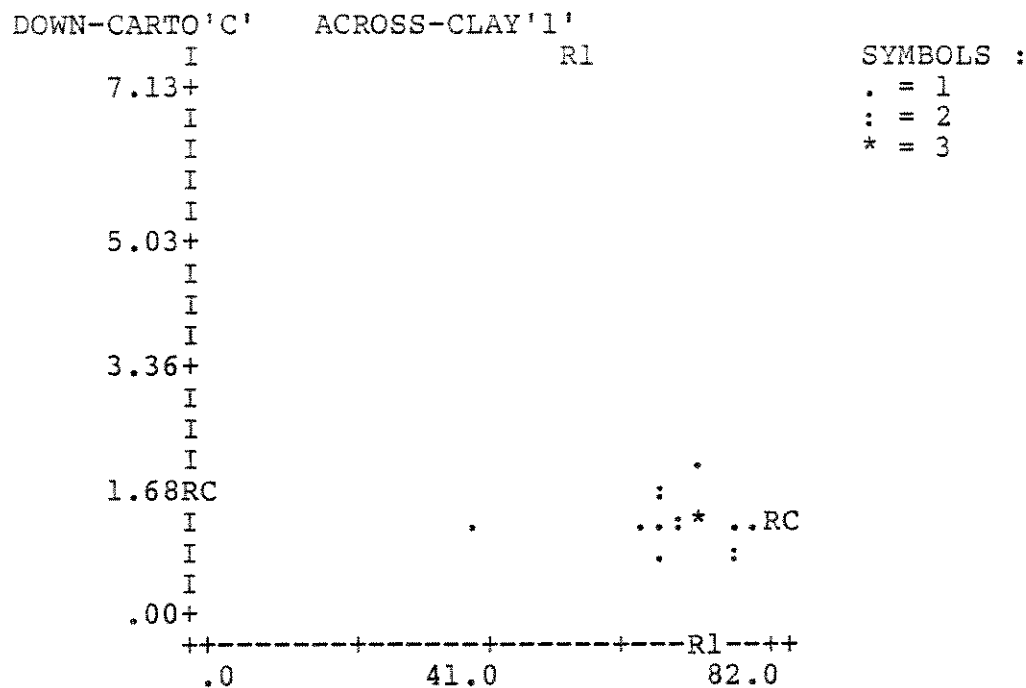


	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
CARTO	1.40	.31	.094	.009	.365	6.6-03	1.20	.32	16
SILT	29.67	4.38				1.33	27.81	4.51	16
SILT	37.88	11.34							52

## CARBON VS. SILT REDUCED

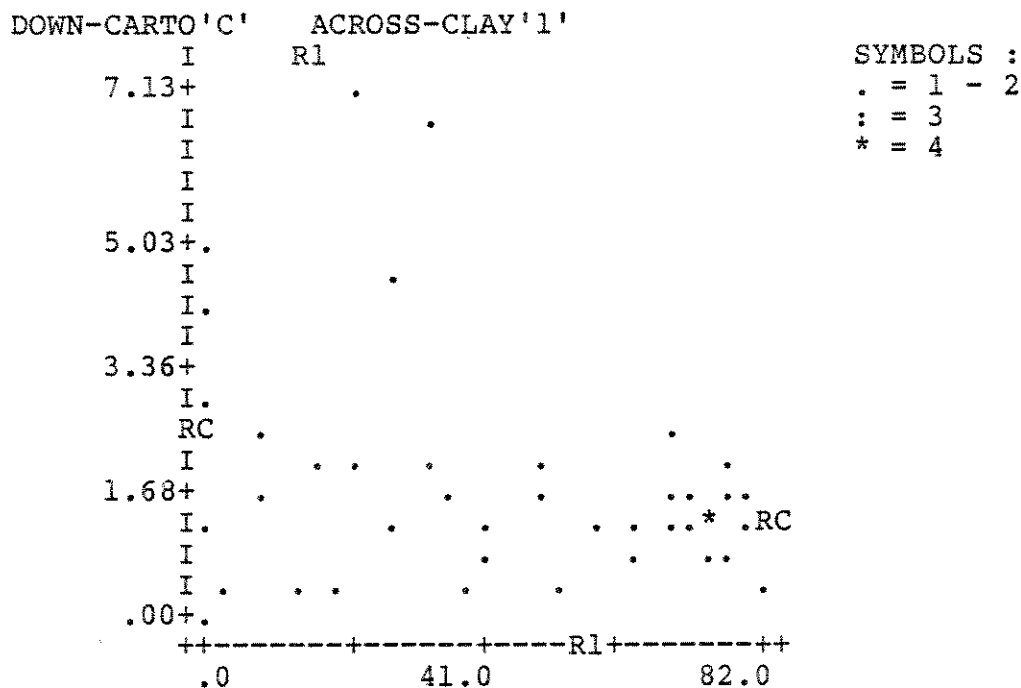


	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
CARTO	1.84	1.48	.581	.337	.000	3.8-02	.26	1.22	47
SILT	41.75	22.79				8.93	25.32	18.76	47
SILT	40.32	19.40							101



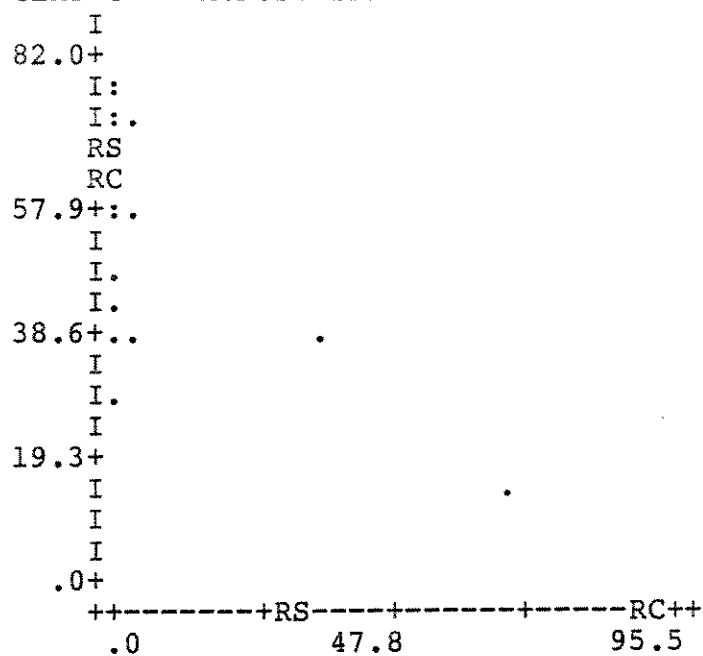
	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
CARTO	1.40	.31	-.094	.009	.364	-3.2-03	1.61	.32	16
CLAY	67.91	9.15				-2.79	71.81	9.42	16
CLAY	59.84	13.19							52

CARBON VS. CLAY REDUCED



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
CARTO	1.84	1.48	-.293	.086	.023	-1.5-02	2.53	1.43	47
CLAY	44.64	28.32				-5.60	54.94	27.38	47
CLAY	47.86	25.31							101

DOWN-CLAY'C' ACROSS-SAND'S'

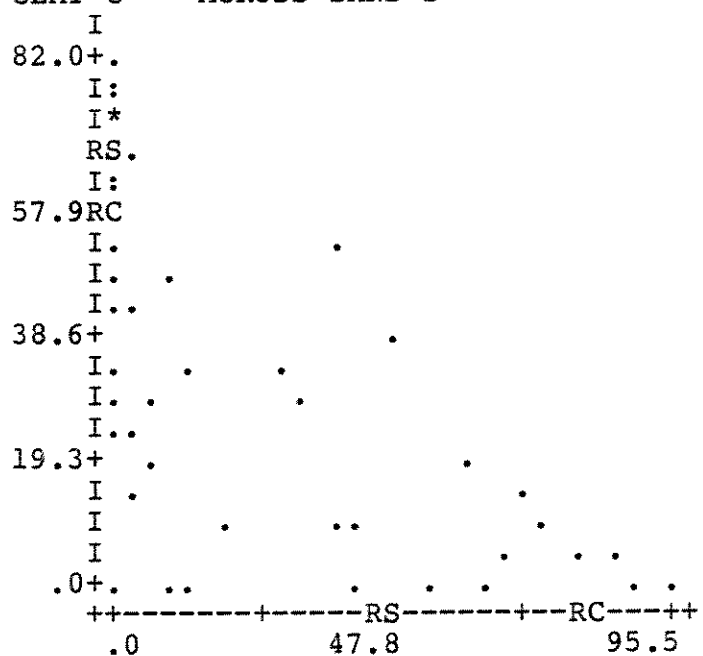


SYMBOLS :  
 . = 1 - 4  
 : = 5 - 8  
 \* = 9 - 12

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
CLAY	59.84	13.19	-.563	.317	.000	-.70	61.45	11.01	52
SAND	2.28	10.54				-.45	29.20	8.80	52

CLAY VS. SAND REDUCED

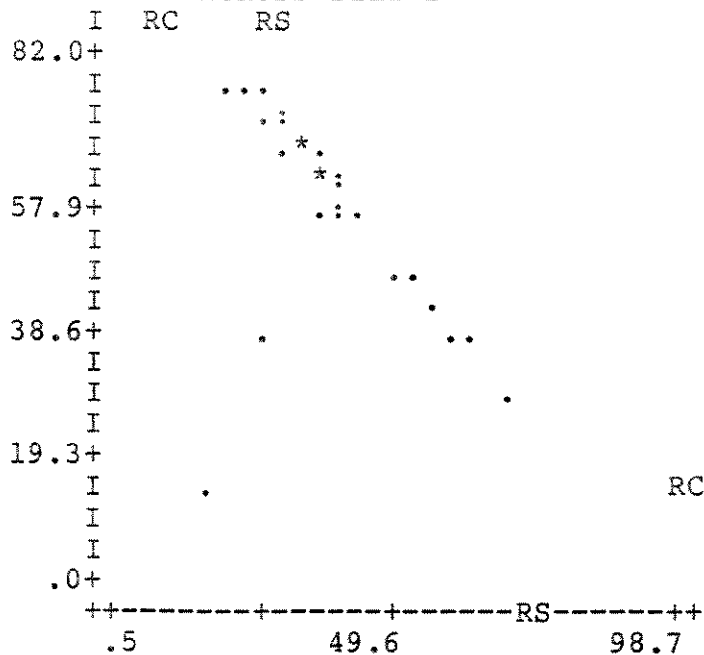
DOWN-CLAY'C' ACROSS-SAND'S'



SYMBOLS :  
 . = 1 - 5  
 : = 6 - 10  
 \* = 11 - 15

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
CLAY	47.86	25.31	-.702	.492	.000	-.73	56.55	18.13	101
SAND	11.95	24.43				-.68	44.36	17.50	101

DOWN-CLAY 'C' ACROSS-SILT 'S'



SYMBOLS :

. = 1 - 3

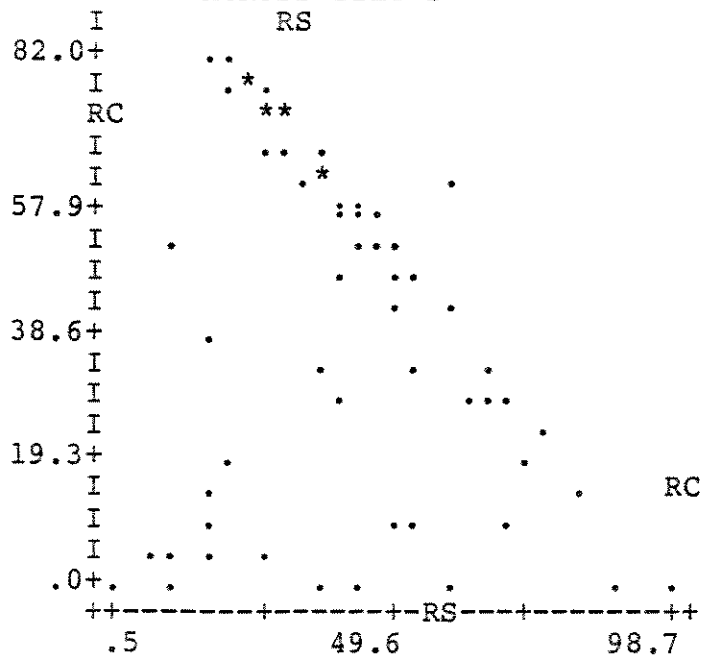
: = 4 - 5

\* = 6 - 8

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
CLAY	59.84	13.19	-.640	.410	.000	-.74	88.06	10.24	52
SILT	37.88	11.34				-.55	70.79	8.80	52

CLAY VS. SILT REDUCED

DOWN-CLAY 'C' ACROSS-SILT 'S'



SYMBOLS :

. = 1 - 3

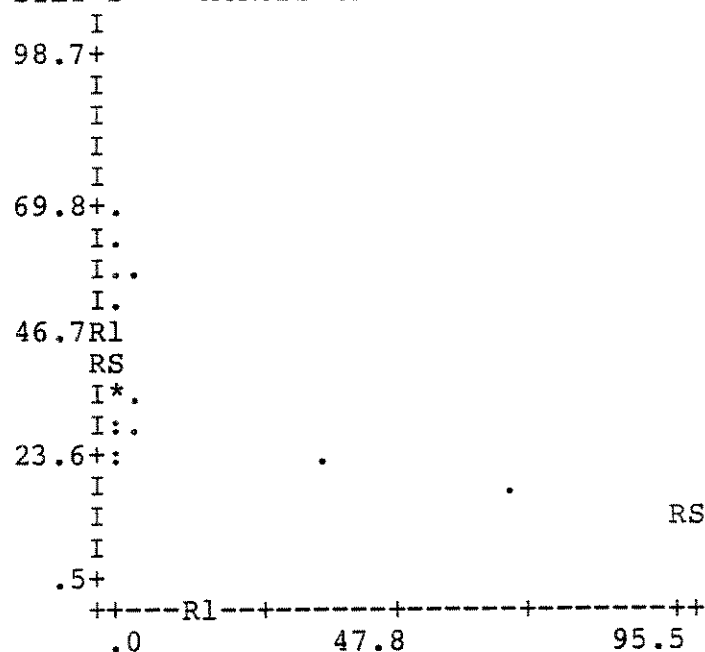
: = 4 - 5

\* = 6 - 8

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
CLAY	47.86	25.31	-.413	.170	.000	-.54	69.56	23.18	101
SILT	40.32	19.40				-.32	55.45	17.76	101

## SILT VS. SAND OXIDIZED

DOWN-SILT'S'      ACROSS-SAND'1'

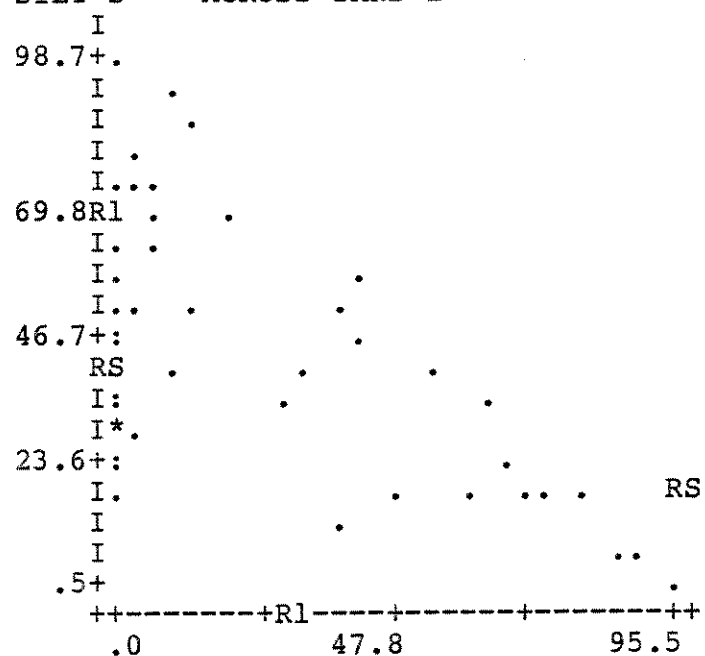


SYMBOLS :  
 . = 1 - 5  
 : = 6 - 9  
 \* = 10 - 13

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
SILT	37.88	11.34	-.274	.075	.025	-.30	38.55	11.01	52
SAND	2.28	10.54				-.26	11.94	10.24	52

## SILT VS. SAND REDUCED

DOWN-SILT'S'      ACROSS-SAND'1'

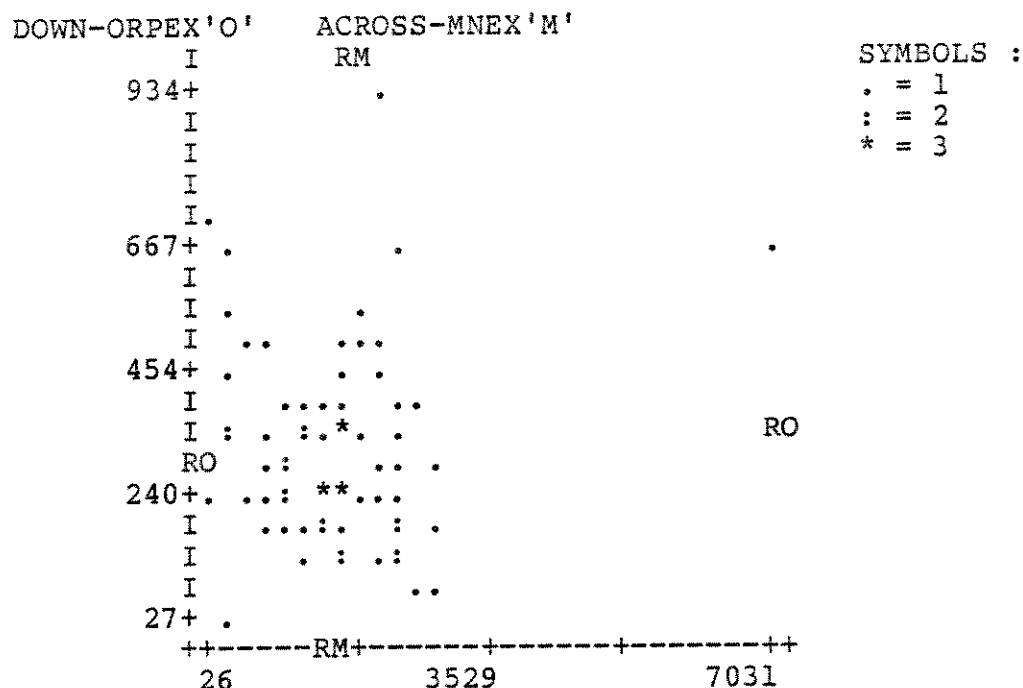


SYMBOLS :  
 . = 1 - 6  
 : = 7 - 11  
 \* = 12 - 16

	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
SILT	40.32	19.40	-.355	.126	.000	-.28	43.69	18.23	101
SAND	11.95	24.43				-.45	29.99	22.95	101

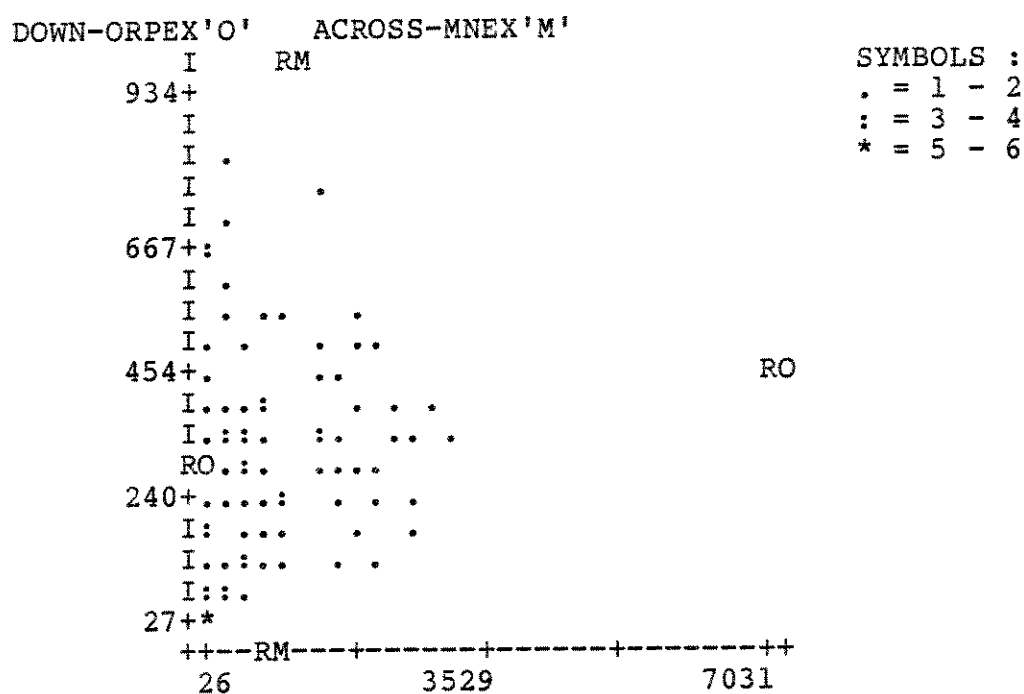
## ORGANIC PHOSPHORUS VS. MANGANESE OXIDIZED

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	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ORPEX	327.61	162.83	.044	.002	.358	7.2-03	316.08	163.86	70
MNEX	1.6+03	996.86				.27	1.5+03	1.0+03	70

## ORGANIC PHOSPHORUS VS. MANGANESE REDUCED



	MEAN	SD	R	RSQ	SIGF	SLOPE	INTCP	SEE	N
ORPEX	315.29	171.10	.101	.010	.147	2.2-02	297.44	171.02	110
MNEX	808.72	781.83				.46	663.39	781.43	110