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V. Subramanian

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V. SUBRAMANIAN
Marine Sciences Centre, McGill University, Montreal, P.Q.

With a mean discharge of 14000 m^2/sec, the St. Lawrence River ranks eleventh among world rivers (Inman and Nordstrom, 1971). Much of the precipitation in the drainage basin occurs in the form of snow; and lakes covering glacial topography make up to 29% of the total drainage area of $50000 m^2$ (d'Anglejan and Smith, 1973; Loring and Nota, 1973). Since the river is flowing out of the Great Lakes, the geology of the water shed is complicated. All the three major rock types are represented in the water shed as well as in the drainage basin. The Canadian Shield and the Appalachian Mountains contribute to the hard-rock part of the basin while the glacial sediments from the Wisconsin age and the Paleozoic Strata constitute the soft-rock part.

In addition to the Great Lakes, the major source of water is the tributaries such as the Ottawa, Richelieu and Saguenay Rivers. As shown by Gibbs (1967) for the Amazon river, the geological complexity of the drainage basin is likely to be reflected in the water chemistry of the St. Lawrence River. Except for the water analyses compiled by Livingstone (1960), no systematic study has so far been made for the St. Lawrence River.

In this report, water quality data obtained from the National Water Quality Data Bank (NAQUADAT) are analyzed graphically to show some of the inter-relationship among different variables. Equilibrium composition of the suspended matter has been derived theoretically from the water analyses, and possible water-sediment reactions are speculated.

RESULTS

Station Location:

Fig. 1 shows the location of the stations selected for the purpose of the present work. Among a large number of stations for which water quality data are available, only a few are chosen so as to be representative of the entire length of the river. Work is currently under progress in the estuary region of the river and the present report is addressed only to the fresh-water region of the St. Lawrence River.

Major Constituents:

Fig. 2 shows the values of total dissolved load at various points between Montreal and Quebec City. The vertical bars in the figure represent seasonal variations. Because of discharge effects, total dissolved load can be expected to vary seasonally (Edwards, 1973; Gibbs, 1967, 1972; Grove, 1972; Livingstone, 1960). Longitudinal variations in the dissolved load can be
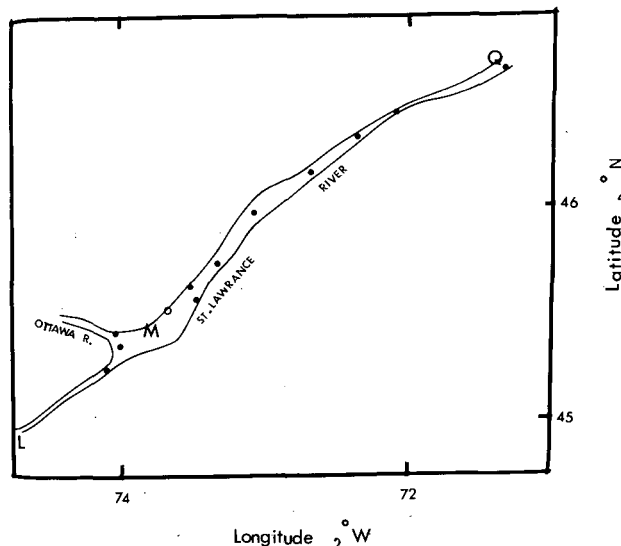

FIG. 1: Location of stations along the St. Lawrence River. M-Montreal; Q-Quebec City; L-Lake Ontario.
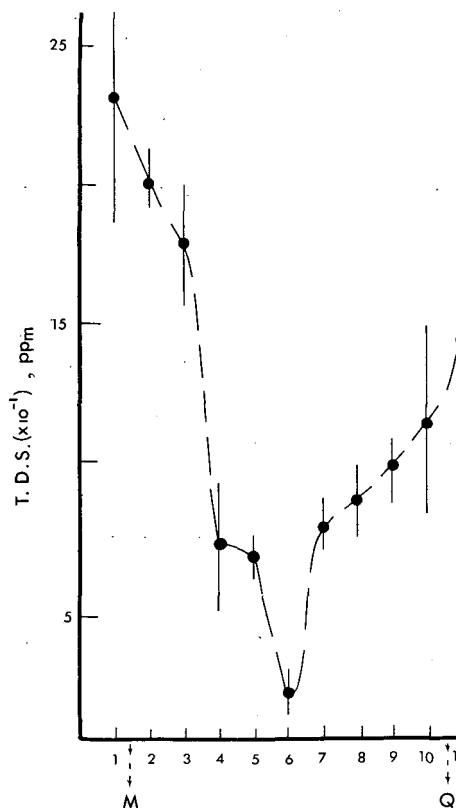

FIG. 2: Seasonal and longitudinal variations in the total dissolved solids (T.D.S.). Dots represent arithmetic mean.

explained by either dilution at localities where a
tributary with a small dissolved load may enter the
main river, or by removal of some salts by the
ecosystem or by inorganic precipitation. On the
other hand, increase in the dissolved load can be
explained by the addition of salts through wastes
from industries located along the length of the
river, or by dissolution of some of the inorganic
phases in the sediments, or by addition of water
from a tributary draining a soft rock basin. In
the case of the St. Lawrence river, the longitudinal
distribution passes through a minima at a point
roughly half way between Montreal and Quebec City.
The removal of more than 75 per cent of the dis-
solved load at this point is due probably to the
entrapment of the river water in a lake-like system
present there, or due to the sample being taken at
the junction of two small tributaries draining the
Canadian Shield area. Heavy industrialization and
urbanization all along the length of the Ottawa
river, around Montreal and also around Quebec city
may account for the higher total dissolved load
observed in these regions.

The world average discharge of dissolved load
is only 117 ppm (Gibbs, 1972) or 120 ppm (Living-
stone, 1960). Even the tropical African rivers
such as the Niger and Senegal Rivers have a max-
imum dissolved load of only 80 ppm (Grove, 1969);
the Ganges and Brahmaputra Rivers, before reaching
their subtropical and sedimentary basin, carry a
maximum of only 140 ppm and 132 ppm respectively
(Government of India Report, 1955; Handa, 1972).
The Amazon River, whose dissolved load is derived
from mountain areas in the drainage basin, carries
only 62 ppm (Gibbs, 1967, 1972). Thus the mass
transfer of the total dissolved load from the
water shed and the drainage basin by the St.
Lawrence River to the Atlantic Ocean may be very
significant, and may be important in the marine
chemistry of the North Atlantic Ocean.

Figure 3 shows the variations in the concen-
trations of major ions with the total dissolved
load. From the fresh water towards the estuary,
the predominating ions in solution will change
from Ca^{++} and HCO_3^- to NA^+ and Cl^-. Since all the
stations considered in this report are located
within the fresh water region of the St. Lawrence
river, changes in the ionic ratios cannot be ex-
plained by sea-water mixing. In Figure 3 is is
seen that the ratio Na/Na+Ca sharply increases
with the total dissolved salts around Montreal
whose position is indicated with an arrow in the
figure; below the arrow, stations are located
between Lake Ontario and Montreal and above that
point, the stations are located between Montreal
and Quebec City. The sharp increases of Na^+
accompanied by a corresponding decrease in Ca^{++}
is probably due to winter salts washed off from
the urban areas into the river. Ruthford (1972) has
observed a high percentage of Na^+ in the sediment
waters from the bottom sediments of St. Lawrence
river near Kingston, Ontario. The behaviour of the
anionic ratios, $(Ca HCO_3/Na+Cl)$, shown in the same
figure, suggest that any increase in Na^+ is also
accompanied by increase in Cl; NaCl used during the
winter months on the streets offers a convenient
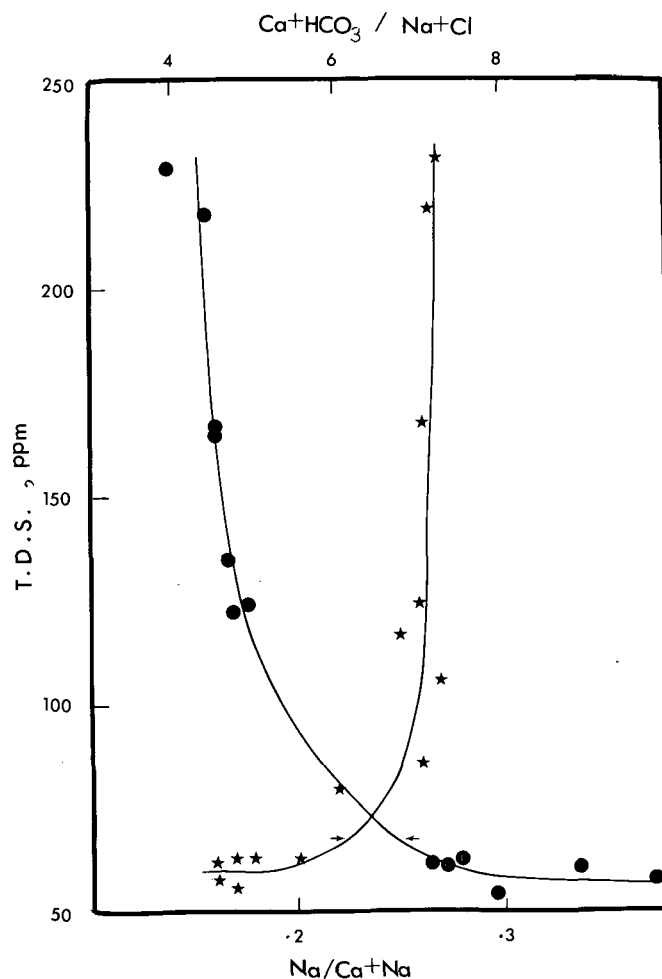source for both Na^+ and Cl^-. The Champlain Sea sed-

FIG. 3: Variations in major ionic ratios with the total dis-
solved solids. Stars= Ca+HCO₃/Na+Cl; Dots=
Na/Na+Ca. Arrow indicates location of Montreal.

iments, part of the drainage basin of the St.
Lawrence River, could be a source for many ions in
the water, particularly for stations between Montreal
and Quebec city.

Figure 4 shows the relationship between the
total dissolved solids and the major anions in the
river water. The vehaviour of Cl/HCO_3 Cl can be
predicted from the previous figure since Na^+ and
Cl^-, on the one hand, and Ca^{++} and HCO_3^- on the
other, could be derived from common sources. Con-
tinuous increase in the SO_4^{--} concentrations with
the total dissolved salts suggests, but does not
prove, that they have common controlling factors.
Sharp increase in SO_4^{--} near Montreal may be due
to the industrial effluents from refineries. Pulp
mills, petrochemicals and chemical industries are
potential contributors of sulphur-bearing materials
to the river waters (Gove and Gellman, 1972;
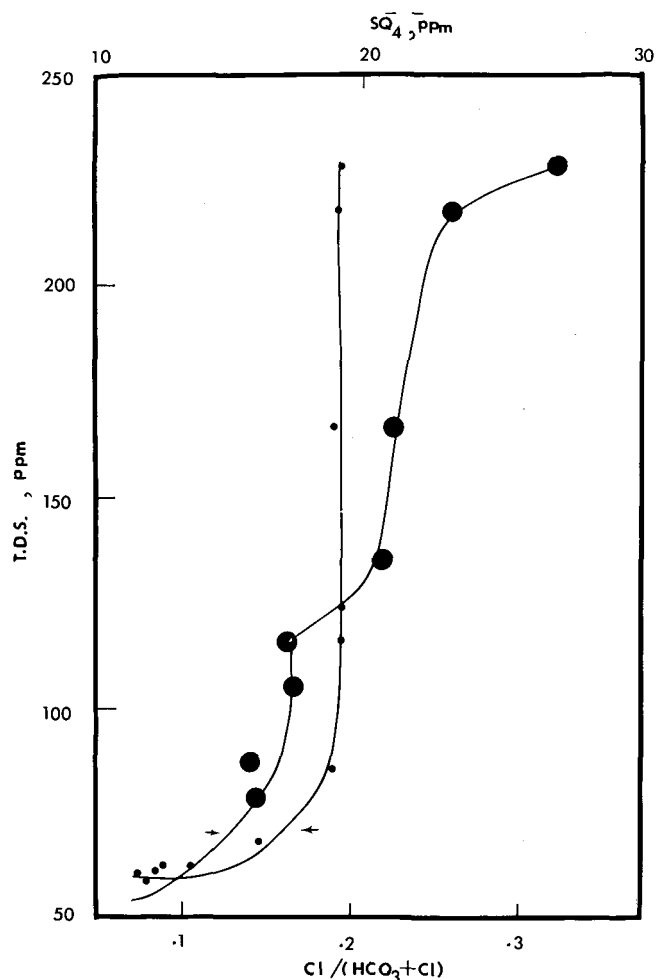Mytelka, 1972).

FIG. 4: Variations in anionic ratios with total dissolved solids
(T.D.S.). Small Dots=Cl-HCO₃+Cl; Large Dots=SO₄⁻.
Arrow indicates location of Montreal.

Figure 5 shows the relationship between total
reactive silica and pH ranges, reactive silica can
be considered to represent all the dissolved silica
species in fresh waters. In silicate reactions,
pH is an important variable (Garrels and Christ,
1965); based on solubility reasoning, acidic waters
should be silica deficient. Figure 5 indicates the
role of two factors in regulating the silica levels
in the river water: (a) Seasonal variation - The
silica numbers have been grouped into seasonal
ranges and the highest values are observed during
the colder months of February-March; lowest values
are observed in the Spring and Summer times of May-
October. (b) pH variation - While a definite and
clearcut relationship is lacking between silica and
pH, a negative correlation is suggested by the plot
obtained from the analytical data.

Silicate minerals are more soluble at higher
pH (Mackenzie and Garrels, 1965). If the silica
content in the St. Lawrence river is controlled
primarily by silicate reactions, then the plot
should have been reversed; it is hence likely that
factors other than mineral-water reactions are
responsible for the observed increase in silica
at lower pH values; the low silica values at higher
pH may be due to sorption of silica by clay miner-
als, as was shown by Siever (1973) in laboratory
experiments. Organic productivity is also an
additional variable in silica chemistry: the
small amount of silica at higher pH values probably
reflects the uptake of silica by organisms in the
warm months of June to October. It is also possible
that the higher silica values reported at lower pH
may represent analysis of colloidal silica (Siever,
1962; Mckeague and Cline, 1963). Even at the high-
est silica concentrations, the St. Lawrence River
water is under-saturated with respect to both
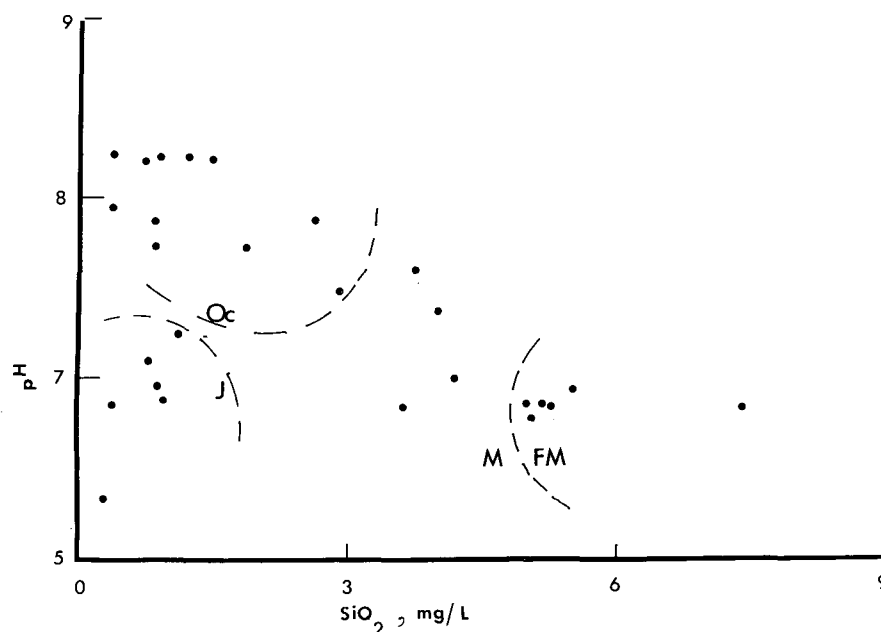quartz and amorphous silica (Helgeson, 1969) and

FIG. 5: Variations in Silica contents with pH. Oc-October; J-June; M-May; FM-February-
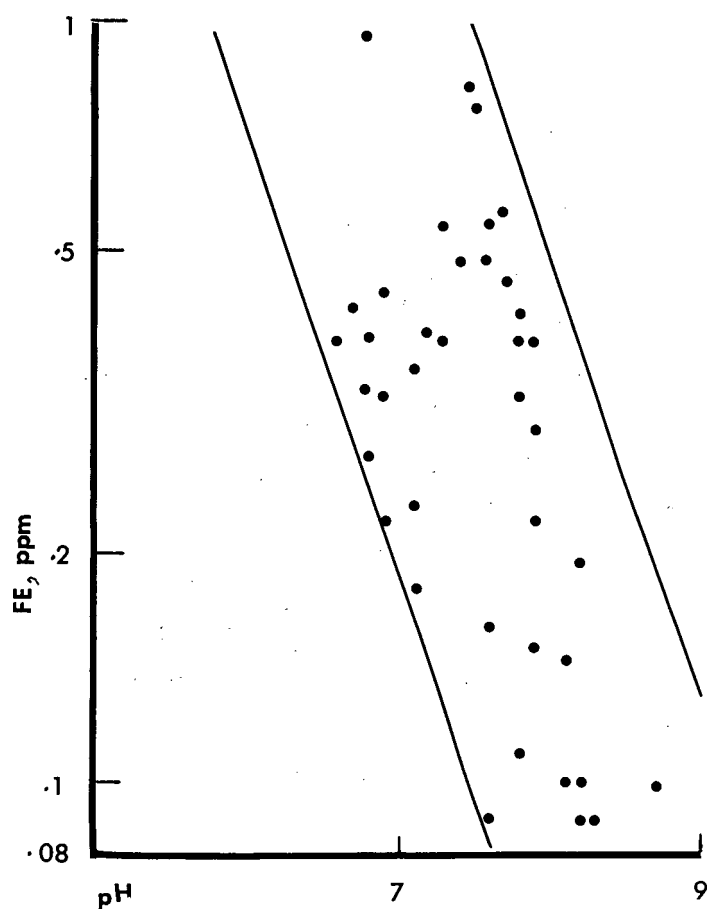March.

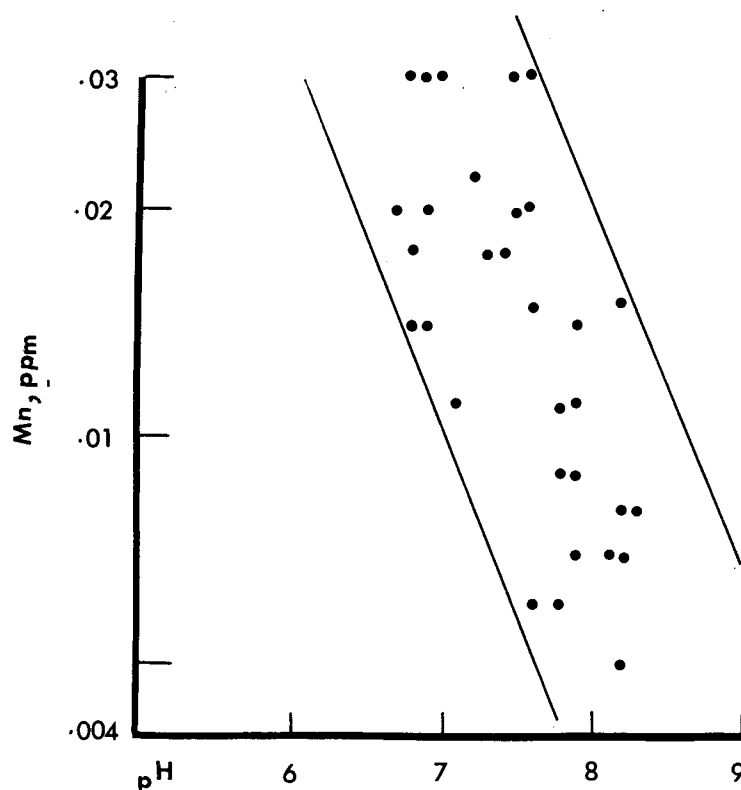FIG. 6:   Variations in total dissolved Fe with pH.

FIG. 7:   Variations in total dissolved Mn with pH.

hence, no silicate mineral is likely to precipitate out of the river water.

Minor Constituents:

Fig. 6   shows the relationship between Fe content and pH of the river water. Even though a definite relationship is lacking, the range of values obtained fall within a restricted area of the plot, as shown by the lines in the figure and from this, a negative correlation can be consider-ed to exist between pH and total dissolved Fe in St. Lawrence River water. Removal of Fe from fresh waters under oxidizing conditions is con-trolled by equilibrium between the water and the oxyhydroxides of Fe (Langmuir and Whitmore, 1971) and, since oxyhydroxides are only sparingly soluble, dissolved Fe in natural waters should be negligible. Organic complexes of Fe can stabilize Fe species in solutions beyond the levels dictated by the solubility products of Fe- Oxyhydroxides, Sulphides and Carbonates (Berner, 1971; Theis and Singer, 1974).   In addition to the absence of any correl-ation between Fe and dissolved organic carbon in these river waters, and lack of any other direct evidence for the presence of organo-metallic com-plexes, the role of organics in the aqueous chem-istry of Fe is only speculative at this stage (Plumb Jr. and Fred Lee, 1972).

In the pH range observed for St. Lawrence River water, the maximum Fe that could be in solution is less than 0.1 ppm (Hem, 1972).   The observed higher values of Fe may (a) reflect analysis of fine colloidal particles of oxyhydrox-ides of Fe which are ubiquitious in natural aqueous systems, or (b) reflect, indirectly, the stabilizing effect of both inorganic and organic ligands in the water (Morgan and Stumm, 1965), or (c) show the effect of the total dissolved salts (salinity) (Bewer et. al. 1974).

In Fig. 7   is shown the relationship between pH and total dissolved Mn.   The behaviour of Mn is very similar to that of Fe.   A scatter of values at any given p^H is more prominent for Mn than for Fe. The highest Mn values reported in the analyses fall within the range expected for equilibrium between hydrous Mn oxides and water (Bricker, 1965).   Under identical Eh and pH conditions, Mn is stable relative to Fe in natural waters (Kruskopf, 1957).

Because of the reported intimate association of Fe and Mn in the weathering cycle (Krauskopf, 1957; Jenne, 1967), a plot of dissolved Fe versus dissolved Mn was made and is shown in Fig. 8. The observed positive correlation suggest that both Fe and Mn in St. Lawrence River water are controlled by the same factors.   Because of the greater ease of formation of Fe-Organics relative to Mn-Organics (Rashid, 1972; Stumm and Morgan, 1970) and also for lack of any correlation between dissolved organic Carbon and Fe as well as Mn (plots not shown), it is unlikely that organic chelation could be a single controlling factor for both Fe and Mn in the water of the St. Lawrence River.   Besides Eh and pH, source-area lithology is also important in the aqueous chemistry of Fe and Mn.   The St. Lawrence River water probably

derives both Fe and Mn from the same minerals in the
source area. Possible mineralogical contributions
are discussed later.

Even though the positive correlation between
Fe and Mn holds good at all seasons, the plot can
conveniently be divided into two seasons as follows:
regions of higher Fe and Mn values representing data
from the month of October, and regions of lower Fe
and Mn values representing data from the month of
May. An insignificant number of data are available
for other months and are not considered here.
Colloidal Fe sorbed onto Mn oxides may possibly
represent high Fe Mn values (Martin et al, 1973;
Gibbs, 1972; Jenne, 1967).

Due to the non-availability of significant
number of analyses, no controls could be evaluated
for other trace metals.

Dissolved Organic C, N and P:

Figure 9 shows the plot of dissolved organic
carbon versus total N. A negative correlation is
evident and suggests that they are derived from two
different sources. Dissolved organic carbon (DOC)
is the result of interaction between water and the
ecosystem. DOC in world average river water is 10
ppm (Livingstone, 1960) and represents nearly a
tenth of the total dissolved load carried by rivers.
Amino acids, proteins, lipids and carbohydrates
constitute the major dissolved organic matter in
natural waters. Based on thermodynamics of equil-
ibrium systems, Thorstenson (1969) concluded that
organics of higher molecular weights are unstable
in most natural waters; in spite of this, higher
molecular weight organics have been reported from
several natural environments, - up to 5 ppm of humic
matter have been reported for river waters (Martin
et al, 1971) and dissolved amino acids in McKenzie
river has been reported to be in the range of 15-
220 ppb (Peake et al, 1972). Since the St. Lawrence
River water has not been fractionated to isolate
individual organic components, no specific source
could be assigned for the DOC.

The source of dissolved N are NH_4^+, amino acids,
dissolved N_2, and NO_3^-. The negative correlation
between DOC and N suggests that dissolved organics
containing amino functional groups are not import-
ant in the present system. Alternately, contribu-
tions from inorganic N could be in excess of that
of amino acids. If the total dissolved organics
are considered to be represented by DOC, then in
the St. Lawrence River they are in the range expected
for any fresh water bodies. Absence or insignifi-
cance or higher molecular weight organics may also
explain the lack of correlation between Fe and DOC.
None of the trace metals such as Zn showed any
correlation with DOC. Since metal-organic complexes
are formed easily with higher organic compounds
such as humic acids, it appears that metals and
also N chemistry in the St. Lawrence River are
primarily influenced by inorganic rather than
organic processes. Though the presence of dissolved
Fe-P complexes are not known so far, UpChurch (1974)
has shown that Fe-P inorganic complexes could exist
in suspension. The positive relationship between
dissolved Fe and P, shown in Figure 10, may again
reflect the same source-area effects. Except over
a narrow range of P-values, P content is independent
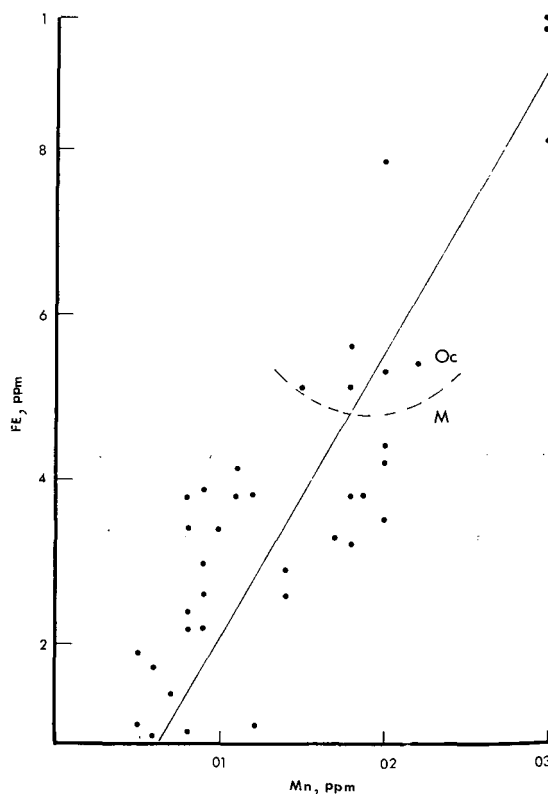of Fe content. The P-values are high compared with

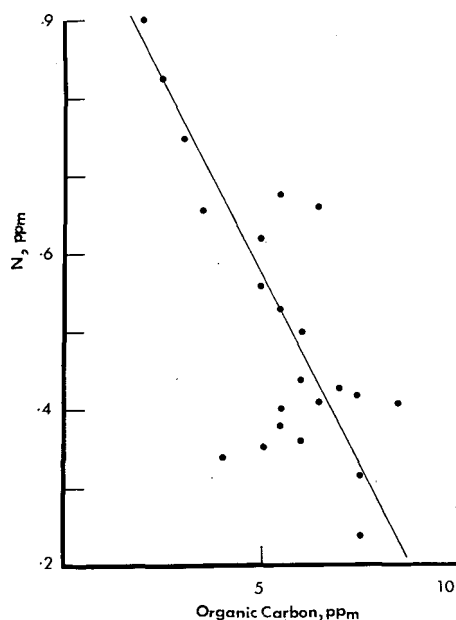FIG. 8: Relationship between total dissolved Fe and Mn.
Oc-October ; M-May.

FIG. 9: Variations in total dissolved N with dissolved
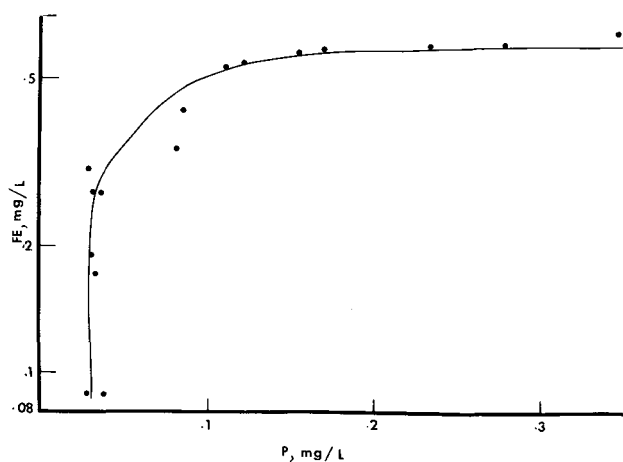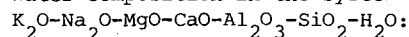organic C.

FIG. 10:   Variations in P with total dissolved Fe.

FIG. 11:   Water composition in the multicomponent system.
pK+ = -Log (K+/H+); pNa+= -Log (Na+/H+);
pMg++= -Log (Mg++/H+); pCa++=-Log (Ca++/H+); pSiO2=
-Log (H4SiO4); Ab-Albite; AS-Amophous Silica saturation;
M-Montmorillonite; IL- Illite; Ch-Chlorite; K-Kaolinite;
G-Gibbsite.

those reported for estuaries (UpChurch et al,
1974) but the higher productivity in the estuary
region should remove P from solution whereas in
the fresh water regions, consumption by the organisms
would be the limiting factor for P.   St. Lawrence
River water appears to be consistent with these
expectations.

Water composition in the system
$K_2O-Na_2O-MgO-CaO-Al_2O_3-SiO_2-H_2O$:

The chemistry of river water can be represented
in a system diagram consisting of the above mention-
ed components.   In the past, such diagrams have
been reported (Drever, 1971; Garrels and MacKenzie,
1971; Jacks, 1973; Helgeson and MacKenzie, 1971;
Kramer, 1967, 1968; Norton, 1974).   Hydrolysis
reactions of silicates or silicate-silicate re-
actions can be written as a function of three
variables - a cation, pH and dissolved silica.
Equilibrium reactions between any two silicate
minerals can thus be represented in an orthogonal
plot consisting of two variables - Cation/Hydrogen,
and SiO_2.

In the diagrams shown in Fig. 11   the
composition of St. Lawrence River water has been
plotted in stability diagrams of silicate minerals
expressed as a function of the three above-mentioned
variables.   Except for a single analysis, the river
water falls in the gibbsite and chlorite area.
Kramer (1967, 1968) has reported that Lake Ontario
samples, from winter and summer months, fall in
the gibbsite and kaolinite areas on similar plots.
Ruthford (1972) has observed illite, chlorite and
mixed-layer clays in the bottom sediments of the
St. Lawrence River near Kingston, Ontario at the
point where the river flows from the Great Lakes.
Gibbsite has not been reported anywhere from the
St. Lawrence basin sediments.   Even in the St.
Lawrence estuary and the Gulf of St. Lawrence,
the mineralogy of sediments reported so far con-
sist of chlorite, illite and mixed-layer clays
with occasional kaolinite but no gibbsite (d'
Anglejan and Smith, 1973; Beltagy, 1974).   Thus
the observed mineralogy is different from that
predicted for the river based on water chemistry.
Possible causes are discussed later.

Assuming (1) the average composition of the
river water is that at Lewis, Quebec, (2) hydroly-
sis data for silicate minerals given by Helgeson
(1969), Kramer (1968) and (3) following the
methods of Helgeson and McKenzie (1971), the
silicate system can be treated simply as a two
component system consisting of pH and silica.
Fig. 12   shows such a plot.   The water compositions
are plotted in the stability diagram as before,
and the predicted mineralogy is the same now as
was the case when the system was plotted in a
seven-component system (Fig. 11).

DISCUSSION

Hydrological data for the St. Lawrence basin
are summarized in Table 1.   Nearly 60 percent of
the daily average drainage at Quebec City (at the
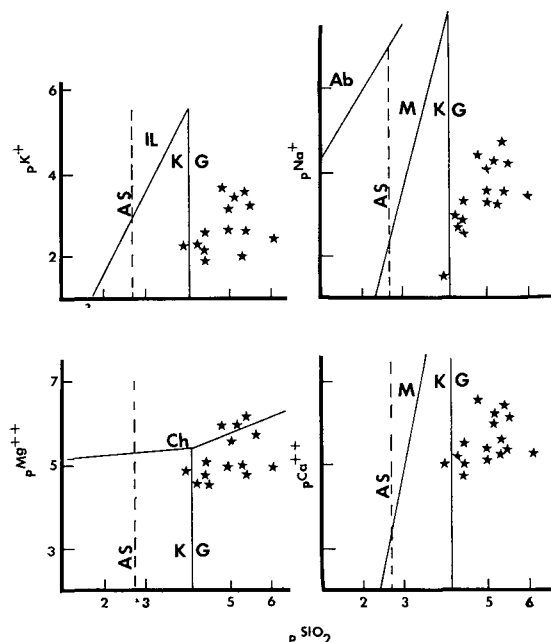end of the fresh water region) can be accounted

Table 1. Data on St. Lawrence River

Source	Drainage Km^2	Station	Discharge m^3/sec	TDS ppm
1. Sedimentary Basin				
Lake Ontario (a)	63973	--	6624	194
Richelieu (b)	19300	Chambly	318	87
St. Francois (b)	8300	Drummondville	2.3	--
2. Canadian Shield Basin				
St. Maurice (c)	42000	Centre de Grand Mere	708	20
Ottawa (d)	89600	Chat Falls	703	--
St. Lawrence (e)	766000	Quebec City	10350	160

a. Data from Ragtozkie, 1974.
b. Data from Annaire Hydrologique, 1970.
c. Data from Can. Comm. Int. Hy. Decade, 1972. TDS data from Saguenay River.
    (Loring and Nota, 1973).
d. Data from Can. Comm. Int. Hy. Decade, 1972.
e. Data from Padre, 1948 and quoted in Loring and Nota (1973).
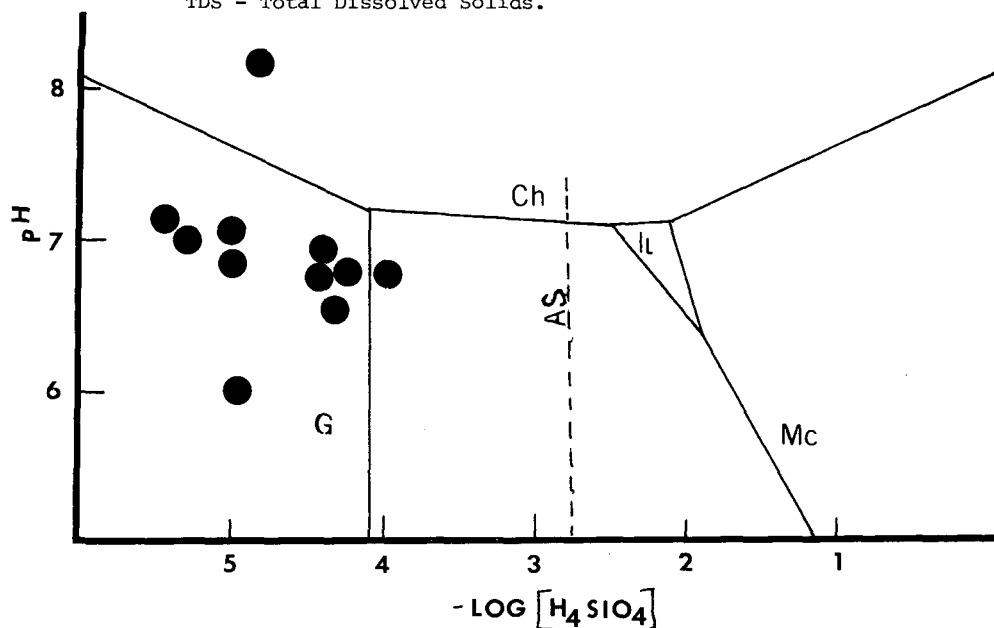TDS - Total Dissolved Solids.

FIG. 12: Water composition plotted on an orthogonal diagram. Abbreviations same as above. Mc-Microcline.

for by water draining a sedimentary basin. This sedimentary water carries a high percentage of dissolved load compared with waters from the Canadian Shield area. Because of the large contribution of Lake Ontario to the drainage of the St. Lawrence river and also because of the presence of the Niagran dolomites in regions adjoining Lake Ontario, St. Lawrence water should be a carbonate water, based on the classification of Garrels and MacKenzie (1971). The high percentage of HCO_3^- in the river water is consistent with the drainage lithology. Only a small increase in the total dissolved load of Lake Ontario in recent years has been reported (Ragotzkie, 1974). Because of the close similarity in the water composition of Lake Ontario and of the river near Quebec City, it can be stated that the

river-water chemistry is essentially the same all along the fresh-water region. Of the four main tributaries, discharge from the hard-rock terrain (Ottawa River and St. Maurice River) is nearly 4.5 times that from the soft-rock basin (Richelieu River and St. Francois River). Thus the water with a high dissolved load from Lake Ontario is diluted by the smaller contribution from the hard-rock regions before the river reaches Quebec City. Thus, dilution, along with possible entrapment of the load at Lake St. Peter half way between Montreal and Quebec City, with possible inorganic precipitations probably account for a small net loss of dissolved load at the end of the fresh-water region of the river (See Table 1).

Except for the Na^+, SO_4^{--} and Cl^{--} contents, the individual elemental composition of the water is not different along the course of the river. While the Na^+ and Cl^- contents can be modified either by additions through winter salts or Champlain Sea sediments, changes in SO_4^{--} content possibly reflect industrial additions. Even at the highest SO_4^{--} values, the St. Lawrence river is under-saturated with respect to all metal-Sulphate phases and hence the SO_4^{--} will remain in the water column of the river. Ruthford (1972) reported increased concentration of SO_4^{--} in the interstitial waters of bottom sediments near Kingston but such an increase may be entirely due to diagenesis.

Major ionic ratios suggest that their concentrations are primarily controlled by weathering processes, based on Gibbs' (1970) classification of river compositions. Precipitation does not appear to have significant effects on the water chemistry of the St. Lawrence River. Because of the dominance of the sedimentary basin, mineral-water reaction, rather than physical weathering is likely to contribute to the water chemistry.

Since the reported composition of suspended matter in the estuary and the gulf predominantly consist of detrital silicates, the chlorite and gibbsite expected to form under equilibrium conditions cannot be distinguished from the detrital phases even if they form through water-mineral reactions. However, gibbsite has never been reported and this may be due to its presence in amorphous forms such as bohemite or both gibbsite and kaolnite react with water to become illite. Such a halmyrolitic reaction is unlikely because of the detrital nature of the suspensoids. The author is currently experimenting with gibbsite and bohemite reactions with fresh water to monitor changes that may be relevant to the St. Lawrence River water chemistry. The author is also studying suspended matter from the river along a transect from the fresh water to completely salt-water region to identify any halmyrolitic reaction taking place in the river. The results should be available in the near future.

The pH control of the chemistry of Fe and Mn in natural water is well known (Hem, 1972), and data from the river indicate that Fe and Mn behave in similar fashion and that both are derived from the same source mineral. Rutherford (1972) mentioned the presence of Mn-rich regions in the Great Lakes and the same could also be the source for Fe. Cronan and Thomas (1972) located ferromanganese concretions in the Great Lakes and solution of these nodules, under favourable conditions, may provide both Fe and Mn to the St. Lawrence River water. Fe values are locally high, often 0.9 ppm; such high values reflect possible analyses of colloidal Fe-hydroxides. The river water is mostly saturated with respect to $Fe(OH)_3$ and the high values may also reflect metastable equilibrium.

In lieu of the large sedimentary drainage basin, the negative correlation between C and N is surprising. Organic matter in sedimentary rocks is common and river-water interaction should mobilize some of them. The Great Lakes have a variety of dissolved organics including those with higher molecular weights (Ragtozkie 1974) and their near paucity in the river suggest some removal processes before the river drains out of the Lakes.

CONCLUSION

In spite of the small drainage of the St. Lawrence River compared with other major rivers of the world, the total dissolved load carried by the river into the North Atlantic may be significant in mass transfer and budget studies. The major ionic composition of the river is essentially the same throughout the fresh-water region. A small net loss if dissolved load is observed which may be due to the presence of Lake St. Peter.

The water chemistry of the river is primarily controlled by rock domination in the water shed. The sedimentary part of the drainage basin contributes the major ions which are slightly diluted by large-volume discharge from the Canadian Shield area. The predicted mineral equilibria from the water chemistry has not yet been observed from the actual mineralogical studies of the suspended matter.

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