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ABSTRACT

Darrell S. Vodopich. Fractionation and control of iron in channelized and swamp drainage streams in North Carolina. (Under the direction of Dr. Charles O'Rear) Department of Biology, East Carolina University, May 1975.

A channelized stream and swamp drainage stream in eastern North Carolina were investigated as to their capacity to transport and fractionate iron. Several water quality parameters were considered with special attention given to organic matter as a control. Between May and September 1974, measurements of dissolved oxygen, pH, temperature, conductivity, flow, organic carbon, and iron, including organically complexed iron, were made and correlated. The two stream systems were found to fractionate and discharge iron differently both qualitatively and quantitatively. The mean total iron concentration of the swamp and channelized streams were 2.06 and 1.46 mg/l respectively. The swamp was consistently higher in both the percentage of total iron dissolved and the percentage of organically complexed iron dissolved. The organically complexed iron concentration of the swamp and channelized streams was an average of 2.7% and 2.1% of the total iron respectively. In both streams over 90% of the organically complexed iron was dissolved. All of the water quality parameters were significantly correlated to the variance in at least one of the iron fractions. Suspended particulate matter was repeatedly indicated to be a major influence on fractionation. The major role of organic matter was shown to be the production of a reducing environment rather than a significant binder of iron.

FRACTIONATION AND CONTROL OF IRON
IN CHANNELIZED AND SWAMP DRAINAGE STREAMS
IN NORTH CAROLINA

A Thesis
Presented to
the Faculty of the Department of Biology
East Carolina University

In Partial Fulfillment
of the Requirements for the Degree
Master of Arts in Biology

by
Darrell Stowe Vodopich

May 1975

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INTRODUCTION

From a biological point of view, heavy metals are of extreme importance. Heavy metals include those with an atomic number greater than 23. Iron, copper, zinc, and manganese are almost universally considered essential for life; at least six more are suspected to be essential for some organisms. Our drainage basins and stream systems play a major role in the dispersal and circulation of these metals throughout the environment. This role is especially important today due to the abundant use of metals in industry and the polluting effluents which are poured into streams.

As with all other elements, metals circulate through the environment in a manner which is dictated by the element's particular chemical characteristics and biological functions. Heavy metals may be functionally described as enzyme activators and pigment structural molecules, and are generally associated with proteins. In addition to the essential heavy metals there are many metals, such as lead and mercury, which are considered contaminants and can be toxic at relatively low levels. These toxic metals compete with the essential metals and disrupt enzyme activity. Three prominent characteristics of heavy metals are important in biological systems. Heavy metals are (1) biologically active at concentrations in the parts per billion range, (2) highly reactive with organic as well as inorganic compounds, and (3) toxic at levels often as low as a few parts per million. For these reasons the exact fate of these metals in stream systems must be known and understood in terms of sources, sinks, physiological effects

on organisms, and time.

Iron is the most abundant metal and probably the most well known in biological systems. Its chemistry has been thoroughly studied. In solution it has two oxidation states. Ferric ions are in the higher oxidation state with a +3 charge, while ferrous ions have a + 2 charge. The ease with which iron undergoes oxidation reduction reactions between these two states and functions as an electron transport system is the greatest contributing factor to its supreme importance in plant and animal physiology.

While in the two major oxidation states, iron may be bound in as many as twelve different molecular and ionic oxides and hydroxides, in addition to the numerous salts. When iron is studied in a natural environment or ecosystem, the solubilities of these various compounds are of utmost importance. In the aquatic system the hydroxide forms of iron are dominant (Stumm 1964) and have very low solubilities. At equilibrium a 1 liter solution containing 1 mole of iron at pH 7.0 and saturated with oxygen would have in true solution only 10^{-15} M Fe^{+3} , 6×10^{-11} M FeOH^{+2} , 2×10^{-8} M $\text{Fe}(\text{OH})_2^+$, 10^{-12} M $\text{Fe}(\text{OH})_4^-$, and 5×10^{-14} M $\text{Fe}^{+2} + \text{FeOH}^+$. Total soluble iron is thus on the order of only one microgram per liter (Stumm 1964).

Virtually no iron should exist in solutions equilibrated with the atmosphere, but analytical findings for real aquatic systems show otherwise. The reasons for this bring us to a discussion of the major controls on iron in the environment. Redox potential, pH, and oxygen tension are often significant controls on solubility, especially in lakes where these parameters may have a wide seasonal range within

the same lake. A decrease in pH, redox potential or oxygen tension will generally increase iron solubility. Equally important is the strong tendency of insoluble iron hydroxides to adsorb and form coatings on suspended or sedimented particles (Jenne 1968). Precipitated iron particles are known to be as small as 100 Angstroms (Lengweiter et al. 1961) and therefore are easily suspended in a stream and readily pass through a membrane filter. For these reasons it is not surprising that most analyses reveal significant "dissolved" iron levels, when the actual molecular species present would dictate otherwise.

Related to the adsorption of hydrous iron oxides is the theory that these adsorbed oxides themselves will occlude other metals in soils or sediments, therefore making them biologically unavailable. E. A. Jenne (1968) has reviewed extensively the literature related to this consequence of adsorbed hydrous iron and manganous oxides and has shown that this may be a most important factor in the availability of Co, Ni, Cu, and Zn in soils and sediments.

Organic matter is another factor known to influence the movement of heavy metals including iron through a stream system (Gibbs 1973, Jenne 1968). Organic matter can vary in concentration within the same system, act as a sink by readily chelating heavy metals, alter the biological availability of these chelated metals, and serve as a fundamental component of the biological food chain. As a secondary objective this study elucidates the importance of some of these features.

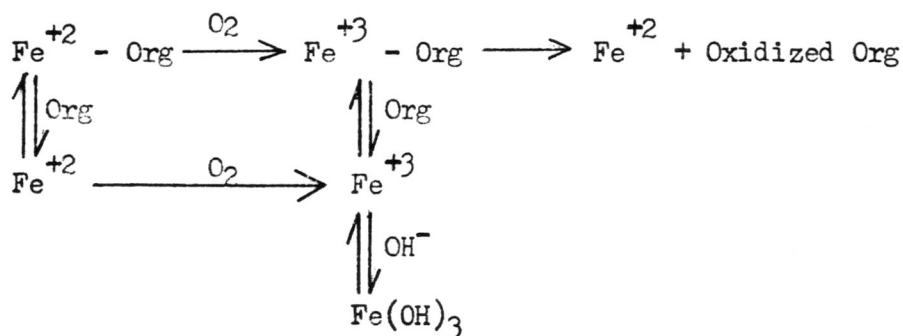
R. K. Cannan and A. Kibrick (1938) were among the first to investigate organic matter control and stated that "the presence of

organic matter in the water may result in adsorption or anionic complex formation" with heavy metals. Most of the ensuing work noted a positive correlation between the organic matter and heavy metal contents of soils (Hibbard 1940, Sommer 1945). Some experimented with the release of heavy metals upon treatment of soils with hydrogen peroxide (Crooke 1956). This led to the theory that the organic matter actually binds enough of the metals to make them significantly unavailable. Jenne (1968) disagrees with this theory. He believes that "the general role of organic matter is to produce a periodic reducing environment (speaking of the terrestrial situation) which maintains the iron and manganese oxides in a hydrous high - surface-area state", thereby making other metals unavailable. If Jenne is correct, occlusion by iron and manganous oxides is responsible for rendering these other heavy metals unavailable, not organic complexation. The data of Sokoloff (1953) also argues against organic matter as a principle sorber of heavy metals in soils. Even though organic matter does have chelating properties, he believes the influence is indirect. In 1958, Martin and Reeve summarized most of the evidence of chelate formation. In 1967 Barsdate conclusively proved the formation of heavy metal complexes by natural organic matter, using gel-filtration technique based on comparing molecular weights of organic matter with and without complexed metals.

In view of these facts, organic matter may exert its influence in a number of ways. It may chelate heavy metals, rendering them unavailable to most biological systems. It may have an indirect

effect by producing a reducing environment which maintains the adsorptive capacity of iron and manganeous oxide coatings, which in turn renders these heavy metals unavailable. This reducing environment caused by anaerobic respiration also may donate electrons to directly reduce heavy metals and make them more soluble.

Most of the evidence concerning the controls on iron in the environment is from experimentation with terrestrial soils. The same concepts apply to the lotic environment and some notable work has been done. Theis and Singer (1974) using aqueous media demonstrated that "tannic acid, gallic acid, pyrogallol and other products of natural vegetative decay can completely retard the oxidation of ferrous for several days..... with the extent of complexation increasing as pH and the organic-ferric ratio increase." The reactions involved are summarized below : (Taken from Theis and Singer 1974)



Note that both ferrous and ferric ions may be complexed organically and that oxidation of ferrous iron occurs even while complexed, although very slowly.

Most of the organic species known to complex iron are soluble, but Barsdate (1970) points out that "the reaction products of these substances, at high concentrations, can be exceedingly insoluble."

Stumm (1970) believes that this chelation results in a colloidal dispersion, but Christman (1970) has not observed any size classes larger than the organic molecules during his work with iron-containing humic materials. Thus the question of the true solubility of the organic metal complexes is problematical but academic in the practical sense.

Ghassemi and Christman (1968) investigated organic iron complexes by observing the nature of the iron-color association at 350 millimicrons. This wavelength is associated with the yellow organic acids. "The degree of association of color molecules with iron was found to be pH dependent, being greater at both high and low pH than in the range of 7-8," (Ghassemi and Christman 1968). J. Shapiro (1964) reported that the "iron-holding" capacity of color increases with pH up to a value of 10.0. Complexation at low pH levels is thought to be directly with ferrous and ferric ions, whereas at high pH levels complexation is probably through simple adsorption of $\text{Fe}(\text{OH})_4^-$ (Shapiro 1964).

Literature on the distribution of total iron in aquatic systems is abundant. Livingstone (1963) states that the average iron concentration for rivers and streams of the world is 0.67 milligrams per liter. Mason (1958) points out that iron concentrations in streams are typically 100 times those in the sea due to the effect of pH (cited in Martin 1971).

Increased pollution by heavy metals has stimulated analysis of basic transport mechanisms of metals in rivers and streams. In the analysis of a natural water, the presence of suspended matter, both

organic and inorganic, has a profound influence on the composition of heavy metal concentrations (Eichholz, Craft, and Galli 1967). Ralph M. Perhac (1974) studied the effect of suspended matter by using continuous flow ultracentrifugation to determine the distribution or partitioning of iron and other heavy metals among different sizes of particulates in a fluvial system. This technique is becoming very popular. Perhac noted that of most metals tested, at least 85% of the metal load was transported in the dissolved fraction, but the highest weight for weight concentration was in the colloidal fraction. Iron and manganese were notable exceptions. Eighty percent of the iron was transported in the coarse particulate fraction ($20,000 \text{ S}$ or 0.15 microns with a specific gravity of 2.65), 1% in the colloidal particulate fraction, and 19% in dissolved solid state (Perhac 1974).

Martin et al. (1971) investigated the correlation between rainfall, humic acid content, and iron content in fourteen west coast Florida streams. Significant positive correlation coefficients between humic acid and iron contents were found. Coefficients, including the rainfall data rather than flow, were not as conclusive but in some cases were significant.

The work of Ronald T. Gibbs (1973) is most significant in that he made field measurements of the amount of iron actually bound organically. He analyzed the waters of the Amazon and Yukon Rivers and found that 6.5% and 11.0% respectively of the iron content was being transported by organic particulates. He did not distinguish between the dissolved iron and the dissolved organically complexed iron. He found 0.7% and .05% of the iron in the Amazon and Yukon

Rivers respectively to be transported in the dissolved state (including dissolved organics). This is a drastic difference from the 19% found by Perhac (1974). Comparing the data of Gibbs and Perhac concerning other heavy metals such as copper and cobalt shows an even greater difference. Gibbs (1973) believes particulate matter to control at least 90% of the heavy metal content. Perhac believes that 90% of the heavy metal content is transported in the dissolved state. Sieburth (1971) also measured the amount of heavy metals complexed organically in a wide variety of natural waters. Using an ion exchange process which was entirely different from Gibbs' process, he found up to 50% of some heavy metals bound organically.

The ecological importance of iron is dependent upon its availability, which in turn is governed by its distribution and speciation (Martin et al. 1971). Since the reduced state of iron is believed to be the physiologically active state in plants (Martin et al. 1971), we would expect organic chelation to be important. Organic chelation affects the oxidation-reduction potential making iron soluble and more available to a plant (Johnston 1964) or animal (Roeder and Roeder 1966). Davies (1970) specifically suggests that "chlorophyll production in phytoplankton, especially chlorophyll 'a', may require the presence of organo-iron complexes." Johnston (1964) agrees with this but states that in natural sea water only a very small percent of the organic matter present need have chelating powers as strong as those of EDTA.

As we have seen, the most important considerations of iron in

the environment include (1) biological essentiality, (2) solubility, (3) transport mechanisms, and (4) organic complexation. This research project was designed to elucidate on the latter three of these considerations as they apply to a swamp and a channelized stream.

The objectives of this project were:

1. To measure the concentrations of organically complexed iron in a swamp and a channelized stream.
2. To determine those factors which significantly govern the general speciation of iron, including the concentration of organically complexed iron.
3. To assess some of the effects of channelization on heavy metal complexing and transportation and to note the biological significance of such effects.

These objectives were carried out by an analysis of simultaneous measurements of water quality factors including dissolved oxygen, pH, flow, conductivity, water temperature, organic carbon, total iron, and organically complexed iron content. These measurements were taken from both a swamp and a channelized stream.

DESCRIPTION OF STUDY AREA

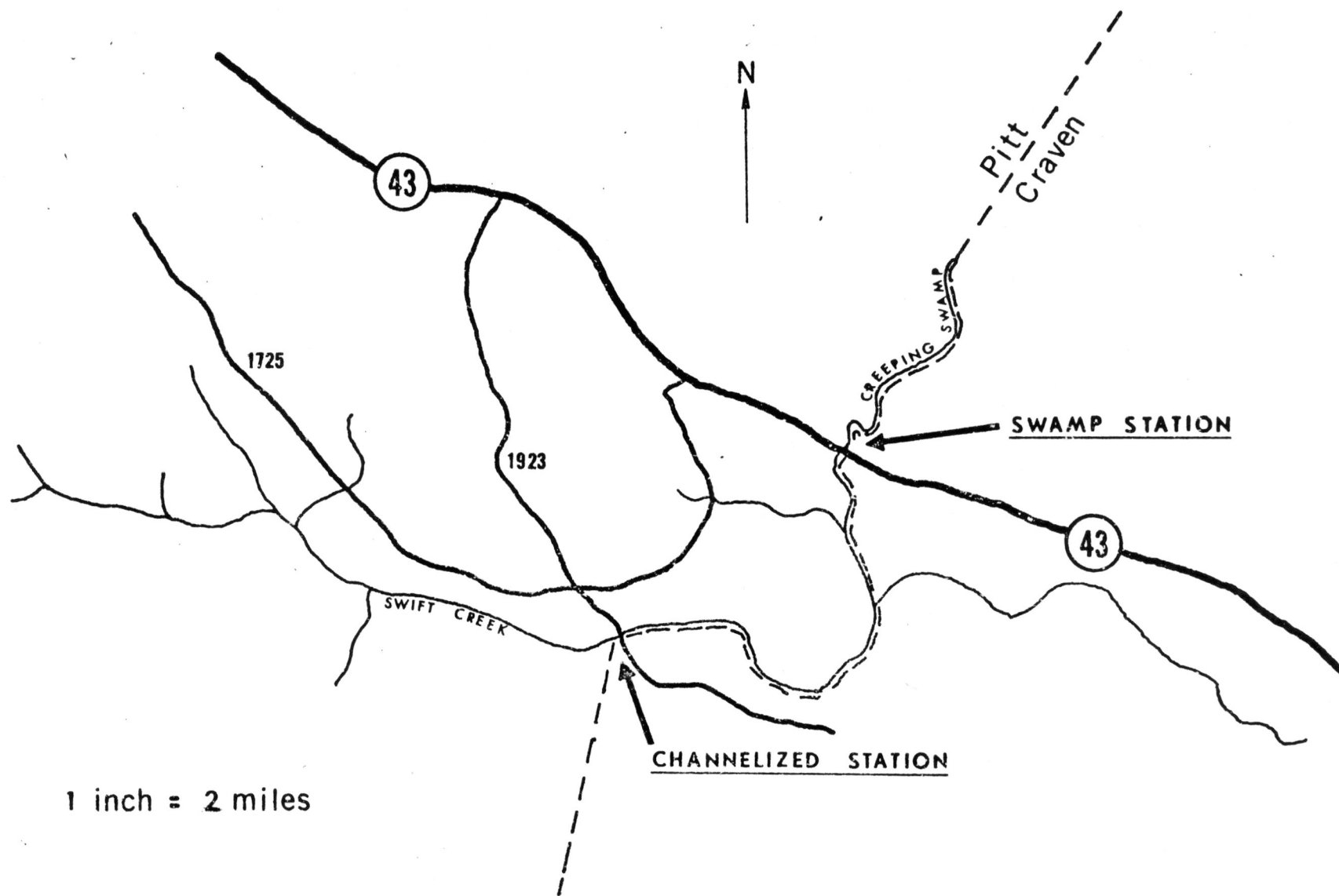
The two study areas are located approximately 7 km from each other on the border between Pitt County and Craven County, North Carolina. Figure 1 illustrates the relative locations. The channelized study area was sampled approximately 25 m upstream from the bridge where Pitt County road #1923 crosses Swift Creek. The site was 12 km east of Grifton, North Carolina. Swift Creek joins Creeping Swamp and both finally empty into the Neuse River about 33 km downstream.

The water passing by the channelized study area had traveled through a minimum of 10 km of channelized stream bed. The first 7 km were channelized in 1937 and the final 3 km, just upstream from the sampling site, were channelized in 1965 (USDA 1969). The first 7-km section had recovered somewhat, but the last 3-km section had no canopy or permanent log obstructions. This section had a flat, sandy bottom with a minimum of rooted aquatic vegetation. At the sampling site the dimensions of the stream ranged between 20-25 m in width and .5-2.0 m in depth. This gave a water discharge range of .2-19.2 m³/s. The approximate drainage area is 376 km² (145 miles²) (USDA 1969).

The swamp sampling site is located where state highway #43 crosses Creeping Swamp. At this point the waters of Creeping Swamp converge and drain through a narrow weir, maintained by the USGS. This point is 12 km west of Vanceboro, North Carolina and 18 km east of Grifton, North Carolina. The watershed covers 70 km² (27 miles²).

The area is characterized by a heavy canopy and a bottom with high organic content. The discharge ranged from .06 - 2.6 m³/s during the study period. Basic water quality data which further describes both these study areas is given in the results section.

Fig. 1. A map of the study areas in Pitt County, eastern
North Carolina.



MATERIALS AND METHODS

Seven complete collections were made beginning on July 30, 1974. In addition limited data was collected on three previous sampling dates (5/22, 6/8, 7/2). This data was limited because a suitable swamp station was not found until July 30th. This date also corresponds with the initial success of the techniques for determining organically complexed iron concentrations. The total of ten sampling dates covered a 128-day period from May 22, 1974 to September 26, 1974. Each sampling day will be referred to by the corresponding number of days since the beginning of the sampling period. May 22, 1974 corresponds to day 1. All collections were made between 0800 and 1100 EDT.

Field Collections and Measurements

Preparation for each field trip included acid washing all collection bottles, glassware and other apparatus with 20% HNO_3 , rinsing five times with distilled water and twice with deionized water. Preparation also included the calibration of all meters by appropriate methods. The dissolved oxygen meter was calibrated 12 - 24 hours previous to each field trip using the Winkler method as described in Standard Methods (Taras ed. 1971).

Water was collected at mid-channel, mid-depth at least 25 m upstream from each bridge crossing. Two liters of water for iron analysis was collected in brown Nalgene plastic bottles. Water for the organic carbon analysis was collected in duplicate 30 ml plastic vials.

Field measurements included pH, conductivity, dissolved oxygen, water temperature, and flow. Conductivity, pH, and dissolved oxygen were measured with standard meters. Temperature was taken using the thermistor associated with the dissolved oxygen meter. Flow rates in the channelized stream were calculated from the stream profile and time-of-travel measurements which were taken at each sampling. Flow rates from the swamp area were determined by use of a rating curve calibrated by the USGS for the concrete weir located at this station.

Five sediment cores were taken at each station on each sampling date. These cores were taken in a rough transect perpendicular to stream flow. Each core was 2.5 cm in diameter and 3.0 - 5.0 cm in depth.

Iron Analysis

All iron analyses were performed using a Perkin-Elmer Model 305B Flame Atomic Absorption Spectrophotometer. The machine settings were those described in the operator's manual listed under "standard conditions." The standard error of the analysis of each iron fraction was determined on a 5-replicate run. This was done to estimate experimental error. The results are given in Table 1 . All filtration was done with membrane filters with a 47 mm diameter and a .45 μ pore size. Before use, each filter was washed with 20 ml of deionized water followed by 20 - 30 ml of previously filtered stream water.

Total iron measurements were made with water previously acidified with HNO_3 to a pH less than 2.0. Dissolved iron

Table 1. The standard error determined for each iron analysis technique.

	N	Mean	SE	%SE
Total iron	5	1.44 mg/l	.01	1.0
Dissolved iron	5	.28 mg/l	.01	3.5
Dissolved organic iron	5	62.0 µg/l	4.0	6.4
Particulate organic iron	5	9.0 µg/l	.9	10.0

measurements were made with water filtered within three hours after collection with subsequent acidification. The particulate iron fraction was determined by subtraction of the dissolved from the total measurement.

The dissolved organically complexed iron was determined by organic extraction. One-hundred ml of the filtrate was extracted twice using 15 ml of methyl isobutyl ketone as the organic extractor. The extracted aqueous layer was acidified and then aspirated directly through the atomic absorption unit. The blanks and standards used were also saturated with methyl isobutyl ketone. The concentration of iron found in this extracted solution was subtracted from the concentration of iron previous to extraction ; this value was taken as the concentration of the dissolved iron that was bound organically.

The particulate iron bound organically was determined by the method outlined by R. T. Gibbs (1973). Two-hundred ml of stream water were filtered and the filtrate removed. Twenty-five ml of 0.5 M $MgCl_2$ were passed through the filter to remove the most loosely bound iron from the particulate matter. A .01 M EDTA solution was then used to remove any "metallic coating" (Gibbs 1973) from the particulate matter. These filtrates were removed. Eighty ml of sodium hypochlorite solution , pH 8.5, were then used to destroy the particulate organics and thereby release the particulate organically bound iron. This iron-containing solution was then acidified to pH 3.0 using HNO_3 with vigorous stirring and aeration. This solution was then concentrated by extraction using ammonium pyrrolidine dithiocarbamate as a chelator and methyl isobutyl ketone

as an extractor. The iron in 80 ml of sodium hypochlorite was extracted into 10 ml of organic solvent. This organic solvent was aspirated through the atomic absorption unit with appropriate standards.

Organic Carbon, Sediment, and Phosphorous Analysis

Organic carbon samples were analyzed in the lab using a Beckman Model 915 Total Organic Carbon Analyzer. Each sample was acidified to pH 2.0 with H_2SO_4 and purged with nitrogen gas to remove the CO_2 resulting from the acidification and subsequent oxidation of the inorganic carbonates. The carbon remaining in solution was termed organic. Water for Total Organic Carbon (TOC) analysis was analyzed after no treatment other than the acidification. Water for the Dissolved Organic Carbon (DOC) analysis was filtered in the field with a syringe-type filter forcing water through a $.45 \mu$ membrane filter. The filters were previously rinsed with stream water to prevent contamination. Particulate Organic Carbon (POC) levels were calculated by subtraction of DOC from TOC.

The sediment cores were oven dried overnight at $60^\circ C$. The sediment was then analyzed for the "percent readily oxidizable material" according to the Walkley and Black's chromic acid procedure (Jackson 1958). The sediment was also analyzed for acid extractable iron as outlined by L. M. Walsh (1971). Each core was analyzed individually for the first three sampling dates. A test was run to compare the average of five individual measurements from the five cores with a single measurement of a homogenous sample composed of an

aliquot from each of the five cores. This was done for each station. The single measurement was within 4% of the average five measurements. Hence, for the remaining sample dates the five dried cores were mixed in the lab and a single analysis was performed. The total phosphorous concentration was determined by the acid-heat digestion technique outlined in Standard Methods (Taras ed. 1971).

All statistical analysis was done by computer utilizing the Statistical Package for Social Sciences (SPSS) programs. Simple correlation and multiple regression comprised the majority of the analyses.

RESULTS AND DISCUSSION

The means, ranges, and standard deviations of the water quality parameters sampled are given in Tables 2 and 3 for both stations. The means, ranges, and standard deviations of the concentrations of the iron parameters, including both inorganic and organically complexed iron, are given in Table 4. The individual iron sample measurements are expressed graphically in comparison with flow rates and organic carbon concentrations in Figures 2-5 for both the swamp and channelized stations. The results of the statistical analysis are expressed as a correlation coefficient matrix (Tables 5 and 6) and as multiple regression equations (Table 7) noting F-values and significance levels.

The dynamics of the water quality parameters, especially in response to flow, are ultimately responsible for the manner in which each stream system handles its nutrients including iron. These dynamics, indicated by appropriate correlations, were found to be consistent with those expected in a typical swamp and channelized stream. In the swamp drainage system a period of rainfall increased the discharge relatively slowly. Higher flows lowered the conductivity, pH, and iron concentration and increased the dissolved oxygen. The organic carbon concentrations increased, but very slowly with a significant lag behind the pulse in flow. The channelized discharge responded very rapidly to a rainfall period. This rise in flow was accompanied by a decrease in pH, conductivity, and dissolved oxygen, but generally increased the iron concentration.

Table 2. The mean water quality values determined for the channelized and swamp stations.

	Channelized			Swamp		
	Mean	Range	SD	Mean	Range	SD
DO mg/l	7.90	5.0-16.33	3.29	3.47	1.3-4.8	1.18
pH	6.05	5.15-6.80	0.45	5.48	5.2-5.9	0.26
Cond umhos	70.80	4.60-110.0	25.78	34.14	26.0-48.0	7.38
Water temp °C	21.40	16.5-23.0	1.95	20.80	16.5-22.5	2.08
Flow m ³ /s	5.93	.22-19.2	6.58	1.01	.06-2.6	1.00
TOC mg/l	11.98	4.00-25.05	6.46	24.40	9.8-37.9	9.41
DOC mg/l	9.47	3.5-19.5	5.22	18.24	8.6-25.5	6.16
POC mg/l	2.51	.5-5.5	2.14	6.15	1.2-13.9	4.64

Table 3. The mean values of phosphate, extractable iron, and readily oxidizable material in sediment for the channelized and swamp stations.

	Channelized		Swamp	
	Mean	Range	Mean	Range
Total phosphate in mg/l	.32	.14-.87	.06	.03-.10
Extractable sediment iron in ppm	74	57-87	89	47-133
Readily oxidizable material	.09%	.05-.15%	33.9%	7.2-63.0%

Table 4. The mean iron values determined for the channelized and swamp stations.

Iron	Channelized			Swamp		
	Mean	Range	SD	Mean	Range	SD
Total mg/l	1.46	0.88-2.54	0.53	2.06	1.25-2.96	0.76
Dissolved mg/l	0.35	.19-.85	0.20	0.89	.56-1.24	0.23
Particulate mg/l	1.09	.65-2.27	0.47	1.17	.21-2.40	0.77
Total organic µg/l	30.30	3.90-51.00	18.90	48.00	7.60-92.11	0.40
Dissolved organic µg/l	27.80	1.80-50.00	17.40	53.60	5.00-90.00	40.50
Particulate organic µg/l	3.20	.50-8.00	2.70	5.50	1.05-18.50	6.50

Fig. 2. A comparison of organic carbon concentrations, iron concentrations, and flow measurements versus sampling days in the swamp.

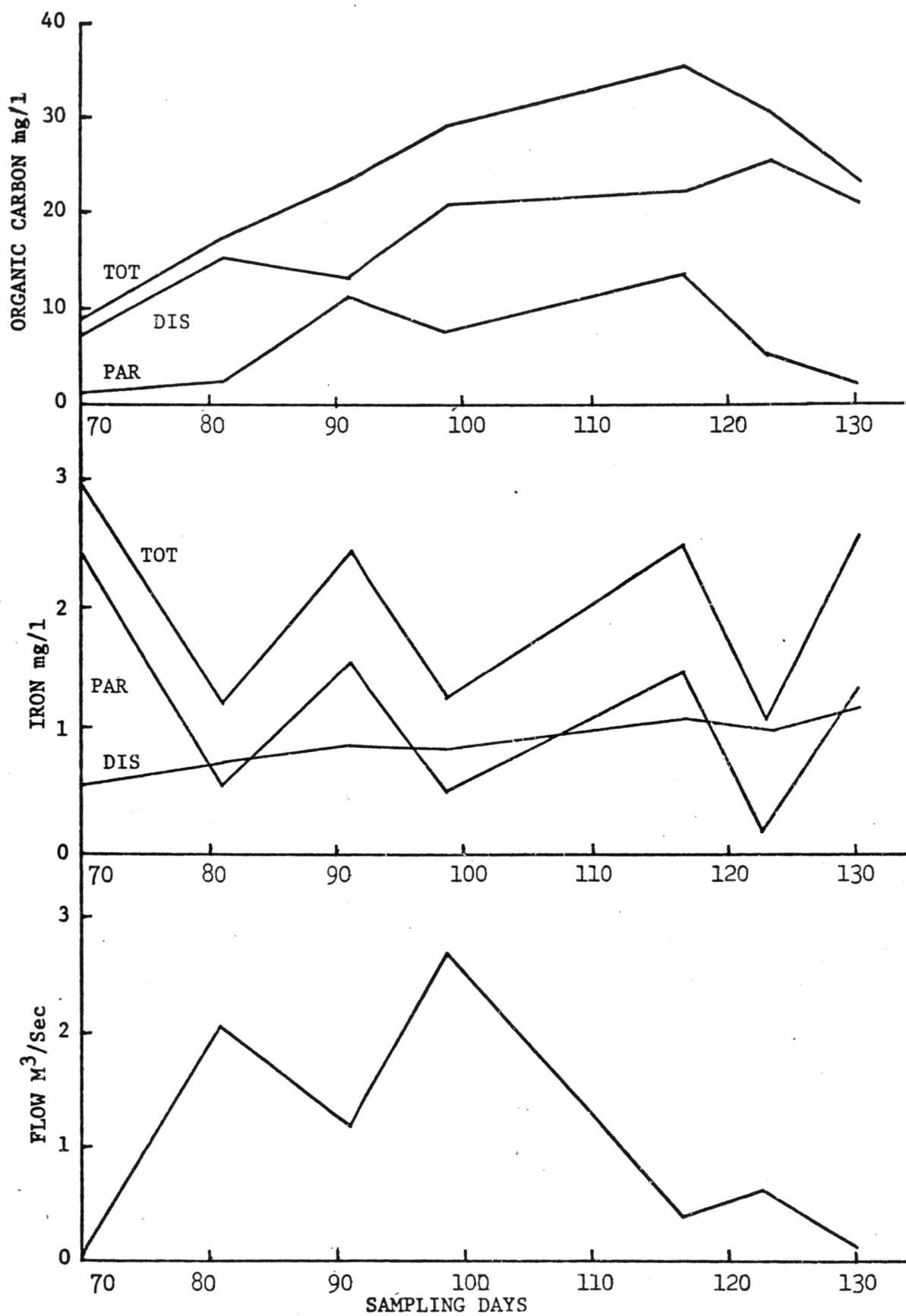


Fig. 3. A comparison of organic carbon concentrations, organically complexed iron concentrations, and flow measurements versus sampling days in the swamp.

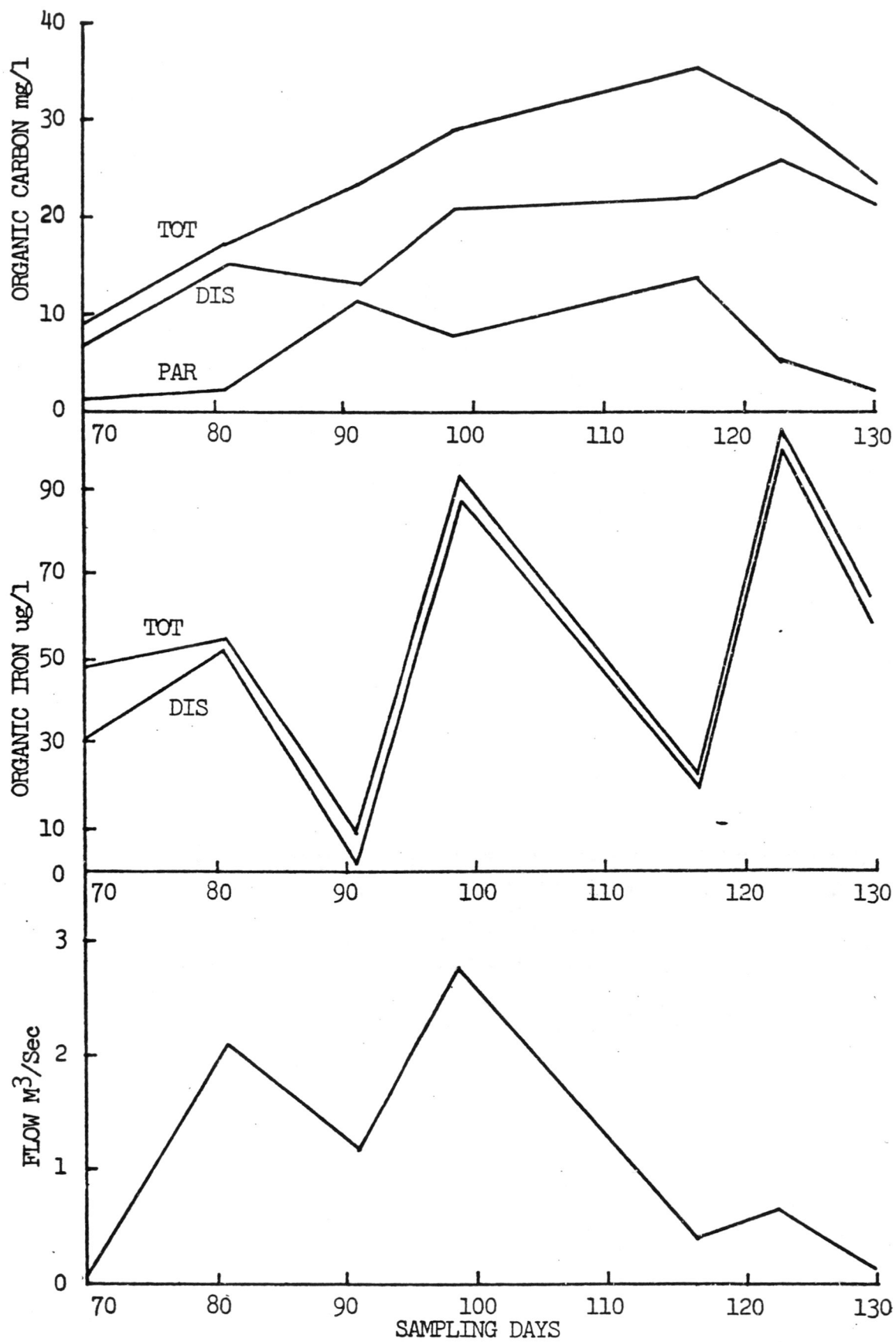


Fig. 4. A comparison of organic carbon concentrations, iron concentrations, and flow measurements versus sampling days in the channelized stream.

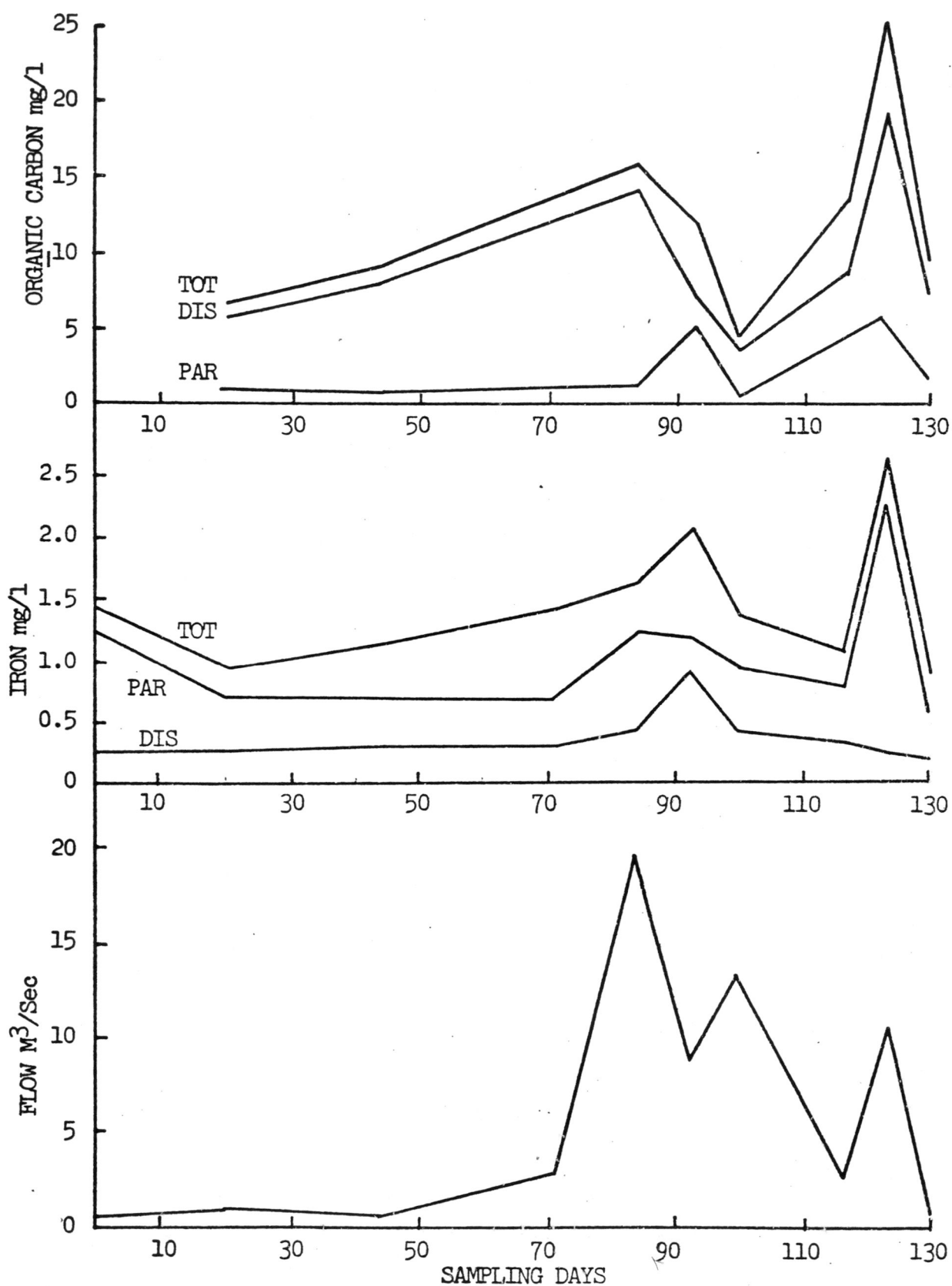


Fig. 5. A comparison of organic carbon concentrations, organically complexed iron concentrations, and flow measurements versus sampling days in the channelized stream.

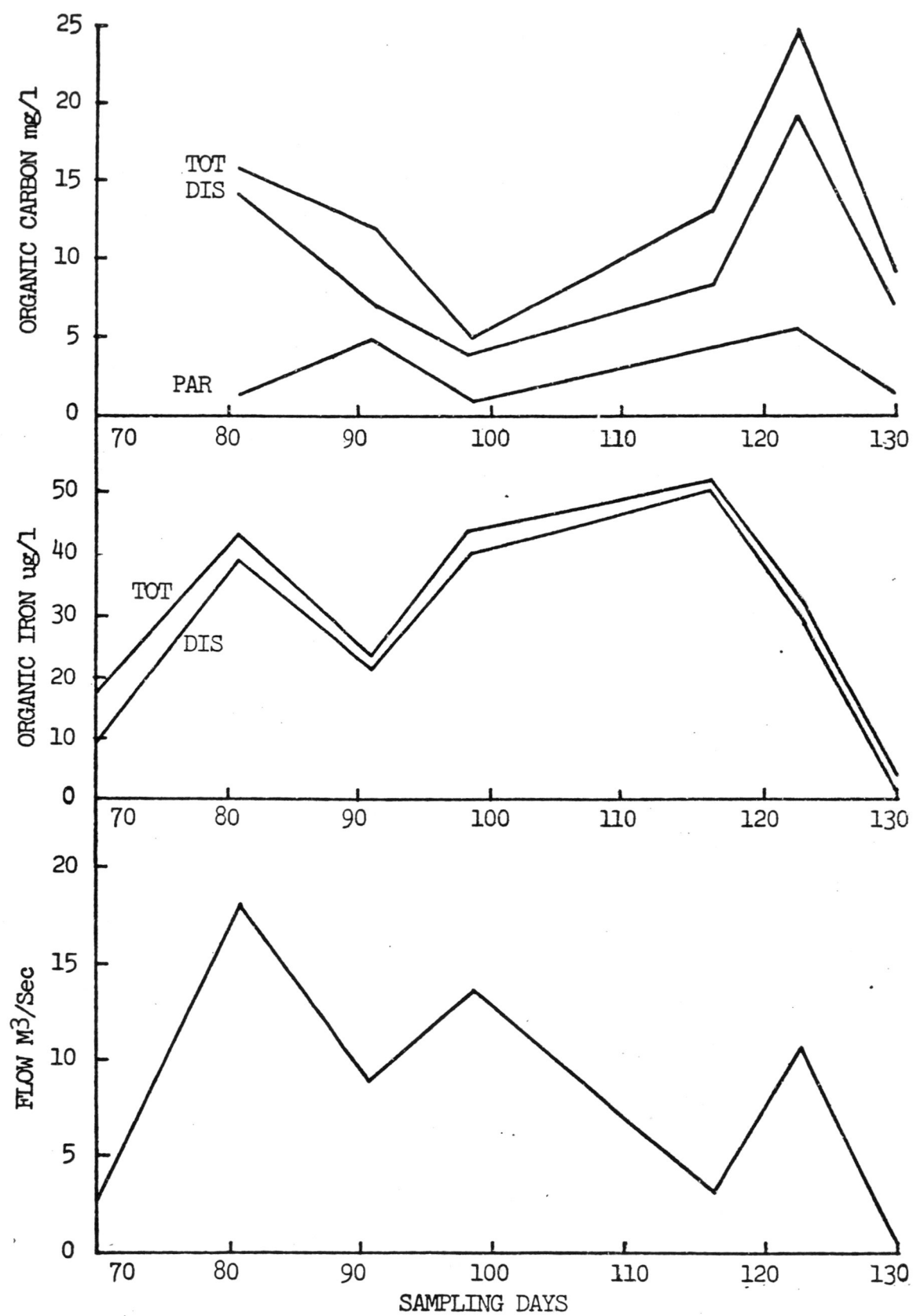


Table 5. Simple correlation coefficients for the swamp station.

	Total Fe	Dis. Fe	Part. Fe	Total org-Fe	Dis. org-Fe	Part. org-Fe	Dis. oxy.	pH	Cond	Water temp.	TOC	DOC	POC	Flow
Total Fe	1.0	.12	.95*	-.50	-.71*	.43	-.55	.17	.41	-.02	-.30	-.52	.07	-.68*
Dis. Fe	.12	1.0	-.17	.05	.17	-.63	.15	.44	-.23	-.71*	.58	.61	.36	-.31
Part. Fe	.95*	-.17	1.0	-.49	-.76*	.67*	-.59	.04	.48	.18	-.48	-.70*	-.03	-.58
Tot. org-Fe	-.50	-.05	-.49	1.0	.97*	.06	.11	-.61	.04	-.54	.13	.23	-.53	.45
Dis. org-Fe	-.71*	.17	-.76*	.97*	1.0	-.14	.03	.03	.07	-.38	.25	.61	-.28	.19
Part. org-Fe	.43	-.63	.67	.06	-.14	1.0	-.81*	-.12	.86*	.28	.80*	-.79*	-.64	-.45
Dis. oxygen	-.55	.15	-.59	.11	.03	-.81*	1.0	-.44	-.96*	-.16	.28	.26	.23	.77*
pH	.17	.44	.04	-.61	.03	-.12	-.44	1.0	.35	.16	.59	.50	.54	-.62
Cond	.41	-.23	.48	.04	.07	.86*	-.96*	.35	1.0	.13	-.36	-.25	-.38	-.69*
Water temp	-.02	-.71*	.18	-.54	-.38	.28	-.16	.16	.13	1.0	-.04	-.29	.28	.09
TOC	-.30	.58	-.48	-.13	.25	-.80*	.28	.59	-.36	-.04	1.0	.90*	.82*	.14
DOC	-.52	.61	-.70*	.23	.61	-.79*	.26	.50	-.25	-.29	.90*	1.0	.50	.17
POC	.07	.36	-.03	-.53	-.28	-.64	.23	.54	-.38	.28	.82*	.50	1.0	.07
Flow	-.68*	-.31	-.58	.45	.19	-.45	.77*	-.62	-.69*	.09	.14	.17	.07	1.0

* significant at the 95% level

Table 6. Simple correlation coefficients for the channelized station.

	Total Fe	Dis. Fe	Part. Fe	Total org-Fe	Dis. org-Fe	Part. org-Fe	Dis. oxy.	pH	Cond	Water temp	TOC	DOC	POC	Flow
Total Fe	1.0	.49	.91*	-.10	-.10	-.09	-.21	-.12	-.62*	.45	.72*	.63*	.63*	.51
Dis. Fe	.49	1.0	.11	.19	.20	-.40	-.51	-.47	-.48	.45	-.01	-.12	.29	.53
Part. Fe	.91*	.11	1.0	-.09	.01	-.27	.01	.12	-.47	.29	.86*	.81*	.63*	.31
Tot. org-Fe	.10	.19	-.09	1.0	.98*	-.15	-.61*	-.25	-.07	.74*	.15	.10	.12	.54
Dis. org-Fe	.10	.20	.01	.98*	1.0	-.30	-.57*	-.22	-.01	.68*	.09	.05	.14	.52
Part. org-Fe	-.09	-.40	-.27	-.15	-.30	1.0	.02	.18	-.42	.14	-.52	-.10	-.90*	-.02
Dis. oxygen	-.21	-.51	.01	-.61*	-.57	.02	1.0	.63*	.43	-.20	-.11	-.07	-.16	-.61*
pH	-.12	-.47	.12	-.25	-.22	.18	.63*	1.0	.34	.06	.25	.29	.05	-.57*
Cond	-.62*	-.48	-.47	-.07	-.01	-.42	.43	.34	1.0	-.32	-.24	-.23	-.14	-.64*
Water temp	.45	.45	.29	.74*	.68*	.14	-.20	.06	-.32	1.0	.21	.16	.23	.41
TOC	.72*	-.01	.86*	.15	.09	-.52	-.11	.25	-.24	.21	1.0	.95*	.68*	.29
DOC	.63*	-.12	.81*	.10	.05	-.10	-.07	.29	-.23	.16	.95*	1.0	.43	.38
POC	.63*	.29	.63*	.12	.15	-.90*	-.16	.05	-.14	.23	.68*	.43	1.0	-.05
Flow	.51	.53	.31	.54	.52	-.02	-.61*	-.57*	-.64*	.41	.29	.38	-.05	1.0

* significant at the 95% level

Table 7. Multiple regression equations.

Channelized Station

1. Total Organic-Fe = $-.00037(\text{Log-Flow}) + .0064(\text{Water temp.}) - .0028(\text{DO}) - .083$
N.S. F= 2.41 D.F.= 3/2 R²= .78
2. Particulate Fe = $.05(\text{TOC}) - .007(\text{Conductivity}) + .04(\text{DO}) + 0.6$
98% Sign. F= 11.07 D.F.= 3/4 R²= .89
3. Particulate Fe = $.06(\text{TOC}) - .007(\text{Conductivity}) + .04(\text{DO}) - .24(\text{pH}) + 1.79$
90% Sign. F= 8.39 D.F.= 4/3 R²= .92
4. Organic-Fe Discharge gr/s = $-37.9(\text{DO}) + 38.1(\text{Flow}) + 377.0$
99% Sign. F= 31.15 D.F.= 2/3 R²= .83
5. Total Fe = $1.03(\text{Part. Fe}) + 0.33$
99% Sign. F= 42.6 D.F.= 1/8 R²= .82

Swamp Station

6. Dissolved Fe = $-.088(\text{Water temp.}) + .55(\text{pH}) - .032(\text{Conductivity}) - .13(\text{DO}) + 1.23$
99% Sign. F= 110.76 D.F.= 4/2 R²= .99
7. Percentage of total Fe bound organically = $1.83(\text{Flow}) - .34(\text{POC}) + .22(\text{DOC}) - 1.02$
99% Sign. F= 321.37 D.F.= 3/2 R²= .99
8. Total Organic-Fe = $-.086(\text{pH}) + .0045(\text{DOC}) - .0038(\text{POC}) + .46$
99% Sign. F= 98.05 D.F.= 3/2 R²= .99
9. Total Fe = $.94(\text{part. Fe}) + .95$
99% Sign. F= 51.6 D.F.= 1/5 R²= .91
10. Total Organic-Fe = $1.04(\text{Dissolved Organic-Fe}) + .003$
90% Sign. F= 9.7 D.F.= 4/3 R²= .94

Variable	Units	Variable	Units
All Fe Parameters	mg/l	Conductivity	umhos
Dissolved Oxygen	mg/l	TOC	mg/l
Water temp.	°C.	DOC	mg/l
Flow	m ³ /s	POC	mg/l

Total Iron

The mean total iron concentration of the swamp was 41% higher than that of the channelized stream. The concentrations in both systems were high compared to other areas of the country. Martin et al. (1971) found total iron commonly between 0.3 - 1.0 mg/l in fourteen gulf coast Florida streams. Silvey (1960) found an average of .03 mg/l in some California natural waters. Angino et al. (1969) found .01 - 0.8 mg/l in the lower Kansas River basin.

In order to assess the factors influencing total iron in the two systems we must look at the particulate and dissolved fractions. The simple correlations between the particulate iron and the dissolved iron in the channelized stream and swamp respectively are 0.11 and -0.17. This low correlation indicates that the two fractions are influenced by different factors. The two fractions will be presented separately.

In the swamp the particulate iron fraction accounted for 90.2% of the variation in the total iron concentration (Table 7, Equation 9). Both total iron and particulate iron had negative correlations with flow (Table 5). Particulate Organic Carbon (POC) was used as an indicator of the total particulate content. The graph of POC and flow versus time (Fig. 2) shows that in this swamp drainage system a rise in particulate matter, in response to a pulse in flow, may lag significantly behind the flow increase. This lag is probably due to the relatively slow velocity of the swamp discharge. High flow has the immediate effect of dilution, but causes a subsequent rise in

particulate concentration, hence the inverse correlation between flow and iron concentration.

The effect of pH, conductivity, and dissolved oxygen on total and particulate iron concentrations in the swamp was considered. High flow was accompanied by decreases in pH and conductivity and an increase in dissolved oxygen (Table 5). A pH decrease would increase the solubility of iron (Stumm 1970). A decrease in conductivity would decrease cation competition for sites on particulate matter (Jenne 1968). An increase in dissolved oxygen would increase formation of insoluble hydroxides and oxides (Stumm 1970). The combined effects of these during high flow were considered. Single and multiple regressions were used to compare total iron and particulate iron concentrations with these factors. No combination yielded significant F-values.

In sharp contrast to the swamp station, the channelized total iron concentration varied positively with flow (Table 6). Similar to the swamp station, 82% of the variation in the total iron concentration may be explained by the particulate iron fraction (Table 7, Equation 5). Therefore, a study of total iron variances is basically a study of the particulate iron variances. A mean of 75% of the total iron was bound particulate.

Particulate bound iron in the channelized stream had a low correlation with flow, but correlations with POC (.63), TOC (.86), and DOC (.81) were quite high. The high correlation with TOC was unexpected because the organic carbon in the channelized area was relatively low plus the fact that only 20% of the already low organic

carbon is in the particulate state. This low level of organic matter with its bound iron was not expected to be a direct contributor of iron to the particulate iron levels. Possibly it was an indirect contributor or just coincidentally parallel. I propose that these high correlations may reflect that the organic carbon levels are indicative of the total particulate levels of the stream. It is this relationship that results in a high correlation between organic carbon and particulate iron.

Single linear regression showed no significant correlation between particulate iron and pH, conductivity, or dissolved oxygen in the channelized area; multiple regression did show significance. The regression of particulate iron with TOC, conductivity, and dissolved oxygen was significant at the 98% level (Table 7, Equation 2). The addition of pH data lowered the significance to the 90% level (Table 7, Equation 3). The regression equation signs of TOC, conductivity, and pH correspond to those found during high flow periods. The sign of dissolved oxygen did not. Oxygen's positive sign illustrates its effect of removing iron from the dissolved state by formation of oxides which adhere to particulate matter and increase the particulate bound iron fraction. We see now that in the channelized stream all the characteristics of high flow, except for the lowering of dissolved oxygen, increase the particulate and therefore total iron levels.

The dissolved iron concentration in the swamp was 48% of the total iron concentration. The graph of the dissolved iron fraction (Fig. 2) shows a gradual slope with an increase corresponding to a

rather continuous high flow during the month of August (sample days 71-102). The increase continues in spite of declining flow during the next twenty days. I propose that much of this fraction is the result of ground water input. Swamp and lowland ground water are acid due to high hydrogen sulfide and carbonic acid content (Ruttner 1953). This acidity, along with the reducing power of organic matter in the soil strata of the drainage basin, results in significant mineralization and iron release into the ground water. The pulse of ground water would be more dampened than the surface flow pulse following high flow, resulting in the slow continuous rise of its dissolved iron input into the swamp. The slow rise of dissolved iron on the graph is evidence of this.

The gradual slope of the dissolved iron level also corresponds with the increase in dissolved organic carbon. The correlation coefficient is $+0.61$. Contrary to this positive correlation, the last three sampling dates show a distinct inverse correlation. Thus the significance of dissolved organic carbon's contribution to dissolved iron levels is questionable. The dissolved iron fraction significantly varies with changes in pH, dissolved oxygen, water temperature, and conductivity. Multiple regression yields 99% significance between dissolved iron and these factors (Table 7, Equation 6). As a comparison to the study's dissolved iron readings, data gathered by a division of the USGS on the concentration of iron in ground water near the swamp station shows much variability with a range of $.03 - 10.0$ mg/l (Sumsion 1970). The average amount is well

over that amount of dissolved iron found in the surface water. This is expected because of rapid oxidation and precipitation of dissolved iron once it reaches the surface.

In the channelized area only 24% of the total iron was dissolved. In contrast to the swamp, an analysis of variance in the dissolved fraction yielded few significant correlations with TOC, DOC, or POC. The factors correlating highest with dissolved iron were flow (.53) and dissolved oxygen (-.51). Hence, these would be the most likely choices as the major controls of dissolved iron concentrations. These controls were not verified by significant regression levels. Multiple regression of dissolved iron with flow, pH, dissolved oxygen, and conductivity also did not yield significant values.

In view of the results and statistical analysis presented thus far, we can now consider the similarities and differences in how these two systems handle the iron present. The differences result from the fact that the swamp is a more acidic, lower oxygenated, highly organic system which responds slowly to rainfall with a slower water velocity. The channelized stream is a quick responding, less acidic, less organic and more oxygenated system.

Both systems maintain the highest proportion of the iron in the particulate fraction, but the ratio of particulate to dissolved iron is greater in the channelized area. In both systems this logically must presume the presence of particulate matter and conditions favoring precipitation of iron. The channelized system maintained more suspended matter indicated by higher turbidity (oral communication 1974 with Jay W. Chapin, Department of Biology Graduate, East Carolina

University, Greenville, N. C.) which was probably a result of the observed greater water velocity. The higher pH and dissolved oxygen levels of the channelized stream also favor precipitation of iron (Stumm 1970).

The response of the total iron concentration to increased rainfall and flow was different in the two systems. The swamp iron concentration went down and the channelized stream iron concentration went up. I propose that the swamp iron concentration decreased because positive changes in pH and dissolved oxygen favor precipitation while the system's response to drainage and water velocity was too slow to suspend the iron and overcome the dilution factor. However, in the channelized stream changes in the pH and dissolved oxygen favored dissolution and thereby greater transport of iron. Also the water velocity favored greater transport of particulate matter with its bound iron. Therefore, in the channelized stream the iron concentration increased with high flow.

The streams have both similarities and differences as to how they discharge iron quantitatively. In both streams the discharge of iron in milligrams per second is very highly correlated positively with flow. Of the two systems studied, the channelized stream exported an order of magnitude more iron than the swamp; this is probably due to the larger drainage area of the channelized stream chosen. The question arises, does a swamp inherently discharge more or less iron than a channelized area? Given the same geology and drainage area, I believe that the swamp would discharge more iron in a given interval of time. This is because the pH and dissolved

oxygen conditions in the swamp are more favorable for dissolution and mineralization, therefore favorable for iron transport. However, the greater ability of a channelized stream to transport iron trapped in the crystalline lattice of suspended sediment must be considered. This iron was not selectively measured in this study. The present data does not conclusively resolve the previous question, but it does suggest the following concept as to discharge.

The channelized drainage basin was observed to rapidly flush after a given rainfall and thereby discharge large quantities of runoff quite rapidly. The swamp discharges a pulse of runoff quite slowly. This is due to morphology. The present data indicates that the effects of this large, rapid pulse of discharge from the channelized stream is further amplified by the change in water chemistry during high flow. As previously noted, when the flow increases the iron concentration increases in the channelized stream. In the swamp when the flow goes up, the iron concentration decreases. There is still a rise in discharge of iron in the swamp, but the decrease in concentration keeps this rise from being as bold as in the channelized area. This relationship is due to changes in the water which affect solubility. When the flow goes up in the channelized area the conditions are favorable for bringing more iron into solution. The particulate levels, which are known to be important in iron transport, also increase. This even further emphasizes the magnitude of iron discharge during a pulse in flow. In summary when the flow increases, both systems discharge more iron but in the channelized system the concentration also goes up. Therefore, an increase in

discharge is amplified in the channelized stream and dampened in the swamp.

The significance of this characteristic of a channelized stream is difficult to pin down. Most environmentalists would consider this a negative aspect because the organisms at the mouth of the stream are subjected periodically to large, rapid influxes of suspended materials and dissolved solids. Favorably, contaminants would be removed from a drainage basin very quickly.

Organically Complexed Iron

Between 0.3% and 6.7% of the total iron in the swamp was complexed organically. The variance in this percentage showed particularly low correlations with organic carbon concentrations; when the organic carbon readings were qualified with flow readings in a multiple regression, 99.7% of the variation of this percentage was explained at the 99% significance level (Table 7, Equation 7). Note particularly that in this equation POC has a negative sign and DOC has a positive sign. The importance of this will be noted below.

A mean of 84% of the total organic-iron is dissolved. This dissolved fraction accounts for 94% of the variation in the total organic-iron (Table 7, Equation 10). Figure 3 clearly shows the close parallel between the dissolved and total concentrations. Figure 3 also shows that there is a definite lag of the organic carbon increase behind a period of high flow. Why does the total organically complexed iron concentrations not parallel the total organic carbon concentrations as one might expect? I propose that this does not happen because DOC

and POC correlated negatively with total, dissolved, and particulate organic-iron (Table 5). If POC is taken as an indicator of the total particulates then I believe that an increase in particulate matter with its high affinity for metallic oxides is responsible for transfer of the electrostatically bound iron from the organic complexes to the inorganic particulate matter. This would mean that particulate matter is a negative control on organically bound iron. More evidence for this effect of inorganic particulate matter is the negative correlation between organically complexed iron and inorganic particulate iron (Table 5). Then the particulate iron goes up (indicating a rise in the total particulate content) and the organically complexed iron goes down.

The control of total organically complexed iron is indicated to be not only influenced by particulate matter but also modified by DOC and pH. DOC and dissolved organically complexed iron have a positive correlation. This correlation would logically be due to organic matter's known capacity for iron chelation (Jenne 1968) both in living organisms and aquatic systems. We now see that the concentration of organically complexed iron is influenced positively by DOC and negatively by particulate matter. In addition to these controls, as the pH decreases, organically complexed iron increases (-.61). I propose that the acidity keeps iron in solution and more available for chelation by organic matter. These cause and effect relationships between organically complexed iron and pH, DOC, and POC are verified by regression. A multiple regression of organically complexed iron with pH, DOC, and POC gave 99% significance (Table 7

Equation 8). Dissolved oxygen and conductivity showed no significant correlations with total organic-iron.

The instantaneous discharge load of organically complexed iron in the swamp varied 100 fold during the sampling period. The increased concentration of organically complexed iron during high flow periods was responsible for this large variation. The discharge load of total inorganic iron varied only 37 fold because flow and concentration were inversely correlated. An average of 4% of the iron discharged from the swamp was organically complexed, but the average concentration of organic-iron was only 2.7% of the total iron concentration.

In the channelized stream, the percentage of the total iron that was organically complexed averaged 2.2%. This was .5% less than that in the swamp, probably due to the lower organic carbon content of the channelized stream. The total organically complexed iron concentration correlated most highly with water temperature, dissolved oxygen, and flow. An increase in flow paralleled an increase in organic-iron (+.53). Multiple regression to total organic-iron with dissolved oxygen, water temperature, and flow yielded no significant F-values. Notably the correlations in the channelized stream of total organic-iron with TOC, DOC, and POC were very low. An average of 82% of the total organic-iron was in the dissolved fraction. Variations in this fraction accounted for 96% of the variations of the total. This is clearly shown in Fig. 5. Regression of dissolved organic-iron with dissolved oxygen and flow gave no significant results.

The particulate bound organic-iron in the channelized stream had a very high inverse correlation with POC ($-.90$). There were also negative correlations with TOC ($-.52$) and inorganic particulate iron ($-.69$). I again propose that POC and particulate iron levels are indicative of the total particulate content. As in the swamp, it would appear that particulate matter is a major controlling factor. As particulate matter goes up, the concentration of particulate organic-iron goes down. The logical, positive effect of POC on particulate organic-iron is negated by the simultaneous rise and negative effect of other particulates as explained for the swamp. The lack of correlation between particulate organic-iron and flow further emphasizes that particulate organic-iron concentrations are specifically governed by particulate levels which do not always correspond directly with flow readings.

The total organic-iron discharge in the channelized stream varied closely with flow ($.97$) and inversely with dissolved oxygen ($-.83$). A rise in dissolved oxygen paralleled a decrease in the total organic-iron discharge load rate. A multiple regression yielded 99% significance to the correlation of organic-iron discharge with dissolved oxygen and flow (Table 7, Equation 4). It should be noted that the true effects of dissolved oxygen are not proven. Dissolved oxygen may have no effect on organic-iron discharge, but still appear in the regression equation due to its significant correlation with flow ($-.61$). Nevertheless, I speculate that since the majority of the organically bound iron is dissolved, it is susceptible to the precipitation effects of a rising dissolved

oxygen content.

The role of organic carbon as a control in both these systems is either as a direct contributor of bound iron or as an agent which produces a more reducing environment. This reducing environment would put more iron into solution. TOC, DOC, and POC concentrations were shown to have only a few significant correlations with some of the iron fractions studied including iron discharge rates. Most of the evidence from the data indicates that the major role is usually that of producing a reducing environment, rather than being a direct contributor to the total iron content. The strongest evidence against direct contribution is the experimental finding that a mean of only 2.5% of the total iron is organically bound. In the swamp, which had the most abundant organic carbon, there were no positive correlations of total organic carbon with total iron, total organic iron, or the discharge load of iron. In the channelized section, no aspect of the organic-iron was found to be correlated positively with organic carbon concentrations. The two major exceptions to this evidence are a +.72 correlation between TOC and total iron in the channelized section and a +.61 correlation between dissolved organic-iron and DOC in the swamp. Even in view of these exceptions, I believe that organic carbon's major role is that of producing a reducing environment. This maintenance of a reducing environment may be the major reason the iron concentrations are higher in the swamp with its greater mean organic content.

A discussion of the major controls, especially organic matter, brings us to the concern of biological significance. Although

biological availability is difficult to define, there are some factors which probably increase availability. In the case of iron, solubility is of utmost importance. The data presented had shown that the swamp has more iron in solution. The mean values of the iron concentrations also show iron to be more abundant in the swamp, but the significance of apparent greater availability is questionable. In addition to having more iron in solution, the swamp also has more iron organically complexed. This complexation adds to the ease of organismic utilization. The swamp has 50% more organic-iron than the channelized section, but this is only a difference of .02 mg Fe/l. Johnston (1964) states that the concentration of organic matter should also be considered, pertaining to availability, since some organic chelators can make iron available to an organism without the matter itself being assimilated. The organic molecule may then recycle. He believes that as little as .05 mg of carbon per liter can maintain optimum availability of iron to marine plankton. There is far more organic carbon than this in both the swamp and channelized streams.

Data comparable to this study's data on the concentration of organically complexed iron is rare. Table 8 gives a brief comparison of the data published by R. T. Gibbs (1973) for the Yukon and Amazon rivers and by Ralph M. Perhac (1972) from two streams in Tennessee. Notably the Amazon and Yukon transport very small percentages of iron in the dissolved state. This was probably due to a large suspended load. The effects of particulate matter have been previously pointed out. The high percentage of iron carried by organic solids also indicates the influence of a large suspended load. The data from

Table 8. A comparison of the measured percentages of iron transported by five different river systems.

Iron	Gibbs(1973)		Perhac(1974)	Vodopich	
	Amazon	Yukon		N.C.	
			Tenn.	Swamp	Channelized
Dissolved	0.7	.05	19.6	49.0	24.4
Particulate	99.3	99.5	80.4	51.0	75.6
Dissolved organic				2.4	1.9
Particulate organic	11.0	11.0		0.2	0.3

the Tennessee River is more on the order of that found in this study. Certainly the major conclusions to draw from this comparison are that variability between systems is high and that particulate matter again is shown to be an important control.

The data gathered still does not resolve the question of pH and its control on organically complexed iron, as expressed by Ghassemi and Christman (1968) and Shapiro (1964). Ghassemi states that the optimum pH for organic color coagulation with iron is 4.5-5.5 for most natural waters. The swamp had a pH range of 5.2-5.9 and had a higher organic-iron concentration than the channelized system of pH 5.8-6.8. This agrees with Ghassemi's pH range; however, I have previously noted the inability in establishing pH as the dominating control.

Shapiro (1964) states that a pH increase up to 10.0 would increase organic chelation. The data presented here shows a negative correlation between pH and organic-iron both in the swamp and channelized streams, and therefore contradicts Shapiro's generalization.

SUMMARY

The two streams involved in this study are quite different in their morphology and basic water quality parameters. The differences in the water quality parameters are obvious after a brief comparison of the means of these water quality values (Tables 2 and 3) and are consistent with those one would expect to find in a typical swamp and channelized stream. The dynamics of these parameters, especially in response to flow are ultimately responsible for the manner in which each stream system handles its nutrients including iron.

Considering these differences, do the systems fractionate and discharge iron differently? Yes, they do in terms of the quality of speciation. The swamp maintains a higher concentration of total iron than the channelized segment. The swamp also maintains an average of twice as much iron in the dissolved fraction. There is also more organically bound iron in the swamp, but the percentage that is dissolved is about the same in both the channelized and swamp streams.

In both streams the discharge of iron in milligrams per second is very highly correlated with flow. The channelized stream exported an order of magnitude more iron than the swamp; this may be due to the larger drainage area of the channelized stream chosen. It was indicated that the effects of a large, rapid pulse of discharge from the channelized stream is further amplified by the change in water chemistry during high flow. The significance of this characteristic is debatable.

The specific parameters which control the partitioning of iron are difficult to determine. All of the parameters were shown to be significant in regards to control of at least one or two of the various iron parameters measured. The major importance of high flow with all its inherent characteristics was to increase the removal of iron, including organically complexed iron, from the drainage basin. Variations of flow in both systems were also accompanied by changes in dissolved oxygen, pH, conductivity, and organic carbon. In the channelized stream, rises in dissolved oxygen had a negative effect on the solubility of the total, dissolved, and particulate iron fractions as well as the total organic-iron fraction. The dissolved iron fraction in the swamp was also shown to vary significantly with dissolved oxygen. The variance in pH was recognized as being a significant control only in the swamp, specifically for the dissolved iron and organic-iron fractions. The pH was not shown to be a dominating control on organically complexed iron, but did show a negative correlation in both the swamp and channelized areas. This contradicts the positive correlation found by previous workers within the pH range studied.

Total particulate matter was indicated numerous times to be a control. In both the swamp and channelized systems, most of the total iron was in the particulate fraction. Although most of the organically bound iron was dissolved, it is believed that other forms still played an important negative role. The general effect of inorganic particulate matter was to adsorb a large percentage of

the iron present. The inorganic particulate matter adsorbed iron so strongly as to remove it from the organic particulates.

Organic carbon and its fractions were shown to have significant correlations with at least some of the iron fractions studied, including iron discharge rates. Most of the evidence from the data indicates that the major role is to produce a reducing environment rather than being a direct contributor of complexed iron. The strongest evidence against direct contribution is the experimental finding that a mean of only 2.5% of the total iron is organically bound. This major role of organic matter may be the major reason the iron concentrations are higher in the swamp.

CONCLUSIONS

1. The swamp has a higher iron content than the channelized stream, probably due to the inherent reducing environment.
2. The amount of iron bound organically was successfully measured to be 0.2-4.7% of the total iron in the channelized stream and 0.8-6.7% of the total iron in the swamp.
3. Most of the organically complexed iron is dissolved.
4. Particulate matter may be the dominating control on iron speciation within a stream system.
5. The pulse of iron discharge in a channelized stream is amplified by a rise in iron concentration during high flow periods. The opposite is true for the swamp.
6. Rainfall and runoff control the discharge of iron from a watershed.
7. Iron is more biologically available as a nutrient in the swamp than in the channelized stream.
8. The major role of a higher concentration of organic carbon in the swamp is probably the maintaining of a strongly reducing environment, rather than serving as a quantitatively large binder of iron.

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