THE BIOAVAILABILITY OF PHOSPHORUS IN THE AVON RIVER

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TO: IN STREAM COMMITTEE
STRATFORD AVON ENVIRONMENTAL MANAGEMENT
COMMITTEE

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INTRODUCTION

A report to the International Joint Commission in 1980 identified a number of information needs regarding phosphorus management strategies for the Great Lakes. One of the requirements for obtaining an increased ability in defining phosphorus management strategies was a better understanding of the bioavailability of various forms of phosphorus.

Historically, the majority of studies have focussed on values of total phosphorus concentration and/or loads. In the past decade several studies (DePinto *et al.* 1981, Williams *et al.* 1980, Cowen and Lee 1976, Sagher 1976) have indicated that algal cultures do not utilize all forms of phosphorus. Therefore, when this historical TP data is used in the development of phosphorus load regulations for controlling eutrophication a number of inadequacies surface. The total phosphorus parameter may be of little relevance to the problem, but what is of concern is that portion, or the forms of P which are available for plant growth and metabolism.

Analytically, phosphorus can be defined as soluble and particulate fractions. It is readily accepted that the soluble orthophosphate is available to algae and other aquatic macrophytes (Logan, 1982). Yet the particulate fraction is composed of a variety of forms of P, not all of which are utilized for plant metabolism.

Chemical fractionation of particulate phosphorus identifies three forms - organic, apatite and non-apatite inorganic. To date laboratory studies on lake sediments and lake tributary suspended sediments indicate that apatite (the mineral form of calcium phosphates) is generally unavailable, organic forms are available to some extent over longer time periods (weeks to months) and that some fraction of the non-apatite inorganic form is readily available for plant use (Williams *et al.* 1980). A schematic diagram indicating the general relationships between P forms and algae is presented in Figure 1.

In order to delineate cost effective management strategies, which will result in reduced phosphorus loadings it is necessary to obtain more information regarding the available phosphorus fractions. This would include an analytical technique for determining the available portion as well as an understanding of the sources, fluxes and temporal variability of biologically available P (BAP).

The availability of particulate phosphorus to algae can be determined by various bioassay procedures. These techniques are costly and time consuming and therefore have led to investigations of the correlation between BAP and chemical phosphorus fractions (Canviro 1982, DePinto *et al.* 1981, Williams *et al.* 1980, Cowen and Lee 1976, Sagher *et al.* 1975, Golterman *et al.* 1969).

While available P has not been found to be in constant proportion to the total sediment P it has been directly related to the non-apatite inorganic (NAIP) fraction (Williams *et al.* 1980). In a widely used fractionation scheme developed by Williams (1976) NAIP is determined with two chemical extraction procedures using NaOH and CDB (citrate dithionite bicarbonate). While they both extract aluminum and iron associated inorganic phosphorus as well as loosely adsorbed P, the CDB extraction is considered to be more rigorous (Canviro, 1982).

Logan *et al.* 1979 considered NaOH-P to be the short term bioavailable fraction while the sum of NaOH-P and CDB-P (NAIP) was considered to be potentially available over longer periods of time. The inorganic portion of the base extractable particulate phosphorus has been noted to have a relatively high biological availability in a number of bioassays (Williams *et al.* 1980, Cowen and Lee 1976, Sagher *et al.* 1975). DePinto *et al.* (1981) used the same chemical fractionation technique as Logan (1979) and compared these values to algal uptake. They found that both the NaOH and CDB fractions correlated significantly with short term biological uptake.

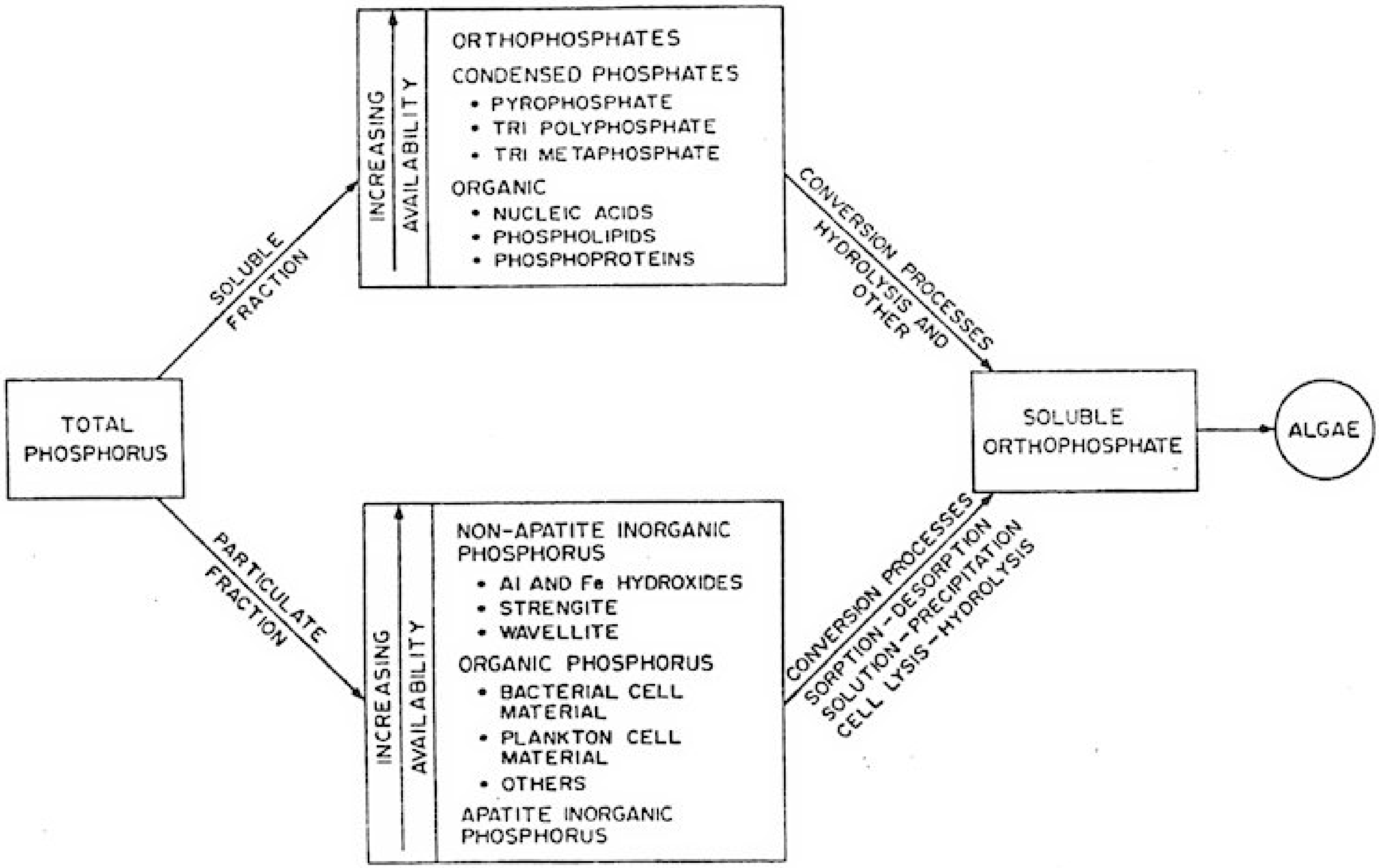


FIGURE 1: Generalized Relationship Between Phosphorus Forms And Algae Availability [From Canviro,1982]

It was apparent from their data that while the rate of release for these two fractions could be different, they were both contributing phosphorus which was utilized by the algae.

Phosphorus inputs to a stream system are a function of three major factors, basin geochemistry (Logan, 1978) land use activities (Omernik 1976) and agricultural practices (Logan, 1977). Three quarters of the diffuse source P loadings to the lower Great Lakes have been noted to be sediment related, with the majority of this material moving in high flow events (Army Corps of Engineers, 1979). The proportion of tributary point source loadings to the lake (both particulate and soluble) is a function of the type of activity discharging effluent and its location in the watershed.

Several studies on Great Lakes tributary basin sediments have attempted to determine the proportion of the sediment P load which is biologically available (DePinto *et al.* 1981, Victore 1981, Logan *et al.* 1979). Victore (1981), sampled five Lake Erie watersheds several times during high flow events and found that TP content of the suspended sediments showed little variation among samples from a given tributary. Greater variation existed among TP samples from different tributaries. This pattern was also evident for the chemically defined P fractions.

Logan *et al.* (1979) analyzed 36 Lake Erie tributaries and sampled predominantly during high flows. He found that the biologically available phosphorus estimated by NaOH-P varied from 30-42% of the total sediment inorganic P, whereas the NAIP portion represented 75-89% of that fraction. DePinto *et al.* (1981), studied the same watersheds as Victore and found BAP (by algal uptake) to range between 6-35% of the total particulate phosphorus. The variability of BAP in the sediment load of a watershed can be seen to be a function of the composition of the sediments, which involves the relationships between the organic, mineral and particle sizes of the particulates.

Studies of wastewater particulate BAP have been carried out by Canviro 1982, Young *et al.* 1982, and DePinto 1980. Young, sampling before, during and after treatment at four sewage treatment plants in the Great Lakes basin found on average that 63% of the total particulate phosphorus was available to algae. DePinto *et al.* (1980), observed that a range of 30-85% of the total particulate P was bioavailable. In this study it was concluded that the various methods of treatment used in the plants to reduce phosphorus had little effect on the relative proportion of BAP to TP. The recent study by Canviro (1982) which compared nine sewage treatment plants in Southern Ontario indicated that digester supernatant (contents) particulates had the highest proportion of BAP (50% of TP) while influent particulates had the lowest proportion of BAP (36% of TP). The BAP of the primary, secondary and filtered effluents generally fell between these values.

The focus of the above mentioned studies has been to emphasize the point source loadings to streams and the total watershed contribution to lakes. While this has aided in evaluating some management problems, the watershed management of diffuse source inputs and the fate of point source inputs in downstream reaches has not been addressed. Carlson *et al.* 1978, suggested that streams have a natural ability to reduce the proportion of bioavailable P contributed from upstream sources. An attenuation of available P could be a function of plant uptake which transfers BAP to stored phosphorus, and/or the settling of particulate materials in slow reaches of the channel. If downstream reductions do occur naturally, the implementation of remedial measures may be more effective in specific critical portions of the watershed.

STUDY OBJECTIVES

In an attempt to evaluate the downstream changes in BAP and their relationships with various activities within a watershed, a one year study was conducted in the Avon River basin of southwestern Ontario. Temporal changes were evaluated by sampling in all seasons and during both high and low flow events. The objectives of this study were: 1) to evaluate the spatial variation of biologically available phosphorus in order to determine the relative importance of contributing sources (point and non-point) of P forms within the watershed, 2) to evaluate the spatial pattern of P forms downstream from the sources, 3) to evaluate the temporal fluxes of biologically available P from the sources, and 4) to discuss alternative management strategies for effective BAP control.

THE AVON RIVER WATERSHED

The Thames River Project (1975) identified the Avon River sub-basin as a site for further study in order to determine optimal solutions to existing water quality impairment problems. A three-year Stratford-Avon River Environmental Management Project (SAREMP) focussed on evaluating urban, rural and in stream options.

The Avon River drains a 166 km^2 area, which is a sub-basin of the Thames River watershed. The topography of the basin is relatively smooth with only 5.4% of the watershed having slopes greater than 5% (Coleman, 1982). The eastern headwater section of the basin exhibits a gently undulating topography while below Stratford the basin is flat, the river banks representing the major breaks in slope. The urban area of Stratford, located approximately in the centre of the basin comprises 11% of the basin area while woodlots account for 8%. Agriculture is the predominant form of land use and is composed of mixed as well as monoculture practices (Coleman, 1982).

On average the annual flows of the Avon River vary between 4.0 m^3/s during spring melt and 0.45 m^3 /s during summer months. Extremely low flows have been recorded with greater than 50% of the total flow originating from the sewage treatment plant effluent. The mean total precipitation (30 year) is 98.15 cm/yr. Roughly three quarters of this falls as rain, the remainder as snow (Greck *et al.* 1982).

METHODS

Sample Sites

Seven sites on the mainstream Avon River were selected for sediment and other water quality parameters. Figure 2 indicates the position of these sample sites within the watershed.

Two upstream sites (1A and 3) were situated in the rural agricultural portion of the basin where the steeper slopes exist, whereas sites 6 and 7 were located within the urban area of Stratford. Site 6 was just downstream of a small urban reservoir and immediately upstream of the sewage treatment plant effluent outfall while site 7 was near the city limits 1.5 km downstream of the sewage treatment plant outfall. A major storm sewer outflow occurs approximately one km upstream of site 7. The three remaining sites were in the downstream reaches of the watershed where agricultural practices again predominate. Site 10 was also the location of a federal stream flow gauge which enabled loading calculations for sediment and phosphorus fractions. Although provincial flow gauges were present at each of sites 1A through 8, the data are very sparse and of limited use in this study.

Field Methods

The field collection of sediment and water samples from the seven sites in the Avon watershed took place on 13 dates over a period of one year. At each site the culvert or bridge, which served as a road crossing, was used as the access point. Two submersible pumps were positioned at one-third and two-thirds of the stream width and were lowered to approximately mid-depth of the stream cross-section in order to obtain a representative suspended sediment sample.

Water and the associated suspended material were collected in 10-50 litre carboys (during periods of high flow and/or turbidity less water volume was required to obtain sufficient sediment). The time of sampling and the temperature of the stream water was recorded along with observations on stream flow and weather conditions. Two, one-litre samples of pumped water were collected for aqueous parameter analysis by the Ontario Ministry of Environment (MOE) laboratory in London (this included total phosphorus TP, dissolved reactive phosphorus DRP, suspended solids SS, nitrogen forms and chloride.

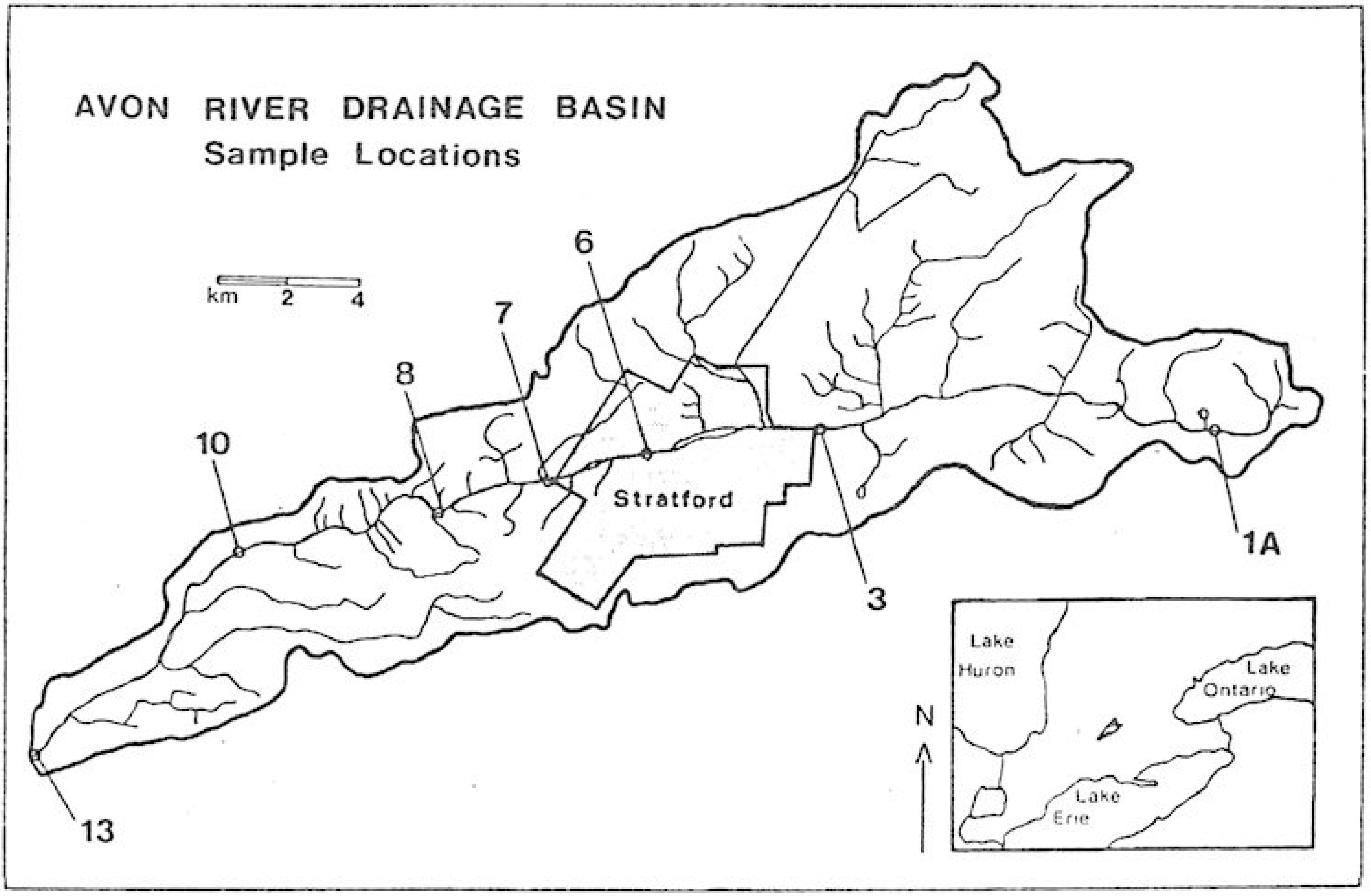


Figure 2: AVON RIVER DRAINAGE BASIN - Sample Locations

The carboys of water were transported back to the, mobile laboratory (located at the sewage treatment plant) and transferred into holding tanks. This water and sediment was then pumped through Westfalia (Model KDD-605) high speed centrifuge (9,400 RPM) to extract the solids, at a rate of six litres per minute.

The sediment collected in the centrifuge bowl was then transferred to a plastic container for freezing and subsequent freeze drying. Following freeze drying, the sediment was weighed to determine the concentration of suspended solids. The freeze dried sediment was stored for future phosphorus fractionation.

The seven sampling sites were sampled in this method over a time period of approximately eight hours. During non-events it was believed that this time period could sufficiently characterize sediment movement along the length of the Avon River. During storm events, the basin response time was faster, such that synoptic data could not be collected at all seven sites. Thus sites 1A, 3, 7 and 13 were sampled. A period of four hours was required to complete this sampling. In spring high flows which persisted for a number of days, enabled synoptic sampling of all sites (assuming they were accessible, i.e., free of ice and snow and/or not exhibiting road flooding).

The thirteen sample dates selected to represent Avon River water-year included a variety of both flow regimes and antecedent conditions. In studies of sediment delivery and/or stream loadings of sediment, qualitative characteristics of each sample period must be assessed in conjunction with the quantitative evaluations of the event. Antecedent conditions within the watershed, such as soil moisture, affect the sediment supply and delivery and therefore must be considered when comparing the relative importance of each sampling date. Table 1 indicates the event date, the Avon River discharge at the federal gauge, as well as the occurrence of precipitation before or during sampling.

TABLE 1. Avon River Sampling Conditions

DATE	APR. 16	MAY 5	JUN. 1	JUL. 6	JUL. 28	AUG. 4	SEPT. 14	SEPT. 21	OCT. 5	DEC. 7	MAR. 23	MAR. 30	MAR. 31
Sampling Conditions	After Storm	Clear	Clear	After Storm	Storm	Clear	Clear	Storm	After Storm	Clear	Spring Malt	Spring Melt	Spring Melt
Site 10 Discharge M^3 /s	0.944	0.531	0.104	0.436	2.500	0.180	0.210	0.268	0.905	0.830	N.A.	N.A.	66.000
P Fractions Sampled	Partic.	Soluble & Partic.	Partic.	Partic.	Soluble & Partic.	Soluble & Partic.	Partic.	Soluble & Partic.	Partic.	Soluble & Partic.	Partic.	Partic.	Soluble & Partic.

Partic. = particulate

Laboratory Methods

Freeze dried sediment was analyzed for the various chemical forms of phosphates. The analytical method used (Canviro, 1982) was an adaptation of the Williams and Mayer (1981) procedure. Fourteen of the 81 samples were also further analyzed with an algal bioassay as developed by DePinto (1981).

In summary, sediment phosphorus is chemically separated into four fractions - total phosphorus, organic, apatite and non-apatite inorganic as per the flow chart illustrated in Figure 3. Organic phosphorus is determined by total extractable P minus total inorganic P (sum of apatite and NAIP). The iron and aluminum associated phosphates are removed by two extractions, the first being a citrate dithionite bicarbonate exposure for 15 minutes at 85°C. This extractant is referred to as CDB-P and includes loosely adsorbed phosphates along with Fe and Al associated phosphates. The residue from this treatment is then exposed to 1N NaOH for 16 hours where the remaining Fe and Al phosphates are removed. The sum of NaOH-P and CDB-P is the NAIP fraction. The residue was exposed subsequently to 1N HCl for 16 hours to determine apatite P directly.

Total extractable phosphorus is not always the same value as total P as the resistant phosphorus forms are not extracted in the HCl, NaOH sequence. These resistant and/or inert P forms are essentially of no interest environmentally, as they do not cycle through the aquatic system. Total extractable P is determined in order to obtain a better estimate of organic P by subtraction. The total P value is derived by measuring the orthophosphorus resulting from strong acid digestion of all forms of phosphorus in the sample.

Due to time and resource restraints, algal assays were performed on only 14 of the collected sediment samples. Six samples from September 14 and March 31, as well as two site 13 samples from August 4 and March 30, underwent both chemical and biological phosphorus extractions.

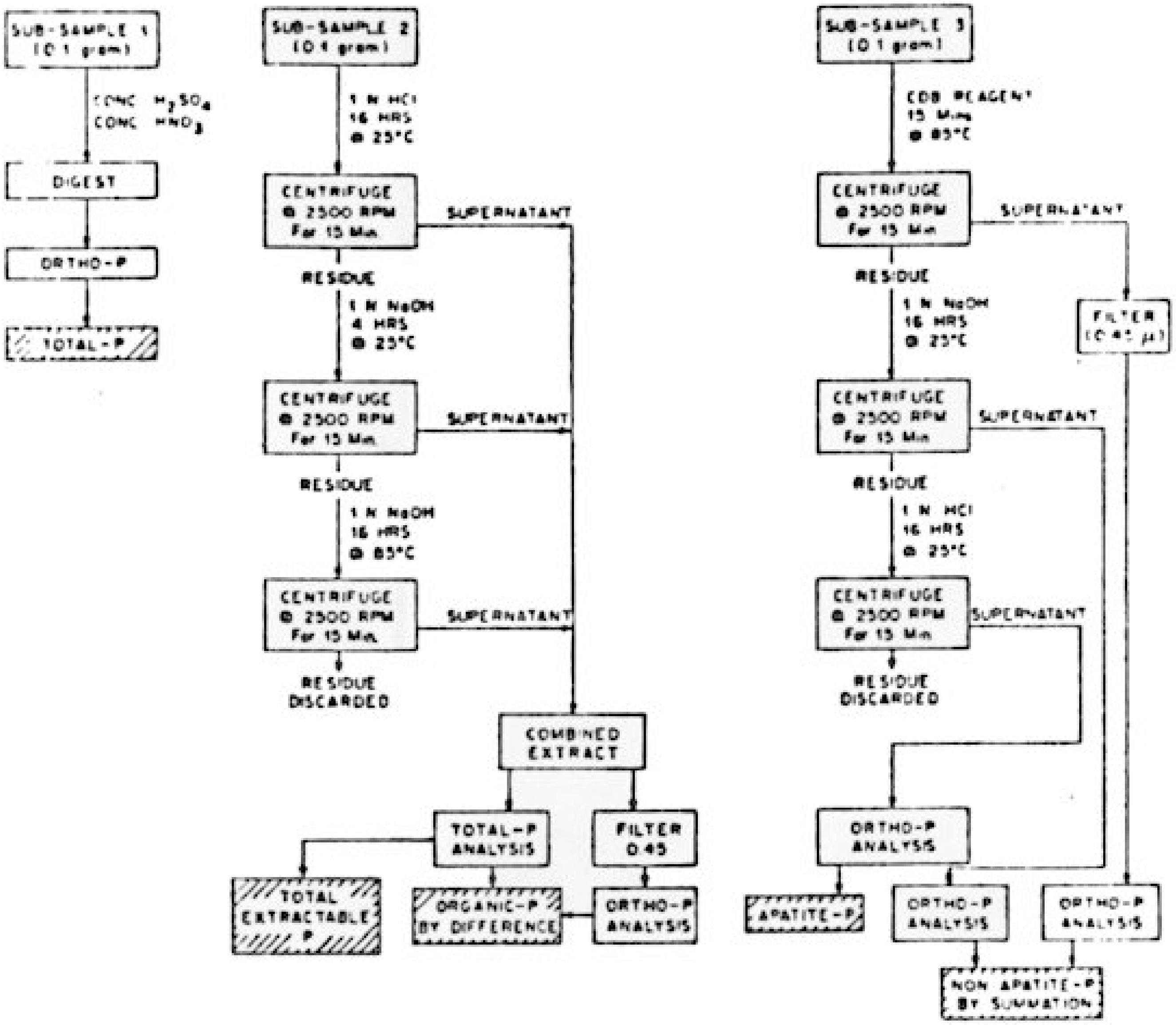


FIGURE 3. Flow Chart For Determining Forms Of Phosphorus In Wastewater Particulates

A dual culture diffusion apparatus (DCDA) (DePinto *et al.* 1981) was used as it allows the algal population to remain separate from the sediment. As well this enclosed system enables better phosphorus mass balance calculations. This DCDA apparatus is pictured in Figure 4. General procedures for obtaining a 14-day phosphorus mass balance follow:

1) A 10-14 day old P-starved uniform algal assay culture of *Selanastrum Capricornutum* was placed in the right side of the DCDA.

2) River sediments suspended in algal growth media (minus P) were introduced into the dark chamber (this was darkened to reduce any indigenous algal growth during incubation).

3) Harvestings of the algal population occurred on the sixth and thirteenth day in order to determine their total P uptake.

4) At the end of the thirteenth day total phosphorus, as soluble and particulate fractions was determined for both chambers.

5) A materials balance on all components of the DCDA was undertaken in order to determine the quantity of bioavailable P.

Figure 5 is a flow diagram of the laboratory techniques used in the algal uptake studies.

RESULTS

The Stratford-Avon sediment and water analysis of phosphate forms are presented here in a variety of ways in order to facilitate an understanding of the spatial and temporal characteristics of the data set.

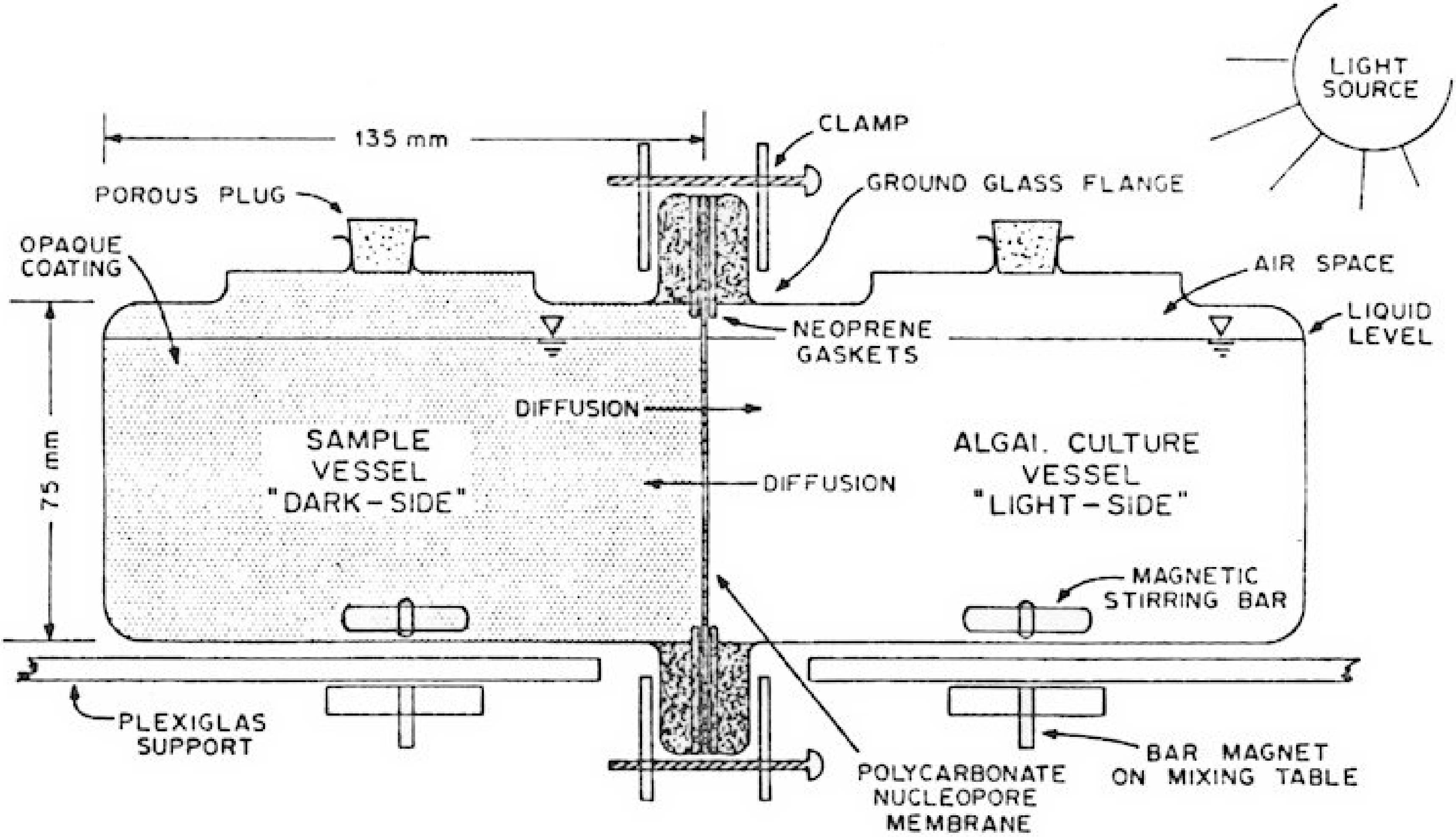
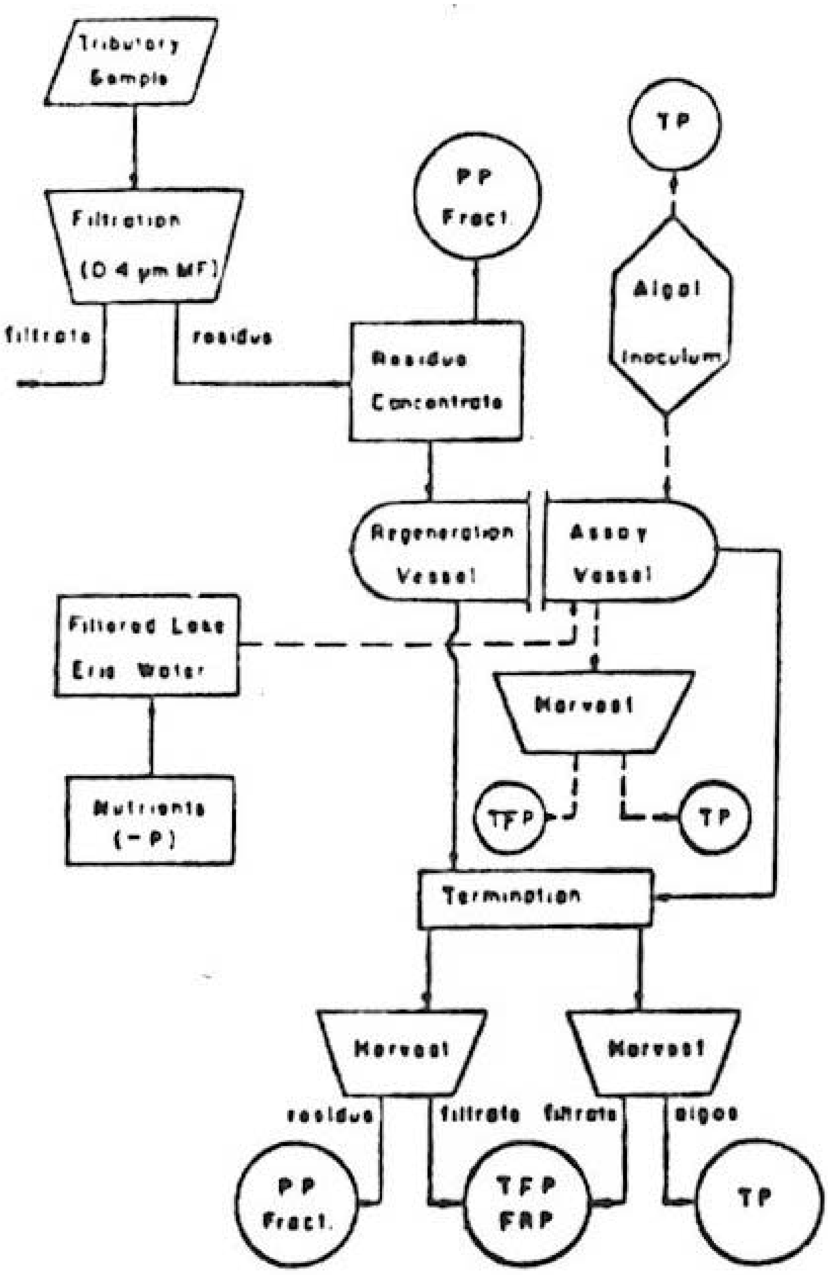


Figure 4. Dual Culture Diffusion Apparatus (DCDA)

Figure 5



Flow chart for DCDA evaluation of available particulate phosphorus in tributary samples. Dashed lines are repetitive step. (TP = Total Phosphorus, PP = Particulate Phosphorus, TFP = Total filtratable P, FRP = Filtratable Reactive P.)

(From DePinto *et al.*, 1981)

Sediment Phosphate Composition

Initially the sediment samples are viewed in terms of phosphate composition. Four phosphate fractions were determined, which together comprise total sediment P. Figure 6 indicates the daily mean values of the fractions for all sample dates. Apatite, the mineral form of phosphate comprises a relatively minor portion of the material moving in the Avon. The storm events of July 28 and September 21 as well as the high flow events of December 7 and spring melt exhibit the largest apatite values. While high flows occurred in April and May 1981, the apatite supply may have been depleted by the earlier high flow of spring melt.

Organic phosphorus comprises a dominant portion of the particulate materials on most of the thirteen sample dates, with the exception of early spring samples. Recall that organic matter is generally considered to be unavailable on the short term, yet if stored along the creek bottom can be mineralized to become available as orthophosphorus.

The non-apatite portion of the sediments fluctuates between 22-54 percent. The secondary Na0H-P extraction consistently removes only a small portion (2-5%) of the total P while the CDB-P extraction comprising the dominant portion of the NAIP component.

By viewing data from thirteen dates sampled over a period of twelve months it appears that the organic-P particulates and the CDB-P particulates exhibit the greatest temporal variation.

Bioavailability as Represented by Extractions

To proceed with an evaluation of sediment bioavailability the selection of a chemical P fraction which best represented the algal assay HAP results was required. Fourteen sediment samples, of the 81 collected underwent algal uptake bioassays as well as chemical P fractionation.

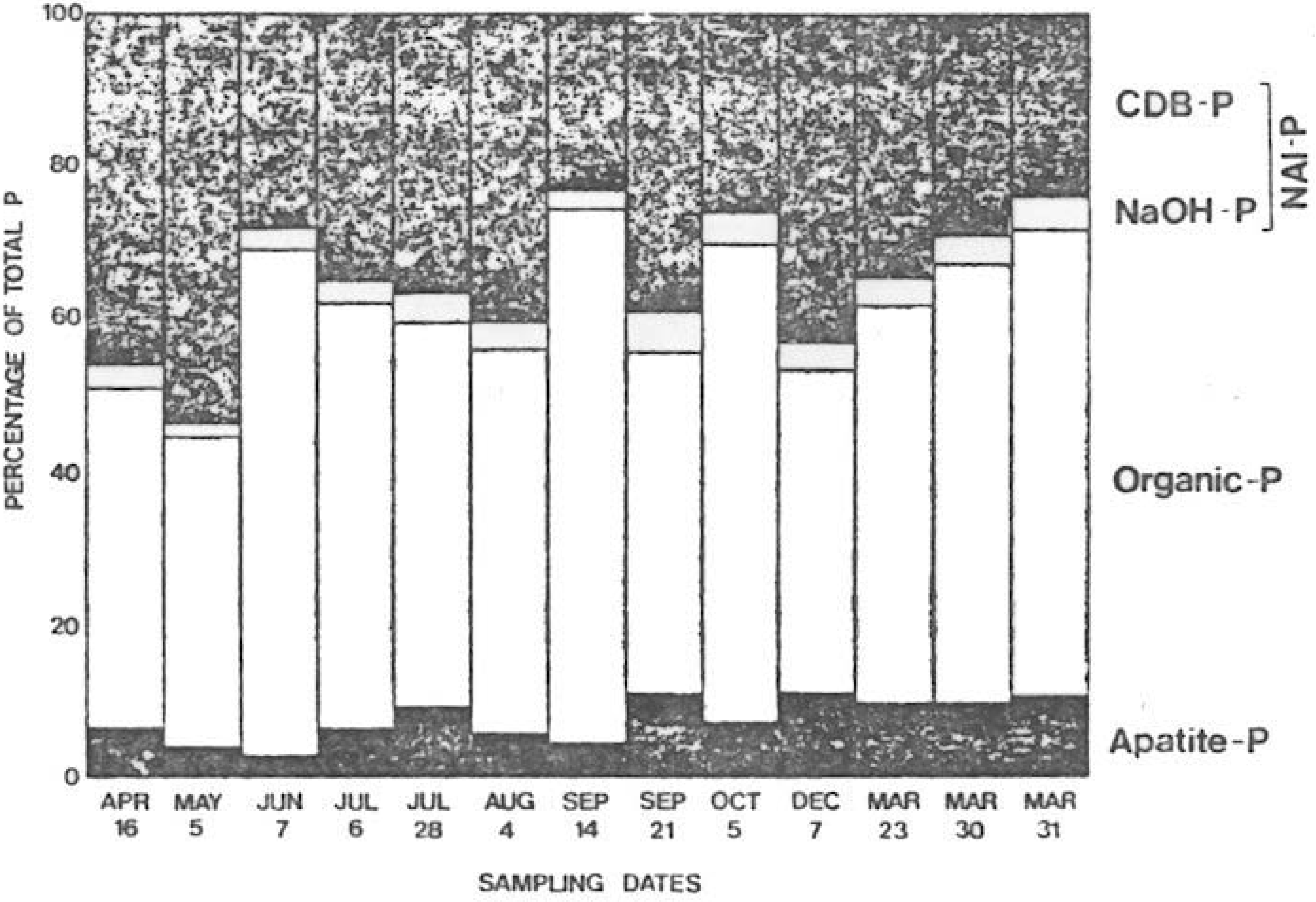


FIGURE 6: Suspended Sediment Phosphate Composition of Avon River Samples

From this sample set it was determined that the CDB-P fraction best represented the short term algal available P. Paired t-tests were performed for both the NAIP and CDB-P fractions with the algal BAP results. While both t values were significant at the 5% level, the CDB-P value was lower, exhibiting a closer fit.

With this selection of CDB-P as the best indicator of sediment BAP, the following results and discussions focus on the inputs, loadings and transfer of the CDB-P sediment fraction in the Avon River. References to particulate BAP (BAP-P) from this point refer to the chemically measured CDB-P portion of the collected suspended particulates.

Variability in the Bioavailable Portion of the Suspended Solids

Downstream and temporal changes in the percentage of the total load which is considered available (CDB-P/TP x 100) are presented as Table 2. The mean values ($\bar{y}$) for each date and station, along with the standard deviations (S.D.) are presented for comparative purposes. While this view of the data does not indicate the amounts of BAP moving in the stream, it does allow an understanding of the changing sediment composition associated with different scales of events. Some indication of the origin and quality of the inputs can be derived from this data set.

The highest values are exhibited by the high flow non-storm events in late spring and early winter. The daily means of the 1982 spring melt samples show a slight decrease over the three sampling days. Fall samples indicate a flow dependent relationship, while five summer mean values are relatively constant over a wide flow regime.

The second approach to viewing the bioavailable material moving in the Avon River involves the calculations of BAP loadings. Calculations involve the use of prorated discharges from a federal gauge at site 10. A 1:1 discharge:area ratio was utilized to calculate discharge at each sample station. But for the upstream sites this ratio was

TABLE 2. CDB/TP Percentage Table, All Sites And All Dates

	AFTER STORM	CLEAR	CLEAR	AFTER STORM	STORM	CLEAR	CLEAR	STORM	AFTER STORM	CLEAR	SPRING MELT SAMPLING			
DATE SITE	Apr. 16	May 5	June 1	July 6	July 28	Aug. 4	Sept. 14	Sept. 21	Oct. 5	Dec. 7	Mar. 23	Mar. 30	Mar. 31	$\bar{y}$ /S.D.
1A	54	58	45	22	28	46	29	25	30	50	N.A.	30	25	36.8 12.8
3	51	42	22	46	42	38	28	73	24	37	28	39	13	36.5 15.3
6	28	42	47	28	N.A.	37	26	N.A.	27	47	N.A.	31	20	33.3 8.4
7	49	67	39	50	46	38	22	28	32	66	28	31	22	39.8 15.0
8	40	55	32	44	N.A.	37	17	N.A.	42	25	26	30	38	35.1 10.5
10	58	45	39	28	N.A.	33	23	N.A.	18	38	43	28	26	34.5 11.5
13	45	67	28	N.A.	33	36	20	31	16	41	50	25	N.A.	35.6 14.6
$\bar{y}$	46.4	53.7	36.0	36.3	37.3	37.9	23.6	39.3	27.0	43.4	35.0	29.3	24.0	
S.D.	10.0	11.0	9.1	11.7	8.2	4.0	4.4	22.6	8.9	12.8	10.8	2.1	8.3	

applied following subtraction of STP discharge (as during low flows this may represent a dominant portion of the flow).

The graphs in Figure 7 indicate the downstream patterns in BAP loadings for the 11 sample dates available (March 23 and 30 exhibited ice flow conditions which inhibits depth gauging). Presentation of the data in this form reveals the relative amounts of BAP associated with different scales of events and different times of the year.

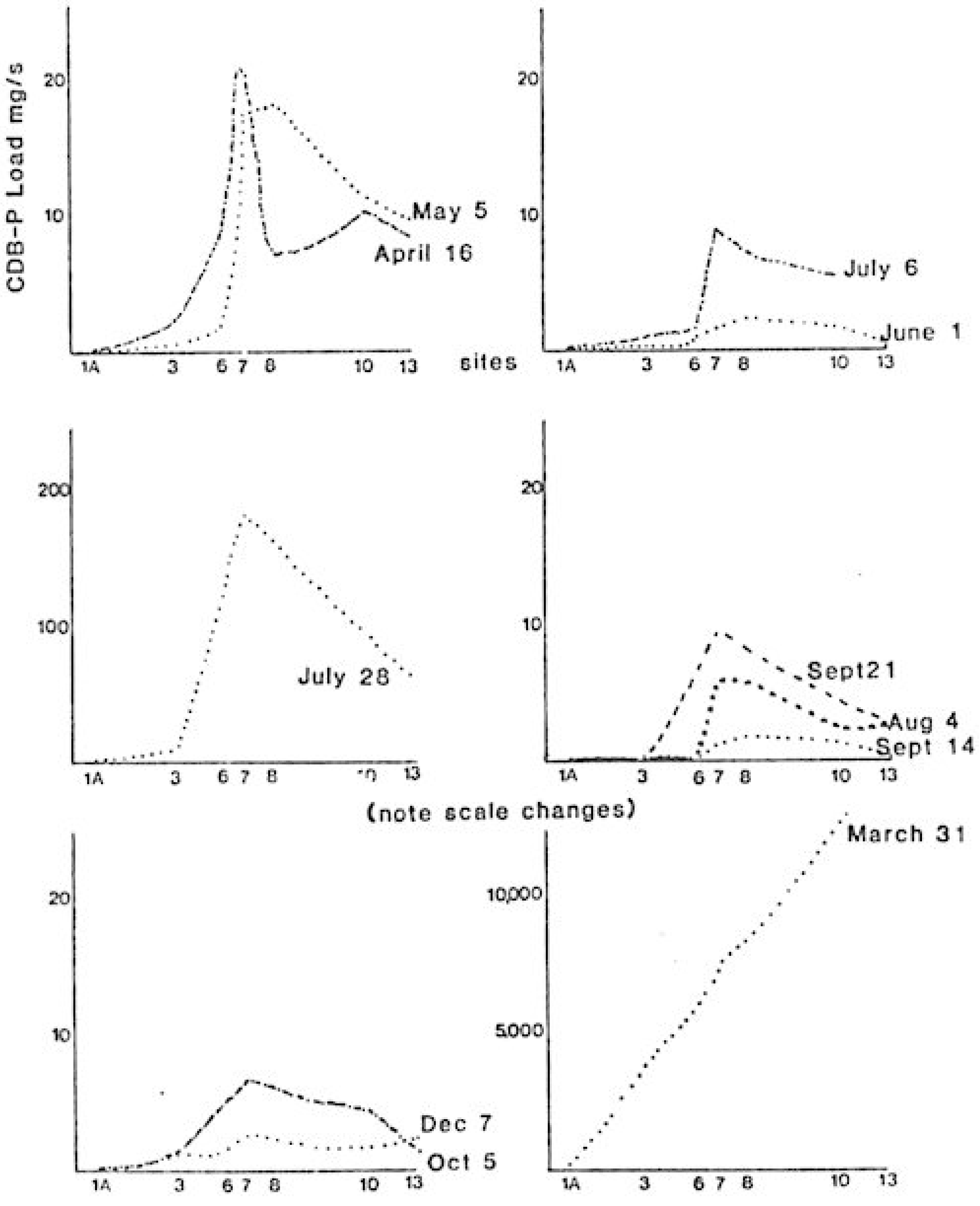
The largest movements of CDB-P occur during spring melt when the sediment supply is abundant and flows are at the annual high values. March 31 is the only date which exhibits an increase in BAP loadings downstream, again a function of extreme flows and abundant sources of material to erode. The loading graphs in Figure 7 exhibit a tendency for peak values to occur at site 7 and then to decrease in a downstream direction. As flow increases downstream, this occurrence is apparently a function of reduced sediment loads downstream, coupled with reduced CDB-P proportions.

The relative importance of the BAP loadings transmitted during the summer storm are apparent from the July 28 data. Note the change in scale on the y-axis, as a peak loading of 180 mg/s at site 7 exceeds all other sample date values excepting those of spring melt.

Unit Distance Loadings of BAP

In order to view the importance of each stream reach and its relative contribution of BAP, unit distant loads to the stream were calculated. Unit area loadings were also a possible choice for comparison, but as the majority of events were not precipitation related it was felt that the lengths of the channel reaches were a more appropriate comparison.

The difference between loadings from one site to the next was divided by the distance between sites to obtain the unit distant loading of BAP.



(note scale changes)

Figure 7: Downstream Loadings Plots for Particulate Bioavailable Phosphorus.

Table 3 indicates the temporal and spatial distribution of the gains and losses of particulate BAP in the Avon system.

The two urban sites, 6 and 7, have the highest mean unit loading for the 13 sample days selected. The two upstream agricultural sites exhibit inputs at all times of the year while the downstream agricultural sites (8, 10, 13) vary between gains and losses.

Total Bioavailable Loadings of BAP

For the six sample dates for which soluble phosphorus was measured, total BAP loadings at sites along the Avon have been calculated. Figure 8 portrays the breakdown of this total BAP flux into the soluble and particulate portions. When the total loads are small such as on Sept. 21 and Dec. 7 the soluble component comprises the dominant portion of the total BAP (even though Sept. 21 was a storm event). In clear weather when the total BAP loads are high (May 5, Aug. 4) the soluble BAP is not noted to increase until site 7. The summer storm (July 28) and the spring melt samples indicate that a notable portion of the total BAP is soluble at all stations.

Urban and Rural Contributions of BAP

A study of the Stratford sewage treatment plant (Canviro, 1982) indicated that the plant has a relatively good removal rate for BAP during normal flows in both summer and winter. Ninety-seven percent of the BAP is removed by the time the material passes through the third process of filtration. On occasion the capacity of the STP is exceeded and the treatment process is bypassed, directing materials to the Avon River. This efficient removal should however be viewed in context with the upstream loadings, in order that the relative impact of STP loadings can be determined.

TABLE 3. Unit Distant Loadings For Stream Reaches (mg/s/km)

Conditions	After Storm	Clear	Clear	After Storm	Storm	Clear	Clear	Storm	After Storm	Clear	Spring Melt	$\bar{y}$	Stream Reach km
DATE	Apr. 16	May 5	June 1	July 6	July 28	Aug. 4	Sept. 14	Sept. 21	Oct. 5	Dec. 7	Mar. 31		
SITE													
1A	0.092	0.057	0.002	0.118	0.674	0.006	0.005	0.019	0.051	0.045	155.256	14.211	2.75
3	0.211	0.062	0.0004	0.079	0.909	0.007	0.001	0.011	0.150	0.133	372.790	34.030	8.88
6	1.318	0.249	0.018	0.079	N.A.	0.039	0.062	N.A.	0.791	0.075	455.194	52.187	4.88
7	1.546	5.461	0.216	2.733	23.331	1.561	0.589	1.244	0.539	0.216	642.233	61.797	2.38
8	-4.302	0.192	0.178	-0.535	N.A.	-0.007	0.149	N.A.	-0.175	-0.103	323.061	-	3.13
10	0.488	0.993	-0.090	-0.302	N.A.	-0.554	-0.077	N.A.	-0.251	-0.676	671.146	-	6.25
13	-0.298	-0.294	-0.153	N.A.	-7.159	0.055	-0.142	0.418	-0.405	0.091	N.A.	-	7.25

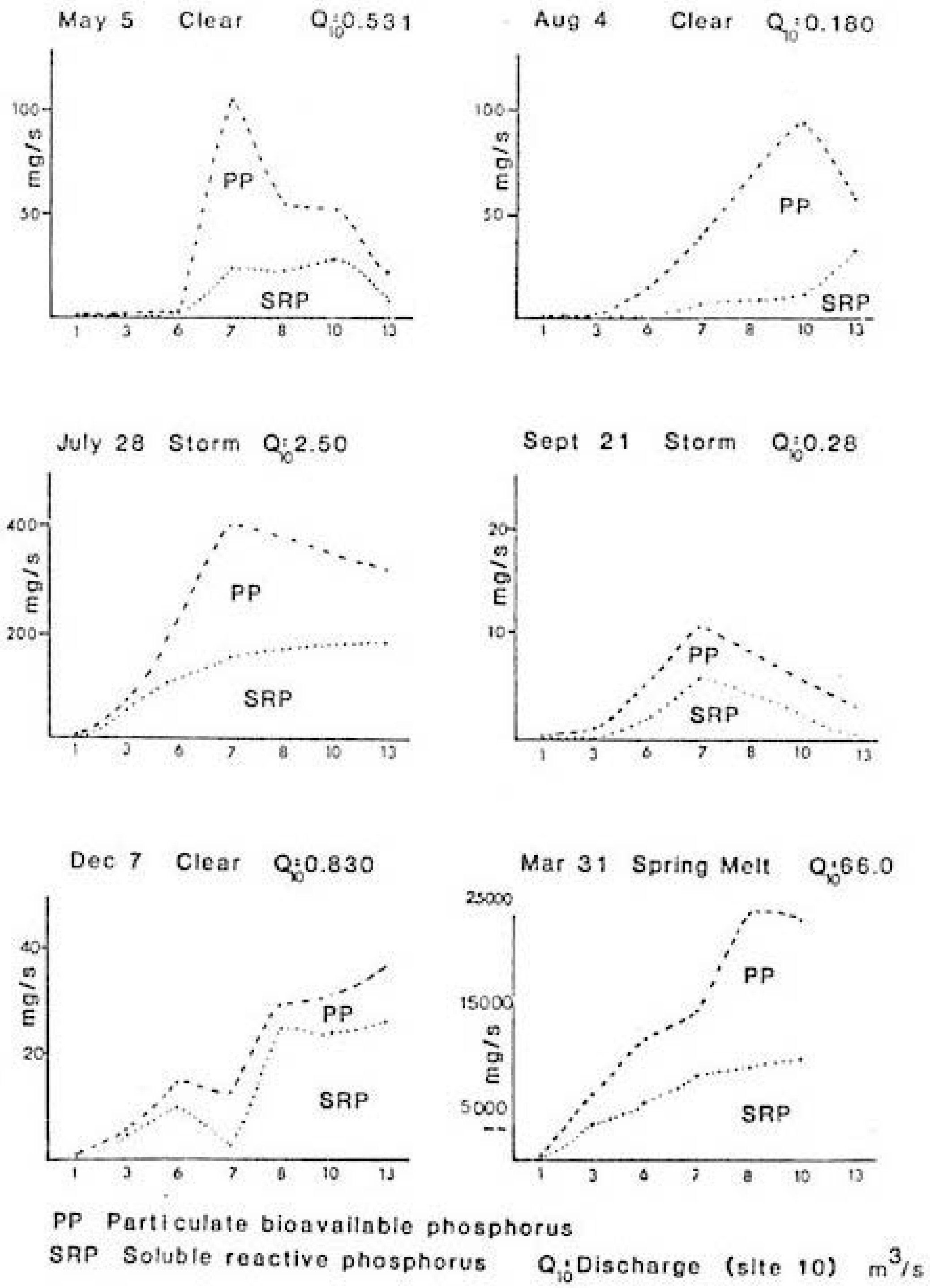


Figure 8: Total Bioavailable Loadings of Phosphorus.

An estimate of the relative importance of the sources of BAP (both soluble and particulate), which included storm sewers, sewage treatment plant effluent and river station loadings, was calculated for the fall storm of Sept. 21. Estimates indicate that on this date an urban storm sewer (Bedford) contributed total BAP loadings of approximately 5.68 mg/s. The sewage treatment plant input 13.06 mg/s, yet the sampling at site 7 indicates a loading of only 10.75 mg/s. Upstream of the city limits at site 3 the total BAP load was 1.79 mg/s indicating that urban inputs played a major role in the loadings of this date.

DISCUSSION

The biologically available loads of both suspended sediment P and soluble P are controlled by a number of factors. To some extent stream discharge (Q) controls the movement of particulate materials (SS), but both Q and SS are affected by energy inputs from precipitation or overland flow. While precipitation and/or melt increases discharge in streams, which allows the transport of material stored on the channel bed, precipitation also impacts energy to the ground surface eroding and carrying material streamward.

Rating Relationships

The relationship between suspended sediment concentrations and discharge are not simply characterized, as the supply of movable material changes with season as well as from event to event. Seasonal differences are expected in the intensity of storms and the condition of the erodible surface (i.e. bare fields versus crops). As well when streams support abundant biomass seasonal releases of this organic matter will affect the sediment transport relationships. Variation of the Q to SS relationship between events is also a function of sediment supply which is affected by the frequency and magnitude of storms and the changing antecedent watershed conditions, such as soil moisture.

While high river discharges are capable of carrying large amounts of suspended sediment the actual amount will be dependant upon the sediment availability, and those forces which are engaged in supplying that material (raindrop impact, overland flow and/or channel scour). The suspended sediment-discharge relationship for the Avon River samples is plotted as a scatter diagram in Figure 9. Strong clustering of data points is noted in the low range of suspended sediment concentration even though the flow varied through three orders of magnitude. The spring melt samples of March 31 single out as a separate group with much greater suspended sediment concentrations associated with these high flows. Sediment supply does not seem to be limited at this point in the year.

Rating relationships for soluble phosphorus versus discharge exhibit different forms in various climatic and geomorphic regions. Again this is a function of the supply of the dissolved substance. Generally the relationship between dissolved solids and discharge is inverse, due to the effect of dilution of baseflow. Inputs of precipitation or snow melt are generally more dilute than the baseflow and therefore decreased concentrations are noted with increased discharge (Gregory and Walling, 1973). Variations in this relationship will occur if sources of the solute near to the stream are flushed by precipitation or overland flow. Surficial phosphorus fertilizers, manure leachates in soil pore water and loosely adsorbed sediment orthophosphates are three sources of P which may be released in periods of increased precipitation or discharge. Again the size of these P stores change with various scales of events and at different times of the year.

Particulate BAP Inputs

In evaluating the contributions of particulate BAP to various stream reaches the association of the CDB with the sediment should first be viewed. While CDB loadings will be controlled by the concentration of suspended sediment, (and therefore indirectly by discharge) the concentration of CDB is affected by other regulating processes or factors. These factors include the presence and type of activities in the area which affect P inputs (such as farming or industry) and the in stream chemical status which regulates the form, utilization and regeneration of available P.

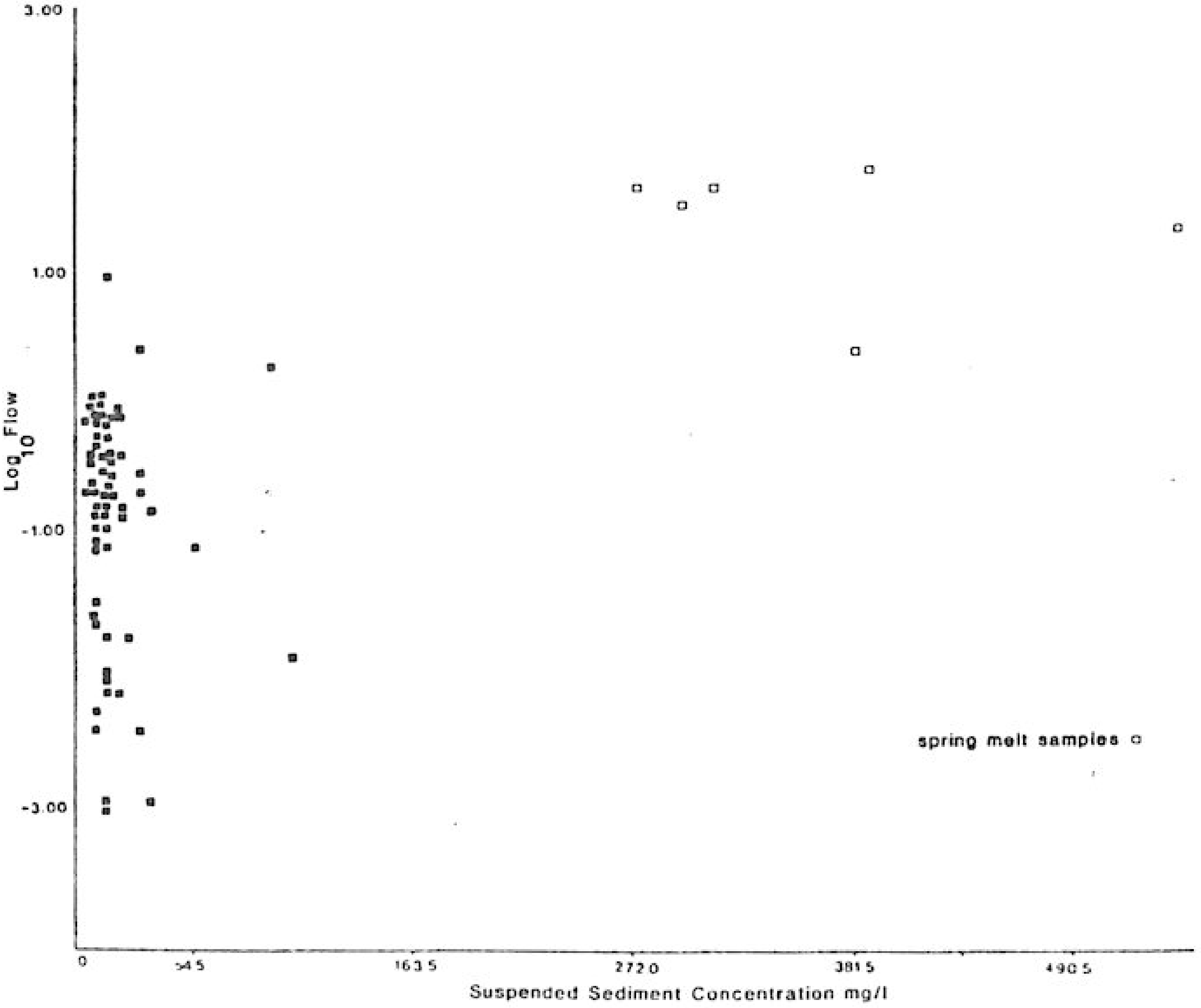


Figure 9: Flow and Sediment Concentration Relationship.

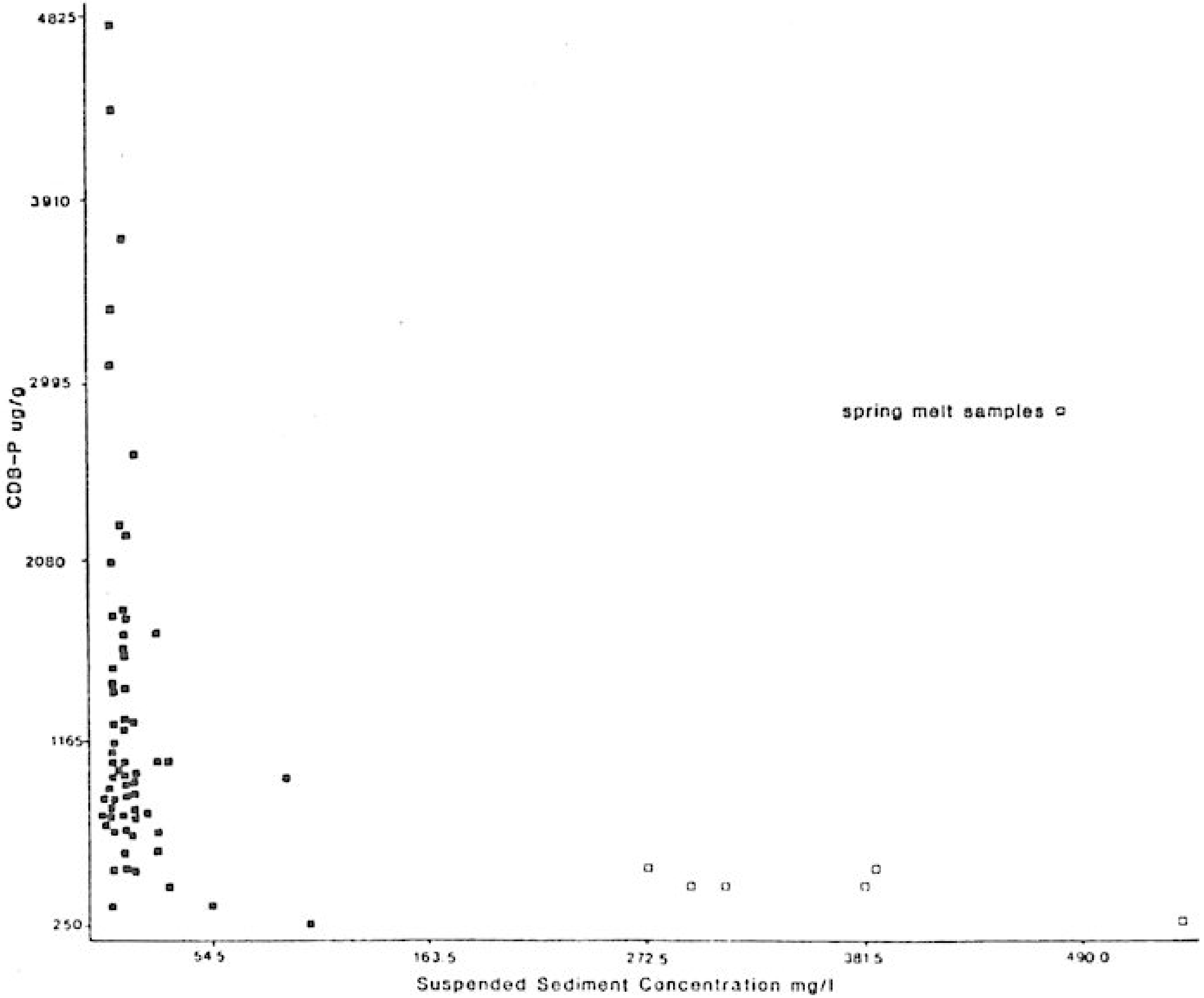


Figure 10: Suspended Sediment and CDB-P Relationship.

Figure 10 indicates the distribution of suspended solids concentration and CDB concentration for the Avon samples. 75% of the data points cluster in the low SS and CDB concentration region while the samples of greatest SS concentration have quite low CDB values. Alternatively the highest CDB concentrations are associated with low SS values. The dilution effect is apparent through the identification of these outlying data points in Figure 10. The spring melt samples of March 31 exhibit the high SS values with low CDB while the high CDB concentrations are all sampled below site 7 during non-precipitation events. Since the majority of sample points are clustered within the area of low SS and CDB concentrations the differentiation of loadings will depend largely on the flow regime.

Seasonal Variations of Particulate Inputs

To identify periods of high bioavailable inputs Table 2 and Table 3 should be viewed in conjunction. Seasonal differences in both particulate loadings and the percentage of material which is bioavailable can be identified.

The highest daily mean values of percent CDB (Table 2) occur on April 16, May 15 and December 7, three non-storm events which exhibited high flows. The two upstream agricultural reaches exhibit high unit distant inputs (compared to other non-precipitation events at these sites), as do the two urban sites. Downstream of site 8 losses of loads occur. Being non-storm events the inputs of suspended sediments could be due to 1) point sources 2) in stream transformations of P, forms to CDB-P or 3) bottom scouring of stored materials. While it is apparent that the increase in percent CDB is associated with a decrease in the percentage of organic matter (Figure 6) this again is more likely due to a lack of organic materials stored for movement at these times of year.

In early spring the concentrations of CDB-P are high at all sites but more so downstream of site 7. To obtain an estimate of STP stream loadings the daily flow rate was used along with the effluent phosphorus concentration for that period of record. Of the 13 BAP sample dates, April 16 and May 5 exhibit the highest total P loadings. Figure 11, which portrays the unit area loadings of particulate BAP for May 5, indicates the dramatic increase in BAP loadings between sites 6 and 7.

Comparatively the upstream agricultural inputs are minor, while reductions of load occur in the downstream reaches.

Intensive sampling during the 1982 spring melt (March 23, 30, 31) reveals that the mean daily values of percent bioavailable particulates tends to decrease as the event continues (Table 2). While channel bottom sediments would be scoured and removed during these annual high flows the majority of input would be derived from surficial sediments in adjacent fields. The flow is noted to be increasing over these three days as does the sediment load (the supply has apparently not become limiting at this stage), yet the proportion of BAP tends to decrease. This is not a marked occurrence, but possibly indicates that the sources of BAP in the sediment supply are diminishing with time. (Potentially this is a function of grain size, as the later higher flows are capable of carrying heavier sediments which are less likely to be associated with available phosphorus. Loadings are not available for all spring melt sample dates but the estimates for the sites sampled on March 31 indicate the voluminous amounts of material moving. To allow a visual comparison of the magnitude of the spring meet particulate BAP transport see Figure 12. Note both the change in scale for March 31 data as well as the fact that BAP loadings do not attenuate downstream on this date.

It is questionable as to whether this event period is of major significance for stream quality management (aside from erosion aspects) as the majority of material appears to be carried through the system to be deposited in either the Thames River or Lake St. Claire. On the falling limb of the multi-day spring melt hydrograph the suspended materials will begin to attenuate downstream, depositing particulate BAP in reaches of the river.

The range in the magnitude of loadings sampled in Summer 1981 have been shown in Figure 12, through the use of the July 28 storm event and the August 4 low flow situation. The relative importance of the summer storm events ability to transport BAP is apparent.

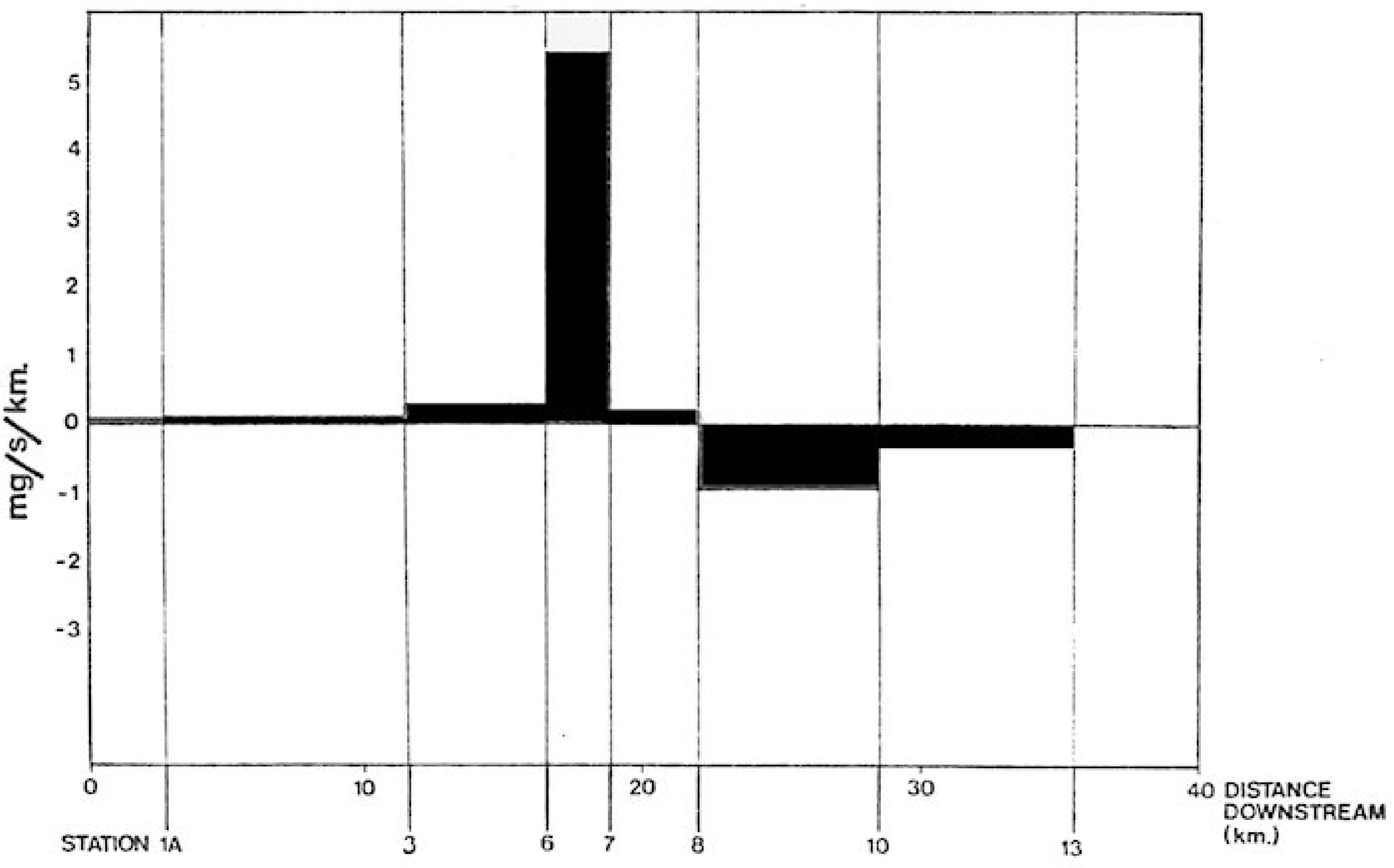


Figure 11: Avon River Stream Reaches -- May 5,1981: Unit Distant Loadings of CDB-P per Kilometer.

In the summer period when aquatic production is high it is perhaps useful to look more closely at the percentage of CDB-P in the suspended material. Although in periods of low flow material may not be moved, the settled sediments as well as those in the water column are available for utilization by plants. The four summer sampling dates (June 1, July 6, July 18, August 14) show a consistency in daily mean CDB-P values. The range between 36-38% involves sampling of an extreme storm event, clean weather and post storm conditions. The mean values do not reflect the flow conditions in this season, yet a closer view of the individual sites over this time period indicates where inputs and reductions may be occurring (to follow later).

Fall samples include September 14, 21 and October 5, which respectively involved clear weather, a storm event and post storm sampling. The mean values of the percentage of BAP appear to be flow related, showing increased proportions with high flows. Loadings for these dates indicate the post storm sampling event of October 5 delivered ,higher loadings than the storm event sampled on September 21. The trend for each of the fall sampling dates is a decrease in loading in the reaches downstream of site 7.

Site Behaviour

Returning to the summer data it appears that site 3 and 7 are zones of external BAP input. Increases of the percentage of BAP occur in both low and high flow as well as during both precipitation events and non events. Site 7 is downstream of the urban storm sewer and sewage treatment plant outfalls, such that phosphorus inputs are expected here in all flow conditions. Similar flow conditions elicit opposite responses from site 1A and 3. The proportion of BAP increases at site 3 during high flows indicating an input to the suspended material from some source while at site 1A, the proportions of BAP are elevated during low flows.

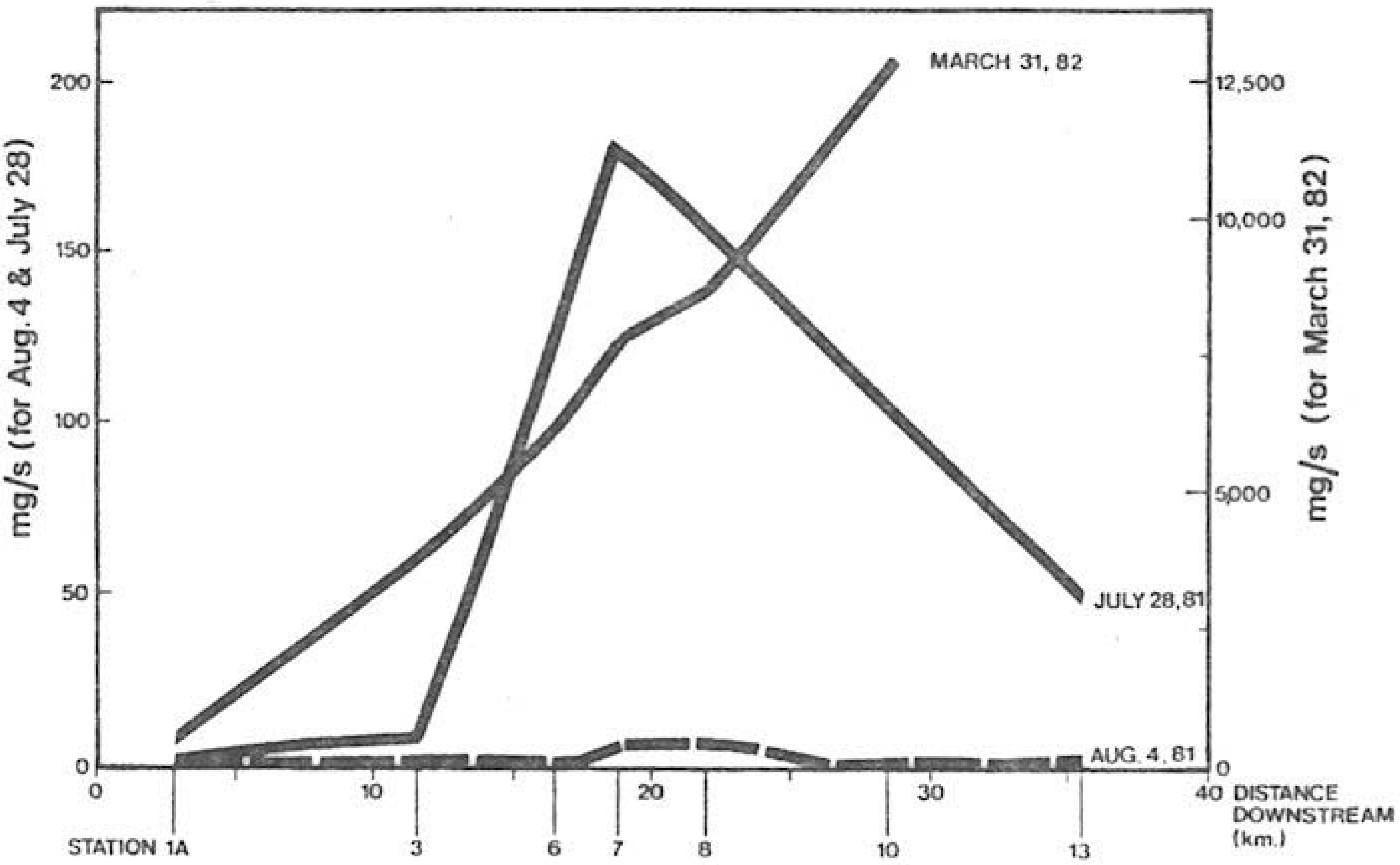


Figure 12: Instantaneous CDB-P Loadings Along the Avon River.

To elucidate the exchanges under these conditions more clearly Figure 13 presents site 1A and 3 summer values of flow, suspended sediment concentration, CDB-P percentages, organic P percentages and total particulate P concentration.

The summer sampling at site A indicates that suspended sediment concentrations are increased during high flow events associated with rainfall (July 6, July 28), yet the proportion of CDB-P is reduced. The storm related inputs of sediments seem to contribute a smaller proportion of CDB. Total particulate phosphorus concentrations are reduced in the high flow events while the proportion of both apatite and organic P are somewhat increased. This indicates that the material stored near site 1A for movement during summer high flows is composed of greater amounts of organic matter and apatite (less available forms) than the material suspended in lows flows. Sediment CDB-P concentrations are diluted during the high flow events. High flow loadings of CDB-P do, however, exceed the low flow contributions due to the increased amounts of lesser content CDB-P) sediment moving in the stream. Summer sampling of site 1A indicates then that CDB-P is abundant in both types of flow events but it is likely available to only the flora in the immediate vicinity during low flows whereas it is transported and dispersed downstream in higher volume events.

Site 3 data shows a similar pattern of summer flows yet the total sediment phosphorus concentration attenuates over the time period. The CDB-P percentages are elevated during high flows and represent a smaller proportion during low flow. It appears that site 3 represents a problem area during summer storm events as the sediment carried by the stream (which in these events would include inputs from bottom scour and/or field erosion) contribute greater concentrations of bioavailable P than that which is suspended in the stream during low flows. Implementation of remedial measures in the fields adjacent to this stream reach would be appropriate as long as the majority of summer CDB-P is not being resuspended from stored bottom materials.

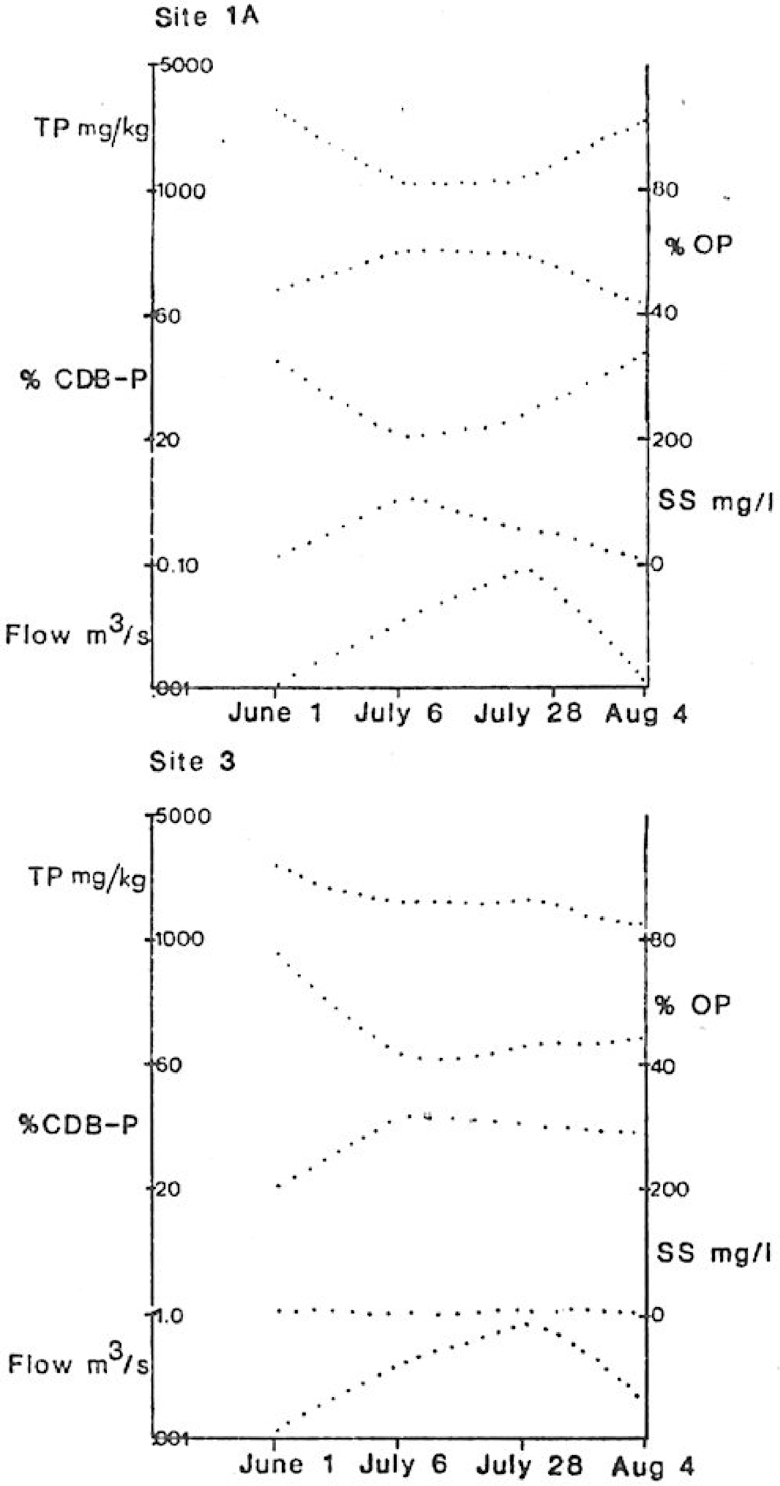


Figure 13: In stream Summer Conditions at Site 1A and 3.

Urban Inputs

In the comparison of the September 21 BAP contributions from significant sources it appeared that the urban inputs exceeded the upstream agricultural contribution. As this was the only event for which storm sewer discharge, STP effluent and river discharge were simultaneously sampled the relative importance of these sources on other dates has been estimated from less direct data.

Histograms of total (SRP and BAP-P) loadings have been prepared for six sample dates (Figure 14). Sites 3 to 7 are presented in this manner to allow an estimate of the upstream agricultural contributions within the stream before it enters an urban area (site 3), the influence of urban inputs at site 6 and the cumulative effects of the STP, urban and agricultural inputs by site 7. Note that the STP loadings are presented here as direct inputs rather than as river loadings at the plant outfall and therefore are additional to the P loadings moving downstream from site 6.

May 5 loadings have previously been viewed in Figure 11, but here the instantaneous STP inputs are shown in relation to site 7 loadings. The soluble STP inputs attenuate in the downstream reach to site 7 while the particulate loading increases. This suggests that SRP is associating with available suspended sediments in the stream water column and moving downstream as sediment associated P. This situation occurs again on Sept. 21 and Dec. 7. High sewage treatment plant SRP inputs are reduced in a short distance while particulate BAP increases in the short stream reach. An alternate explanation of this phenomena would be the utilization of SRP in biological uptake with an increase in particulate BAP due to erosion or resuspension in this reach. As the observed changes occur during various types of events and at several different times of the year, it would seem that the first explanation is more suitable. The SRP is considered to be most easily available to plants and therefore this alteration of SRP to BAP-P renders a portion of the sewage treatment plant inputs less available. Reductions of suspended solids upstream of this reach could alter this exchange process.

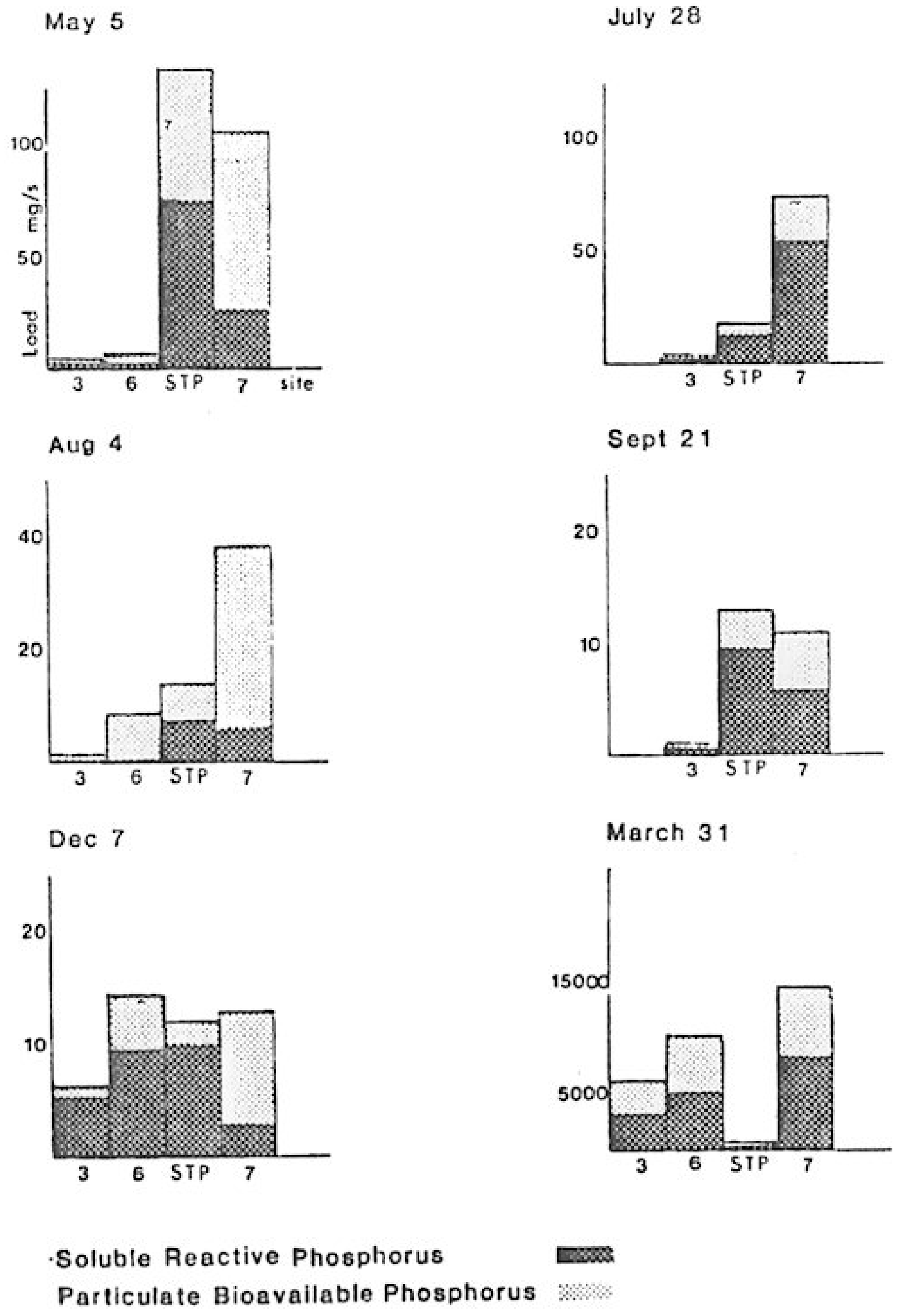


Figure 14: Downstream Loadings of Total BAP.

The storm event of July 28 indicates that soluble urban runoff inputs were high in the distance between site 3 and 7. SRP increases dramatically, all of which cannot be explained by the STP inputs. Upstream agricultural inputs are again minimal compared to the urban component. This urban drainage contribution is also noted to be of significance on December 7 when the site 6 SRP values equal those of the sewage treatment plant. A two-fold increase of both SRP and BAP-P occurs between site 3 and 6 indicating the influence of urban inputs. For these six sample days, the total upstream agricultural inputs of BAP appear important only during the spring melt period and the high flow non-storm event of December 7.

While the soluble portion of available P is generally thought to be dominant in low flows and diluted in higher flows, it appears that this does not hold true in all cases for this area. The histogram for August 4 indicates that in low summer flows SRP comprises the smaller portion while particulate BAP is dominant. Possibly the SRP values are depressed because rooted and floating plants have utilized it in these periods of low flow.

The July 28 storm event and the March 31 snow melt data exhibit extremely high proportions of SRP. The influence of STP inputs can be evaluated in Figure 14, but in referring back to Figure 8, it becomes apparent that soluble inputs are occurring during these storm/melt events at most sites along the stream. While urban storm sewer and STP inputs could explain the SRP increases at site 6 and 7, the upstream and downstream agricultural proportions are not portraying the classical dilution effect. The high percentage of soluble P loadings in these agricultural areas may be due to the influence of the drainage which would act to increase both the amount and rate of SRP transfer to the streams during rainfall or melt events.

CONCLUSIONS

Transfers and inputs of particulate BAP in the Avon River have been evaluated on thirteen sample dates over a period of twelve months. Temporarily the fluxes of biologically available P are greatest during spring melt and minimal during summer low flows. In this data set an intense summer storm moved more material than several longer term rainfall events.

The biologically available component of the sediment moving in stream was not depleted at any time in the year and was noted to be highest in the late spring/early summer. The BAP portion varied between 17 and 73 percent of the material suspended in the stream.

The in stream BAP loadings are greatest at site 7 downstream of both urban and sewage treatment plant inputs. This holds true for all flow conditions and seasons excepting spring melt. The other urban site, upstream of the treatment plant exhibits the second highest unit distant loads. The two upstream agricultural sites contribute BAP in all flow conditions and seasons, but the are smaller in magnitude. While the downstream agricultural areas are potential sources during precipitation events, there is a general tendency for unit load losses of BAP to occur in the downstream region of the Avon River.

The point sources of the sewage treatment plant and storm sewers coupled with diffuse urban runoff appear to be the major contributors in this case. Evidence of exchanges between the particulate and soluble loads immediately downstream of the sewage treatment plant indicate that possibly the transport of sediment in the stream is useful as it acts to adsorb soluble P, the most accessible form of phosphorus. Soluble P inputs appear to be elevated in the agricultural areas during storm events. It is suggested that the tile drains are facilitating the transfer of soluble P to the stream during precipitation events. This quantification of soluble and particulate available phosphorus transported in the Avon River deals only with that material which is potentially available for growth. The occurrence and behaviour of aquatic organisms at these sites on these dates has not been evaluated in this study.

The development of in stream management strategies for the Avon River requires that the knowledge of temporal and spatial loadings of BAP be interfaced with information regarding the life cycle and nutrient requirements of in stream biotic species.

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