ABSTRACT

Streams which drain a single general rock type have a constant concentration (± 10%) of dissolved ions while discharge may vary by two orders of magnitude. It is concluded that at all times the water flowing in a stream is from the ground water system. The increased discharge during flood flow is from increased flow of ground water into the stream and is not from overland flow or shallow, near-surface, horizontal, subsurface flow.

The change in composition accompanying a change in discharge of large streams and the Susquehanna River results from the change in the proportions of the total flow composed of type waters of constant composition. This change in the flow proportions is due to the different hydrologic responses to precipitation inputs of basins underlain by different single rock types.

The in-river precipitation of mine-drainage-injected Mn and Fe was studied at a pH of ∿ 7. For Mn the removal from solution appears to be first order. The rate constant is 10^3 times greater than the extrapolated autocatalytic rate constant of previous laboratory experiments. The study of the removal of Fe from solution yields a first order rate constant consistent with previous laboratory experiments.

Pb^{210} has been used as a tracer to study the fate of trace metals. The study of soils shows that they are virtually 100% efficient for Pb^{210} scavenging (on organic matter). The Pb^{210} in soils can only be removed from the system by erosion of the soil material.

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As a result, metals similar to Pb^{210} have a mean life of 2000 years in soil profiles. Mine-drainage-injected Pb^{210} has been used to study trace metal removal kinetics in the river. At a pH of ∿ 7 the removal of Pb^{210} from solution has a first order half time of < 1 day.

The Mn, Fe and Pb^{210} data show that there is no pronounced natural seasonal variation in the concentration of dissolved trace metals. The Mn data indicate that mine drainage dominates the variation of Mn seen at the river mouth. While the natural variation in particulate Mn seems to mimic that resulting from mine-drainage-injected Mn, it is on a very subdued level.

The amount of dissolved U^{238} in streams is related to the amount of rock weathered. Conversely, the U^{234} in solution is dependent on the residence time of the stream water as ground water. The U^{234}/U^{238} activity ratio of dissolved U is due to a combination of the above phenomena.

The dissolved and particulate U data show that U is removed from solution onto the suspended sediment in the Susquehanna. This process may be a natural phenomenon and would contribute to the soluble U delivered to the oceans.

Tributaries receive their water from the ground water system with dissolved Fe and Mn which precipitate in the streams. Fine-grained bottom sediments in the river are a source of dissolved Fe and Mn which move into the river water and precipitate. Biological activity within the river and soil erosion introduce organic matter capable of sequestering trace metals. Contrary to laboratory predictions based on a static system, the dynamic system with continuous production of materials that sequester trace metals results in the unidirectional removal of these metals from fresh water. This demonstrates that an isotope such as Pb^{210} may indeed be a tracer of a whole group of elements in the natural system although the *in vitro* chemistry of Pb is different in detail from other heavy metals.

THE GEOCHEMISTRY OF MANGANESE, IRON, URANIUM
LEAD-210 AND MAJOR IONS IN
THE SUSQUEHANNA RIVER

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The development of the neutron activation technique employed in this study materialized from discussion with M. Bender of the University of Rhode Island and L. Benninger of Yale. M. Bender also provided laboratory space at RINSC for the neutron activation work and for some flameless atomic absorbtion analyses of dissolved manganese in water samples.

Discussions of many aspects of this study with L. Benninger, G. Brass and J. Thomson were beneficial.

Sampling could not have been completed without the able assistance of L. Lewis. Additional technical assistance was provided in the laboratory by G. Goshgarian, K. VonDamm and G. Benoit. T. Eisensmith maintained the electronic equipment. B. Brockett Kimler drafted the figures. The typing of A. Phelps is appreciated.

In addition to her technical assistance in sampling, the patience and understanding of my wife, Linda, has contributed greatly to the completion of this work.

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I. INTRODUCTION

The fate of trace metals in fresh water systems is important to the study of natural processes and in assessing the impact of anthropogenic injections of metals into the system. It has been well documented that the oxides of manganese and iron are intimately involved in the localization of trace metals (Goldberg, 1954; Krauskopf, 1956; Jenne, 1968) and that the history of the manganese and iron oxides is also significant (Kharkar et al., 1968; Murray 1975a, 1975b). Consequently, the inclusion of a study of iron and manganese in a study of trace metals is necessary.

A direct study of the stable trace metals in terrestrial systems is plagued by several problems arising from the widespread use of these same metals by modern technology. This widespread use of metals gives rise to a heterogeneous injection of trace metals into the environment. Therefore, it is not feasible logistically to study all trace metal sources in a large scale study. As a result, stable trace metal analyses may represent only patchiness due to these injections and would be of limited use for further elucidation of mechanisms. In addition, contamination of samples during sampling and laboratory analysis is a common problem, especially for Pb. Rama et al. (1961) demonstrated that Pb^{210}, a naturally occurring radioactive isotope of lead, can be used as a tracer in a river system. Therefore, a study using Pb^{210} as a heavy metal tracer was initiated because it is free from the problems mentioned above for stable metals.

The study of uranium is interesting in itself, as it is an important element in geochemical and economic terms. It too, however, has value as a tracer of transition metals (particularly Mo and Cr) and is included in this study for that reason as well.

Another aspect of geology in which rivers are intimately associated is chemical weathering and erosion. One area of interest is the rates of these processes in silicate terranes compared to carbonate terranes, and an investigation of this is undertaken. Several recent studies (Judson and Ritter, 1964; Meade, 1969; Gibbs, 1967) suggest that modern day erosion rates determined from river sediment transport data cannot be used to estimate erosion before man became an active agent in the process. The method of study employed in this thesis allows an examination of this problem. This study method also provides an instructive view of the relationship of stream discharge and water composition, as they are related to the hydrologic response of a region to precipitation inputs.

The Susquehanna River was chosen for this study for several reasons. The data of Schubel (1972) indicated some interesting seasonal variations in dissolved manganese and iron and particulate manganese, copper, nickel and zinc at the mouth of the Susquehanna River. A reconnaissance study of coal mine drainage pollution in the basin (Biesecker and George, 1966) indicated a very advantageous arrangement for studying Fe and Mn precipitation, especially in the West Branch of the Susquehanna. The pioneering study of Pb^{210} in the Colorado River System (Rama et al. 1961) suggested that mine drainage would be high in Pb^{210} relative to other stream water. This arrangement provides the opportunity to study manganese, iron and the heavy metal tracers in a natural system; i.e., a dynamic, flowing river as opposed to a laboratory beaker.

Two additional points make the Susquehanna River adaptable to the method of study. The basin is part of an area of well-studied geology and land use. Also, the streams and main river have been part of the USGS monitoring system for discharge, dissolved species and sediment for many years, providing a basic framework within which to design the study.

The method of study employed was to sample the region in a representative fashion and to process the samples immediately in the field to prevent changes. The establishment of type areas based on geology and stream composition was undertaken to help resolve the processes that influence the above-mentioned parameters. These areas were sampled in conjunction with the main river to ascertain the source of variation for both trace metals and major elements, both with discharge and season.

In conjunction with the sampling of the type areas and location of significant injections of a specific water type, profile sampling (i.e., at sequential stations along the river) was employed to study reactions that occur in the river.

Filtration of samples was performed in the field immediately after sampling to minimize changes due to manganese, iron and trace metal reactions.

Organization of the Thesis

In Chapter II the basis for the selection of type areas and their applicability to the entire basin is established. Sampling and analytical techniques are also discussed. Chapter III is a presentation of the major ion data for the type areas and the main river along with a discussion of the implications of this major ion data for the geohydrology of the basin. Also, models are presented for calculating water and ion provenance for use in studies of precipitation in the river. The last section of Chapter III is a discussion of total denudation rates; i.e., the combination of chemical weathering and erosion. Chapter IV is a discussion of the manganese and iron variations observed in the river and a study of the precipitation rates of these elements in a river system. It also provides the basis for field studies of the tracers Pb^{210} and uranium. Chapter V is a discussion of the use of Pb^{210} as a tracer and the results of the experiments. Chapter VI discusses the uranium data outlining river reactions and pointing out some important considerations of uranium supply to the oceans by streams. Chapter VII is a summation of the thesis results and suppositions and is a synthesis of all the separate chapters into a general model for the river.

II. GEOLOGY AND GENERAL WATER CHEMISTRY OF THE SUSQUEHANNA RIVER SYSTEM AS RELATED TO WEATHERING AND TRACE METAL STUDIES

The purpose of this study is to understand some of the processes which are operative in the transport of materials via rivers from the continent to the coastal environment. The study is concerned with the transport of major ions in solution as a result of chemical weathering, the erosion of soils and rock material and mechanisms governing metal transport in the terrestrial system. In regards to certain elements--the major ions--the river is probably a conduit flow which is the total of its tributaries, while in regards to others--Fe, Mn and trace metals--reactions may occur in the river to affect the concentrations in solution and in particles.

The river system is too large to sample all the tributaries in detail, and a widespread, cursory study of such samples might prove to be of limited value. Therefore, a method of study had to be devised which would be logistically feasible and provide the necessary data to solve problems. The uniform climate throughout the basin eliminates it as a variable in the selection of areas of study, although it is a constraint in temporal considerations of sampling. The Susquehanna River drains an area of diverse geology--the Central Appalachians in Pennsylvania, New York and Maryland. The geology of the basin is a very deterministic factor. The land forms and related land use (e.g., the presence of forests) are directly controlled by the geology. Similarly, the hydrologic response of an area is closely related to the geology. It is also generally known that the geology has an influence on the ions dissolved in the ground water and streams of an area. Therefore, it was expected that a concentration of study on areas of well-defined geology, type areas, would be very valuable in understanding the main river.

In order to proceed, it must be demonstrated that there is a definite relationship between the geology of an area and the concentration of ions in the streams draining the region and, furthermore, that areas can be chosen which are representative of others. In this chapter the geology of the Susquehanna River basin is discussed so that regions of representative geology (type areas) may be identified for detailed study. Published data for major elements in streams of the region, mostly USGS water quality data, are then examined in light of the geology to determine if the relationship between water quality and geology is sufficiently good to provide the basis of a detailed study. Finally, the sampling program based upon this preliminary work is described.

Geology

The Susquehanna basin lies within four physiographic provinces of the Appalachians and the coast. From the headwaters in the northwest to the mouth of the river at Chesapeake Bay these are designated: 1) the Plateau Province, 2) the Valley and Ridge Province, 3) the Triassic Lowland, and 4) the Piedmont Province (Figure II-1).

The Plateau Province lies on the northwest flank of the Appalachians and extends its full length. It can be divided into a high plateau and low plateau area (Figure II-1). In the Susquehanna basin the High Plateau area is generally unglaciated, while the Low Plateau to the east is extensively glaciated and covered by Wisconsin till and moraine (Gray et al., 1960; Randall and Coates, 1973). The bedrock underlying the Plateau Province ranges from Devonian to Pennsylvanian in age in the Susquehanna basin. While there are some gentle folds near the southeast flank of the province, the rocks are generally flat lying. On a regional basis the upper Paleozoic rocks exposed here form a gentle synclinorium plunging to the southwest with its axis near the center of the province (Rodgers, 1970; Gray et al., 1960).

The rocks exposed at the surface of the High Plateau range in age from Devonian to Pennsylvanian. The Devonian and Mississippian rocks are shale, siltstone and sandstone--most of which are terrestrial, although some of the lower Devonian rocks are of marine origins (Colton, 1970). A most notable feature of these rocks is a virtual lack of carbonate beds mapable on any scale (Colton, 1970; Gray et al., 1960). The lowest Pennsylvanian of this region is the Pottsville Group, which is composed of sandstone, shale and some thin, occasionally mineable coals but, like the underlying Devonian and Mississippian, lacks carbonate beds. The overlying Pennsylvanian rocks are the Allegheny and Conemaugh groups that contain cyclothems of sandstone, shale, limestone and coal (Colton, 1970).

Due to the Coal Basin Synclinorium and the distinct lithological differences above and below the Pottsville, the High Plateau is distinctly divisible on the basis of the bedrock geology into two regions. The southwest portion of the plateau is underlain exclusively by lower to middle Pennsylvanian rocks containing the bituminous coal and black shales, while the bedrock to the northeast is Devonian to lowermost Pennsylvanian. The demarcation line between the two areas is approximately the West Branch of the Susquehanna River and Sinnemahoning Creek. To the south of this line the only rocks exposed at the surface are the coal-bearing Pennsylvanian rocks. To the north, in the coal-free region, the bedrock is dominantly Devonian and Mississippian clastic rocks. There are, however, scattered outliers of the Pennsylvanian Pottsville and Allegheny groups on some of the flat-topped hills of the dissected plateau within this "coal-free" region.

The northern end of the High Plateau has been glaciated, and some of the tributaries to the West Branch of the Susquehanna River (Pine Creek, Lycoming Creek and Loyalsock Greek) contain glacial outwash deposits. But most of the streams of the High Plateau which flow over extensive glacial till and moraine deposits drain into tributaries of the North Branch of the Susquehanna draining the Low Plateau.

The bedrock of the Low Plateau is the same Devonian rock exposed in the High Plateau, but due to its lower elevation it was glaciated extensively during Pleistocene time, resulting in extensive glacial deposits which cover the bedrock (Randall and Coates, 1973; Gray et al., 1960). Much of this debris is derived from the adjacent bedrock of New York (Randall and Coates, 1973). A study of the areas of maximum glacial erosion in New York shows that the glacial till and moraines should be composed of material derived from the Silurian to Devonian strata surrounding the Finger Lakes region (Staheli, 1971; Dennison 1975) and should therefore contain a variable mixture of carbonate and clastic silicate rocks. In fact, pebble counts in the glacial material near the Pennsylvania-New York border in New York show that carbonate pebbles range from 0 to 22% at different sites (Randall and Coates, 1973). It can be assumed that the fine materials of the till are of the same general composition as the pebbles.

The rocks of the Valley and Ridge Province range in age from Cambrian to Pennsylvanian. The major feature of the stratigraphy is the occurrence of a Cambro-Ordovician carbonate series overlain by an Ordovician to Silurian silicate, clastic sequence which is in turn overlain by a Siluro-Devonian carbonate sequence. The remainder of the section above the Devonian carbonates is Devonian, Mississippian and Pennsylvanian silicate clastics similar to the same formations in the Plateau Province (Colton, 1970). Although the anthracite coal-bearing beds of the Valley and Ridge are time equivalents of parts of the Allegheny and Conemaugh groups of the Plateau Province, there is considerably less mapable carbonate in the coal measures of the anthracite region (Wood et al., 1962; Colton, 1970). From descriptions of the Ordovician-Silurian and Devonian and younger clastics it is clear that they differ in age but not in gross mineralogy.

The rocks of this province have been tightly folded into parallel synclines and anticlines (Rodgers, 1970), which results in the exposure of many rock units within a small area (the carbonates and shales in the valleys, with sandstone at the ridge crests). In addition to the tight folds of the province, there is a large-scale regional deformation resulting in a synclinorium in the anthracite region and an adjacent anticlinorium, the highest point of which (structurally) is the Nittany arch. The result is the exposure of Cambrian to Devonian rocks (carbonate-bearing) in one area and Devonian to Pennsylvanian rocks free of carbonate beds in the anthracite region. The Susquehanna River flows approximately at the boundary between these carbonate-containing and carbonate-free terranes.

Between the southeastern-most sandstone ridge of the Valley and Ridge just upriver from Harrisburg to the Triassic rocks of the Triassic Lowland is a broad, open valley with subdued relief, the Great Valley. Structurally this area is equivalent to the Valley and Ridge Province and is included in it (Rodgers, 1970). The rocks of the valley are the Cambro-Ordovician carbonates and the Ordovician Martinsburg shale, all of which are also exposed in the Valley and Ridge to the northwest (Colton, 1970; Gray et al., 1960).

As alluded to above, the southeastern boundary of the Valley and Ridge is the Triassic rocks. For the most part the Valley and Ridge is unglaciated, although the Illinoian and Wisconsin ice sheets extended into the Susquehanna River in the Wilkes-Barre area (Leverett, 1934; Gray et al., 1960).

The Triassic Lowland is bounded on the northwest side by a normal fault which helped form the basin in which these rocks were deposited. The rocks, all considerably tilted but not folded, are mostly redbeds of sandstone, siltstone and shale (and occasional thin beds of limestone) with flows and intrusive bodies of basalt (Rodgers, 1970). Microscopic examination of the clastic rocks shows that they often contain carbonate cement and authigenic-carbonate minerals (Glaeser, 1966).

The Piedmont Province is bounded on the northwest by the overlapping Triassic sediments and on the southeast by the similarly overlapping Cretaceous sediments (Rodgers, 1970). In the Susquehanna basin this southeast boundary intersects the river at the mouth.

The Piedmont contains primarily two major rock units (Rodgers, 1970). Just south of the Triassic is a series of rocks, Cambrian clastics and Cambro-Ordovician carbonates similar to those of the Great Valley, which occur in a wedge centered on the Susquehanna River. Southeast of this zone is a broad expanse of generally pelitic schists of the Wissahickon Formation (Southwick and Fisher, 1967). There is very little carbonate in this part of the Wissahickon; and although the grade of metamorphism is recorded locally by the appearance of garnet, the composition of these rocks is similar to the clastic sequences of the Valley and Ridge and Plateau Provinces.

Water Quality

Climate and Evapotranspiration

The climate of the Susquehanna River basin is considered to be humid continental type. As the basin extends over 3° of latitude and a terrain of different provinces and spatial relationships in regards to the prevailing westerlies and the Atlantic seacoast, there is a small gradation in temperature and precipitation throughout the basin. The gradation for all parameters is from the Plateau region in the headwaters to the Piedmont near the Atlantic coast at the river mouth.

The mean annual temperature on the Plateau is 8.5°C (47°F) and ranges to 14°C (57°F) near the mouth of the river on the Piedmont.

Precipitation is reported to be fairly uniformly distributed throughout the year with a tendency towards increased rainfall during the spring and summer. Basin-wide the mean annual precipitation is ∿ 104 cm (41 inches). The Plateau regions of Pennsylvania and New York receive a mean annual precipitation of 104 cm (41 inches). The Valley and Ridge Province receives about 101.6 cm (40 inches) per year. The Piedmont, Pocono Mountain and the area between the Piedmont and Poconos receive about 114.3 cm (45 inches), with the extra 10.3 cm (4 inches) above the basin average mostly as a result of summer storms from the Atlantic Ocean.

Most of the precipitation falls as rain, although the ground of the entire region can be snow covered at sometime during the winter. The heaviest snowfall occurs on the Plateau in the river headwaters and decreases by a factor of 2 to the river mouth. On the Piedmont it is estimated that the fields are snow covered about one-third of the winter season (Dailey, 1974).

Of the approximately 41 inches of rainfall over the Susquehanna basin, long-term discharge of the Susquehanna River indicates that about 50% of it is returned to the atmosphere by evapotranspiration (USGS, 1975).

Composition of Streams

The major source of data for ascertaining the composition of streams comes from the widespread monitoring of water quality by the USGS. Table II-1 shows the streams for which the USGS data has been examined to ascertain the relationship between stream compositions. Also included in the table are both the bedrock associated with each stream channel as well as references to the USGS publications in which the water data are given.

Under the same climatic conditions rocks of similar composition will weather to produce effluent waters of similar compositions. Miller (1961), for example, has shown that small streams draining single rock types in the Sangre de Cristo Range of New Mexico tend to have similar compositions. Thus, variations in stream composition should reflect the influences of different rock types under varying climatic regimes.

Variation at a single station

On areas underlain by rocks composed predominantly either of silicate minerals or of carbonate minerals, sampling over an annual cycle shows small variations of the concentrations of dissolved constituents with changing discharge. Typically, the concentration of dissolved constituents will vary within 10% of a mean value, while discharge will change by one to two orders of magnitude.

An example is shown in Figure II-2 for Young Womans Creek, a tributary to the West Branch of the Susquehanna River near Renovo (see SR-5e of this study for exact location). This stream flows over the best-defined lithologic end member of the study area; i.e., the silicate sedimentary rocks of the coal-free region of the High Plateau Province (see: Geology section, this chapter). While there is a scatter of data around a composition of ∿ 28 mg/ℓ of total dissolved solids, the bulk of the data shows little change in composition with change in discharge (USGS, 1971b, 1972a, 1973b, 1972c, and 1974a).

Water quality data for streams that drain terranes of both carbonate and silicate rocks or that are affected by mine drainage do show significant changes of dissolved solids concentration with changing discharge. The variation is generally a dilution of dissolved constituents with increasing discharge. Even though there are variations, they are subdued enough (∿50% dilution with maximum change in discharge) that the data of different streams can be compared at similar stages of discharge.

Stream to stream comparisons

The fact that the compositions of streams are more sensitive to rock type in the drainage basin than to discharge shows that meaningful comparisons of water composition from stream to stream can be made. For the streams in the Susquehanna drainage basin (Table II-1) the compositions are closely related to the geology of the area drained by the stream. Areas underlain by silicate rocks--the Devonian-Mississippian clastics of the High Plateau, the schists.and gneiss of the Piedmont, and the clastic rocks of the Valley and Ridge Province--are drained by streams of nearly the same composition. These include Young Womans Creek, Mix Run, Driftwood Branch of the Sinnemahoning (High Plateau); Octararo Creek (Piedmont); and Antes Creek at Rauchtown (Valley and Ridge). These streams contain less than 50 ppm total dissolved solids, 5 to 20 ppm $SO_4^=$, 10 to 30 ppm HCO_3^-, less than 10 ppm Ca and less than 2 ppm Mg. A few streams of the glaciated Low Plateau have similar element concentrations.

Streams draining carbonate terranes have a distinct composition quite different from the streams draining the dominantly silicate terranes. Comparison of streams draining the Cambro-Ordovician carbonates, such as Spring Creek (Valley and Ridge) and Conestoga Creek and tributaries (Piedmont), to those draining Siluro-Devonian carbonates, such as Messer Run at McVeytown, Pa., shows no significant differences in composition. These streams contain ∿ 250 ppm total dissolved solids, 5 to 20 ppm $SO_4^=$ (as do the silicate streams), ∿ 200 ppm HCO_3^-, 50 ppm Ca and 10 ppm Mg.

Since most of the carbonate rocks are exposed in the tightly folded Valley and Ridge Province, most streams also drain considerable areas underlain by the clastic silicate rocks in the section below and above the Siluro-Devonian carbonates. As a result, these streams have intermediate compositions determined by the volumes of water contributed to the stream by the two different, closely spaced terranes. As discussed earlier, these intermediate streams show more change in concentration with changing discharge than the end member streams. This will be discussed further in a later section (see: Mixing Models, Chapter III). Many of the streams draining the glaciated Low Plateau have compositions that resemble the carbonate or intermediate streams. Since the tills of this area are a variable mixture of Paleozoic sedimentary rocks (see: Geology, this chapter), it is not too surprising that the streams range in composition from silicate to carbonate end member composition as do the streams on the much better-defined bedrock geology of the High Plateau and Valley and Ridge.

It is well recognized that acid drainage from various coal mining operations in the Susquehanna River basin constitute another distinct water type (Biesecker and George, 1966). In general, streams affected by mine drainage can be described as those with greater than 30 to 40 ppm $SO_4^=$, variable HCO_3^-, ∿ 20 ppm Ca and 5 to 10 ppm Mg.

Sampling

Goals of the Study

Seasonal variations in dissolved and particulate concentrations of Mn, Fe and some trace metals have been reported at the mouth of the Susquehanna River (Schubel, 1972). It has been shown above that the water composition of a stream is closely related to the bedrock geology. Therefore, it was possible to choose representative areas (type areas) underlain by one general rock type to assess the source of metals contributing to the seasonal variation. Furthermore, sampling sites were spaced along the river and at the mouths of major tributaries both to detect sources that the type area sampling might omit and to assess the changes in water composition along a major river during several different times of the year.

Selection of Sample Sites

As can be seen from the distribution of sample sites within the basin (Figure II-3, Table II-2), the sampling for this study was concentrated on the West Branch of the Susquehanna River sub-basin and the Susquehanna River below Sunbury. An important factor in this selection of sample sites was the presence in the West Branch of the Susquehanna River basin of all the type waters discussed above. In contrast, the North Branch of the Susquehanna River basin is much less characterized because it comprises mainly the glaciated Low Plateau region. In addition, the arrangement of the West Branch in relation to mine-drainage inputs provided the opportunity to use this phenomenon in a study of geochemical tracers as well as the opportunity to explore the extent of such perturbations on the natural regime.

Most mine drainage addition to the West Branch occurs above Keating (SR-5a, Figure II-3). Only small amounts of low alkalinity silicate type water is added from Keating to Lock Haven (SR-6) (a river distance of ∿ 30 miles), resulting in a relatively constant pH of 4 to 4.5 over this distance. At Lock Haven the relatively high influx of alkalinity from Bald Eagle Creek quickly neutralizes the acid and raises the pH to greater than 6. Because the slope of the pH versus alkalinity curve (at equilibrium with atmospheric CO_2) significantly above the bicarbonate end point is small and the majority of the water added to the West Branch below Bald Eagle Creek is low alkalinity silicate type water, the pH is in the range of 6.5 to 7.5.

Along this path the major changes in chemical properties such as pH affect the behavior of metals in solution. As this behavior is the essence of this study, the choice of sampling sites is clearly controlled by the awareness of such changes.

Choice of tributary sampling sites

From the preliminary study of the geology and related stream water compositions, it is apparent that there are three type areas: silicate terranes, carbonate terranes and mined Pennsylvanian coal areas.

The stream initially chosen to represent drainage from silicate terranes was Pine Creek (SR-8, Figure II-3). It was chosen because it drains a large area of the High Plateau and is a major tributary to the West Branch of the Susquehanna River below Lock Haven. However, mid-way in the study the data indicated the possibility of contamination by mine waters. This was substantiated and another tributary basin was located where it is well established that no coal mining has occurred. The basin selected for study is near the headwaters of the Driftwood Branch of Sinnemahoning Creek. The sites are shown on the map for part of the Rich Valley 7 1/2 minute quadrangle (Figure II-4). The most upstream mining which has occurred in this basin was minor and located on the south side of the first tributary to the Driftwood Branch below the sample area. The sample network included one site on the Driftwood Branch (RV-1), four springs (RV-3, RV-4, RV-5, and RV-7), two ephemeral streams (RV-2 and RV-8) near two of the above-mentioned springs, and one well in the valley alluvium (RV-6). The basin is sparsely populated and is > 96% forest of deciduous type. The samples taken from these sites were to be compared to one another and to other Plateau tributaries at each sampling time and throughout the sampling cycle.

Buffalo Creek (Union Co., Pa.) was chosen as representing the drainage directly to the river from carbonate terranes. It was chosen because it drains a relatively broad valley underlain by the Siluro-Devonian carbonate sequence discussed earlier (see: Geology). Furthermore, it is a tributary flowing directly into the West Branch of the Susquehanna which was being studied in some detail. As discussed earlier, there are two major carbonate sequences exposed in the Valley and Ridge of the Central Appalachians. Almost all of the drainage from the Cambro-Ordovician carbonate terranes flows into Bald Eagle Creek and the Juniata River which, because of their quantitative significance to the Susquehanna River, have been sampled individually. Therefore, of the several streams that directly enter the Susquehanna from carbonate terranes, the Buffalo Creek drainage is geologically an excellent representative.

Based on USGS data for stream water quality, Chest Creek and Clearfield Creek were sampled as streams draining fairly large areas of the bituminous coal area of the High Plateau Province. However, subsequent analysis of these samples showed an apparent diminuition of mine drainage inputs into these streams, although Clearfield Creek is still acid and high in $SO_4^=$, Mn and Fe--clear indices of acid mine water. Later, Moshannon Creek near Osceola Mills, Pa., was sampled since it contains more mine drainage than Clearfield Creek. The determination of a mine drainage type water composition can be estimated from the data for these sample sites. It appears that the mine drainage from the bituminous regions is similar to that from the anthracite region (Biesecker and George, 1966).

Sample Sites on the West Branch of the Susquehanna River above Lock Haven

The sites near the head of the river were established to ascertain water compositional changes near the head as more mine drainage was added downriver. The site at Bower, Pa., (SR-2) corresponds to a USGS water quality station and allows comparison of the data of this study to that of present and past USGS data. The site (SR-2a) below the Curwensville Dam (at another gaging station) was occupied to determine the effect of small reservoirs on the chemical properties of a stream. The site at Karthaus (SR-5) was originally established to sample water quality after massive addition of mine drainage to the West Branch. However, it became obvious that the river was not well mixed at this site since Moshannon Creek entered the river a short distance upstream. Therefore, a site was established at Keating (SR-5a) above Sinnemahoning Creek where most of the mine drainage had been added and the river should be well mixed. Four additional sites from Keating to Lock Haven were occupied to study reactions in this section of river. The site at Lock Haven (SR-6) also served as a measure of water composition being input into the area of acid neutralization below Bald Eagle Creek.

Sample sites on the river from Lock Haven to the mouth of the Susquehanna River

Below Lock Haven to the confluence of the West Branch and the North Branch sample stations were placed about every 20 miles (SR-9, SR-10, SR-13, SR-13a). In all cases an effort was made to locate the site so that the local effects from inflowing tributaries would be minimized. Below the confluence the sites were relatively widely spaced (SR-14, SR-16, SR-17), mainly to assess water composition after mixing of the major tributaries. The sites at Marietta (SR-16) and Conowingo (SR-17) were established also to evaluate the effects of the three reservoirs behind the hydroelectric dams between Marietta and Conowingo. In addition, the Marietta site was one occupied for previous geochemical studies (Turekian and Scott, 1967; Brass, 1973) by workers at Yale University. The site at Conowingo (SR-17) represents the composition of materials entering Chesapeake Bay and can be compared to the closely spaced sampling reported by Schubel (1972).

Major tributaries

Several tributaries to the West Branch of the Susquehanna or to the Susquehanna River were sampled routinely. Sinnemahoning Creek at Keating (SR-5b) was sampled as it is the only large tributary to the West Branch of the Susquehanna River between Curwensville and Lock Haven. Bald Eagle Creek at Lock Haven (SR-7) mixes with the West Branch of the Susquehanna River to produce an entirely new river regime after the confluence. Pine Creek (SR-8), discussed earlier under type waters, was also sampled due to its quantitative importance as a tributary to the West Branch not far downriver from Lock Haven.

The discharge of the North Branch of the Susquehanna River at Danville, ∿ 10 miles upriver from where a sampling station was established (SR-12), is about the same as for the West Branch at Lewisburg. The Juniata River, which primarily drains the Valley and Ridge Province, was sampled near Newport, Pa. (SR-15).

Variation in water quality in cross sections

At a number of times the USGS has sampled the main branches of the Susquehanna River in cross sections. The sampling station on the West Branch of the Susquehanna is at Lewisburg, and the data indicate that except for periods of lowest flow the West Branch is well mixed from bank to bank (USGS, 1964, 1972a).

From numerous cross section samples of the Susquehanna at Harrisburg Anderson (1963) concluded that the Susquehanna River below Sunbury is not mixed efficiently: the east bank (left bank to an observer facing downstream, Gary et al., 1972) samples are high in $SO_4^=$ due to mine drainage influence on the North Branch and several tributaries above the Juniata River between Sunbury and Harrisburg, and the west bank (right bank) samples are high in HCO_3^-, Ca^{++}, and Mg^{++} due to mixing of the Juniata River with the Susquehanna River. However, these cross-sectional variations at Harrisburg may all be ascribed to local inputs. On the west bank (right bank) only a few hundred meters upstream from the cross section site Conodoguinet Creek--with very high alkalinity, Ca^{++} and Mg^{++} compared to the Susquehanna River--(Anderson, 1963) enters the river. Similarly, on the east bank (left bank), Strong Creek flows into the Susquehanna just upriver from Harrisburg and has its source in the anthracite coal region. Although no water quality data are available for this stream, it, like most other streams arising in coal country, is probably polluted by $SO_4^=$ rich mine drainage.

Similar cross sections at Marietta, Pa., and Columbia, Pa., (separated by only a few miles along the course of the river) show no significant inhomogeneities between right-bank samples and the middle of the river. There are no major tributaries on this side of the river for some distance upriver. Clearly, these data show that whatever the cause of the right bank inhomogeneity at Harrisburg, it is wiped out by the time the river reaches Marietta (a distance of ∿ 20 miles along the course of the river). This also speaks for local effects in causing the inhomogeneities at Harrisburg since otherwise the inhomogeneities would have to persist for a distance of up to 70 miles. At Marietta and Columbia there is a high $SO_4^=$ anomaly on the left bank, but again there is a nearby upstream source for this $SO_4^=$, Swatara Creek (McCarren et al., 1961).

Therefore, it must be concluded that when sample stations are located at reasonable distances downstream from local sources, the river is well mixed and a nearshore sample will be representative of the river water.

Frequency of Sampling

Part of the goal of this study was to determine the nature of the seasonal variation observed at the mouth of the Susquehanna and to determine the relationship of element fluxes to river and stream discharges. These goals were met with an approximately bimonthly sample spacing over a period of 15 months from April 1973 to June 1974.

Sampling Equipment Used and Types of Samples Taken

An important aspect of this study is that filtration of samples was carried out in the field and was completed within 1 to 2 hours of sample collection. The filtration system is operated by pressurizing a jerrican containing the water and suspended sediment. The water, a bucket surface sample, is forced through one of these filter types:

1. 47 mm, 0.4 μm pore diameter membrane filters--used for particles only, water volume filtered measured with a graduated cylinder

2. 47 mm, 0.45 nominal pore size, glass fiber filters--particles only, volume of water filtered measured
3. 142 mm, 0.4 μm pore diameter membrane filters (Nuclepore)--used to collect water and particles for stable element analyses. (Also, at certain sites additional particle and filtered water samples were taken for radionuclide analyses).

At sites where samples of particles and filtered water for radionuclide analyses were taken, unfiltered samples were also taken. Generally a 4 to 6 ℓ unfiltered sample was taken and acidified for later analysis to determine if the field filtration process was quantitative, especially in regards to Pb^{210}. At two sampling times large-volume, unfiltered, unacidified samples were collected at seven sites. These samples were later filtered in the laboratory and the water then acidified. The particles and water were analyzed for U^{238} and U^{234} and also Ra^{226} and Pb^{210}. A complete discussion of sample identification markers is given in Appendices I, II and III.

Other field data include in situ pH measurements with a portable pH meter and measurement of air and water temperatures with a mercury thermometer. Initially alkalinity titrations were performed in the field; but since these values agreed with alkalinities determined on field-filtered, unacidified aliquots in the lab, the field titrations were discontinued after the first two field trips (Table II-3). Samples were collected for analysis of dissolved oxygen by first pickling them in the field by adding the manganous sulfate and alkaline iodide solutions and then later performing a Winkler titration in the laboratory after acidification with sulfuric acid (Strickland and

Parsons, 1972). Including the radionuclide samples, about 220 samples sets (consisting of filtered water and particles on filters) were taken for analysis (Table II-4).

Data Collected for This Study

The following elements have been determined in the filtered water: Fe, Mn, U^{238}, U^{234}, Pb^{210} and Po^{210} as well as Na^+, K^+, Ca^{++}, Mg^{++}, $HCO_3^=$, $SO_4^=$ and Cl^-. The particles have been analyzed for Fe, Mn, Al, Ra^{226}, Pb^{210}, U^{238}, U^{234} and organic matter.

Dissolved Na^+, K^+, Ca^{++} and Mg^{++} were determined by flame atomic absorption spectrophotometry (AAS) on a Perkin-Elmer 303. Analytical precision for replicate analyses of these four cations is ± 5% of the concentration. Dissolved Fe has been determined using the reagent ferrozine as discussed by Stookey (1970), with the elimination of the boiling step which was not necessary with these samples. An analytical precision of about ± 5% was obtained for dissolved iron. Dissolved manganese has been determined by flame AAS with a Perkin-Elmer 303 utilizing direct aspiration for samples > 1 ppm and standard additions for samples < 1 ppm, and with a Heated Graphite Atomizer-Atomic Absorption Spectrophotometry (HGA-AAS) system (Perkin-Elmer 360 with a Heated Graphite Atomizer [HGA] 2100 furnace) at the Rhode Island Nuclear Science Center (RINSC), Narragansett, R.I. Analytical precision in both cases was about ± 5% to ± 10%. Good agreement was obtained between sample aliquots analyzed by flame AAS utilizing standard additions and flameless AAS. Sulfate was determined by a spectrophotometric technique utilizing the $FeSO_4^+$ complex (Goguel, 1969). The precision of the sulfate method is about ± 10% of the concentrations. Chloride and alkalinity were determined by potentiometric tritration utilizing Gran plots (Gran, 1952, 1950; Jagner and Åren, 1970). Precision of the Gran tritations for chloride and alkalinity is less than ± 5% of the concentration, with some repeated titrations yielding a precision of ± 2%. Chloride was determined in the June 1974 samples by using a chloride electrode (Coleman) and double junction reference electrode to obtain a calibration curve determined with chloride standards. Direct electrode determination of chloride has a precision of about ± 10%. The U^{238}, U^{234} and Po^{210} are determined by alpha counting after extraction from solution by coprecipitating with Fe(OH) and chemical purification. Pb^{210} is determined by alpha counting its daughter, Po^{210}, after ingrowth from a purified state. Details of the radionuclide analytical methods are discussed by Benninger (1976). Errors reported for the radionuclide analyses are based only on counting statistics.

Particulate analyses for U and Pb^{210} are as above, except that first the samples were totally dissolved in HNO_3-HF. In addition, Ra^{226} was determined by the Rn^{222} emanation technique (Turekian, Kharkar, and Thomson, 1973). Particulate organic matter was determined by weight loss on ignition of the samples on the 47 mm glass fiber filters. Particulate Mn and Al were determined by Instrumental Neutron Activation Analysis (INAA) at the Rhode Island Nuclear Science Center utilizing an internal standard of Yb for flux and dead time corrections (Appendix IV). Duplicate analyses indicate a combined sampling and analytical precision of about ± 5% for particulate manganese.

TABLE II-1. SUSQUEHANNA RIVER BASIN STREAMS: GEOLOGICAL MATERIAL AT THE SURFACE AND USGS PUBLICATIONS REPORTING WATER COMPOSITIONS

Sample Site Stream and Location	Stream Bed Geology	WSP-1132	WSP-1162	WSP-1186	WSP-1197	WSP-1250	WSP-1290	WSP-1350	WSP-1400	WSP-1450	WSP-1520	WSP-1741	WSP-1881	WSP-1941	WSP-1947	WSP-1954	WSP-2011	WSP-2091	WSP-2141	WRDNY 1971	WRDNY 1972	WRDNY 1973	WRDP 1969	WRDP 1970	WRDP 1971	WRDP 1972
Susquehanna River above Conklin, N.Y.																										
Schenevus Creek at Schenevus, N.Y.	g										M															
Susquehanna River at Colliersville, N.Y.	g						M																			
Otego Creek near Oneonta, N.Y.	g										M															
Flax Island Creek near Otego, N.Y.	g																M									
Susquehanna River at Otego, N.Y. and Unadilla, N.Y.																	P	P		P	P	P				
Ouleout Creek at East Sidney, N.Y.	g										M															
Butternut Creek at Morris, N.Y.	g										M					M										
Unadilla River near New Berlin, N.Y.	g						M				P															
Unadilla River at Rockdale, N.Y.											P															
Susquehanna River near Great Bend, Pa.																			M					P	P	P
Snake Creek near Montrose, Ra.	g,s																M	M	M							
Susquehanna River at Conklin, N.Y.							M		P													P				
Chenango River System																										
Chenango River at Greene, N.Y.	g						M				P															
Red Brook near Smithville Flats, N.Y.	g																M									
Red Brook at Smithville Flats, N.Y.	g																M									
Genegantslet Creek at Smithville Flats, N.Y.	g																P	P	P							
East Branch Tioughnioga Creek near Cortland, N.Y.	g										M															
West Branch Tioughnioga Creek at Homer, N.Y.	g										M										P	P				
Tioughnioga River at Cortland, N.Y.	g										P										P					

TABLE II-1. (Continued)

Sample Site Stream and Location	Stream Bed Geology	WSP-1132	WSP-1162	WSP-1186	WSP-1197	WSP-1250	WSP-1290	WSP-1350	WSP-1400	WSP-1450	WSP-1520	WSP-1741	WSP-1881	WSP-1941	WSP-1947	WSP-1954	WSP-2011	WSP-2091	WSP-2141	WRDNY 1971	WRDNY 1972	WRDNY 1973	WRDP 1969	WRDP 1970	WRDP 1971	WRDP 1972
Otselic River near Upper Lisle, N.Y.	g						M							M												
Otselic River at Cinncinnatus, N.Y.	g													M												
Tioughnioga River at Itaska, N.Y.	g						M																			
Susquehanna River at Johnson City, N.Y.																				P	P	P				
Susquehanna River at Waverly, N.Y.							M																			
Chemung River System																										
Kirkwood Creek near North Cohocton, N.Y.	g																M									
Cohocton River at Avoca, N.Y.	g						M																			
Fivemile Creek near Kanona, N.Y.	g																P	P	P	P	P	P				
Campbell Creek near Kanona, N.Y.	g						M																			
Cohocton River near Campbell, N.Y.	g						M			P																
Canisteo River at Arkport, N.Y.	g						M																			
Canacadea Creek near Hornell, N.Y.	g						M																			
Canisteo River at Hornell, N.Y.	g						M																			
Canisteo River at West Cameron, N.Y.	g						M				P															
Crooked Creek at Tioga, Pa.	g,s																									P
Crooked Creek at Little Marsh, Pa.	g,s																M	M	M							
Crooked Creek at Crooked Creek, Pa.	g,s									M																
Corey Creek near Mainesburg, Pa.	s									P	P	P	P		P	P	P									
Elk Run near Mainesburg, Pa.	s									P	P	P	P		P	P	P									

TABLE II-1 (Continued)

Sample Site Stream and Location	Stream Bed Geology	WSP-1132	WSP-1162	WSP-1186	WSP-1197	WSP-1250	WSP-1290	WSP-1350	WSP-1400	WSP-1450	WSP-1520	WSP-1741	WSP-1881	WSP-1941	WSP-1947	WSP-1954	WSP-2011	WSP-2091	WSP-2141	WRDNY 1971	WRDNY 1972	WRDNY 1973	WRDP 1969	WRDP 1970	WRDP 1971	WRDP 1972
Tioga River at Tioga, Pa.	s						M				M								M					P	P	P
Cowanesque River near Lawrenceville, Pa.	s																		P				P	P	P	P
Tioga River at Lindley, N.Y.	s															M										
Tioga River near Erwins, N.Y.	s						M																			
Chemung River at Big Flats, N.Y.	g,s																									
South Creek at Fassett, Pa.	g,s																M	M	M							
Chemung River at Wellsburg, N.Y.	g																			P	P	P				
Chemung River at Chemung, N.Y.	g						M	P									P	P								
Saterlee Creek at Athens, Pa.	g,s																M									
Susquehanna River from below the confluence with the Chemung River to the confluence with the West Branch Susquehanna River																										
North Branch Sugar Creek tributary near Columbia Cross Roads, Pa.	g,s																		M							
Tomjack Creek near Bourne, Pa.	g,s																M	M	M							
Susquehanna River at Towanda, Pa.					P	M		P																		
East Branch Wyalusing Creek at Lawton, Pa.	g,s																M	M	M							
Little Tuscarora Creek at Laceyville, Pa.	g,s																M	M	M							
Meshoppen Creek near Springville, Pa.	g,s																M		M							
Hop Bottom Creek at Brooklyn, Pa.	g,s																M	M	M							
South Branch Tunkhannock Creek near Dalton, Pa.	g,s																		M							
Susquehanna River at Falls,Pa.		P	P	P	P	P	P			M									M					P	P	P

TABLE II-1. (Continued)

Sample Site Stream and Location	Stream Bed Geology	WSP-1132	WSP-1162	WSP-1186	WSP-1197	WSP-1250	WSP-1290	WSP-1350	WSP-1400	WSP-1450	WSP-1520	WSP-1741	WSP-1881	WSP-1941	WSP-1947	WSP-1954	WSP-2011	WSP-2091	WSP-2141	WRDNY 1971	WRDNY 1972	WRDNY 1973	WRDP 1969	WRDP 1970	WRDP 1971	WRDP 1972
Lackawanna River at Forrest City, Pa.	s,cl	M	M																							
Lackawanna River at Carbondale, Pa.	s,cl	M	M																							
Lackawanna River at Archbald, Pa.	s,cl	M												M		P	P	P	P				P	P	P	P
Lackawanna River at Old Forge, Pa.			PM	P	P					P		M	P	M		M	P	P	P				P	P	P	P
Susquehanna River at Wilkes-Barre, Pa.										M																
Toby Creek at Luzerne, Pa.	s,cl	M	M																							
Harvey Creek at West Nanticoke, Pa.	s	M	M																							
Hunlock Creek at Hunlock Creek, Pa.	s	M	M																							
Susquehanna River near Hunlock Creek, Pa.																			M					P	P	P
Shickshinny Creek at Shickshinny, Pa.	s,cl	M	M																							
Susquehanna River at Shickshinny, Pa.		M	M															M								
Susquehanna River at Mocanaqua,Pa.																	M									
Wapwallopen Creek at Wapwallopen, Pa.	s		M	M																						
Susquehanna River at Berwick, Pa.																	M	M								
Nescopeck Creek at Nescopeck, Pa.	s,cl		M	M																						
Briar Creek at Briar Creek, Pa.	s,cr	M	M																							
Fishing Creek near Bloomsburg, Pa.	s,cr																P	P	M							
Tomhickon Creek near Zion Grove, Pa.	s,cl																M	M	M							
Catawissa Creek at Catawissa, Pa.	s,cl	P	M	M																						
Susquehanna River at Danville, Pa.			P	P	P	P	P			P	P	P	P	P	P	P	P	P	P				P		P	P
Mahoning Creek at Danville, Pa.	s,cr	M	M																							

TABLE II-1. (Continued)

Sample Site Stream and Location	Stream Bed Geology	WSP1132	WSP-1162	WSP-1186	WSP-1197	WSP-1250	WSP-1290	WSP-1350	WSP-1400	WSP-1450	WSP-1520	WSP-1741	WSP-1881	WSP-1941	WSP-1947	WSP-1954	WSP-2011	WSP-2091	WSP-2141	WRDNY 1971	WRDNY 1972	WRDNY 1973	WRDP 1969	WRDP 1970	WRDP 1971	WRDP 1972
West Branch Susquehanna River																										
Wilson Run at Newburg, Pa.	s,cl																M	M	M							
West Branch Susquehanna River at Bower, Pa.												M				P										
West Branch Susquehanna River at Curwensville, Pa.											M	M	P													
Montgomery Creek at Hyde, Pa.	s,cl																M	M	M							
Beaver Run near St. Augustine, Pa.	s,cl																		M							
Killbuck Run near St. Augustine, Pa.	s,cl																		M							
Wyerough Run near Flinton, Pa.	s,cl																		M							
Slate Lick Run near Frugality, Pa.	s,cl																		M							
Burgoon Run at St. Augustine, Pa.	s,cl																		M							
Slate Lick Run tributary near Frugality, Pa.	s,cl																		M							
Little Clearfield Creek at Kerrmoor, Pa.	s,cl																M	M	M							
Cowley Run at Sizerville, Pa.	s																M	M	M							
Driftwood Branch of Sinnemahoning Creek at Sterling Run, Pa.	s															P	P	P								
Driftwood Branch of Sinnemahoning Creek at Cameron, pa.	s										M															
Mix Run near Driftwood, Pa.	s																M	M	M							
Sinnemahoning Creek at Sinnemahoning, Pa.	s,cl											P	M	M	P	P	P	P	PM				P	P	P	P
East Fork Sinnemahoning Creek near Logue, Pa.	s																M	M								
First Fork Sinnemahoning Creek at Sinnemahoning, Pa.	s										M															P
West Branch Susquehanna River at Keating, Pa.														M												

TABLE II-1 (Continued)

Sample Site Stream and Location	Stream Bed Geology	WSP-1132	WSP-1162	WSP-1186	WSP-1197	WSP-1250	WSP-1290	WSP-1350	WSP-1400	WSP-1450	WSP-1520	WSP-1741	WSP-1881	WSP-1941	WSP-1947	WSP-1954	WSP-2011	WSP-2091	WSP-2141	WRDNY 1971	WRDNY 1972	WRDNY 1973	WRDP 1969	WRDP 1970	WRDP 1971	WRDP 1972
Kettle Creek near Westport, Pa.	s,cl										M															
Kettle Creek at Westport, Pa.	s,cl										M															
West Branch Susquehanna River at Renova, Pa.																M	P	P	P				P	P	P	P
Young Womans Creek near Renovo, Pa.	s																M	P	P				P	P	P	P
West Branch Susquehanna River at Hyner, Pa.											M															
Queens Run near Lock Haven, Pa.	s																M	M	M							
West Branch Susquehanna River at Lock Haven, Pa.		P	P	P	P					P	M	P	P	P	P	P	P	P	P				P	P	P	P
Spring Creek near Axemann, Pa.	cr																P	P						P		
Bald Eagle Creek near Milesburg, Pa.	s,cl,cr									P	P							P	P				P	P		
Bald Eagle Creek at Blanchard, Pa.	s,cl,cr									P	P	P	M	P	P	P	P	P					P	P	P	P
Marsh Creek at Blanchard, Pa.										P	P						M									
Big Run at Orviston, Pa.	s,cl																M	M	M							
Beech Creek at Monument, Pa.	S,cl													M				M	P				P	P	P	P
Beech Creek at Beech Creek Station, Pa.	s,cl													M												
Bald Eagle Creek at Beech Creek Station, Pa.	s,cl,cr																M	M								
Bald Eagle Creek at Mill Hall, Pa.	s,cl,cr																M	M								
Little Fishing Creek at Mill Hall, Pa.	cr,s																M	M	M							
Fishing Creek at Mill Hall, Pa.	cr,s																M	M	M							
West Branch Susquehanna River at Chatham Run, Pa.												M														
Babb Creek at Morris, Pa.	s,cl																M	M	M							
Pine Creek at Cedar Run, Pa.	s,cl																P	P	M							
Trout Run at Cammal, Pa.	s																M	M	M							
Pine Creek near Jersey Shore, Pa.	s,cl				M												M									
Antes Creek at Rauchtown, Pa.	s																M	M	M							

TABLE II-1 (Continued)

Sample Site Stream and Location	Stream Bed Geology	WSP-1132	WSP-1162	WSP-1186	WSP-1197	WSP-1250	WSP-1290	WSP-1350	WSP-1400	WSP-1450	WSP-1520	WSP-1741	WSP-1881	WSP-1941	WSP-1947	WSP-1954	WSP-2011	WSP-2091	WSP-2141	WRDNY 1971	WRDNY 1972	WRDNY 1973	WRDP 1969	WRDP 1970	WRDP 1971	WRDP 1972
Mill Creek at Roaring Branch, Pa.	s																M	M	M							
Lycoming Creek near Trout Run	s,cl					M	M																			
Little Loyalsock Creek near Dushore, Pa.	s,g																M	M	M							
Elk Creek near Estella, Pa.	s,g																M	M	M							
Loyalsock Creek at Loyalsock, Pa.	s,cl,g					M	M																			
Little Muncy Creek at Lairdsville	s																M		M							
West Branch Susquehanna River at Lewisburg, Pa.		P	P	P	P	P	P			P	P	P	M	Mx		P	M	Px	P				P	P	P	P
Mud Creek at Washingtonville, Pa.	s,cl																M	M	M							
Susquehanna River: Sunbury to the Juniata River																										
Susquehanna River at Sunbury, Pa.												M				Mx	M	Mx	M							
Shamokin Creek near Shamokin	cl,s																P									
Shamokin Creek at Weigh Scales	cl,s		M	M								P	MP													
Penns Creek at Penns Creek, Pa.	cr,s		M													P	M	P	P				P	P	P	P
Middle Creek near Beavertown, Pa.	cr,s																M	M	M							
Middle Creek near Selinsgrove, Pa.	cr,s	M	M																							
Mahony Creek at Dornsife	s,cl		M	M																						
West Branch Mahantango Creek at Oriental, Pa.	cr,s																M	M	M							
West Mahantango Creek near McKees Half Falls, Pa.	cr,s	M	M																							
East Mahantango Creek near Dalmatia, Pa.	s,cl		M	M															M							
Wiconisco Creek at Elizabethville, Pa.	s,cl		M	M																						
Armstrong Creek near Enders, Pa.	s																	M	M							

TABLE II-1. (Continued)

Sample Site Stream and Location	Stream Bed Geology	WSP-1132	WSP-1162	WSP-1186	WSP-1197	WSP-1250	WSP-1290	WSP-1350	WSP-1400	WSP-1450	WSP-1520	WSP-1741	WSP-1881	WSP-1941	WSP-1947	WSP-1954	WSP-2011	WSP-2091	WSP-2141	WRDNY 1971	WRDNY 1972	WRDNY 1973	WRDP 1969	WRDP 1970	WRDP 1971	WRDP 1972
Armstrong Creek at Halifax, Pa.	s																M	M	M							
Powell Creek at Union Church near Enterline, Pa.	s																	M	M							
Juniata River System																										
Sugar Run at Altoona	s,cl																M	M	M							
South Bald Eagle Creek near Tyrone, Pa.	cr,s,cl	M																								
South Bald Eagle Creek at Tyrone, Pa.	cr,s,cl	M																								
Little Juniata River at Pinecroft, Pa.	cr,s,cl	M																								
Little Juniata River above Tyrone, Pa.	cr,s,cl	M																								
Little Juniata River below Tyrone, Pa.	cr,s,cl	M																								
Little Juniata River above Spruce Creek, Pa.	cr,s,cl	M																								
Little Juniata River at Barree, Pa.	cr,s,cl	M																								
Frankstown Branch Juniata River near Williamsburg, Pa.	s,cr	M																								
Frankstown Branch Juniata River below Williamsburg, Pa.	s,cr	M																								
Clove Creek at Larke		M																								
Frankstown Branch Juniata River at Alexandria, Pa.	s,cr	M																								
Frankstown Branch River at Huntingdon, Pa. (also Juniata River at Huntingdon, Pa.)	s,cr	M	P	P	P					P					P	P	P	P	P				P	P	P	P
Frankstown Branch River below Huntingdon, Pa. (also Juniata River below Huntingdon, Pa.)	s,cr	M																								

TABLE II-1. (Continued)

Sample Site Stream and Location	Stream Bed Geology	WSP-1132	WSP-1162	WSP-1186	WSP-1197	WSP-1250	WSP-1290	WSP-1350	WSP-1400	WSP-1450	WSP-1520	WSP-1741	WSP-1881	WSP-1941	WSP-1947	WSP-1954	WSP-2011	WSP-2091	WSP-2141	WRDNY 1971	WRDNY 1972	WRDNY 1973	WRDP 1969	WRDP 1970	WRDP 1971	WRDP 1972
Laurel Run at McAlevys Fort, Pa.	s																M	M	M							
Standing Stone Creek at Huntingdon, Pa.	s,cr	M																								
Mile Run at Schellsburg, Pa.	s,cl																		M							
Shawnee Branch tributary near Schellsburg, Pa.	s,cl																		M							
Raystown Branch Juniata River near Manns Choice, Pa.																	M									
Bobs Creek at Weyant, Pa.	s,cl																M	M	M							
Cove Creek near Rainsburg, Pa.	cr																M	M	M							
Raystown Branch at Saxton														M												
Great Trough Creek at Marklesburg, Pa.	cr	M																								
Raystown Branch Juniata River near Huntingdon, Pa.	cr,s		P	P						P				M	P	P	M	P	P				P	P	P	P
Juniata River at Mill Creek, Pa.		M																								
Juniata River at Mount Union, Pa.		M																								
Aughwick Creek near Three Springs, Pa.		M																								
Messer Run at McVeytown, Pa.	cr																M	M	M							
Kishacoquillas Creek at Reedsville, Pa.	s,cr	M																								
Juniata River at Lewistown, Pa.		M																								
Juniata River near Lewistown, Pa.		M																								
Lost Creek near Mifflin town, Pa.	s,cr																M	M	M							
Juniata River at Mifflin town		M																								
Narrows Branch Tuscarora Creek at Concord, Pa.	cr,s																M	M	M							
Tuscarora Creek at Port Royal, Pa.	cr,s	M																								

TABLE II-1. (Continued)

Sample Site Stream and Location	Stream Bed Geology	WSP-1132	WSP-1162	WSP-1186	WSP-1197	WSP-1250	WSP-1290	WSP-1350	WSP-1400	WSP-1450	WSP-1520	WSP-1741	WSP-1881	WSP-1941	WSP-1947	WSP-1954	WSP-2011	WSP-2091	WSP-2141	WRDNY 1971	WRDNY 1972	WRDNY 1973	WRDP 1969	WRDP 1970	WRDP 1971	WRDP 1972
Raccoon Creek at Donnally Mills, Pa.	cr,s																M	M	M							
Cocolamus Creek near Millerstown, Pa.	cr,s	M																								
Buffalo Creek at Newport, Pa.	cr,s	M																								
Little Buffalo Creek near New Bloomfield, Pa.	cr,s																M	M								
Juniata River at Newport, Pa.		PMP		P	P	P	P	P	P	P	P	P	P	P		P	P	P	P				P	P	P	P
Susquehanna River from confluence with the Juniata River to the mouth																										
Susquehanna River at Duncannon, Pa.													M													
Bixler Run near Loysville, Pa.	cr,s										P	P	P	P	P	P	P	P	P				P			
Sherman Creek at Shermans Dale, Pa.	cr,s													M					M							
Sherman Creek near Duncannon, Pa.	cr,s		M																							
Doubling Gap Creek at McCrea, Pa.	s																M	M	M							
Conodoquinet Creek at Hogestown	cr,s						M																			P
Spring Creek tributary near Harrisburg, Pa.	cr,s																		M							
Susquehanna River at Harrisburg, Pa.		P	P	P	P	P	M			P	P	P	P	P	P	P	P	P	P				P	P	P	P
Dogwood Run near Dillsburg, Pa.	m,cr																M	M	M							
Swatara Creek at Swatara Gap	s,cl,cr																		M							
Swatara Creek near Hummelstown, Pa.	s,cl,cr	M	M																							
Swatara Creek at Harpers Tavern, Pa.	s,cl,cr		M	M								PMP														
Fishing Creek at Newberry, Pa.	T										M															
Conewago Creek near Bellaire, Pa.	T																M	M	M							
Conewago Creek near Elizabethtown, Pa.	T		M																							
Bermudian Creek near York Springs, Pa.	T																M	M	M							

TABLE II-1. (Continued)

Sample Site Stream and Location	Stream Bed Geology	WSP-1132	WSP-1162	WSP-1186	WSP-1197	WSP-1250	WSP-1290	WSP-1350	WSP-1400	WSP-1450	WSP-1520	WSP-1741	WSP-1881	WSP-1941	WSP-1947	WSP-1954	WSP-2011	WSP-2091	WSP-2141	WRDNY 1971	WRDNY 1972	WRDNY 1973	WRDP 1969	WRDP 1970	WRDP 1971	WRDP 1972
Latimore Creek near York Springs, Pa.	T																		M							
Beaver Creek at Rossville, Pa.	T																	M	M							
Beaver Creek near Lewisberry, Pa.	T																M									
West Conewago Creek near Manchester, Pa.	T													M					M							
South Branch Codorus Creek near York	m,cr																P									
Codorus Creek near York, Pa.	m,cr		P							M							M									
Susquehanna River at Marietta, Pa.													Mx													
Little Chickies Creek at Mt. Joy, Pa.	cr,s		M																							
Susquehanna River at Columbia, Pa.										Mx																
Otter Creek near New Bridgeville, Pa.	m																M	M	M							
Little Muddy Creek near Reamstown, Pa.	T		M														M	M	M							
Cocalico Creek near Oregon	cr,s		M																							
Lititz Run at Oregon	cr		M																							
Mill Creek at Lancaster	cr,s		M																							
Conestoga Creek at Lancaster, Pa.	cr,s	P	P	P						M		P	P	P	P	P	P	P	P				P	P	P	P
Little Conestoga Creek	cr,s		M																							
Susquehanna River at Holtwood, Pa.																								P	P	P
Muddy Creek at Castle Fin, Pa.	m																		M							
Muddy Creek near Homeville	m		M																							
East Branch Octararo Creek near Homeville, Pa.	m		M																							
Octararo Creek at Lees Bridge near Glenroy, Pa.	m		M																							
West Branch Octararo Creek near Spruce Grove, Pa.	m		M																							

TABLE II-1 (Continued)

Symbol Key

bedrock Key:

g = glacial = glacial cover over the bedrock
s = silicate clastic = sandstone, shale, mudstone, arkose
cr = carbonate = limestone and dolomite
cl = coal = coal bearing section
T = Triassic sediments = arkose, sandstone, shale, and carbonate
M = metasilicates = schist, gneiss and quartzite

WSP = Water Supply Paper (USGS) data are reported in two sections of these papers: 1) permanent sites (P) and 2) miscellaneous sites (M)

WRDNY = Water Resource Data for New York (USGS)

WRDP = Water Resource Data for Pennsylvania (USGS)

TABLE II-2. SUSQUEHANNA RIVER BASIN SAMPLE SITE LOCATIONS AND DESCRIPTIONS

Sample Number	Latitude	Longitude	County (Pa.)	Township	Comments
SR-1	40°52'07"	78°43'13"	Clearfield	Bell	Chest Creek, east side, 50 m upstream of bridge at Ostend, Pa, Westover, Pa. 7.5' quad.
SR-2	40°53'49"	78°40'39"	Clearfield	Greenwood	WBSR, USGS gaging station, Bower, Pa.
SR-2a	40°57'40"	78°31'09"	Clearfield	Curwensville	WBSR, US Corps Eng. gaging station, Curwensville, Pa.
SR-3	41°04'09"	78°21'39"	Clearfield	Goshen	Lecontes Mills, Pa. 7.5' quad. 75 m upstream of confluence with Trout Run. WBSR at Shawville, north bank, 75 m downstream of bridge for Rt. 910.
SR-4	41°00'51"	78°24'30"	Clearfield	Boggs	Clearfield Cr., 85 m upstream from bridge for Rt. 153.
SR-4a	40°57'48"	77°56'30"	Clearfield	Copper	Moshannon Cr., north side, at Rt. 53 bridge, 4.5km west of Moshannon and intersection of Rts. 53 and 144; Karthaus, Pa. 7.5' quad.
SR-5 west east	41°06'59"	78°06'34"	Clearfield Centre	Karthaus Burnside	WBSR, west side 5m upriver from Rt. 879 bridge. east side 50 m upriver from bridge for Rt. 89 Karthaus 7.5' quad.
SR-5a	41°15'18"	77°53'53"	Clinton	East Keating	WBSR 0.87km upriver from confluence with Sinnemahoning Cr.

TABLE II-2. (Continued)

Sample Number	Latitude	Longitude	County (Pa.)	Township	Comments
SR-5b	41°15'38"	77°54'51"	Clinton	East Keating	Sinnemahoning Cr., 1.0km upstream from confluence with WBSR.
SR-5c	41°19'30"	77°38'09"	Clinton	Chapman	WBSR, above Huff Run.
SR-5d	41°19'24"	77°45'04"	Clinton	Noyes	WBSR, near USGS gaging station at Renovo. Samples collected ∿ 30m upriver of Peters Run.
SR-5e	41°20'56"	77°41'54"	Clinton	Chapman	Young Womans Cr., 10m upstream east side of old Rt. 120 bridge.
SR-5f	41°16'27"	77°36'04"	Clinton	Grugan	Renovo East, Pa. 15' quad. along Rt. 120 between Renovo and Lock Haven (4 mi. SE of Hyer bridge).
SR-5g	41°24'48"	78°11'48"	Cameron	Lumber	Driftwood bridge of Sinnemahoning Cr., at Sterling Run, Pa. east bank upstream side of bridge, gaging station on west bank; Cameron, Pa. 7.5' quad.
SR-6	41°08'23"	77°26'31"	Clinton	Lock Haven (south side)	WBSR, at Lock Haven, Pa., each of Rt. 664 bridge--samples taken on Woodward side up to Oct. 1973;
				Woodward (north side)	samples taken on Lock Haven side in Oct. and after.
SR-7	41°07'36"	77°25'59"	Clinton	Castanea	Bald Eagle Cr., at bridge for road to Castanea from Lock Haven ∿ 3km upstream from confluence with WBSR.

TABLE II-2. (Continued)

Sample Number	Latitude	Longitude	County (Pa.)	Township	Comments
SR-8	41°11'48"	77°17'33"	Clinton	Pine Creek	Pine Cr., 3.54km upstream from confluence with Susquehanna River.
SR-9	41°11'48"	77°14'18"	Lycoming	Nippenose	WBSR, (east channel) April only each bank, under bridge for Rt. 44, near Antes Fort.
SR-9	41°13'31"	77°07'07"	Lycoming	Susquehanna	WBSR 0.70km upriver from Penn Central RR bridge over Susquehanna at Nisbet.
SR-10	41°09'55"	76°52'03"	Lycoming	Muncy Creek	WBSR, SE bank ∿ 100m upriver of bridge for Rts. 54 and 405.
SR-10a	41°12'43"	75°45'26"	Lycoming	Muncy Creek	Muncy Creek, under bridge for Rt. 405 near junction of Rts. 405 and 442 ∿ 2km NE of Munch, Pa.
SR-11	40°58'19"	76°54'02"	Union	Kelly (north bank) Buffalo Valley (south bank)	Buffal Cr. (∿ 1.78km) ∿ 107 mi. upstream from confluence with WBSR.
SR-12	40°53'23"	76°47'17"	Northumberland	Northumberland	NBSR, NW bank ∿ 3 km upriver from confluence with WBSR.
SR-13	40°53'03"	76°47'51"	Northumberland	Northumberland	WBSR, NE bank, under bridge for Rt. 11.
SR-13a	40°53'31"	76°49'37"	Union	Union	WBSR, SW bank ∿ 3.5km upriver from confluence with NBSR near Winfield, Pa.

TABLE II-2. (Continued)

Sample Number	Latitude	Longitude	County (Pa.)	Township	Comments
SR-14	40°29'26"	76°57'11"	Perry	Watts	Susquehanna River west side at roadside park ∿ 2km SE of Montgomery Ferry along Rt. 11-15; Halifax, Pa. 7.5' quad.
SR-14a	40°39'35"	76°55'06"	Snyder	Chapman	McKees Half Falls at roadside park along Rt. 11-15 (Dalmatia, 7.5' quad) Susquehanna River west side, ∿ 3km upriver from confluence with Mahantago Cr.
SR-15	40°28'48" 49°29'34"	77°07'42" (April 73) 77°08'00" (others)	Perry Perry	Howe Howe	Juniata River, east bank near USGS gaging station at Newport, Pa.
SR-16	40°02'30"	76°32'54"	Lancaster	Marietta	Susquehanna River ∿ 1.5km upstream from gaging station at Chickies Rock within the Marietta Corp. boundary.
SR-17	39°39'20" 39°39'33"	76°09'53" 76°09'53"	Harford* (west) Cecil* (east)		Sus. R. 0.17km downriver from Conowingo Dam Sus. R. 0.51km upriver from confluence with Octoraro Cr. 0.78km downriver from Conowingo Dam.

*State of Maryland.

TABLE II-3. ALKALINITY: FIELD TITRATION VERSUS LABORATORY GRAN TITRATIONS, JUNE 1973

Site	Field Alkalinity*	Lab Alkalinity*
SR-10	0.225	0.197
SR-12	0.895	0.904
SR-13	0.580	0.559
SR-14	0.645	0.619
SR-15	1.418	1.450
SR-16	1.250	1.248

*Milliequivalent/ℓ

TABLE II-4. SAMPLES COLLECTED FOR THIS STUDY

Sample	1973						1974			
Site	April	June	August	Oct-Nov	November	December	January	March	April	June
SR-1	X	X	X	X						
SR-2	X	X	X					X		X U
SR-2a			X							
SR-3	X	X	X							X *
SR-4	X	X	X	X			X	X		X U
SR-4a								X		X U
SR-5 east	X	X	X							
SR-5 west		X	X							
SR-5a		X	X					X +		X * +
SR-5b		X	X					X		X *
SR-5b										X
SR-5c		X	X							
SR-5d								X		
SR-5e								X		
SR-5f								X		
SR-5g										X *
SR-6	X	X	X	X *				X	X	X *
SR-7 center	X									
SR-7 north		X	X	X				X		
SR-7			X							X U
SR-8 center	X									
SR-8 west		X	X	X *			X	X +	X	X * +
SR-9 144	X									
SR-9 Nisbet		X	X					X		X *
SR-10	X	X	X	X				X		X *
SR-10a								X		
SR-11	X	X	X	X *			X	X +	X	X * +

TABLE II-4. (Continued)

	1973						1974			
	April	June	August	Oct-Nov	November	December	January	March	April	June
SR-12	X	X	X	X			X	X	X	X *
SR-13	X	X	X							
SR-13a			X	X *			X *	X * +	X	X * +
SR-14	X	X	X	X			X	X	X	X *
SR-14a										X *
SR-15	X	X	X	X			X	X		X * +
SR-16	X	X	X	X			X	X		X U
SR-17 east	X	X								
SR-17 west			X	X *			X *	X * +		X * +
RV-1					X	X	X	X +	X	X * +
RV-2						X		X		
RV-3						X		X		X *
RV-4						X	X	X		X
RV-5	X					X	X	X		X *
RV-6							X			
RV-7								X		X
RV-8								X		
SM-spring										X
JML Pond			X							

X = filtered - 1 liter unacidified, 2 liters acidified; particles

* = 4 liters or 8 liters filtered and acidified plus the particles from filtration; 4 liters or 6 liters unfiltered and acidified.

U = 4 liters or 6 liters unfiltered and acidified collected without a corresponding 4 or 8 liter filtered aliquot.

+ = 15 to 40 liters unfiltered and unacidified

FIGURES

FIGURE II-1

THE PHYSIOGRAPHIC PROVINCES OF THE APPALACHIANS IN RELATION TO THE SUSQUEHANNA RIVER BASIN

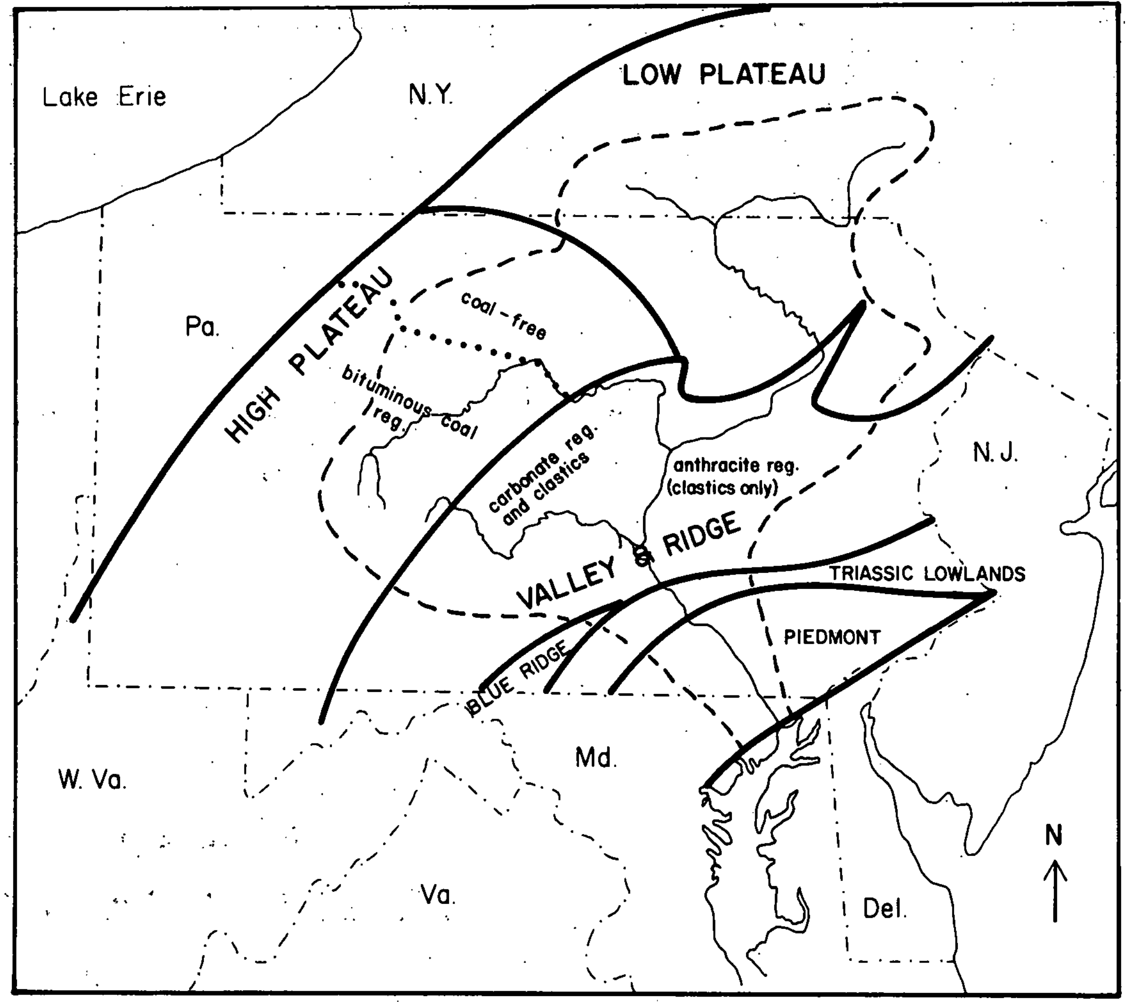


FIGURE II - 2

YOUNG WOMANS CREEK

t ds vs. discharge

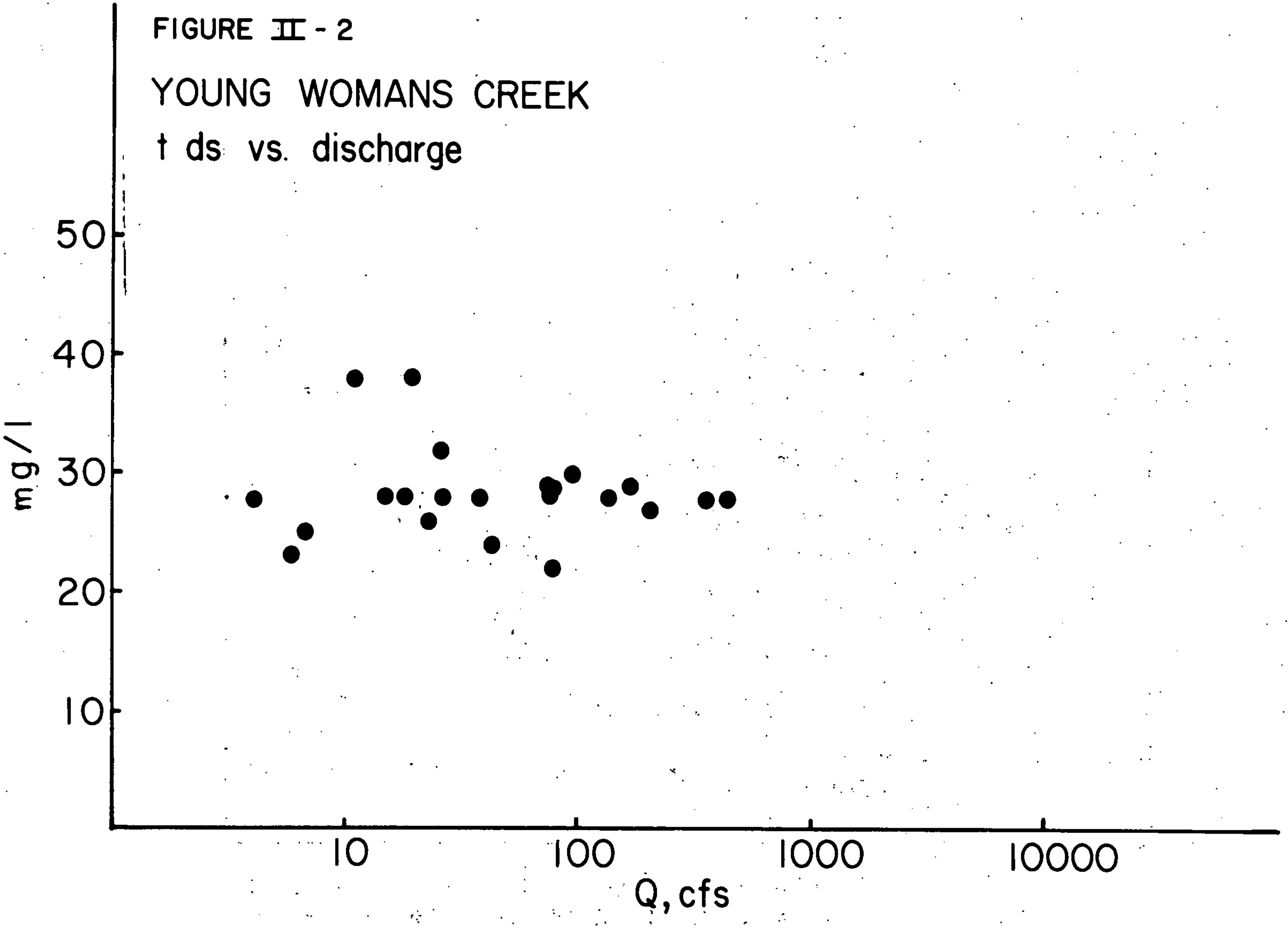
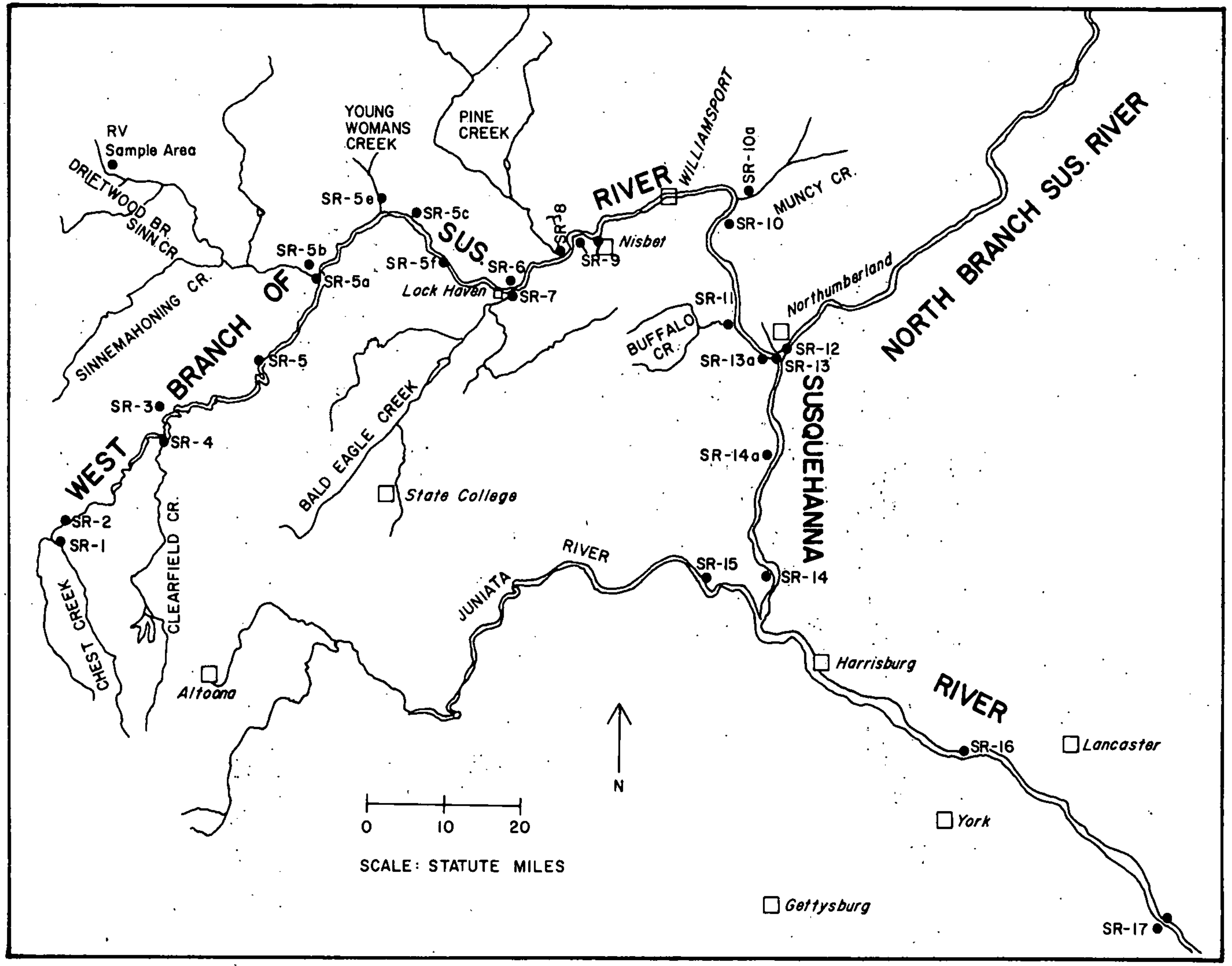


FIGURE II-3
SUSQUEHANNA RIVER SAMPLE SITES



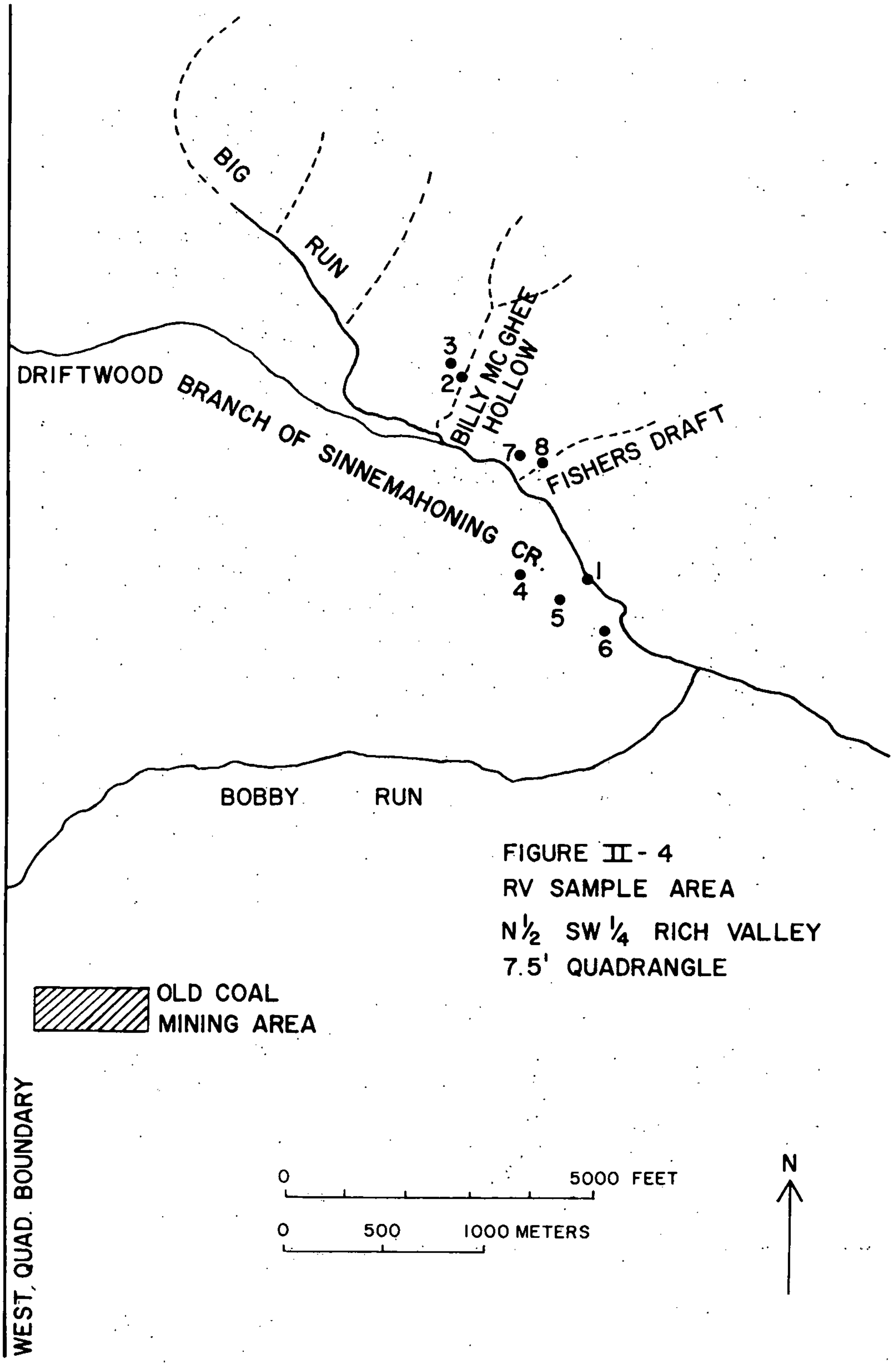


FIGURE II - 4
RV SAMPLE AREA
N½ SW¼ RICH VALLEY
7.5' QUADRANGLE

III. GEOHYDROLOGY OF THE SUSQUEHANNA RIVER SYSTEM: TYPE WATERS, COMPOSITION-DISCHARGE RELATIONS, MIXING MODELS, AND DENUDATION RATES

In the previous chapter it was shown that over a large geographical area streams of the Susquehanna tributary system draining terranes of one general rock type will have characteristic compositions that are constant with changing discharge. In this chapter the different water types are defined and their role in mixing to produce the observed variations in stream water composition is discussed. More detailed mixing models are discussed which can be used to study the behavior of trace constituents in the water after mixing. Finally, denudation rates of the type areas are considered and used to make an estimate of the erosion rate of the entire basin.

Type Waters

Silicate Rocks

Rich Valley sample area

As was discussed in the section on sample selection in Chapter II, a small area in the coal-free region of the High Plateau underlain by Devonian and Mississippian sandstones, siltstones and shales was chosen as a type area for silicate rock drainage.

Four springs, two ephemeral streams near two of the springs, one well and the stream draining the area (The Driftwood Branch of

Sinnemahoning Creek) comprise the studied samples. Site locations are shown in Figure III-1 and described in Table III-1. The ephemeral streams were sampled as the most likely to show the effects of surface runoff after a storm (Davis and DeWiest, 1966; Sherman, 1949) if, indeed, this was the mechanism generating flood flow. The data for all sites are shown in Tables III-2 through III-9. Since the ratios of the cations and $SO_4^=$ to one another are nearly constant, the discussion of one element is sufficient to understand the data.

The Ca data for the springs (their discharges are ungaged) is shown in Table III-10. Although they differ from one another somewhat in composition, the composition of individual springs is relatively constant with time.

The two ephemeral streams, RV-2 and RV-8, and their adjacent springs, RV-3 and RV-7, respectively, were sampled during periods of high runoff in December 1973 and March 1974. Comparison of the ephemeral stream and spring data for the pairs (RV-2:RV-3 and RV-7:RV-8) shows a strong similarity in composition of streams and springs. For the two times of sampling for the RV-2:RV-3 pair the stream is slightly more dilute than the spring. For the RV-7:RV-8 pair Ca is slightly higher in the stream than in the spring at the single time of sampling, March 1974.

The Driftwood Branch of Sinnemahoning Creek (RV-1) data when compared to spring, well and ephemeral stream data in the region indicate that all compositions are virtually identical. Indeed, the variation of composition of the stream with discharge (Figure III-2) is strikingly small. There is only a 10% range in Ca, Mg and K concentrations with an order of magnitude variation in discharge.

The RV sample area data, which are examples of the water type for pure silicate drainage, may be summed up as follows. The well, springs and streams are of similar composition, and for the mainstream only a small change in concentration of dissolved species is observed with large changes in discharge.

Young Womans Creek

Young Womans Creek was sampled once during the course of this study but has been sampled regularly for several years by the USGS. The geology and land use patterns are very similar to the RV sample area (and most of the rest of the coal-free region of the High Plateau; see: Geology, Chapter I). In fact, the USGS has established this stream as a hydrologic bench-mark station because it is representative of areas of the Plateau that are at the present and presumably in the future will be free of pronounced encroachment of human activities.

Like the RV area, the ratios of cations and sulfate do not vary much, so only the Ca data will be discussed as above. The Ca data from USGS publications (1971b, 1972a, 1972c, 1973b, 1974a) are plotted in Figure III-3 against discharge. The concentration of Ca shows an approximately 10% dilution for a 100-fold increase in discharge. My Ca analyses for March 1974 for this stream (SR-5e), the Driftwood Branch average (RV-1) and Muncy Creek (SR-10a) are also indicated. It can be seen that there is good agreement between my measurement and that of the USGS; hence the data can be used without alteration for this study. Comparison of the Young Womans Creek and Driftwood Branch (RV-1) data show that both streams are the same approximate concentration and show a similar small dilution of concentration with increasing discharge.

The apparent dilution that is observed could be due to a small component (10 to 20% at maximum discharge) of rain water. However, the data for Young Womans Creek, which extend over a five-year period, imply another interpretation.

The dilution of Ca (and other elements) appears to be more seasonal than directly discharge related. The concentration of calcium in the summer when the discharge is also the lowest is about 10 to 20% greater than in the fall, winter and spring. Although discharge is generally seasonal (i.e., low discharge in the summer and high discharge in the winter), the stream discharge in the summer can reach values equal to the discharge during the winter. At these different times of the year the concentration of calcium will be different for nearly the same discharge. A pulse of stream discharge following a storm or snow melt in the summer or winter results in juxtaposed high and low discharges in a short time interval. Under these conditions the concentration of calcium is the same even though the discharges are quite different.

Piedmont

Data for the composition of streams draining the Piedmont Province, underlain by schists and other metasedimentary silicate rocks of the Wissahickon formation, is available from two sources. Cleaves et al. (1970) studied a basin in Maryland for more than a year with periodic sampling of water composition and discharge. Their data show a relatively small change in the concentrations of major ions with changing discharge and a similarity of composition to the streams of the High Plateau and Valley and Ridge discussed previously. Data from USGS (1954a) sampling of Muddy Creek and tributaries to

Octararo Creek, all of which are on the Wissahickon formation, indicate no change in concentration with changing discharge. The streams draining the metasedimentary silicate rocks of the Piedmont and those draining the silicate sedimentary rocks of the High Plateau and Valley and Ridge do not vary in composition with changing stream discharge. Furthermore, the compositions of all of these streams do not differ from one another by more than 10%. Therefore, it is possible to determine an average composition for all the streams draining such terranes (on all scales) which can be used in the proposal model to be discussed later. This composition is given in Table III-11 and is based on the RV and Young Womans Creek data of this study.

Carbonate Rocks

Spring Creek drainage basin

The drainage basin of Spring Creek is bounded by ridges composed of Ordovician and Silurian clastic rocks, but most of the basin inside these ridges is underlain by Cambrian and Ordovician limestones and dolomites (Gray et al. 1960). Studies of the carbonate springs of this area (Shuster and White, 1971; Langmuir, 1971) show that while individual springs may differ from one another in composition (especially those in limestone as compared with those in dolomites), the composition of each spring does not very much with changing discharge. The movement of ground water in this terrane is either via a widespread system of relatively low permeability (diffuse springs) or through sink holes and other channel features of limited areal extent and very high permeability (conduit springs). Long-term studies of the diffuse springs show that the variation in dissolved solids is less than 5% for discharges which differ by up to a factor of 2. Even for the conduit springs the change in dissolved solids ranges only from 10 to 24%, while discharge differs by more than an order of magnitude (Shuster and White, 1971; Langmuir, 1971). Some of the variation in the conduit springs is attributed to sequestering of runoff from the adjacent clastic ridges after storms (Jacobson and Langmuir, 1974).

Spring Creek, the stream draining this area, has been analyzed for a few years by the U.S. Geological Survey (1971a, 1971b and 1972a). The concentrations of Ca and Mg versus discharge from USGS reports are plotted in Figure III-4. There is no significant change in concentration (within 10%) of either element for more than a fourfold increase in discharge. Therefore, Spring Creek, like the carbonate springs of the area, does not vary in composition in response to storm flow.

Other carbonate regions

No other region underlain by carbonate rocks is as well studied as the Spring Creek basin. However, USGS data (1971a, 1972a and 1974a) for streams such as Conestoga Creek and Messer Run which are underlain dominantly by carbonate rocks indicate that the concentration of ions in Spring Creek is representative of streams draining areas of carbonate rocks in the Susquehanna basin. This composition is given in Table III-11.

Mine Drainage

Chest Creek (SR-1) and Clearfield Creek (SR-4) were initially sampled as representatives of streams massively affected by mine drainage. Both streams, however, as measurements indicated, had made some degree of recovery from early mining operations and thus did not qualify as true end members of water types.

Moshannon Creek (SR-4a) most closely approximates a mine drainage stream water type. Moshannon Creek drains an area underlain by the Allegheny Group of the Pennsylvanian and receives mine drainage from coal mining operations.

While Moshannon Creek was sampled only twice, it can be seen that its variation in composition with changes in discharge is small when compared to Clearfield Creek (Figure III-5). This implies a relatively constant composition for the mine drainage. On the assumption, defined later, that the lower the flow the greater the mine drainage component of Moshannon Creek, a composition estimated for lowest flow from available data provides the best estimate of the mine drainage water type. This estimated composition is given in Table III-11.

Calculation of charge balance for the mine drainage type water composition listed in Table III-11 indicates a cation deficit of 0.57 milliequivalents. First, within the error of ±10% that is attached to the total cation charge and anion charge the balance is made. Second, the type water would contain several trace metal cations in significant concentrations (Hollyday and McKenzie, 1973; Gang and Langmuir, 1974). These additional cations would yield the required electrical neutrality.

Significance of Constant Composition with Changing Discharge

The constancy of composition with changing discharge, where it occurs in a stream, provides an important constraint on modelling the hydrologic regime not only of that stream but of a larger class of streams. A hydrograph is a plot of the discharge of a stream versus time (Figure III-6 is a generalized example). The classical approach to the analysis of the hydrograph of a stream in response to a storm has been to assign various amounts of the hydrograph to different components of flow (Figure III-6). Sherman (1949) and others assumed for physical reasons that the pulse of water above the base flow, which is assumed to be ground water, is the result of water flowing over the land surface. The overland flow component is calculated by extrapolating a line (<u>ab</u> in Figure III-6) connecting the base flow on either side of the flood peak. Later students pointed out, however, that real overland runoff was seldom observed (see: Lull and Reinhart, 1972, for a summary). Hence, more recent hydrology texts and writings have created a near-surface flow component comprised of infiltrated rain water which flows very rapidly to the stream and is independent of the ground water (Figure III-7). This component is called interflow (Davis and DeWiest, 1966). The resolution of a flood event into components of flow then changes somewhat. The proportion attributed to base flow (= ground water) is the same, but the flood peak is, in this case, attributed mostly to the interflow component and some to overland flow. Nonetheless, this still states that the flood peak should be composed of rain water. With an order of magnitude change in discharge the concentration of elements such as Ca and Mg would be expected to be reduced by about a factor of 10. However, as has been pointed out in this section, streams draining single rock types exhibit little change in composition with such variations in discharge. Clearly, this shows that the classical approach to hydrograph resolution is wrong. It thus becomes a fundamental problem for both hydrology and geochemistry to explain how a stream responds so rapidly to a storm event but yet the water added to the stream has the same concentration as the base flow which is tapping the ground water system.

This observation raises problems as to how chemical weathering occurs. One way of explaining the stream data is to have a near-surface flow component (interflow) and to have weathering proceed at a very rapid rate. A second proposal is the presence of some kind of buffering system for each terrane, such as soil moisture. However, if that were the case, it would be hard to obtain a constant composition with variable rain and soil moisture conditions. A third alternative is that the water from precipitation displaces older ground water into the stream by increasing ground water discharge during storms or snow melt.

There is direct evidence for this last option. A recent study of tritium in the snow pack, ground water and stream of a basin in Switzerland has shown that the strongly coupled response of stream discharge with snow pack melting is accommodated by ground water flow to the stream rather than overland flow or interflow. The water from the melting snow pack enters the ground water system and by a mechanism not completely understood displaces older ground water into the stream (Martinec, 1975).

The streams of the Susquehanna basin probably respond in a similar fashion in regard to rain and snow inputs, but detailed tritium hydrology has not been done for this basin. Indeed, no other major river basin has been measured with this point of view during sampling.

Intermediate Streams

Many streams draining the High Plateau, Valley and Ridge, and the Piedmont flow over regions that are relatively large-scale mixtures of the two geologic terranes and mine drainage-affected regions discussed earlier (see: Geology, Chapter I). Since each of these regions is drained by streams of a characteristic composition, it is reasonable to expect streams draining a combination of terranes to have a composition intermediate to the end members. Examination of the data for Buffalo Creek (Figure III-8, Table III-12), underlain by Ordovician-Silurian clastics and Siluro-Devonian carbonates, shows that it can be thought of as a mixture of Spring Creek type water and Driftwood Branch (RV-1) type water. Similarly, the data for Clearfield Creek (SR-4), which is underlain by the coal-bearing beds of the Pennsylvanian, can be thought of as a mixture of mine drainage and Driftwood Branch type water.

Streams of the Low Plateau and the Triassic Lowland have a range of compositions but, again, they can be attributed to mixtures of carbonate and silicate waters.

These stream compositions differ from the type waters in that the concentration of dissolved species does vary significantly with changing discharge. The calcium and magnesium ion concentrations for Buffalo Creek are shown plotted against the discharge at the adjacent Penns Creek (in the absence of discharge data for Buffalo Creek) in Figure III-8. The decrease in concentration with increased discharge has been interpreted previously as dilution by overland flow. It will be shown by the following discussion, however, that the concentration change is actually attributed to a change in proportions of the two type waters found in this area and that dilution by "pure" rain water is minimal.

Unit Hydrographs and Flow Duration Curves

Unit hydrographs

A unit hydrograph is a graph of discharge (above base flow) versus time for a runoff-producing rain falling on a basin for a given unit of time (Sherman, 1949). This construct is a basic tool used in predicting stream flow in response to storms. It may also be used to compare the flow characteristics of different streams in response to such storms. An example of a unit hydrograph based on Sherman's (1949) discussion is shown in Figure III-9. There are aspects of the unit hydrograph which are important: the basal width of the hydrograph (line ad in Figure III-9) is reasonably constant regardless of the storm magnitude for a given basin; storms of the same magnitude will produce nearly the same peak discharge in the basin; and a very important observation is that the time-to-peak-discharge is independent of storm magnitude. Therefore, two storms such as storm a and a smaller one, storm b, shown in Figure III-9 will have their peak discharge at the same time after the storm. These features are very uniform for a given stream, and unit hydrographs can be determined for streams of interest.

Flow duration curves

A flow duration curve is a plot of the ln discharge versus cumulative frequency that discharge reaches or exceeds a given discharge. As with unit hydrographs, these curves can be used to demonstrate the discharge response of different streams. The flatter the curve (Figure III-10), the less change there is between low and flood flow. The steepness of the curves are directly related to the storage capacity of the drainage basin (Searcy, 1959). Consequently, a basin with a high storage capacity, such as a carbonate terrane, will have a relatively flat curve such as a in Figure III-10. Similarly, areas of low storage, such as shales, will have a curve like c in Figure III-10. Basins with intermediate storage capacities will have flow duration curves somewhere between the other two, similar to b in Figure III-10.

While time is not a direct variable in flow duration curves, it is possible to generalize the relationship between these curves and unit hydrographs which are also related to the storage capacity of the basin. A basin with high storage capacity and a flat flow duration curve such as a in Figure III-10 for a given storm will have a unit hydrograph with a relatively large ratio of basal width/peak discharge, as shown for curve a in Figure III-11. A basin with low storage capactiy and a relatively steep flow duration curve such as c in Figure III-10 for a given storm will have a unit hydrograph with a smaller basal width/peak discharge ratio, as shown for curve c in Figure III-11. Also the peak discharge occurs earlier for curve c than curve a, as it is a general rule that the time-to-peak discharge decreases with storage capacity of the basin.

Variability of Stream Composition with Discharge

In regions where different rock types compose the bed rock the streams draining those areas will have hydrographs that are combinations of the unit hydrographs of basins on individual rock types. From studies of stream discharge data Heerdegan and Reich (1974) have derived unit hydrographs for Spring Creek, which drains a carbonate terrane, and for Corey Creek, which drains a silicate sedimentary terrane near the border between the High and Low Plateau Provinces in Pennsylvania. The generalized plot of these two unit hydrographs is shown in Figure III-12. These unit hydrographs can be considered to represent the drainage from the carbonate and silicate terranes of the Susquehanna basin. If a stream drains an area of mixed terranes types (since the main branch flow is a sum of the smaller streams on the type terranes), it can be seen that with the advent of flood flow the percentage of the main branch flow composed of drainage from silicate terranes will increase. Since it has been shown previously that the concentration of ions is much less in the silicate drainage than in the carbonate drainage but that both are constant (see: Type Waters this Chapter page 51), the increasing percentage of silicate flow will result in a dilution in the stream.

Streams affected by mine drainage are very similar to the case discussed above. However, in this case it is the act of mining which greatly increases the storage capacity of that part of the basin. The remainder of a basin will be an undisturbed silicate terrane. In a study of the Tradewater River basin, Kentucky, (Grubb and Ryder, 1972) the effect of mining on stream flow was demonstrated. Flow duration curves from their paper are shown in Figure III-13 for streams in basins that were unmined (steep curve), mined (flat curve) and for basins that contain mined and unmined areas (intermediate curve). From the discussion of unit hydrographs and flow duration curves it can be seen that the unit hydrographs for the mined and unmined areas would be as shown in Figure III-14. Therefore, with the advent of a storm, the flow of the main branch would be comprised of an increased percentage of drainage from the unmined areas. Drainage from the unmined area is relatively dilute compared to mine drainage, so with increased main stream flow there is a dilution of dissolved species simply by mixing different proportions of components of constant composition. Cases of large increases of mine drainage after storms have been recorded, but these are the result of failure of drainage control features in mined areas (Biesecker and George, 1966).

The exact relationships of a basin are dependent on the area occupied by the different terranes discussed above. In the model to be proposed below these components of flow may be resolved out of intermediate streams and the proportion of flow from each type terrane can be determined.

Conclusions

Most streams and rivers are of an intermediate type as discussed above in that they drain areas underlain by a variety of rock types. Therefore, studies of them have shown variation of composition with discharge, and this obscures the fundamental principles operating in the drainage basin:

1. The relatively constant concentration of ions in streams draining areas underlain by single rock types

2. The lack of an overland flow or interflow component of low ion concentration
3. The mixing of different water types (of constant composition) in different proportions with changing discharge of the main stream, resulting in the variations of dissolved species with varying discharge

Models for Rivers of the Susquehanna Type

General Model

If the flow of a river is composed of different components of flow--end member compositions contributed from tributaries and ground water as discussed previously--then at any time the total discharge, Q_T, is related to the components of the flow (Q_i) by the equation

1) $\Sigma Q_i = Q_T$

This equation can be called the water mass balance equation. Mass balance considerations also enable one to describe the relationship of the dissolved concentration of an element to that in the various components by the equation

2) $\Sigma Q_i C_i = Q_T C_T$

Q_T = total discharge

C_T = the concentration of the element in the total flow

Q_i = discharge of component i of the total flow

C_i = concentration of the element in component i of the total flow

Dividing equation 2) by Q_T results in

$$C_T = \Sigma \frac{Q_i}{Q_T} C_i = \Sigma a_i C_i$$

where a_i = the proportion of the total flow made up of flow component i

It was shown earlier that the water flowing in the Susquehanna River is a mixture of the three type waters discussed. Using the concentrations of the type waters for the Susquehanna River, the proportion of the total flow made up of the silicate, carbonate and mine drainage water types can be calculated for the time of sampling. The results for the Susquehanna River at Conowingo are shown in Table III-14 using the Mg^{++} and $SO_4^{=}$ data in Table III-13. These values are representative of the water provenance; i.e., the amount of flow contributed to the river by areas underlain by the type rock areas.

This estimate of water provenance is subject to possible errors that would lead to misestimates of components. First would be the presence of a major uncharacterized source of water and dissolved ions for which there is no model component. The most likely source of such a component is road salt, municipal pollution, and/or industrial pollution. One way to remove part of this potential error is to subtract out cations in proportion to the excess chloride or to use elements in the model for which the pollution is a minor component. In the model, therefore, Mg and SO_4 are used because the dominant flux from the basin must be from rock weathering and/or, as may be the case for a fair amount of the $SO_4^{=}$, from precipitation.

A second problem arises with the terranes which are small-scale mixtures of carbonate and silicates. It is possible that while the ratio of ions derived from either type of mineral will be the same as for the type terranes, the actual concentration of ions in the flow could be different. However, it appears from some of the USGS data for streams of the Low Plateau Province that the actual range of stream compositions is from silicate type to carbonate type, so this may be a secondary concern.

Both of these objections can be largely overcome if the proportions of flow are calculated for the Juniata River where there are no glacial deposits and less obvious pollution, such as mine drainage, than in the total Susquehanna basin. These calculated proportions are shown in Table III-16 based on the model and the Mg^{++} and $SO_4^=$ data in Table III-15. The results confirm the presumed smaller proportion of mine drainage in the Juniata River compared to the Susquehanna. Other calculations would be required to assess the relative importance of road salt and municipal pollution on the two rivers.

Once the proportions of flow are calculated, one can calculate the proportion of the flux of elements from each type terrane by using the type water concentrations, C_i. This approach then shows the source of the ions. The proportion of ions derived from each source can be compared to the proportion of water derived from each source. The proportion of water from each source over an annual period will approximate the proportion of the basin area occupied by each type terrane if evapotranspiration is equal for all of them.

Since the derivation of ion provenance is not really dependent on ion concentrations but rather the ratios of ions, this approach actually gives the proportion of ions weathered from carbonate, silicate and mine spoil minerals. The proportion of Ca^{++}, Mg^{++} and $SO_4^=$ from each type water is calculated for the Susquehanna River at Conowingo at various times (Table III-17).

Discussion of Other Models

In the classical approach to hydrology it is presumed that there are components of flow in a flooding river; i.e., base flow = ground water and surface runoff = precipitation. The further restriction is generally made that $Q_{\text{base flow}}$ (Q_b) is constant. It should be noted that if one is trying to determine the C_i's by the use of such a model as Drake and Ford (1974) have for two Canadian rivers, one is forced to assume Q_b = constant and is known in order to solve for the concentrations of the components of flow. Clearly, however, it is only a first approximation to assume Q_b = constant, as both this thesis and Martinec (1975) have shown. In the absence of small subbasin data along with the major river data as is the case in this thesis the above assumption does yield interesting results: a very concentrated base flow component and a more dilute component of flow. These results also show that the diluting component is considerably different from the precipitation on the basin. The region drained by these Canadian rivers, the Canadian Rockies, is a sedimentary terrane of carbonates and silicate sedimentary rocks as Drake and Ford (1974) point out in their paper. It is therefore quite likely that their derived components of flow represent differences in discharge of the two type waters as was discussed in an earlier section of this chapter. It must be further noted that these derived components will be in error by an amount proportional to the actual variation in the base flow discharge, which is assumed constant.

Mixing Model for River Reactions

For the study of certain elements in the river a more specific model for mixing is required. The main reason for this is the kinetics of precipitation or removal from solution of elements such as Mn and Fe. Because the concentration of these elements can change with time, it is necessary to sample as nearly as possible the actual inputs into the system. The basis for the specific models, including sections of the river covered and the model inputs, is discussed below. The equation sets representing the models are given in Appendices V and VI. Using the models, the proportion of flow from the model sources is calculated from the major ions. Once the proportion of flow from each source is calculated for a sample point a model concentration for Mn, Fe and Pb^{210} can be calculated.

Between Keating, Pa., and Lock Haven, Pa., the only major tributary to enter the West Branch of the Susquehanna River is Sinnemahoning Creek, which was sampled. The majority of small streams entering the river in this stretch drain the coal-free region of the High Plateau Province, and their composition is assumed to be the same as that of the Driftwood Branch (RV-1). There is a small amount of mine drainage introduced into this stretch, and it will be taken as the composition of Moshannon Creek. The set of equations that describe the model is given in Appendix V.

At Lock Haven, Bald Eagle Creek enters the West Branch of the Susquehanna and the character of the river changes dramatically. The sample of the WBSR taken at Nisbet is presumed to represent the mixture of the West Branch, Bald Eagle Creek and Pine Creek. The drainage added to the river between Nisbet and the confluence flows off the High Plateau and from the Valley and Ridge. Streams flowing off the Plateau are represented by Pine Creek in this part of the model; the Valley and Ridge drainage is represented by Buffalo Creek. The set of equations representing this section of the river is given in Appendix VI.

In principle, models could be constructed to describe the composition of the river at any point from the confluence of the West Branch of the Susquehanna and the Susquehanna River at Northumberland to the mouth of the river near Conowingo. However, the complexity of mine drainage additions from the anthracite coal region in terms of Mn concentrations makes this a futile exercise. Consequently, specific models are not constructed for the Susquehanna below the confluence of the two main branches at Northumberland.

The proportion of flow components at a site can be calculated from these models using the major ion concentrations in the type waters and at the sites of interest. From these proportions it is possible to calculate model concentrations of other elements of interest at any point where samples are taken. An interesting aspect of this model approach is that even if the river is not completely mixed, a model concentration for the particular parcel of water sampled can be calculated. The proportions of the total flow from source waters have been calculated for sites of interest and are shown in Tables III-18 and III-19. These constants will be used in the following chapters to calculate the expected concentration of Fe, Mn and Pb^{210} at various sites.

Denudation Rates

Denudation of a terrain, removal of mass from the upland region to the seacoast, occurs by transport of ions dissolved during chemical weathering and by the erosion of solid material from soils and rocks. The total denudation rate of a region is the rate of chemical weathering plus the rate of erosion. It must be noted that chemical weathering occurs by precipitation moving through the soil and into the ground water system which supports the stream flow. Erosion, on the other hand, occurs by erosion of stream banks and gullies. Hence, the rates of chemical weathering and erosion are not coupled since completely different processes are involved in each phenomenon.

Present Day Chemical Weathering Rates

Chemical weathering rates may be calculated by determining the long-term flux of dissolved elements from a drainage basin of known areal extent. In this section the chemical weathering rates of type terranes will be calculated. Together with the denudation calculated for erosion alone, chemical weathering will comprise the total denudation rate. The information derived for type areas may then be used to assess a total denudation rate determined for the entire Susquehanna River system.

Spring Creek

It has been shown earlier in this chapter that the stream draining the Spring Creek basin is of a constant composition (± 10%) regardless of discharge. Therefore, the flux may be calculated by computing the amount of solutes derived from rock weathering and multiplying this concentration by the flux of water per unit area of drainage basin.

Spring Creek is gaged for discharge at a site in the interior of the Carbonate Valley, near Axemann, Pa., and at a site just before it enters Bald Eagle Creek where it flows out of the Carbonate Valley through a sandstone ridge, at Milesburg, Pa. When the discharge data at the two sites are converted to depth of runoff per unit area of drainage basin (USGS, 1972c, 1973b, 1974c, 1975), a large discrepancy is noted. At Axemann, the mean annual discharge for the four-year period of record (1971-1974) is equivalent to 17.34 inches/year (44.04 cm/yr) while at Milesburg the discharge is equivalent to 23.29 inches/yr (59.16 cm/yr) for the same four-year period of record. With a mean annual rainfall of approximately 41 inches (104 cm) (Dailey, 1974), if the Axemann data represented the total flow for the up-basin area, the amount of water lost by evapotranspiration would be ∿ 70%. On the other hand, the data at Milesburg indicate an evapotranspiration loss of ∿ 50%, which is much like the amount for the entire Susquehanna basin (USGS, 1975). The answer to this discrepancy lies in the hydrology of the basin. A schematic of the basin is shown in Figure III-15. The basic feature is a basin filled with very porous permeable rocks (the carbonates) enclosed by much less-permeable rocks. Some of the precipitation falling on the basin above Axemann flows through the ground water system, but it cannot be lost from the entire basin because of the enclosing clastic rocks. Therefore, at the exit of the basin all the flow must be surface runoff which is gaged for Spring Creek at Milesburg. Since this is the case, the discharge of Spring Creek at Milesburg is much more representative of fluxes than that near Axemann; hence the Milesburg discharge will be used in the computations. The discharge of Spring Creek at Milesburg is equivalent to 0.0505 ℓ/cm^2/yr.

The concentration of dissolved solids will be that at Axemann, Pa. As stated earlier, the concentration is fairly constant with time. However, only some of the ions come from rock weathering; the others are contributed from cyclic salt and domestic and industrial pollution. Since the rocks being weathered are limestone and dolomite, the dominant ions from weathering should be Ca, Mg and HCO_3^- (and $CO_3^=$). For the calculation of rock-derived ions removed from this carbonate terrane all the Ca and Mg is assumed to come from the rocks and 1/2 of the bicarbonate and carbonate is presumed to come directly from the rock (the other 1/2 of HCO_3 is contributed during weathering from the H_2CO_3 formed during the decomposition of soil organics derived from the fixation of atmospheric CO_2). All the silica is assumed to come from rock weathering. Although some Na, and probably some $SO_4^=$, is contributed by weathering, neither of these elements nor chloride is included as a weathering product. They are all attributed to either cyclic salts or pollution. None of the nitrate and phosphate is included as these are from pollution sources. From the average composition of Spring Creek shown in Table III-11 a calculated concentration of 173 mg dissolved solids/ℓ can be attributed to rock weathering.

With a discharge of 0.0505 ℓ/cm^2/yr containing 173 mg/ℓ rock solutes, a chemical denudation rate of 8.7 gm/cm^2/10^{3}yr results.

Driftwood Branch of Sinnemahoning Creek

The denudation rate for the drainage basin of the Driftwood Branch above Sterling Run will be calculated. This site was chosen because of the availability of long-term discharge data and because it is one of the sites included in a detailed, sediment transport study of the Susquehanna basin. This basin, as noted earlier, lies in the coal-free region of the High Plateau. At RV-1 the composition is very nearly constant, and this site has minimal chance for addition of elements other than by weathering and the cyclic salt. Consequently, the concentration of the Driftwood Branch at the RV-1 site corrected for cyclic salt will be used as the solute contribution from rock weathering at the Sterling Run gaging station.

The average dissolved-solids content of the water is shown in Table III-11. None of the bicarbonate is included in the calculation of rock-derived solutes since all of it is probably contributed during weathering from H_2CO_3 formed from the decomposition of soil organics derived from the fixation of atmospheric CO_2. The sulfate is excluded completely from the calculation since the rocks of this area are mostly non-marine and there is known to be a significant contribution of $SO_4^=$ in the rain to this entire region from atmospheric pollution (Cogbill and Likens, 1974). Again, no phosphate or nitrate is assumed to come from rock weathering. The amount of material derived by rock weathering transported out of the basin in solution is 7.5 mg/ℓ.

The average discharge for the Driftwood Branch at Sterling Run for the 61 years of record is 12.6 m^3/s. This discharge spread over the entire basin is equivalent to 22.27 in/yr (56.6 cm/yr) (USGS, 1975), which corresponds to about 54% of the total mean annual rainfall. The above runoff, 0.0566 ℓ/cm^2/yr, taken with the average concentration of 7.5 mg dissolved solids/ℓ results in a chemical denudation rate of 0.00042 gm/cm^2/yr, or 0.42 gm/cm^2/10^3 yr.

Moshannon Creek basin

As noted earlier, Moshannon Creek is dominantly a mine drainage stream; i.e., most of the solutes in it are derived from the oxidation of pyrite and subsequent attack on the rocks by the sulfuric acid produced. The concentration for this calculation will be taken as the end member composition for Moshannon Creek (see Table III-11). The concentrations of the elements are corrected for Cl from cyclic salt (a trivial correction in this case). In addition to the chloride correction, the concentration of SO_4 at RV-1 is subtracted from the total sulfate, as this represents atmospheric pollution (same approximate amount of evapotranspiration). The resulting concentration of rock-derived solutes is 360 mg/ℓ.

Moshannon Creek has been gaged at Osceola Mills for a considerable period of time, so the denudation rate for the basin above that point will be calculated. The average discharge for the 34 years of record is 3.09 m^3/s, which is equivalent to 21.51 in/yr (54.6 cm/yr) if spread evenly over the entire basin (USGS, 1975).

The average discharge of 0.0546 ℓ/cm^2/yr together with the solute concentration of 360 mg/ℓ results in a chemical denudation rate of 0.0197 gm/cm^2/yr, or 19.7 gm/cm^2/10^3 yr.

Discussion

The calculated chemical denudation rates for the three types of terranes show that rates for the silicate clastic terranes are the slowest; that those for carbonate terranes are about 21 times greater; and that the rates for mine drainage areas are the highest, being 46 times greater than normal silicate terranes. A similar result for streams draining the Appalachians was obtained by Feltz and Wark (1962) in the Potomac River basin of Maryland and Pennsylvania. The ratio of their rates of chemical denudation for silicate to carbonate to mine drainage was about 1:20:30.

Present Day Erosion Rates

The U.S. Geological Survey has an extensive water quality program which includes the Susquehanna River basin with very good coverage. Part of the routine sampling at many of the stations includes detailed sampling for suspended sediment. In a comprehensive synthesis of the data for the Susquehanna basin, Williams and Reed (1972) have determined the sediment yields of many sub-basins representative of specific conditions as well as the total yield of the basin as a whole. Included in this study are basins which have been described and classified in this study as type terranes. Of special interest are the data for the Driftwood Branch at Sterling Run and for Spring Creek near Axemann. Also included are stations which should show the effect of mining on sediment yields.

The data for the Driftwood Branch of Sinnemahoning Creek is equivalent to an erosion rate of 2.3 $gm/cm^2/10^3$ yr. This basin is so little affected by agriculture and urbanization that this number probably represents the actual natural erosion rate.

The Spring Creek drainage basin, on the other hand, is a region of intense farming and a fair amount of urbanization associated with the community of State College, Pa. In spite of this, the number for total sediment transported is equivalent to only 3.66 gm/cm^2/10^3 yr. Other streams draining similar basins but with much less urbanization (e.g., Kishacoquillas Creek at Reedsville, Pa., and Bixler Run at Loysville, Pa.) have erosion rates of more than 50% of this value. In fact the Juniata River, which drains mostly the Valley and Ridge Province, has a total erosion rate 75% of the Spring Creek rate. Therefore, while the Spring Creek erosion rate may be high because of the intensive activities of man in the basin, the rate is probably not larger than a factor of two of the natural rate. Consequently, for the establishment of denudation rates for comparisons to other areas a value of 1/2 of the present day rate, or 1.8 gm/cm^2/10^3/yr, will be used as an estimate of the natural rate.

Sediment data was collected for the West Branch of the Susquehanna River at Bower, Pa., a station on the headwaters of that tributary. During much of the period of data collection the region above this site was subjected to considerable coal mining activity. In spite of what might be expected, the denudation rate calculated for this sub-basin is about 4.4 gm/cm^2/10^3 yr, or less than twice the rate for a similar undisturbed area, the Driftwood Branch. Williams and Reed (1972) point out this surprisingly low sediment yield from such an extensively disturbed terrane and attribute it to internal drainage of the mined areas. Therefore, an erosion rate for erosion in a mine drainage terrane in the bituminous coal region will be taken to be that for the West Branch at Bower.

It should be pointed out that the anthracite coal region of the Valley and Ridge Province shows a much more pronounced increase in erosion rates over terranes such as the Driftwood Branch which are presumed to have the natural rate. There, some of the basins have denudation rates up to four times that of the Driftwood Branch basin.

Total Present Day Denudation Rates

The total denudation rate is taken to be the sum of the chemical weathering and erosion rates. The individual rates and the total rates for each of the three basins discussed above are shown in Table III-20. The rate for the Driftwood Branch is 2.7 $gm/cm^2/10^3$ yr; that for Spring Creek is 10.5 $gm/cm^2/10^3$ yr; and that for Moshannon Creek is 24.1 $gm/cm^2/10^3$ yr.

While it is interesting that a mined area has such a high denudation rate compared to other terranes, it is not surprising. Nevertheless, it is of some surprise that the denudation rate for the Spring Creek basin is three times greater than that for the Driftwood Branch basin. One might expect that, after being exposed to the processes of chemical weathering and erosion for more than 200 million years, regions of mixed terranes such as the Valley and Ridge (as well as the adjacent Plateau) would achieve steady-state, relative positions and would all be reduced at the same rate. But if the above data represent natural rates, it is clear that this is not the case and that the Carbonate Valley floors are being denuded three times faster than their adjacent ridges and the Plateau.

Closer examination of the data shows that it is the chemical weathering rate which makes the Spring Creek denudation rate greater than that for the Driftwood Branch. The erosion rates for the two regions are nearly the same.

Both chemical weathering and erosion rate determinations are subject to inaccuracies when determined from recent data as the time interval sampled may not be representative. For chemical weathering the amount of material removed in solution is simply proportional to the discharge because, as it has been argued above, the type area stream composition does not vary with discharge. Periods of discharge during sampling significantly different from the mean would cause some error (as much as 20% for the recent record for Spring Creek). Similarly, erosion rates based on short-term data may misestimate the sediment flux from a basin if major floods (such as the June 1972 flood on the Susquehanna induced by Hurricane Agnes) are not included. Since sediment load increases exponentially with discharge (Leopold and Maddock, 1953), these large events would carry large amounts of sediment. Different areas could be affected differently by the large floods. Bank erosion would be more efficient in the silicate terranes than the carbonate terranes as the unit hydrograph for a given storm has a much higher peak discharge on the former terrane. The effect would be to move the total denudation rates of the two types of areas more closely together.

If one converts the mass denudation rate to a rate in terms of vertical elevation by assuming a density of 2.6 gm/cm^3, the difference in the rates for the carbonate and silicate terranes is -30 meters/10^6 yr. Today the difference in elevation between the Plateau top and the carbonate valleys is about 200 meters. If it is assumed that the current denudation rates were constant with time and that at a previous point in time erosion and chemical weathering started to act on a nearly horizontal surface (perhaps the Cretaceous), the present discrepancy in altitudes could be produced in less than 10 million years. Obviously, then, the denudation process must vary with time, or the process of regional uplift including numerous variations in local rates varies through time. Most likely the denudation rates of different areas vary with time.

Elevation is an important factor in the erosion rate of a region. The high elevation areas of the United States such as the Colorado Plateau and the Cascade Mountains have erosion rates ten times that of the low lying parts of the U.S. (Judson and Ritter, 1964). In the Appalachians it could be expected that if the area were uplifted to higher elevations the rates of erosion of silicate and carbonate terranes might come into balance, as erosion becomes the dominant denudation parameter. Large climatic variations would not affect the long-term erosion rates of the region since the area has been neither arid nor tropical for the last 100 million years.

Regional Denudation Rates

The study of Williams and Reed (1972) is detailed enough that rates of natural erosion can be estimated. In fact, their data show that the erosion rate for the Susquehanna at Harrisburg or for the Juniata River at Newport is representative of the erosion rate for the Appalachians. Former erosion rates (Judson and Ritter, 1964) seem to have been calculated without an attempt to eliminate areas with anomalously high erosion rates due to man's local activities. The inclusion of the Schuylkill River data in the computation of the regional rate (Judson and Ritter, 1964) is a good example. The Schuylkill drains the anthracite coal region of the Valley and Ridge and one of the most urbanized areas in Pennsylvania, both of which, according to the data of Williams and Reed (1972), cause increased local sediment transport out of the basin. As a result of the inclusion of such data, the regional erosion rate calculated for the North Atlantic region is probably 60% greater than the natural rate. As Judson and Ritter noted, their rate is nearly twice as great as an earlier estimate made by Dole and Stabler (1909). The inclusion of data by Judson and Ritter not representative of natural erosion in the Appalachians has led to this discrepancy. In fact, the rate determined by Dole and Stabler (1909) is more representative of the rate of erosion for the Appalachian region.

TABLE III-1. RV AREA SAMPLE SITES SHOWN IN FIGURE III-1: RICH VALLEY, CAMERON CO., PA.

RV-1	Driftwood Branch of Sinnemahoning Creek, 900 meters upstream from confluence with Bobby Run
RV-2	Ephemeral stream, at the mouth of Billy McGhee Hollow (near the spring RV-3)
RV-3	Spring, Billy McGhee Hollow, 5 meters (elevation) above the ephemeral stream site (RV-2) on the hillside
RV-4	Spring, Barton Farm, 40 meters above the valley floor on a north-facing hillside
RV-5	Spring, near the valley floor at the base of the north-facing hillside above, behind Jay M. Lewis' (JML spring) house
RV-6	Well, middle of the valley (∿ 3 meters deep) behind Earl Hockenberry's house
RV-7	Spring, south-facing hillside, near ephemeral stream RV-8
RV-8	Ephemeral stream, at the mouth of a small hollow, 100 meters from spring RV-7

γ

TABLE III-2. DRIFTWOOD BRANCH OF SINNEMAHONING CREEK RV-1. MAJOR ION CONCENTRATIONS, mg/ℓ

	November 1973	December 1973	January 1974	March 1974	April 1974	June 1974 (filt.)
Na^+	1.44	0.95	0.88	1.04	0.72	0.94
K^+	0.39	0.48	0.47	0.45	0.48	0.41
Ca^{++}	4.62	4.06	3.64	3.96	3.56	4.32
Mg^{++}	1.33	1.16	1.03	1.17	1.02	1.20
$SO_4^=$	10	10	12	12	11	4
HCO_3^-	9.88	6.16	4.03	4.27	3.36	4.03
Cl^-	1.32	0.99	1.25	1.29	0.80	0.88

TABLE III-3. BILLY McGHEE EPHEMERAL STREAM, RV-2. MAJOR ION CONCENTRATIONS, mg/ℓ

	December 1973	March 1974
Na^+	0.95	0.88
K^+	0.55	0.46
Ca^{++}	4.80	4.66
Mg^{++}	1.25	1.18
$SO_4^=$	13	16
HCO_3^-	7.02	5.55
Cl^-	0.62	0.59

TABLE III-4. BILLY McGHEE SPRING, RV-3. MAJOR ION CONCENTRATIONS, mg/ℓ

	December 1973	March 1974	June 1974 (filt.)
Na^+	1.40	1.16	1.52
K^+	0.66	0.56	0.53
Ca^{++}	5.76	5.10	6.84
Mg^{++}	1.71	1.61	2.00
$SO_4^=$	13	18	11
HCO_3^-	14.9	9.52	14.76
Cl^-	0.59	0.65	0.53

TABLE III-5. BARTON FARM SPRING, RV-4. MAJOR ION CONCENTRATIONS, mg/ℓ

	December 1973	January 1974	March 1974	June 1974 (filt.)	June 1974 (unfilt.)
Na^+	0.97	0.92	0.96	1.06	1.05
K^+	0.28	0.47	0.47	0.35	0.47
Ca^{++}	6.82	6.34	6.62	8.28	8.46
Mg^{++}	1.45	1.32	1.41	1.77	1.78
$SO_4^=$	12	13	15	9	
HCO_3^-	13.7	10.8	12.2	15.55	14.03
Cl^-	0.66	0.85	0.62	0.48	0.42

TABLE III-6. JML SPRING, RV-5.
MAJOR ION CONCENTRATIONS,
mg/ℓ

	April 1973	December 1973	January 1974	March 1974	June (filt.) 1974	June (unfilt.) 1974
Na^+	1.20	1.07	1.04	1.10	1.22	1.23
K^+		0.18	0.42	0.35	0.34	0.33
Ca^{++}		3.88	3.54	3.78	4.22	4.18
Mg^{++}		1.01	0.92	1.00	1.11	1.10
$SO_4^=$		10	10	12	5	
HCO_3^-		5.92	4.15	4.88	3.90	3.48
Cl^-	0.94	0.61	0.50	1.94	0.60	0.43

TABLE III-7. HOCKENBERRY'S WELL, RV-6.
MAJOR ION CONCENTRATIONS, mg/ℓ

	January 1974
Na^+	0.72
K^+	0.35
Ca^{++}	4.90
Mg^{++}	0.85
$SO_4^=$	13
HCO_3^-	7.26
Cl^-	0.51

TABLE III-8. FISHERS' DRAFT SPRING, RV-7.
MAJOR ION CONCENTRATIONS, mg/ℓ

	March 1974	June 1974	
		(filt.)	(unfilt.)
Na^+	0.96	1.17	1.15
K^+	0.40	0.64	0.65
Ca^{++}	4.88	6.60	6.58
Mg^{++}	1.35	1.80	1.79
$SO_4^=$	15	9	
HCO_3^-	8.54	14.09	13.60
Cl^-	0.69	0.34	0.31

TABLE III-9. FISHERS' DRAFT EPHEMERAL STREAM, RV-8.
MAJOR ION CONCENTRATIONS mg/ℓ

	March 1974
Na^+	0.96
K^+	0.45
Ca^{++}	6.18
Mg^{++}	1.29
$SO_4^=$	17
HCO_3^-	9.64
Cl^-	0.60

TABLE III-10. DISSOLVED Ca^{++} FOR RV SITES (mg/ℓ)

	1973		1974			
Site	Nov	Dec	Jan	March	April	June
RV-1 (stream)	4.6	4.1	3.6	4.0	3.6	4.3
RV-2 (ephemeral stream)		4.8		4.7		
RV-3 (spring)		5.8		5.1		6.8
RV-4 (spring)		6.8	6.3	6.6		8.3
RV-5 (spring)		3.9	3.5	3.8		4.2
RV-6 (well)			4.9			
RV-7 (spring)				4.9		6.6
RV-8 (ephemeral spring)				6.2		

TYPE III-11. TYPE WATER COMPOSITIONS*

	Silicate Driftwood Branch		Carbonate Spring Creek		Mine Drainage Moshannon Creek	
	mg/ℓ	meqvl/ℓ	mg/ℓ	meqvl/ℓ	mg/ℓ	meqvl/ℓ
Mn^{++}					4	0.146
Fe^{+3}					8	0.430
H^{+}					1.259	1.259
Na^{+}	1	0.043	4	0.174	4	0.174
K^{+}	0.4	0.010	2	0.051	1	0.025
Ca^{++}	4.0	0.200	50	2.495	44	2.196
Mg^{++}	1.1	0.090	18	1.481	21	1.728
HCO_3^{-}	6	0.098	210	3.443	0	0
$SO_4^{=}$	10	0.208	22	0.458	300	6.246
Cl^{-}	1	0.028	12	0.338	10	0.282
SiO_2	5		5		7	
pH	7.2		8		2.9	
		$\Sigma^{+} = 0.343$ $\Sigma^{-} = 0.334$		$\Sigma^{+} = 4.201$ $\Sigma^{-} = 4.239$		$\Sigma^{+} = 5.958$ $\Sigma^{-} = 6.528$

*Estimated from several analyses so an error of at least ±5% on the total anion and cation charges is possible.

TABLE III-12. BUFFALO CREEK, SR-11.
MAJOR ION CONCENTRATIONS
mg/ℓ

	April 1973	June 1973	August 1973	Oct-Nov 1973	January 1974	March 1974	April 1974	June 1974
Na^+	2.81	1.95	3.33	1.52	1.95	1.98	1.62	2.24
K^+	0.70	0.81	1.35	2.11	0.64	0.76	1.02	0.43
Ca^{++}	15.8	23.6	35.6	10.7	17.1	18.4	13.7	21.1
Mg^{++}	4.18	7.30	11.00	2.60	4.90	5.82	3.88	6.33
$SO_4^{=}$	12	17	28	22	15	16	14	23
HCO_3^-			139.9	27.6	56.5	67.3	46.2	75.82
Cl^-	3.41	4.03	6.53	3.10	3.74	4.00	3.23	6.68

TABLE III-13. SUSQUEHANNA RIVER, CONOWINGO, MD., SR-17
MAJOR ION CONCENTRATIONS, mg/ℓ

	East		West				
	April 1973	June 1973	August 1973	Oct-Nov 1973	January 1974	March 1974	June 1974
Na^+	4.17	5.56	9.13	10.84	4.76	5.38	7.40
K^+	1.06	1.51	2.12	2.13	1.06	0.88	1.40
Ca^{++}	13.2	23.3	30.2	32.7	16.1	17.1	25.8
Mg^{++}	3.50	6.92	10.65	11.30	4.70	5.44	8.30
$SO_4^=$	26	55	83	85	36	42	61
HCO_3^-			52.2	59.0	30.3	31.5	47.09
Cl^-	5.72	7.57	10.38	13.34	6.98	7.04	18.0

TABLE III-14. WATER PROVENANCE: PROPORTION OF THE TOTAL FLOW OF THE SUSQUEHANNA RIVER AT CONOWINGO COMPOSED OF THE TYPE WATERS, CALCULATED FROM $SO_4^{=}$ AND Mg^{++}

	1973				1974		
Type Waters	April	June	August	Oct-Nov	Jan	March	June
Mean discharge*	3851	702	104	1325	3455	1430	422
Silicate (a)	0.86	0.69	0.47	0.60	0.80	0.76	0.60
Carbonate (b)	0.09	0.17	0.29	0.15	0.11	0.13	0.23
Mine drainage (c)	0.05	0.14	0.24	0.25	0.09	0.11	0.17

*m^3/sec

TABLE III-15. JUNIATA RIVER, NEWPORT, PA., SR-15
MAJOR ION CONCENTRATIONS, mg/ℓ

	April 1973	June 1973	August 1973	Oct-Nov 1973	January 1974	March 1974	June 1974
Na^+	3.50	5.68	10.00	4.22	4.33	5.28	5.25
K^+	1.16	1.82	1.65	2.30	1.01	0.86	1.17
Ca^{++}	14.4	26.0	26.6	16.1	18.2	18.9	20.0
Mg^{++}	3.80	6.65	8.72	4.20	5.00	5.20	5.15
$SO_4^=$	22	27	34	27	23	24	25
HCO_3^-		88.5	99.6	45.1	53.4	61.3	63.81
Cl^-	4.93	7.52	12.82	6.24	6.10	7.13	12.03

TABLE III-16. WATER PROVENANCE: PROPORTION OF THE TOTAL FLOW OF THE JUNIATA RIVER AT NEWPORT COMPOSED OF THE TYPE WATERS CALCULATED FROM $SO_4^=$ AND Mg^{++}

	1973				1974		
Type Waters	April	June	August	Oct-Nov	Jan	March	June
Mean discharge*	447	109	25	490	266	118	110
Silicate (a)	0.93	0.93	0.56	-	0.78	0.77	0.77
Carbonate (b)	0.03	0.01	0.37	-	0.18	0.19	0.19
Mine drainage (c)	0.04	0.06	0.07	-	0.04	0.04	0.04

*m^3/sec

TABLE III-17. ION PROVENANCE FOR THE SUSQUEHANNA RIVER AT CONOWINGO

	April 1973	August 1973	January 1974	June 1974
Ca fraction from rock weathering				
Silicate	0.32	0.06	0.25	0.10
Carbonate	0.46	0.56	0.46	0.56
Mine drainage	0.21	0.37	0.30	0.33
Mg^{++} fraction from rock weathering				
Silicate	0.26	0.05	0.19	0.08
Carbonate	0.45	0.49	0.42	0.50
Mine drainage	0.29	0.47	0.40	0.43
$SO_4^=$ fraction from type areas				
Silicate	0.33	0.06	0.21	0.10
Carbonate	0.08	0.08	0.07	0.08
Mine drainage	0.58	0.87	0.72	0.82

TABLE III-18. KEATING TO LOCK HAVEN MODEL: PROPORTIONS OF FLOW ATTRIBUTED TO MIXING WATERS, VALUES AT SITE SR-6

	WBSR + Sinn. Cr.	Silicate	Mine
	a	b	c
June 1974	0.72	0.27	0.01
August 1973	0.61	0.33	0.06
March 1974	0.87	0.12	0.01
June 1974	0.55	0.39	0.06

TABLE III-19. LOCK HAVEN TO NORTHUMBERLAND MODEL: FLOW PROPORTIONS FOR THE WATERS MIXING TO GIVE THE WBSR FLOW

	Nisbet a	Pine Creek b	Buffalo Creek c
August 1973			
SR-10	0.61	0.39	0
SR-13a	0.61	0.18	0.21
SR-13	0.99	0.10	- 0.09
June 1973			
SR-10	0.67	0.33	0.00
SR-13	0.76	0.19	0.05
March 1974			
SR-10	0.63	0.36	0.01
SR-13a	0.62	0.06	0.32
June 1974			
SR-10	0.63	0.37	0.00
SR-13a	0.56	0.11	0.33
Two component model	a	b + c	
April 1973			
SR-10	0.43	0.57	
SR-13	0.64	0.36	
October 1973			
SR-10	0.59	0.41	
SR-13a	0.61	0.39	

TABLE III-20. RATES OF CHEMICAL WEATHERING, EROSION AND TOTAL DENUDATION IN TYPE REGIONS OF THE SUSQUEHANNA RIVER BASIN

	Denudation Rates (in units of $gm/cm^2/10^3$ yr)			
Stream Basin	Chemical	Erosion*	Total	Total $(m/10^6/y)$**
Spring Creek	8.7	1.8	10.5	40
Driftwood Branch of Sinn. Cr.	0.4	2.3	2.7	10
Moshannon Creek	19.7	4.4	24.1	92

*From the data of Williams and Reed, 1972
**Assuming ρ = 2.6

FIGURES

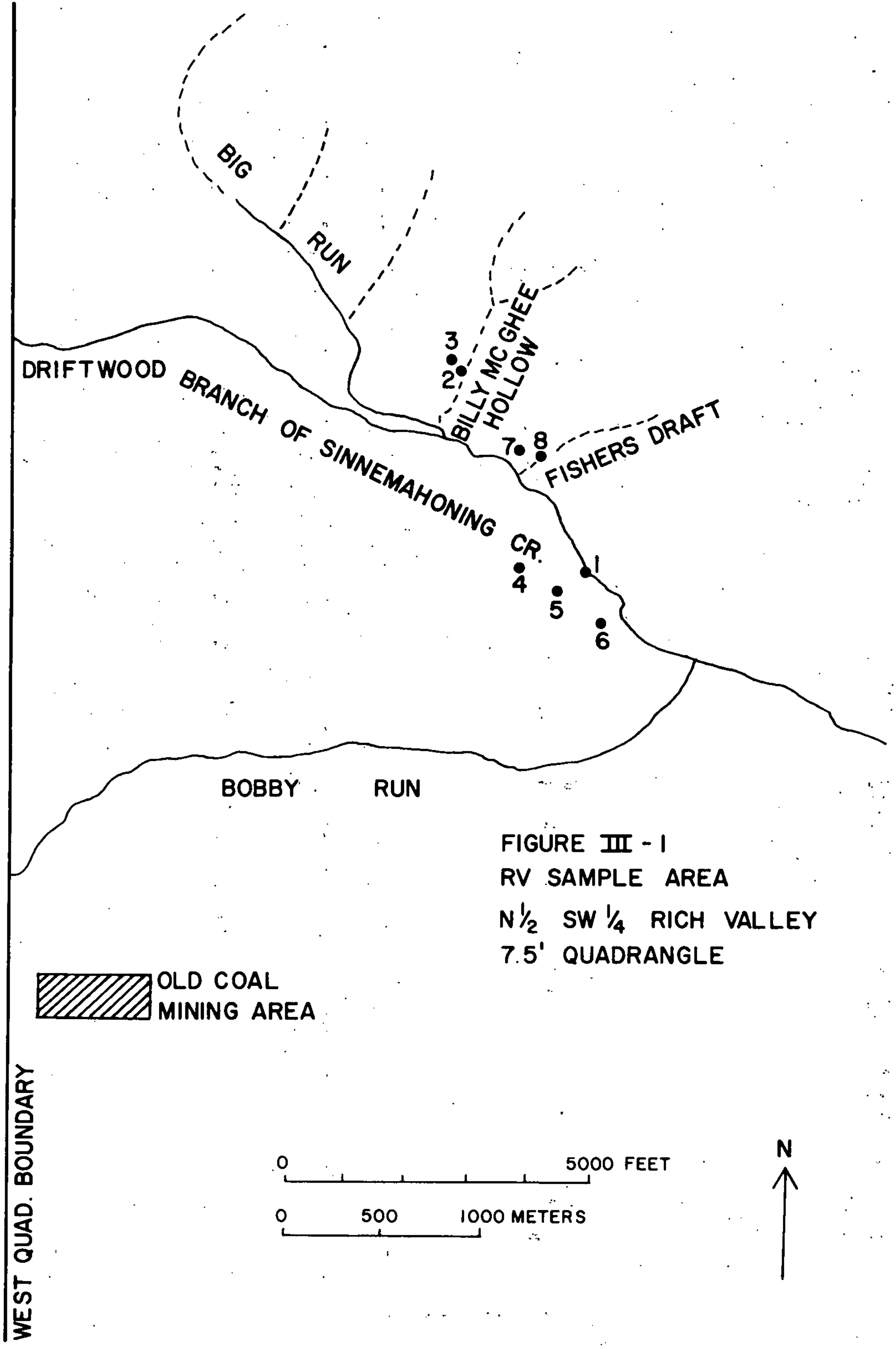


FIGURE III - 1
RV SAMPLE AREA
N$\frac{1}{2}$ SW$\frac{1}{4}$ RICH VALLEY
7.5' QUADRANGLE

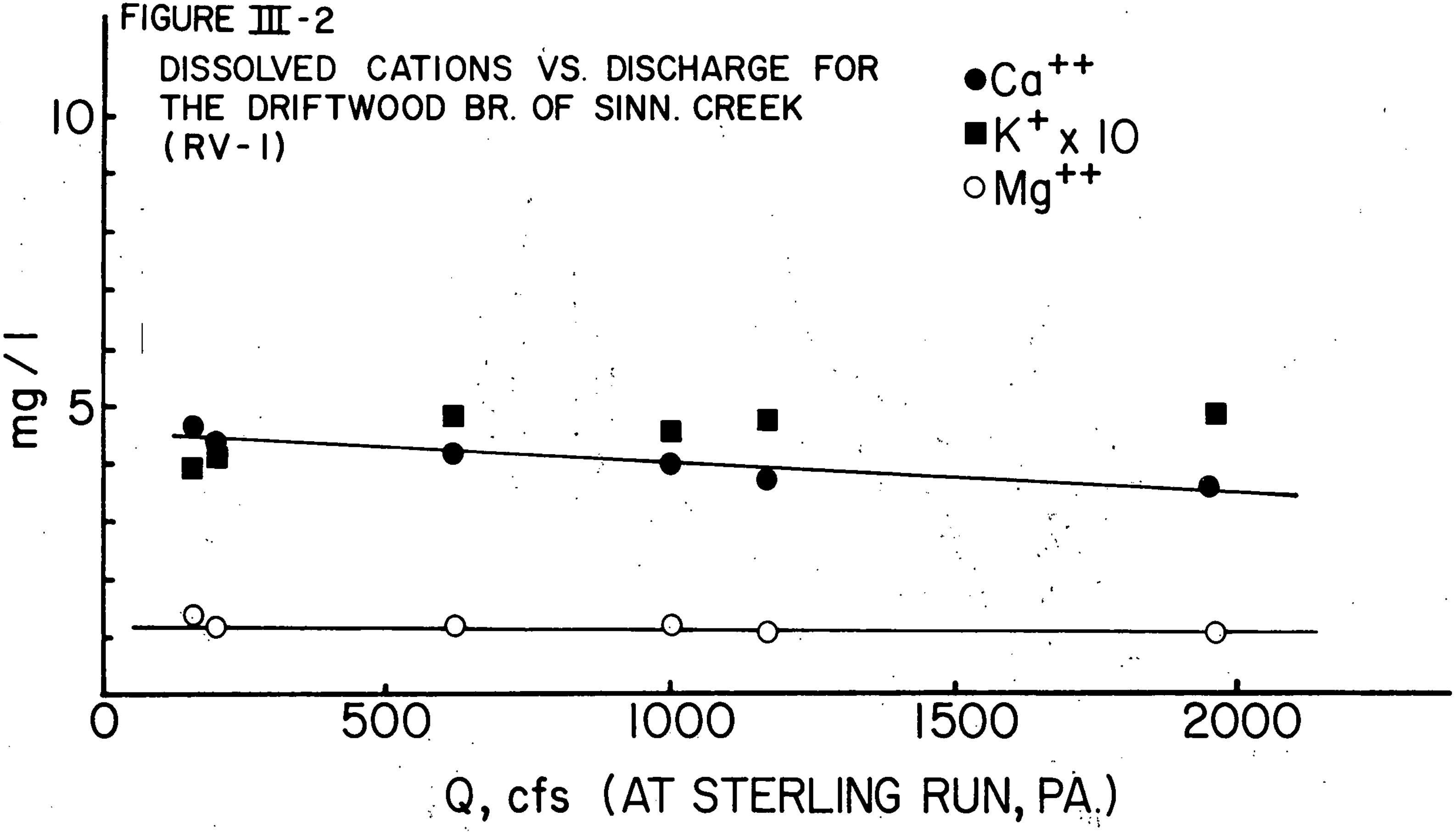


FIGURE III-2

DISSOLVED CATIONS VS. DISCHARGE FOR THE DRIFTWOOD BR. OF SINN. CREEK (RV-1)

FIGURE III - 3

YOUNG WOMANS CREEK (USGS site)
Oct. 1967 - Sept. 1972

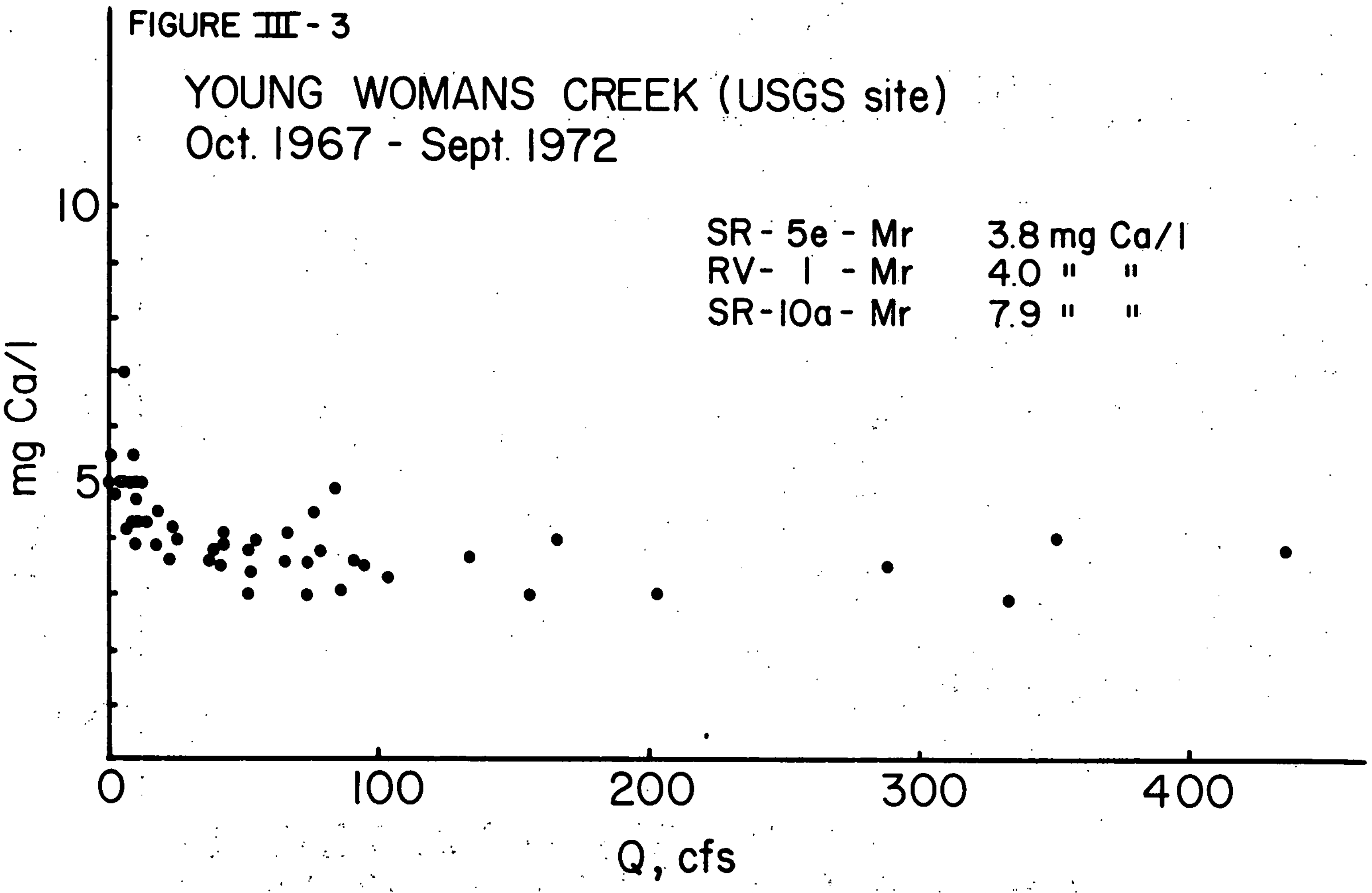
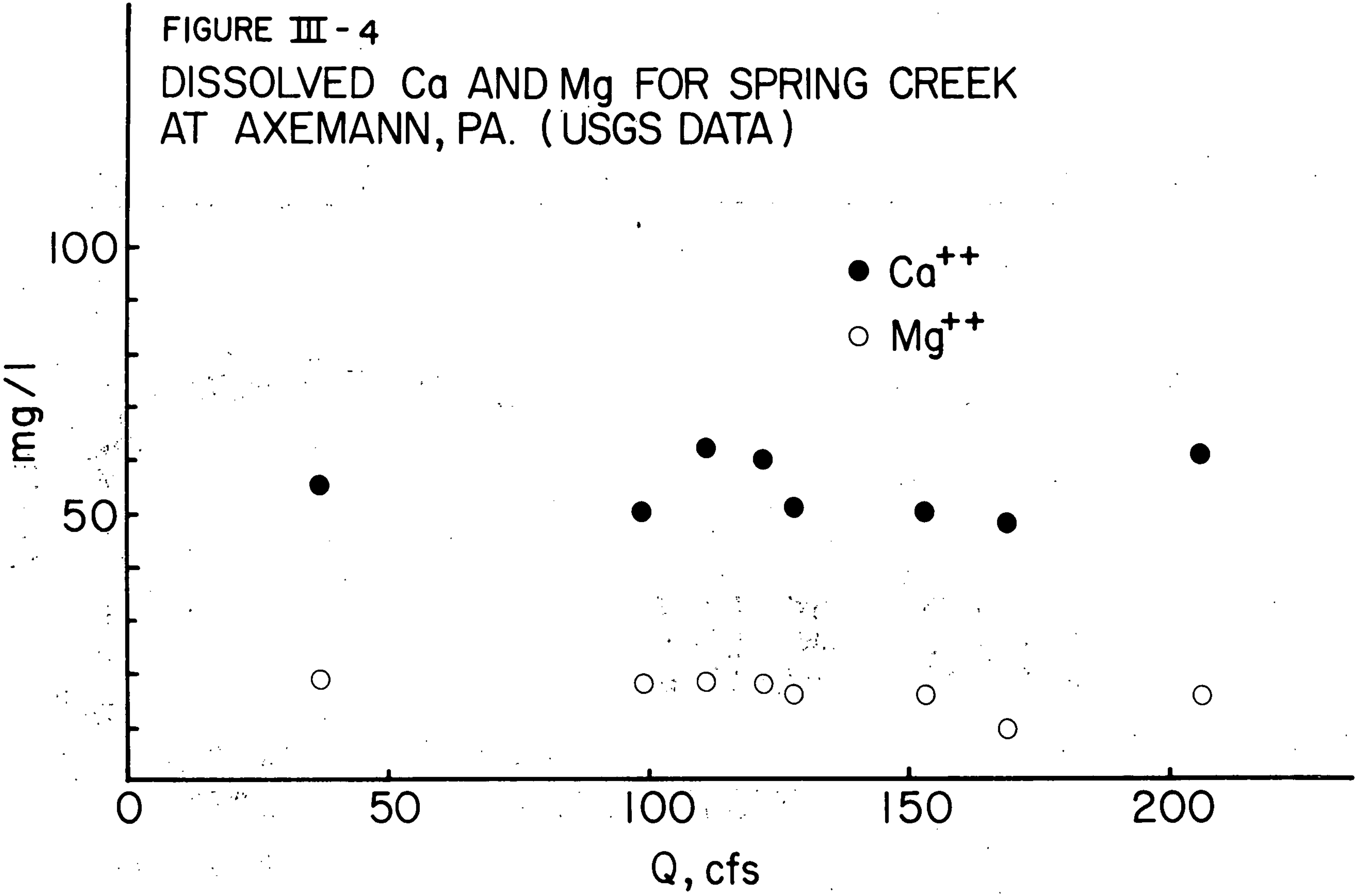


FIGURE III - 4

DISSOLVED Ca AND Mg FOR SPRING CREEK AT AXEMANN, PA. (USGS DATA)



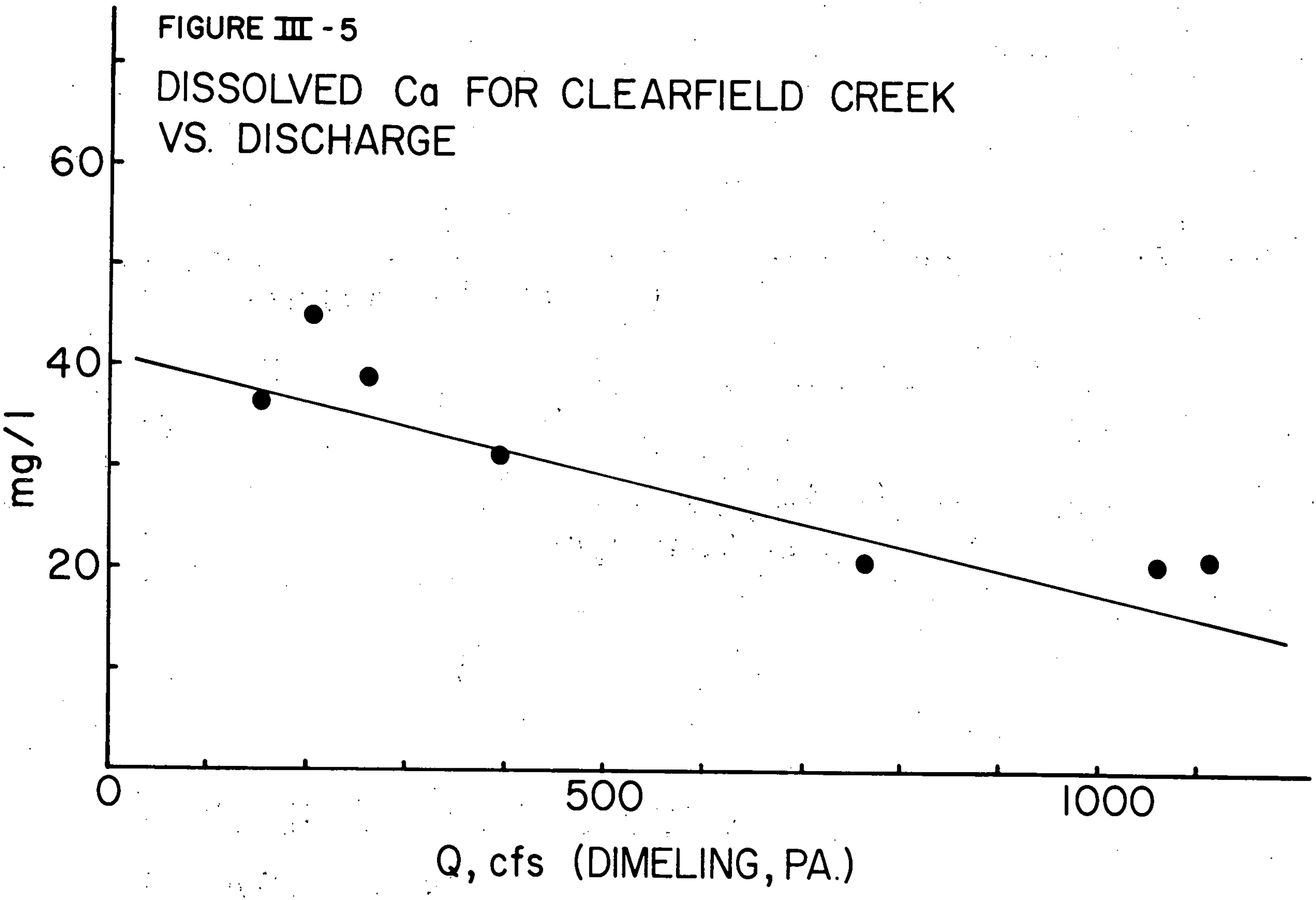


FIGURE III - 5

DISSOLVED Ca FOR CLEARFIELD CREEK VS. DISCHARGE

FIGURE III - 6

GENERAL HYDROGRAPH

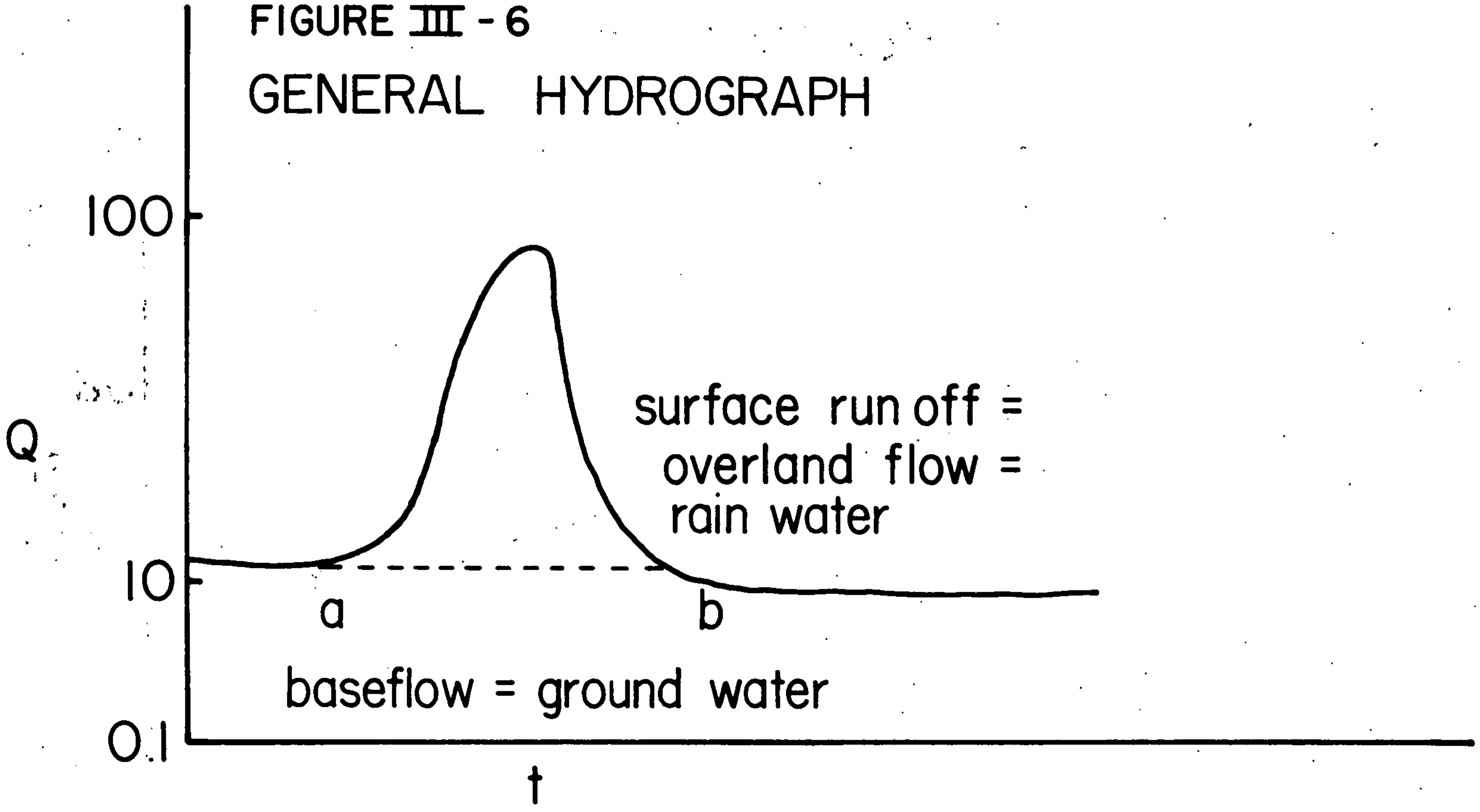
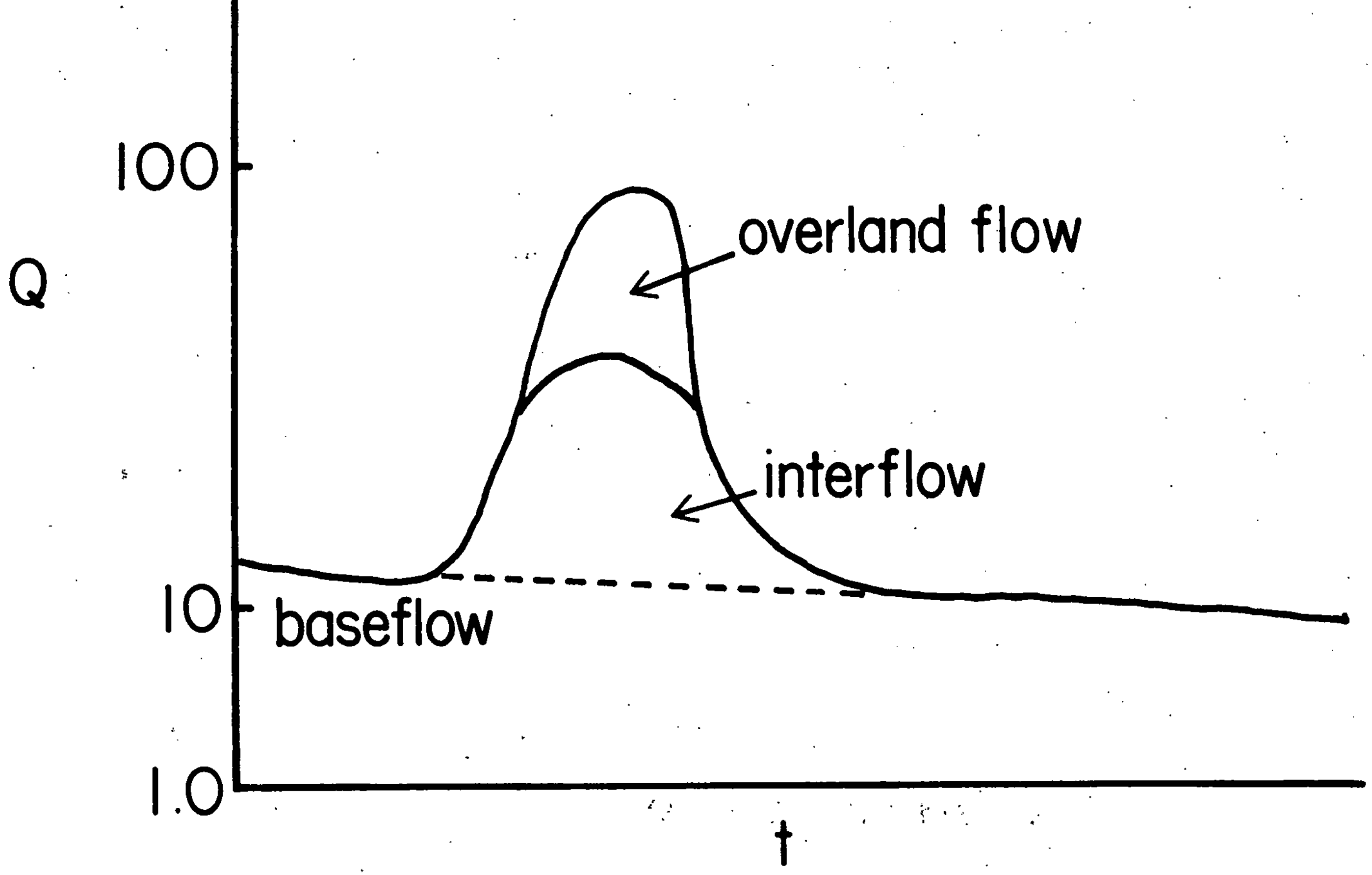


FIGURE III -7
HYDROGRAPH RESOLUTION



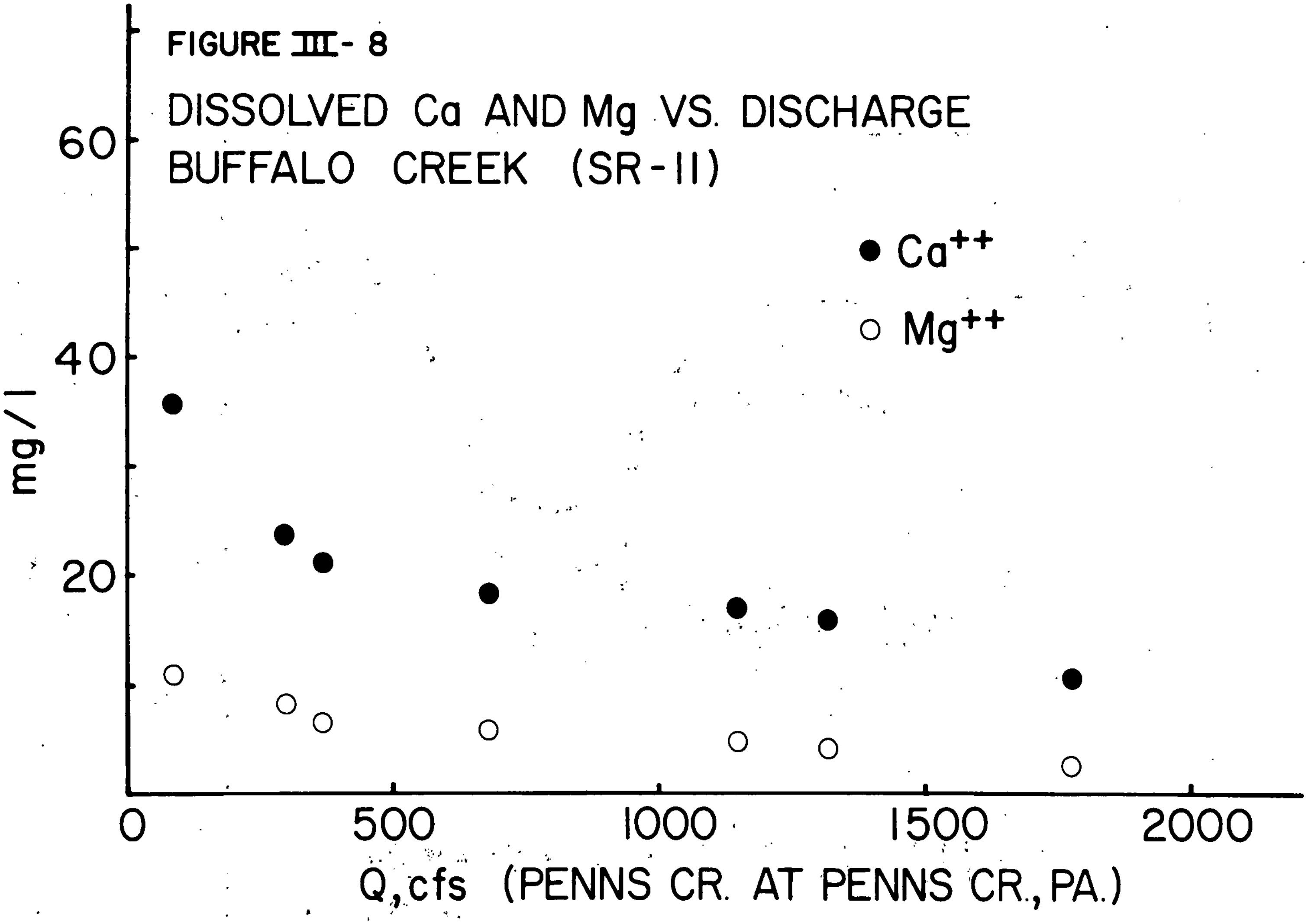


FIGURE III- 8

DISSOLVED Ca AND Mg VS. DISCHARGE
BUFFALO CREEK (SR-11)

FIGURE III - 9

UNIT HYDROGRAPH

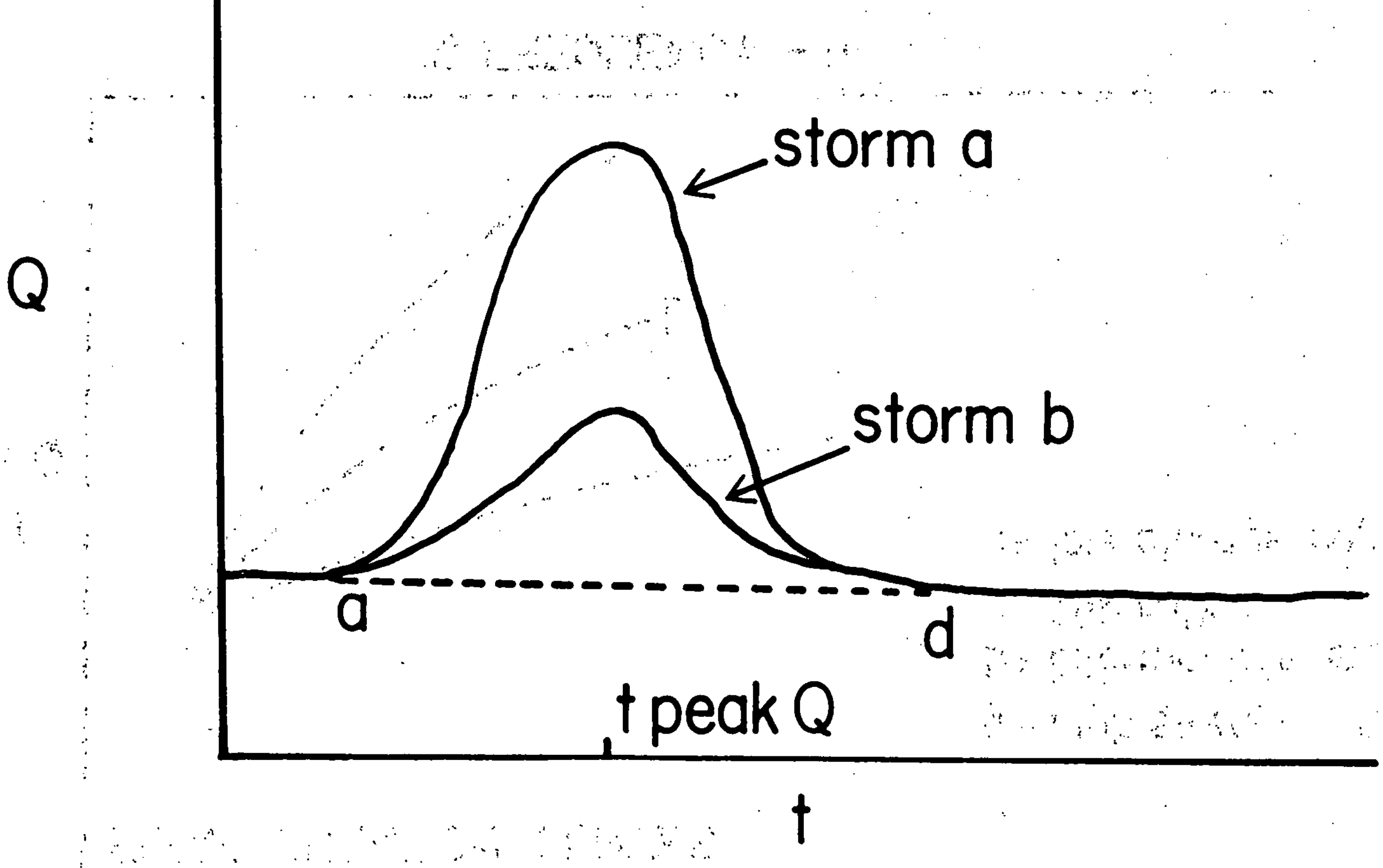


FIGURE III - 10

FLOW DURATION CURVES

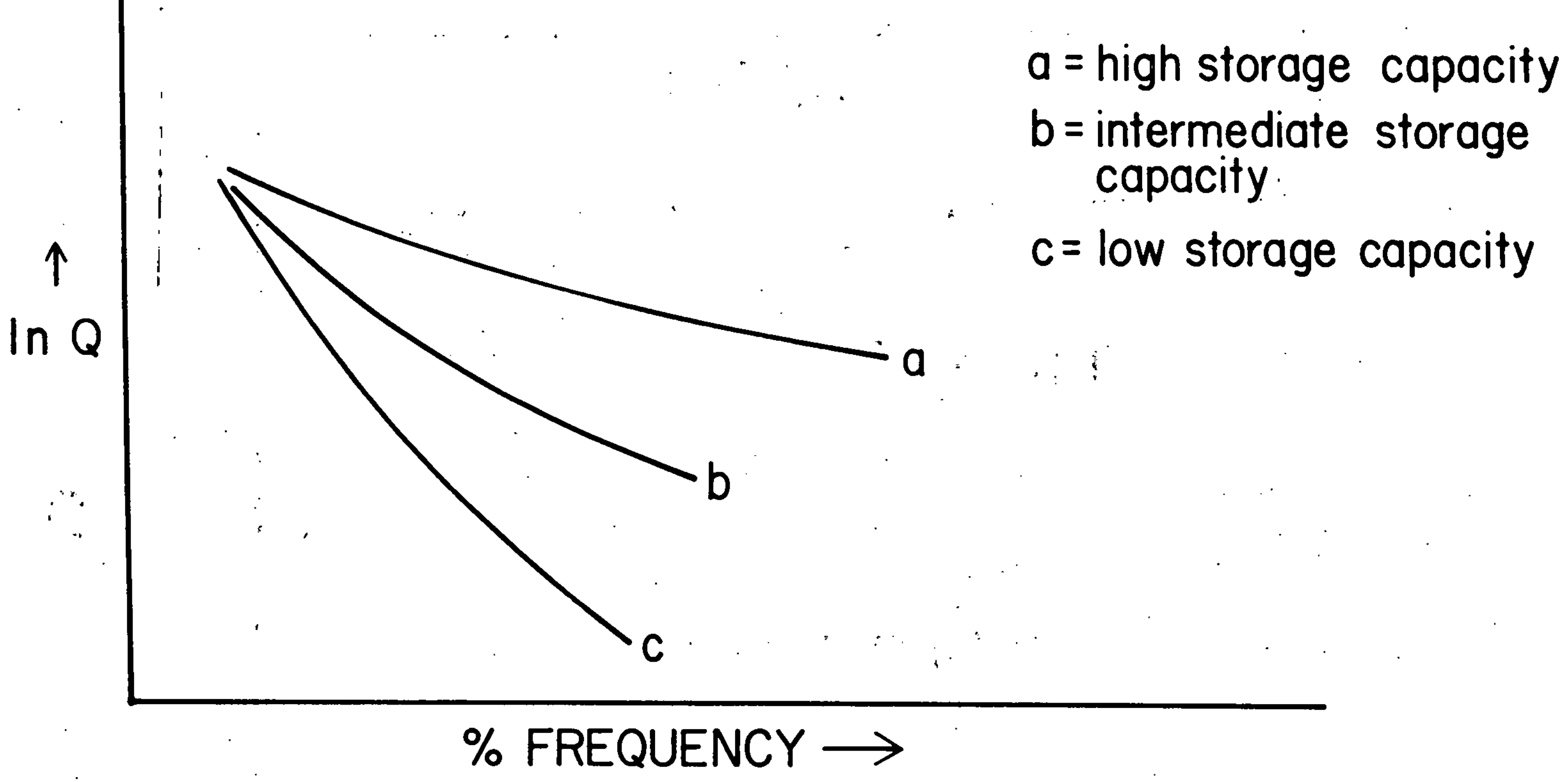


FIGURE III-11

UNIT HYDROGRAPH RELATIONSHIP TO THE FLOW DURATION CURVES OF FIGURE III-10

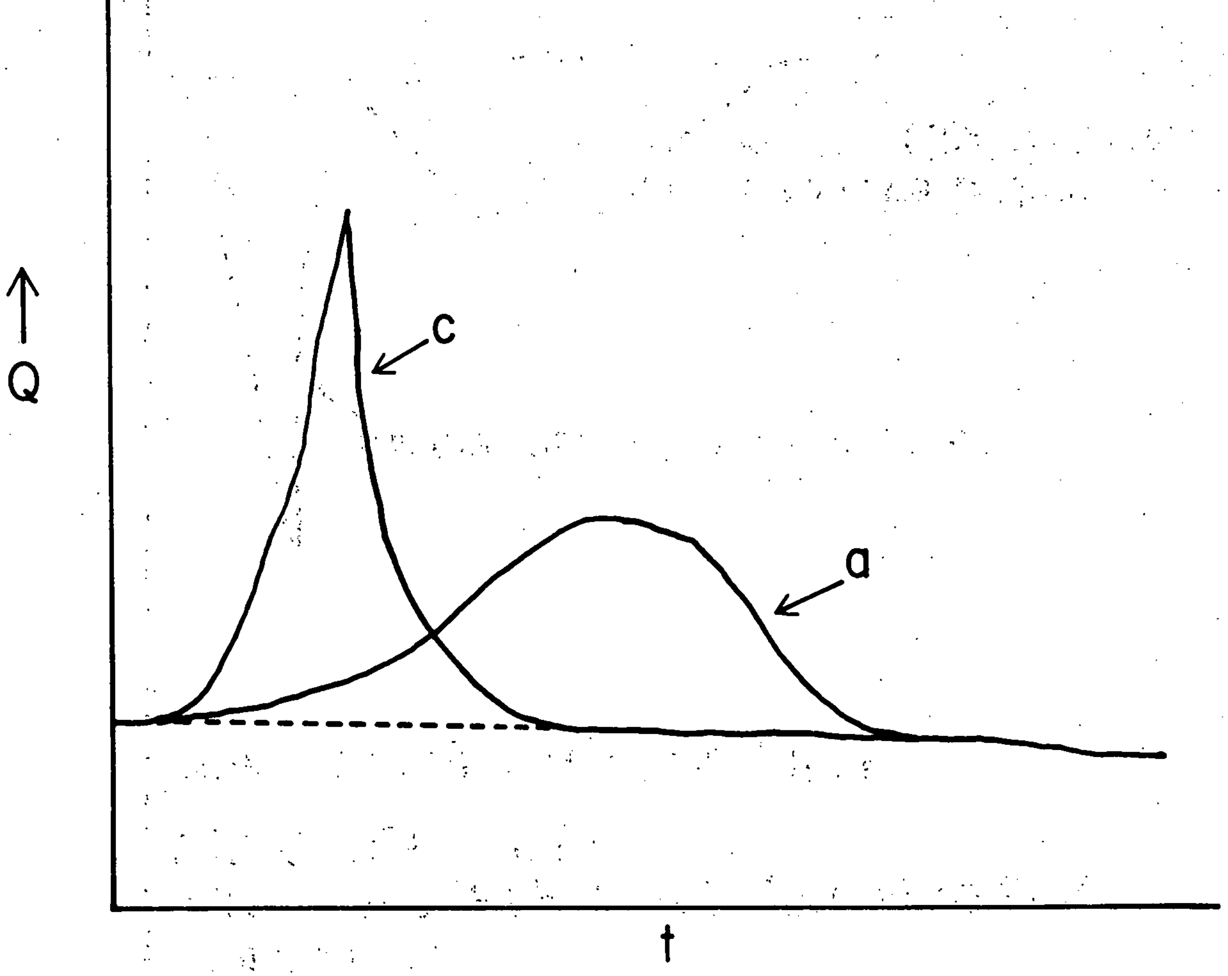


FIGURE III - 12

UNIT HYDROGRAPHS FOR SPRING CREEK AND COREY CREEK

(after Heerdegen and Reich, 1974)

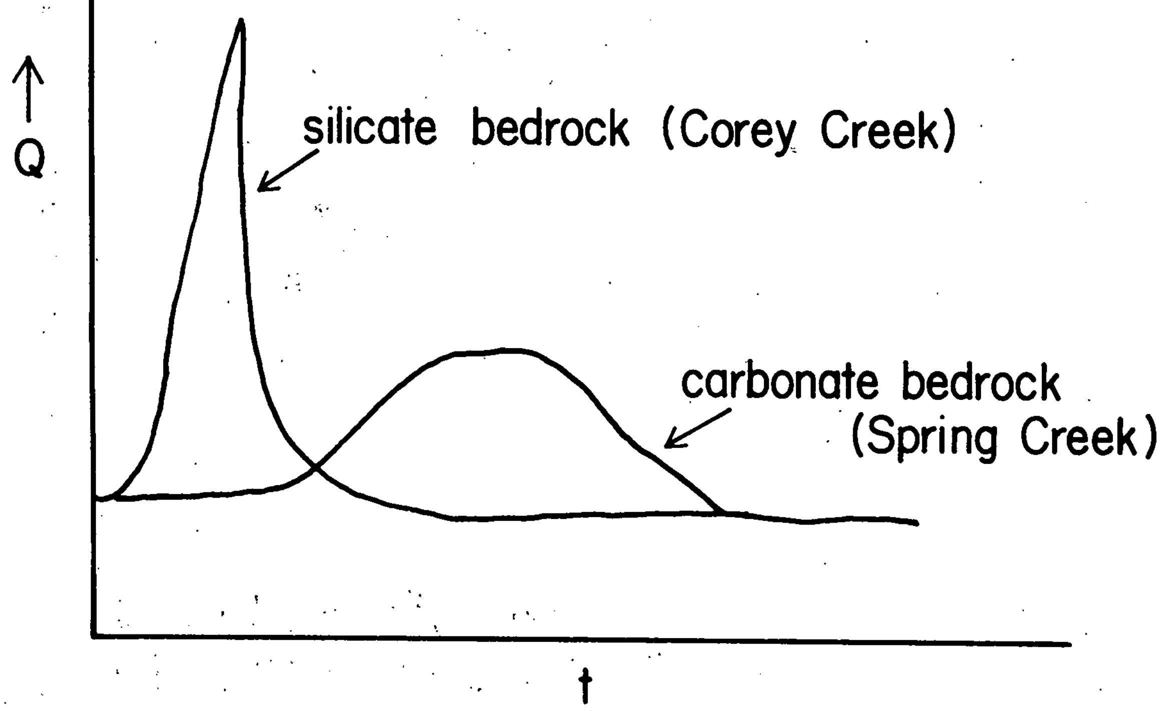


FIGURE III - 13

FLOW DURATION CURVES
Tradewater River Basin
(after Grubb and Ryder, 1972)

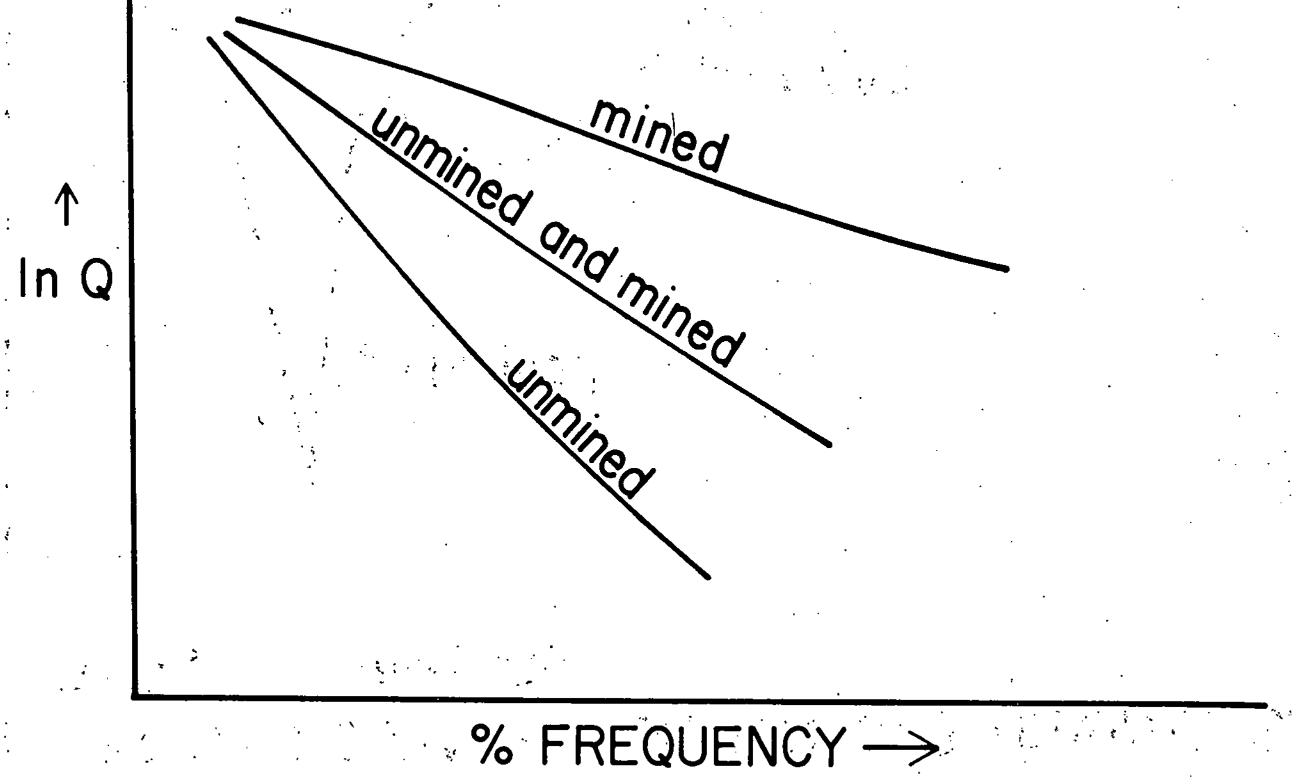


FIGURE III-14
UNIT HYDROGRAPHS FOR MINED & UNMINED BASINS
Tradewater River Basin

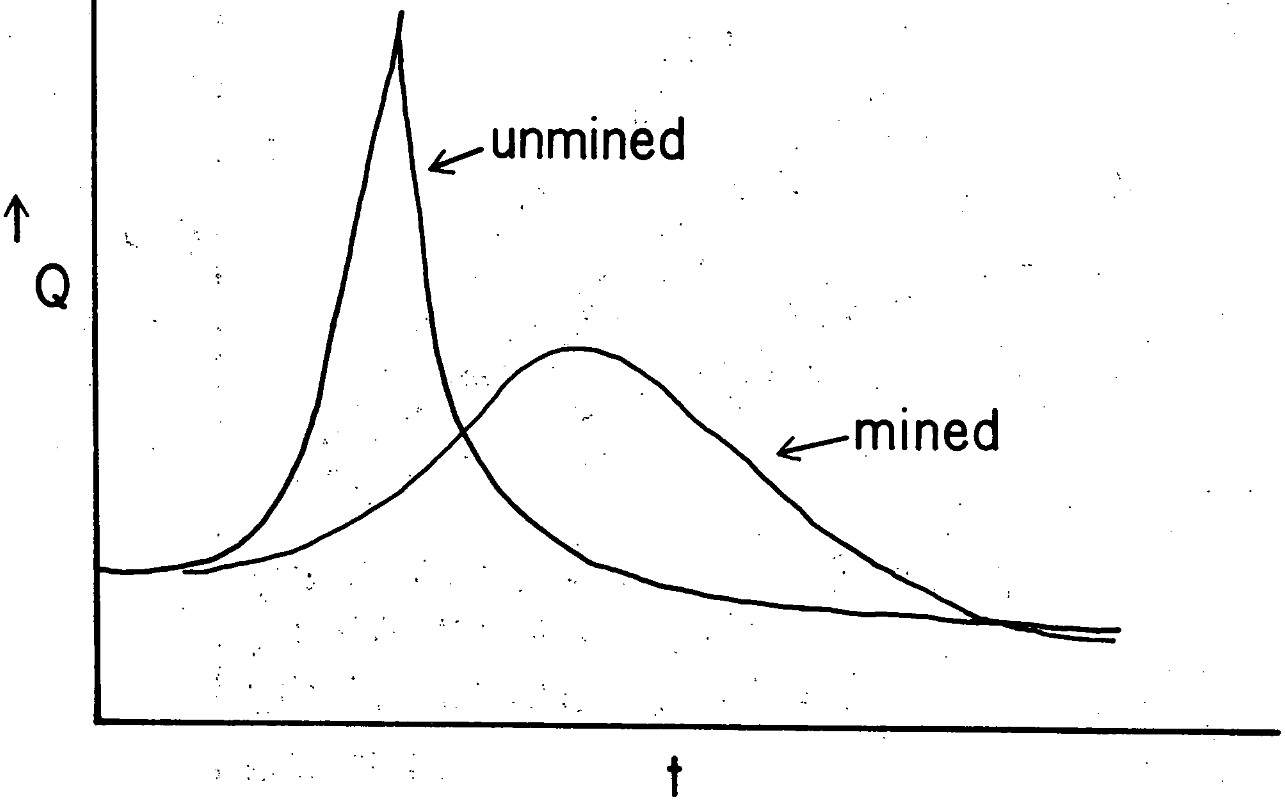
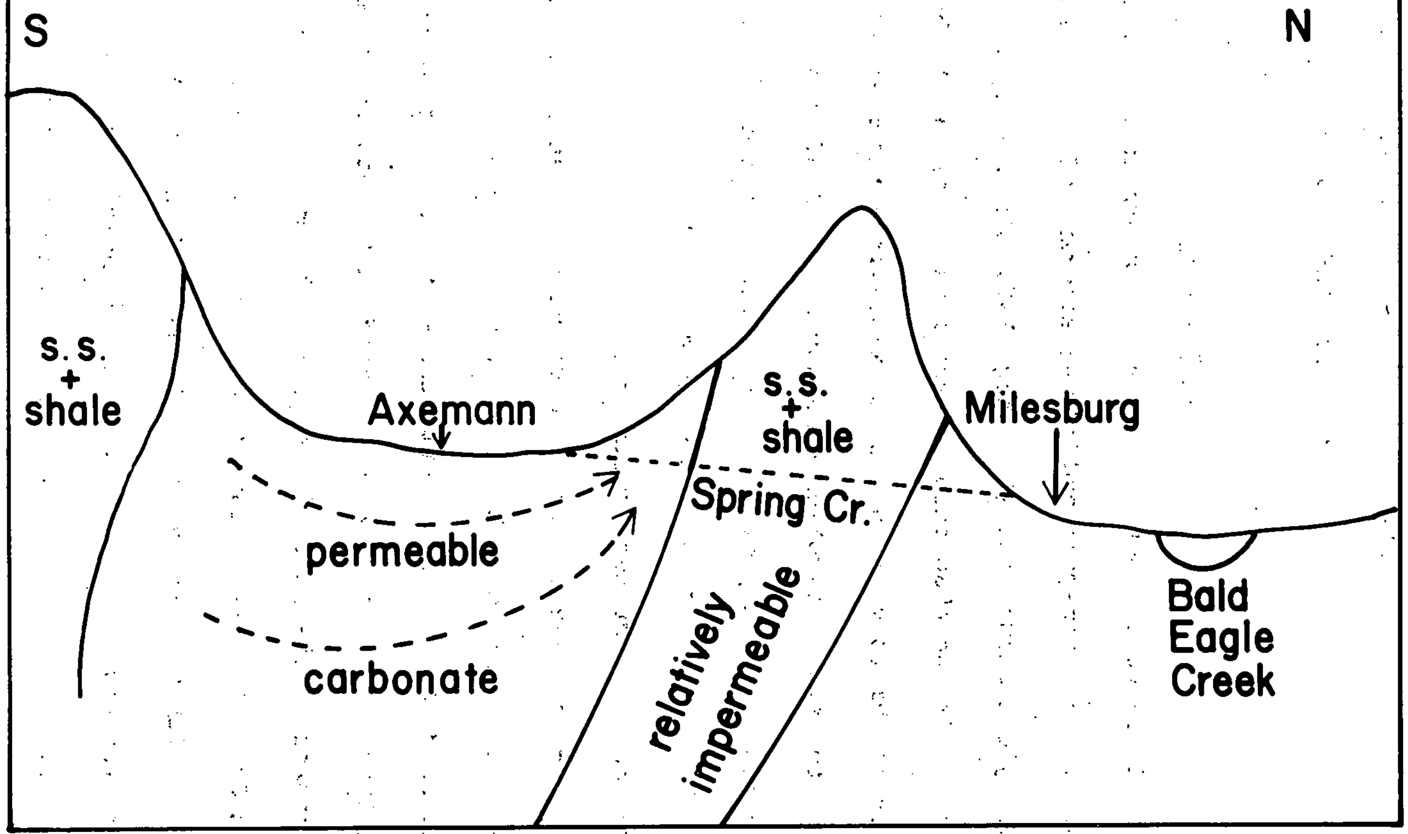


FIGURE III - 15

SPRING CREEK BASIN, CROSS SECTION



IV. GEOCHEMISTRY OF MANGANESE AND IRON IN THE SUSQUEHANNA RIVER SYSTEM

Introduction

It is well known that Mn and Fe hydroxides play an important role in the transport and/or sequestering of trace metals in diverse geological situations (Goldberg, 1954; Krauskopf, 1956; Jenne, 1968). Studies of the absorption capabilities of Mn and Fe hydroxides show that the history of Mn and Fe oxides in streams is important in regard to metal absorption (Kharkar et al., 1967; Murray, 1975a, 1975b). Therefore, a study of Mn and Fe in conjunction with the other aspects of this study was thought to be a useful venture in studying metal transport in the terrestrial system.

Schubel (1972) has found seasonal variations in dissolved and particulate Mn concentrations at the mouth of the Susquehanna River. Higher dissolved Mn concentrations and lower Mn concentrations in the particulate fraction were observed in the winter and early spring compared to the rest of the year. The concentrations of Cu, Ni, Zn and Co on the particulate fraction were also shown to vary sympathetically with Mn. In sediments taken at Marietta, Pa., in June 1966 Turekian and Scott (1967) similarly showed high concentrations of Mn and several trace metals relative to the various crustal rocks from which they could have been derived.

Schubel (1972) proposed that the cyclic variation in Mn and trace metals was due to a natural cycle of vegetation decay and release of metals in the winter and spring. Turekian and Scott (1967) noted that the stream sediments from the eastern U.S. rivers, high in trace elements and Mn, were also high in organic matter.

Knowledge of the controls in manganese transport in streams is clearly necessary to the understanding of the flux of metals to estuaries, and a major aspect of this study is devoted to this element.

Dissolved Manganese in the Type Regions

Silicate Regions

As discussed earlier (Silicate Type Terrane, Chapter II) the Driftwood Branch of Sinnemahoning Creek above the point of sampling is not much affected by human activities, including coal mining. It has been shown that it is representative, at least in terms of the major elements, of streams draining areas underlain by silicate rocks (exclusive of basalts and ultramafics) in the Susquehanna River basin. Examination of the dissolved (< 0.4 μm) Mn concentrations for the Driftwood Branch (RV-1) shown in Table IV-1 indicates that there is no significant variation in manganese concentration of the stream, regardless of discharge or season of the year. Furthermore, the concentration of Mn is very low, averaging around 12 ppb. A single determination of the dissolved Mn was made on a sample collected in March 1974 from Young Womans Creek (RV-7), a stream draining an area very similar to that of the Driftwood Branch (see: Type Waters, Silicate Rocks, Chapter III). The concentration of 2 ± 4 ppb indicates that, like the Driftwood Branch, Young Womans Creek is not a significant source of Mn in terms of the total flux from the Susquehanna basin.

The springs and ephemeral streams of the RV sample area contain no measurable dissolved Mn. This probably reflects the fact that the springs and ephemeral streams are fed by very near surface ground water, while the Driftwood Branch receives its water from a slightly deeper (perhaps more reducing) ground water source.

Initially Pine Creek (SR-8) was sampled as being representative of silicate terranes for manganese as well as for major elements. However, from the maganese concentrations shown in Table IV-1 it can be seen that they are considerably greater than those for the RV-1 site. Since Pine Creek receives a small amount of mine drainage (Biesecker and George, 1966) it is likely that this is the source of the manganese, as will be discussed below.

In March 1974 Muncy Creek was sampled as part of a survey to determine what is a representative concentration of manganese of water flowing into the Susquehanna below Lock Haven. The value of 28 ppb is more like the value for Pine Creek (37 ppb) than for the Driftwood Branch (9 ppb). While this is not a large enough concentration to account for those observed by Schubel, it is greater than silicate terranes represented by the Driftwood Branch. Like Pine Creek, the Muncy Creek drainage basin includes outliers of Pennsylvanian coal measures. While the extent of mining is unknown, it may be that a small amount of mine drainage enters the stream. Also, the stream drains the glaciated section of the High Plateau Province with numerous swamps and ponds that could contribute dissolved manganese.

Carbonate Terranes

The manganese data for Buffalo Creek (SR-11) in Table IV-1 show that there is a seasonal or discharge-related trend to the concentration. High discharge is characterized by a concentration of 10 to 20 ppb, while summer and fall concentrations range from 20 to 50 ppb. Actually the variation is not very pronounced, and much of the time the concentration is not very different from that of Pine Creek. The tendency towards higher Mn concentration at lower flow is probably due to the dominance of older, deeper ground water from the carbonate rocks over the ground water from silicate rocks as was discussed earlier (see: Intermediate Streams, Chapter III).

Mine Drainage

In a survey of streams in the Appalachian region affected by mine drainage the data of Biesecker and George (1966) show that every stream affected by mine drainage (both from the bituminous and anthracite regions) contains dissolved Mn from 0.1 to 2 ppm. In fact, an examination of data for streams affected by mine drainage shows that high dissolved Mn concentrations are as ubiquitous a feature of mine drainage as low pH and high sulfate and high dissolved Fe concentrations.

For this study streams affected by mine drainage were sampled over an extended period of time to determine whether there was a variation. Clearfield Creek (SR-4) in Clearfield County, Pa., was sampled throughout the study period. It is a mine-drainage-affected stream whose pH is always less than 4.5. As discussed earlier (see: Type Waters, Mine Drainage, Chapter III), it became apparent that while Clearfield Creek was significantly polluted by mine drainage, it also showed the effects of dilution by silicate type water during periods of high flow.

The dissolved Mn data for Clearfield Creek (SR-4) are shown in Table IV-1. There is a pronounced variation in dissolved Mn with the lower values ($\sim$ 1000 ppb) during periods of high flow (April 1973, January and March 1974) and higher values during periods of low stream flow (August and October 1973, June 1974). Mn is not supersaturated with any of its compounds in the stream, so the variation must be explained by another means. In fact, the variation of Mn looks just like that for any of the major ions (Ca^{++}, Mg^{++}, $SO_4^{=}$) in Clearfield Creek (Table IV-2). The variation of these major ions has been explained by mixing a concentrated component of the ions (mine drainage) with a more dilute component from the surrounding unmined silicate rocks (see: Chapter III, Type Waters, Mine Drainage). Similarly, dissolved Mn is high in mine drainage and low in streams draining silicate areas (Driftwood Branch, RV-1; Young Womans Creek, SR-5e). Since at low flow the stream contains a large proportion of mine drainage than at other times, the concentration of Mn is highest at low flow. As the discharge of the stream increases, the proportion of the flow composed of the unmined silicate rock component increases and the Mn concentration is correspondingly diluted.

Near the end of the study period Moshannon Creek (SR-4a) in Centre and Clearfield Counties, Pa., was included in the sampling. While the discharge for Moshannon Creek at Osceola Mills differs by a factor of 2 between the two samples, the Mn varies by only about 10%. This is because Moshannon Creek is very dominantly a mine drainage stream, as can be seen from the high $SO_4^=$ (∿ 300 ppm), low pH and high dissolved Fe.

Dissolved Manganese in the Main River

As discussed in Chapter II, sampling at each time was started near the headwaters and was carried out progressively to downriver stations. The composition of the main river in terms of Mn will be due both to the Mn concentration and discharge of the different tributaries contributing to the flow and to reactions occurring in the river which affect the Mn concentrations. Two types of data comparison must be made. The first is to follow a parcel of water downriver and decipher how the Mn concentration observed at each point is determined at the time of sampling. In the second method the fact that the river is composed of different proportions of the flow components at different times of the year (at different river discharge) is considered. The concentrations of Mn observed at each site over periods of seasonal change and at different river discharge are related to the mixing model and subsequent reactions in the channel.

Profile Concentrations

As one proceeds downstream from the headwaters of the West Branch of the Susquehanna River to near the mouth of the Susquehanna River at Conowingo, Maryland, (SR-17) changes take place in the manganese concentration. The following discussion traces these changes along the course of the river.

Upper West Branch of the Susquehanna River to Shawville

The West Branch of the Susquehanna River arises in the bituminous coal region of the Appalachian High Plateau in Pennsylvania. Near its headwaters the river is affected by mine drainage, as indicated by sulfate concentrations considerably above the 10 to 20 ppm that is considered as background levels from weathering and atmospheric input. The pH of the river is greater than 5 to 5.5 in this part of the river as the alkalinity is not totally consumed by the mine drainage acid. Sample sites SR-1, SR-2, SR-2a and SR-3 represent this section of the river from Chest Creek at Ostend, Pa., (SR-1) to the West Branch at Shawville (SR-3). At any one time, such as August 1973, (Table IV-1) the Mn concentration is relatively high compared to normal silicate stream concentrations and increases downriver to SR-3. This increase correlates with a downstream increase in sulfate (an indicator of mine drainage) and qualitatively with the observation that mine drainage streams enter the river between SR-1 and Shawville (SR-3). Samples SR-2 and SR-2a were taken above and below the Curwensville Dam on the West Branch to see what effect ponding has on the concentration of Mn in the stream. Table IV-1 shows that there is no measurable effect on concentration.

Shawville to Lock Haven

From below Shawville (SR-3) to Lock Haven the West Branch is massively affected by mine drainage, as indicated by low pH (3.5 to 4.5) and high dissolved sulfate. From the geology of the basin, from observation of the streams entering the river in this area, and from the model calculations to be discussed below it is apparent that most of the mine drainage is added to the river between Shawville and the confluence with Sinnemahoning Creek (Sinnemahoning Creek is an important mine drainage contributor). However, the water added below the confluence with Sinnemahoning Creek is too low in alkalinity and discharge to neutralize the acid waters; hence the river pH remains low all the way to Lock Haven (SR-6). The sample sites on this stretch of the river are SR-5 east and SR-5 west (Karthaus), SR-5a (Keating), SR-5d (Renovo), SR-5c (Hyner), SR-5f (between Renovo and Lock Haven) and SR-6 (Lock Haven).

While SR-5 east and SR-5 west are at the same location but on opposite sides of the river, the concentration of Mn is considerably different. The higher concentration of SR-5 east results from the input of water high in dissolved Mn from Moshannon Creek only a short distance upriver on the same side. The concentrations at SR-5a to SR-6 are high but generally decrease downstream to Lock Haven (SR-6). Equilibrium calculations show that the equilibrium concentration of Mn with respect to MnO_2 (Bricker, 1965) is not exceeded in this section of the river.

From the model for mixing of the West Branch of the Susquehanna River from Keating to Lock Haven (Chapter III, Mixing Models) it is possible to calculate the concentration of Mn at each point downriver from Keating, assuming that Mn is not lost from solution. Comparison of this calculated value to the measured value at Lock Haven (SR-6) and a few intermediate locations is shown in Table IV-3. In general, the calculated value is nearly the same as the measured value and indicates that, as expected from equilibrium calculations, no Mn precipitation occurs in this section of the river.

West Branch of the Susquehanna: Lock Haven to Northumberland

At Lock Haven, Bald Eagle Creek flows into the West Branch of the Susquehanna River. Bald Eagle Creek is relatively high in alkalinity since it drains a carbonate terrane. As a result, the acid in the West Branch is neutralized and bicarbonate becomes stable, resulting in a river pH > 6 at sites down river from the confluence with Bald Eagle Creek. Because the river P_{CO_2} is not greatly different from atmospheric P_{CO_2} and relatively little alkalinity is introduced below Bald Eagle Creek to Northumberland, the pH in this region of the river is generally in the range of 6.5 to 7.5 (Table IV-4 and Figure IV-1). Bald Eagle Creek flows through the valley that lies at the boundary between the Valley and Ridge Province and the bituminous coal region of the High Plateau Province. One of its tributaries, Beech Creek, drains an area of coal mining and adds enough manganese to Bald Eagle Creek to increase the dissolved Mn concentrations to between 100 and 700 ppb. The Mn in the West Branch at Lock Haven and that in Bald Eagle Creek constitute the major sources of Mn to the river in this region. The tributaries between the confluence with Bald Eagle Creek and Northumberland are low in dissolved Mn.

On the assumption of conservative mixing of waters, a model concentration at sample sites in this section of the river can be calculated as above. It is assumed that mixing of the West Branch and Bald Eagle Creek is completed before the water flows past Nisbet (SR-9), which is 21.6 miles downriver from the confluence with Bald Eagle Creek. Thereafter all drainage added to the West Branch is assumed to have the composition of Pine Creek or Buffalo Creek. At certain times, such as April 1973 and October 1973, the composition of Pine

Creek and Buffalo Creek are nearly the same in terms of Mn and sulfate concentrations, so it can be assumed that the system is composed of two components--the West Branch at Nisbet (SR-9) and the tributary water added which is representative of both Pine Creek and Buffalo Creek--and thus reduces to a two component model.

A further problem of these comparisons is that a sample was not taken at Nisbet (SR-9) in October 1973. The requisite material balance is made in order to test the validity of the assumption that the composition of the river at Nisbet is due to the conservative mixing of the proper ratios of the West Branch at Lock Haven, Bald Eagle Creek and Pine Creek. Since the mean daily discharge of each component is known from USGS stream gage data, it is possible to calculate the theoretical proportion of flow at Nisbet for each component. Then, as discussed earlier (see: Chapter III - Mixing Models), the theoretical concentration at Nisbet (SR-9) may be calculated from the expression:

$$C_{i,N} = a\,C_{i,LH} + b\,C_{i,BEC} + c\,C_{i,PC}$$

where

$C_{i,N}$ = concentration of ion i in the West Branch at Nisbet

$C_{i,LH}$ = concentration of ion i in the West Branch at Lock Haven

$C_{i,BEC}$ = concentration of ion i in Bald Eagle Creek

$C_{i,PC}$ = concentration of ion i in Pine Creek

a = proportion of the flow from the West Branch at Lock Haven

b = proportion of the total flow at Nisbet from Bald Eagle Creek

c = proportion of the total flow at Nisbet contributed from Pine Creek

The parameters a, b, and c and the values of mean daily discharge used to calculate them are shown in Table IV-5. Using these parameters and the above mass balance equation, model concentrations of Mg, SO_4, and Mn at Nisbet were calculated for April, June, and August 1973 and March and June 1974. The result compared to the measured concentration of the same parameter at Nisbet indicates a conservative mixture of the above three components, even for Mn (Table IV-6). It is possible to calculate a value for the Nisbet site in October of 1973 for which a direct measurement is lacking, since samples from the contributary streams were collected.

Below Nisbet water low in Mn is added to the river, and downriver sites (SR-10, SR-13 and SR-13a) consequently show lower concentrations of Mn than those at SR-9 (Table IV-1)--due to dilution, in part, and possibly due to removal by reaction. Using the model for the West Branch between Lock Haven and Northumberland discussed in Chapter III (Mixing Models), it is possible to calculate the concentration of Mn expected at any sample point if dilution with tributary waters was the only process operating. The calculated value and the actual measured concentration are plotted against the station distance downriver from the confluence with Bald Eagle Creek in Figures IV-2 through IV-7. It is apparent from these data that the measured concentrations at sites below Nisbet are considerably less than those expected from dilution alone during June, August and October 1973 and June 1974. However, for April 1973 and March 1974 the measured values are slightly less than the theoretical value. It can be concluded from this data that Mn is being removed from solution in the West Branch below Nisbet at most times, with the exception of less removal in late winter and early spring.

Susquehanna River below the confluence of the West Branch and the Susquehanna at Northumberland

In principle it should be possible to use a model to calculate the expected concentration of Mn at sites downriver from Northumberland since samples of both major branches have been taken. However, there are several tributaries to the Susquehanna below Sunbury which drain the anthracite coal regions of the Central Appalachians. The data of Biesecker and George (1966) show that most of these streams are affected to varying degrees by mine drainage and hence contain high concentrations of Mn. Furthermore, there is the real possibility that the North Branch of the Susquehanna at Northumberland is not homogenized as other mine drainage streams enter the river on the side opposite the sample site (SR-12) only a short distance upriver. Therefore, it is not possible to make a meaningful calculation of expected (dilution only) Mn concentrations at any point below the confluence. Several interesting observations concerning dissolved Mn can be made, nonetheless.

Concentrations of Mn at Montgomery Ferry (SR-14) are lower than a mixture of the West Branch (SR-13a) and the North Branch (SR-12). This is partially due to dilution, but precipitation of Mn between Northumberland and Montgomery Ferry is not precluded.

For the sample sites on the Susquehanna River at Marietta (SR-16) the data clearly show the effect of relatively local additions. As discussed earlier (Chapter II, Sample Site Selection), the river is not totally mixed at Marietta. On the side where the samples were taken, mine drainage-affected water from Swatara Creek (and perhaps other upstream, east bank sources; Anderson, 1966) causes higher $SO_4^=$ concentrations than for the middle or opposite bank samples. This effect is also shown by my data, as at numerous times the $SO_4^=$ and Mn concentrations at Marietta (SR-16) are greater than those in the Juniata River (SR-15) and the Susquehanna River at Montgomery Ferry (SR-14), which together must compose more than 90% of the discharge at Marietta. These high $SO_4^=$ and Mn concentrations (Table IV-1 and Table IV-7) are attributed mainly to the mine drainage from Swatara Creek. Swatara Creek is also the most downriver tributary to contribute coal mine drainage to the Susquehanna River.

There is no further addition of mine drainage-dominated streams between Marietta (SR-16) and Conowingo (SR-17), but there are three dammed reservoirs that could perturb the system. Sample sites SR-16 and SR-17 were used to see whether this is the case. It was shown that small-scale ponding on one of the tributaries had no measurable effect, but the larger scale of these main trunk hydroelectric dams may be expected to show some effect. Generally, the concentration of Mn at Conowingo (SR-17) is less than that at Marietta which is generally compatible with a conservative mixing model. In August 1973 and June 1974 (Table IV-1), however, the Mn concentration at Conowingo (SR-17) is considerably <u>greater</u> than the Mn concentration at Marietta--an effect clearly not explainable by mixing.

It is well known that stratified lakes are subject to a build-up of Mn concentrations in the anoxic bottom waters, with the Mn being contributed from either the bottom sediments or suspended sediment in the reducing water (Hutchinson, 1957). It is very likely that stratification and build-up of Mn in the bottom waters occur during the summer and that some of this water is drawn through the hydroelectric generating system to emerge below the dam at Conowingo (SR-17). This provides a reason for the recorded high Mn concentration at these times.

Particulate Manganese in the Type Regions

Silicate type region:Driftwood Branch

Sampling of the Driftwood Branch (RV-1) of Sinnemahoning Creek did not extend over the entire sample period, but it was included for a long enough period of time to ascertain the trend for Mn concentration in the stream-suspended sediment. The concentration of Mn in suspended particles (> 0.4μm pore diameter membrane filters) is plotted versus time in Figure IV-8. Mn concentrations of around 700 ppm occur during the winter and spring (periods of higher stream discharge) and concentrations of 1500 ppm in the early summer (period of lower stream discharge).

Carbonate Type Regions: Buffalo Creek

Sampling of Buffalo Creek extended over the entire sample period. The data for particulate Mn show (Figure IV-9) a clear trend much like the incomplete cycle shown for the silicate type region streams. The suspended sediment (> 0.4μm) has about 700 ppm Mn during the winter and spring (periods of higher flow) and Mn concentrations ranging up to 2000 ppm during the summer (periods of low flow).

Mine Drainage Streams

Clearfield Creek was sampled throughout the sample period. The data for particulate Mn show that the concentration is always around

500 ppm (Table IV-8), regardless of time. Similarly, the two samples from Moshannon Creek (SR-4a) average about 500 ppm.

Particulate Manganese: Main River Profile

The regions of the river of interest are an acid portion of the river from above Keating to Lock Haven and the river segment from below Lock Haven to the mouth of the Susquehanna River.

At times of high flow (April 1973, March 1974) the Mn concentration in the suspended sediment in the West Branch between Keating and Lock Haven is 500 to 600 ppm and shows no discernible trend (see Table IV-8). However, at times of low flow (summertime) such as June 1974 the particulate Mn at Lock Haven appears to be significantly greater than at Keating.

Below Lock Haven, at lower river flow (June, August, 1973; June, 1974), there is a pronounced downriver increase in the Mn concentration of the suspended sediment (Figures IV-11, 12, 16).

At times of higher flow or during the winter and spring there is only a slight increase, if any, in particulate Mn concentration downriver (Figures IV-10, 13, 14, 15).

Comparison of the Marietta site to that at Conowingo shows that in two instances the Mn concentration in the suspended sediment at Conowingo is less than that at Marietta (Table IV-10). These are also the same samples for which the dissolved Mn at Conowingo is greater than that at Marietta (see above). The implication is that reduction of Mn oxides in the suspended sediment and solution occurs at depth in the reservoir, diminishing the particulate Mn concentration and increasing the soluble concentration.

Manganese Removal from Solution

The dissolved and particulate data for the river indicate that Mn removal from solution occurs. A detailed study of the kinetics of the process can be made for one stretch of the river. Between Bald Eagle Creek and the confluence of the West Branch and North Branch at Northumberland, changes in dissolved Mn concentrations are due to dilution of low Mn water and by removal from solution, with the pH remaining between 6.5 and 7.5. This enables modelling. Rates of removal cannot be determined below the confluence of the West Branch and North Branch because of the uncertainty in regard to input of Mn from tributaries draining the anthracite coal region of the Central Appalachians (see: Mixing Model, Chapter III).

In order to use the data obtained from river sampling in a rate study, two important conversions must be made. First, the distance between sample stations must be converted to transit time for the water. Second, the observed concentrations of dissolved manganese must be corrected for dilution so that the changes due only to Mn removal from solution can be studied.

Conversion of Distance to Time

As part of its stream gaging program the USGS periodically measures gage height, width, depth, mean velocity and discharge at the established gaging sites. Using these data (obtained from the USGS--David Barton, written communication, 1975) plots of the logarithm discharge versus the logarithm of mean velocity have been made for the river gaging sites at Williamsport (Figure IV-18) and Lewisburg (Figure IV-19). Using these rating curves, the mean river velocity at the gaging stations can be determined for the time of sampling using the discharge data.

Since both the discharge and the velocity of a river system increase downstream (Leopold and Maddock, 1953), an average velocity between stations is used in the calculations.

Dilution Correction

The West Branch of the Susquehanna River at Nisbet (SR-9) is a homogeneous mixture of the West Branch of the Susquehanna River at Lock Haven (SR-6), Pine Creek (SR-8) and Bald Eagle Creek (SR-7), as shown earlier in this chapter (see: West Branch of the Susquehanna: Lock Haven to Northumberland and Table IV-6). Below Nisbet it is assumed that the composition of the water added to the river by tributaries can be represented by a combination of the water compositions in Pine Creek and Buffalo Creek at the time of sampling.

Between Nisbet (SR-9) and Northumberland (SR-13a) the West Branch of the Susquehanna River and its tributaries are such that the tributary waters mix with the West Branch only a short distance upriver from the sample sites. (This is suggested from the model calculations discussed in Chapter III and shown in Table III-19 and is supported by field observation of river plumes when a muddy tributary--Sinnemahoning Creek--mixed with clear West Branch of the Susquehanna River water.) Therefore, the progression of events for manganese in the West Branch would be continuous precipitation of the manganese present in solution from just downstream of Nisbet (SR-9) to Northumberland and rapid dilution just before each of the sample sites (SR-10 and SR-13a). As the dilution relative to the sample site is nearly instantaneous, the concentration may be corrected so that at the sample site it will represent the value prior to dilution. This corrected value is the value that reflects only precipitation of Mn and which would have been found if sampling at each site had been done just upstream of the diluting tributary. As was discussed earlier in Chapter III, the concentration of an element at any point in the river below Nisbet can be described by the equation

1) $C_T = a\,C_1 + b\,C_2 + c\,C_3$

where

C_T = the concentration of the elment at the sample site

C_1 = the concentration of the element in the West Branch before mixing with the tributaries

C_2 = the concentration of the element in Pine Creek

C_3 = the concentration of the element in Buffalo Creek

a = the proportion of the total flow at the sample site that is attributed to the West Branch at Nisbet

b = the proportion of the total flow at the sample site that is attributed to the Pine Creek composition

c = the proportion of the total flow at the sample site that is attributed to the Buffalo Creek composition

In the case of manganese the equation is

2) $C_{Mn_T} = a\,C_{Mn_1} + b\,C_{Mn_2} + c\,C_{Mn_3}$

The term C_{Mn_T} is the value measured at the sample site after Mn precipitation and then dilution. The tributary types with manganese concentrations C_{Mn_2} and C_{Mn_3} are assumed to be added immediately above the sample site, so none of this manganese is removed. The term C_{Mn_1} then represents the concentration of Mn in the West Branch before immediate dilution by tributary water but after precipitation of the initial Mn. It is therefore related to the concentration at Nisbet, being the manganese concentration after precipitation. Solving equation 2) for C_{Mn_1} yields:

$$C_{Mn_1} = \frac{C_{Mn_T} - b\,C_{Mn_2} - c\,C_{Mn_3}}{a}$$

The values of C_{Mn_1} calculated for the sites of interest are in Table IV-9 and are the manganese concentrations used in the following sections to determine reaction rate constants.

Reaction Rate Constants

To obtain an approximation of the reaction rate constants for manganese removal in the river a model must be used to obtain the necessary data. The basis of the model has been discussed in detail in preceding parts of this thesis. The following lists a summary of the assumptions used in the model (Model conditions):

1. Nisbet is the starting point
2. At Nisbet the river is a homogeneous mixture of the West Branch of the Susquehanna River, Bald Eagle Creek and Pine Creek (see this chapter: West Branch of the Susquehanna River: Lock Haven to Northumberland)
3. At sites down river of Nisbet the manganese concentration is that obtained in the preceding section (C_{Mn_1}) and reflects only removal from solution (This is equivalent to an experiment with constant solution volume)
4. Time between stations is obtained as discussed above in the section: Conversion of Distance to Time
5. P_{O_2} is atmospheric
6. pH = 6.5 to 7.5

For a first order reaction of the form

$$\frac{dc}{dt} = -kc \qquad \text{or} \qquad \frac{d(\ln c)}{dt} = -k$$

a plot of ln c versus time will yield a line whose slop is equivalent to the rate constant of the reaction. For Mn, the dissolved Mn ($<0.4\mu m$) is used for the term c.

The manganese concentrations as ln[Mn] versus time are plotted for sites SR-9, SR-10, SR-13 and SR-13a in Figures IV-20 through IV-22. Three groupings are seen from these figures: April 1973 and March 1974; June 1973, August 1974 and June 1974; and October 1973. The straight line fitted to April 1973 and March 1974 plots has the smallest slope of the three groups. The other two groups have essentially the same slopes.

The data can be compared more directly on a plot of ln $[\frac{Mn_t}{Mn_o}]$ versus t

where Mn_t = Mn at sample site (dilution-corrected)

Mn_o = initial Mn concentration (SR-9)

t = time down river from SR-9.

Two groups of data are indicated in a plot of this type (Figure IV-23). Morgan (1964) has shown that in the laboratory at high pH (> 9) Mn oxidation and removal from solution is an autocatalytic process. The experimental data for an autocatalytic process yield a convex upward curve when plotted on a coordinate system such as that used in Figure IV-23, whereas a first order reaction would yield a straight line. The March and April data cannot be fitted to such an autocatalytic curve. The June and August data (Figures IV-21 and IV-22) individually could fit a convex curve. It is possible in Figure IV-23 to fit one general autocatalytic line through these data. The October 1973 data appear to fit a straight line and could therefore be first order. It is also possible, given the relatively short time available in October, that these data represent the initial part of an autocatalytic curve which has not had enough time to show the increased rate, as is the case with the other data.

If the data are the result of an autocatalytic removal of manganese from solution, the difference in slope between the March and April data and the June and August data is not necessarily due to a difference in the constant of the reaction. As Morgan (1964) points out, the velocity of reactions on a ln $[\frac{Mn_t}{Mn_o}]$ versus t plot will be different for an autocatalytic reaction if the initial concentrations are different. In this case, the initial concentrations of April and March are about 1/2 of the initial concentrations for June, August and October (Table IV-10). The differences in the slopes for the data sets are like the differences between Morgan's (1964) experiments with variable initial manganese concentrations. Morgan shows that for autocatalytic reaction experiments with different initial manganese concentrations but the same rate constant, the data from all experiments should fit a straight line when plotted as ln $[\frac{Mn_o}{Mn_t} - 1]$ versus $Mn_o \cdot t$. Because the plot requires the terms ln $[\frac{Mn_o}{Mn_t} - 1]$ and because for all but the most downriver site in March and April $Mn_o \cong Mn_t$, the March and April data cannot be plotted for comparison. However, all the other data can be plotted and are shown in Figure IV-24 (see Table IV-10 for the term $[\frac{Mn_o}{Mn} - 1]$). As can be seen, the data do not all fall on a single straight line. If the two data points from each sampling time are connected by straight lines, two sets of parallel, but offset lines are seen. The June 1973 and June 1974 data form one set of two offset lines, and the August 1973 and October 1973 data form the other. These offsets indicate that the initial concentration of manganese alone may not account for different reaction rates in the river. It is likely, then, that the reaction rate seen between April and March and the other times may be due to more than differences in initial manganese concentrations if the removal of manganese in the river occurs according to an autocatalytic mechanism.

Due to the large errors that may be involved in calculating the manganese concentrations and the time of the sample downriver, it is possible that the data shown in Figure IV-23 could be fit to two straight lines: one line through the March and April data and another through the June 1973, August 1973, October 1973 and June 1974 data. It is not easy given the present data to choose whether a first order or autocatalytic reaction is occurring in the West Branch of the Susquehanna River.

It is possible to compare rate constants for Mn removal from solution obtained from laboratory experiments to rate constants determined from the Susquehanna River data. Morgan (1964) defines a rate constant, K_{OBS}, for the autocatalytic reaction that may be obtained by plotting the data as $\ln [\frac{Mn_o}{Mn_t} - 1]$ versus time. The observed rate constant, K_{OBS}, is calculated from the expression

$$K_{OBS} = \frac{\ln 10}{[Mn]_{tot.}} \cdot \frac{\Delta \log_{10} [\frac{Mn_o}{Mn_t} - 1]}{\Delta t}$$

From data in the pH range 8.8 to .96 Morgan obtains a linear relationship between $\ln K_{OBS}$ and pH (Figure 5-18, Morgan 1964). Extrapolating this relationship to pH 7 gives a predicted rate constant K_{OBS} of $\sim 10^{-2}$ ℓ mole^{-1} min^{-1} that must be considered a maximum value since the experimental Po_2 = 1 atmosphere and the field $Po_2 \approx 0.2$ atmosphere. The data for the West Branch of the Susquehanna River is plotted in Figure IV-25 on the coordinates indicated above. Using an average slope of 10^1/30 hr and $[Mn]_{tot} = 2 \times 10^{-5}$ mole/ℓ, a K_{OBS} of $10^{1.7}$ ℓ $mole^{-1}$ min^{-1} is calculated according to the above expression. This rate constant is $\sim 10^4$ times greater than that predicted from laboratory experiments, indicating that removal of Mn occurs much more rapidly in the West Branch of the Susquehanna River than in vitro experiments at comparable initial Mn concentrations.

The preceding discussion effectively eliminates the use of in vitro kinetic models for streams. Therefore, the role of other parameters such as inorganic and organic particles may dominate the kinetics. This being the case, the reactions will appear to be first order in Mn. In some early work on the oxidation of dissolved Mn, Hem (1963) concluded that in a solution containing only Mn and its oxidation product (a solid Mn oxyhydroxide) the reaction was autocatalytic once some Mn oxide had formed. However, he later showed (Hem, 1963b and 1964) that inorganic surfaces (a feldspathic sand in his experiments) acted catalytically to greatly increase removal rates over his sand-free systems at the same Mn concentrations. Furthermore, the reactions appear to be first order in Mn. Extrapolation of Hem's (1964) sand-catalyzed rate constant to a pH of ~ 7 using his plot of rate constant versus pH indicates a first order rate constant of $\sim 5 \times 10^{-4}$ min^{-1}. An average line drawn through the data for June, August, October 1973 and June 1974 plotted as $\ln \frac{Mn_t}{Mn_o}$ versus time (Figure IV-23) has a slope which indicates a rate constant of $\sim 6 \times 10^{-4}$ min^{-1}. The agreement in rate constants between the value extrapolated from Hem's data and the data for the Susquehanna River is much better than the comparison with autocatalytic constants.

The relationship of this observation with theory can be seen by the following. Morgan (1967) has suggested that Mn oxidation follows the rate expression

$$\frac{d[Mn^{+2}]}{dt} = k_1\ [Mn^{+2}] + k_2\ [MnO_2]\ [Mn^{+2}]$$

where $[Mn^{+2}]$ = the dissolved manganous ion

$[MnO_2]$ = the oxidized solid Mn in the system (moles/vol.)

k_1 = a first order rate constant

k_2 = a rate constant due to autocatalysis

t = time

The term $[MnO_2]$ is the expression of the effect of the solid Mn oxyhydroxides acting as a catalyst in the oxidation and removal of Mn from solution. Considering Hem's (1963b, 1964) results, it is clear that substances other than solid MnO_2 can act as catalysts. The autocatalytic rate expression contains a first order term $k_1[Mn^{+2}]$ and the autocatalytic term $k_2[MnO_2][Mn^{+2}]$. It should be noted that for a system with an initial catalyst present in a constant amount ($[MnO_2]$ = constant) the rate expression becomes

$$\frac{d[Mn^{+2}]}{dt} = k_3\ [Mn^{+2}]$$

where $k_3 = k_1 + k_2\ [MnO_2]$

which is a first order expression. In experiments containing an initial amount of catalyst it is clear that the above term should be substituted into the autocatalytic rate expression in place of the k_1 constant, which is applicable to systems with no initial catalyst like in Morgan's experiments. The result is to make the term k_3 a function of all the catalysts other than that produced by Mn precipitation in the expression

$$\frac{d[Mn^{+2}]}{dt} = k_3 [Mn^{+2}] + k_2 [MnO_2] [Mn^{+2}]$$

Rearranging,

$$\frac{d[Mn^{+2}]}{dt} = (k_3 + k_2 [MnO_2]) [Mn^{+2}].$$

The rate constant determined for a system will be very sensitive to the value of k_3. As k_3 increases, the overall autocatalytic rate constant would increase at the same Mn concentration. At some point when $k_3 >> k_2 [MnO_2]$ the expression should become first order since the autocatalytic contribution becomes trivial.

In natural systems the rate constant, k_3, will be dependent on catalytic surfaces that are generally abundant. In a system like the region of the Susquehanna used in the rate study, several solids are available to catalyze the reaction. Mn coatings and Fe coatings on mineral grains, clay minderal surfaces and organic solids may act to catalyze the reaction and to produce the relatively large rate constant observed in the natural system as compared to laboratory studies.

It is further possible that bacterial action may aid the oxidation step and act as a catalyst. Stumm and Morgan (1970) point out that for the oxidation of Fe^{+2} to Fe^{+3} in acid medium, bacteria such as Ferrobacillus Oxidans participate in Fe^{+2} oxidation and produce reaction rates two or three orders of magnitude greater than in bacteria-free Fe solutions. According to Hem (1963) there are bacteria which act to catalyze the oxidation of the manganous ion. Zajic

(1969) reports several bacteria active in Mn^{+2} oxidation and suggests the prospect that there are more. Bacterial catalysis of manganese oxidation would be analogous to increasing the effective catalytic surface area discussed above.

An additional means of activating the removal of Mn from solution would be the direct removal by organisms. Oborn (1964) has shown that Bacterium precipitatium Kalin is capable of depositing solid Mn compounds from water. While he thinks this may play a major role in mediating elemental concentrations in water, it probably is not the dominant mechanism operating in the Susquehanna River. However, it must be kept open as a possible mechanism, especially in systems with low natural inputs of dissolved Mn. Again, it would be equivalent to a catalyst.

Discussion

From the consideration of the removal mechanism proposed by Morgan (1964) and modified to include other catalysts in the system, the results of this study are fairly consistent with those of Morgan (1964) and Hem (1963a, 1963b, 1964). In the natural system with an abundance of catalytic material the rate constant calculated as being autocatalytic is much greater (x $10^{3.7}$) than in the laboratory system having no initial catalyst present. It can be seen that Hem's apparent first order removal with a sand catalyst is consistent with the mechanism discussed above. The agreement of the first order rate constant determined from the Susquehanna River data with Hem's extrapolated rate constant may be fortuitous, although it is expected that both should be much greater than initial catalyst-free systems. It is tempting to argue that since the rate constants agree so well, the removal mechanism in the Susquehanna is first order and that in similar systems a first order removal of Mn from solution should be expected. But, the final answer must be based on better data. It can be stated, however, that for much of the Susquehanna where enough Mn is not precipitated to change the Mn content of the sediment in a downstream direction, the removal of Mn will be a first order mechanism with a rate constant similar to that determined for the West Branch data.

The dissolved and particulate Mn data show that in the sections of the main river where the pH is above 6 the mine injected Mn is always precipitating. The rate constant for this process is much greater than most laboratory experiments predict and is greater at higher water temperatures ($20^{o}C$) than at lower water temperatures ($5^{o}C$). Based on the data shown in Figure IV-24, the first order rate constants are 5.57×10^{-4} min^{-1} ($20^{o}C$) and 6.42×10^{-5} min^{-1} ($5^{o}C$). Using the Arrhenius equation for the temperature dependence of the rate constant ($K_i = A \exp - E_a/RT$), an activation energy (E_a) of 22.6 Kcal/mole is calculated for the manganese removal process.

The information that has been presented on the rate constants can be used to explain the Mn variations observed in the river with time at a station.

The manganese concentration for the main river is related to discharge, but in different ways for different parts of the river. Highest Mn concentrations at low flow in the summer and early fall and lowest Mn concentrations during high flow occur below Shawville to Lock Haven, where it is documented by the large acid mine drainage contribution. Manganese concentrations along this acid course do not exceed the solubility product constant of any of the possible compounds. Since the Mn concentration is below saturation, its time variation at a site is explained by the component mixing model for type waters presented in Chapter III. Dissolved Mn is high in mine drainage and low in silicate type waters. Therefore, at high flow when the silicate drainage becomes a larger proportion of the flow, the Mn concentration is reduced. The station at Nisbet (SR-9) displays this same variation as it has been shown that it is a simple linear combination of the West Branch at Lock Haven, of Bald Eagle Creek and of Pine Creek. The precipitation of Mn has not commenced at the Nisbet site. Since there is little, if any, Mn removal in the acid portions of the stream, the downstream change in Mn is due only to dilution.

The most interesting variation of dissolved Mn is observed at all the stations on the Susquehanna from the mouths of the two main branches to the mouth of the river near Conowingo.

In the rest of the river (SR-13, SR-13a, SR-12, SR-14 and SR-16) the variation of dissolved manganese with time and discharge is opposite of that observed above Lock Haven. At high flow the dissolved manganese is high, while at low flow the manganese concentration is low. This positive correlation of manganese concentration with increasing discharge results in a correlation with season of the year since discharge is seasonal. The variation of manganese concentration at Conowingo (SR-17) follows the above trend, with the exceptions noted earlier that the release of Mn in the reservoir during the summer causes high Mn concentrations.

Several phonomena combine to produce the observed trend. First, during the winter and spring the water temperatures are lower and the rate constant for Mn removal is smaller than during the summer when the water is warmer (other factors may contribute to the larger summer-fall rate constant). Second, the winter-spring period is a time of higher discharge than in the summer, and therefore the water is flowing faster (up to four times faster). The combination of the differences in the rate constants and river flow velocity means that, at the same initial concentration, much more Mn would remain in solution at the mouth of the river during the winter-spring period than during the summer and fall. It has been observed that the source of the high Mn concentrations in the river is mine drainage and that the trend for the Mn source is toward high dissolved Mn at low flow and the converse at high flow, which would counteract the above trend. However, the effect of river flow velocity and difference in the rate constants between winter and summer is such that the difference in Mn concentration at the source (a factor of ∿ 2) is overcome. Therefore, the increase of dissolved Mn with increasing discharge is a result of flow velocity and Mn precipitation kinetics. This trend in Mn concentration observed at the river mouth has been attributed to seasonal vegetative decay in the Susquehanna basin by Schubel (1972). The best explanation, as discussed above, is related to the mine drainage inputs, river flow velocity and Mn precipitation kinetics. The Susquehanna at its mouth is overwhelmed by mine drainage Mn; hence natural mine drainage-free trends cannot be ascertained.

All of the sites on the main river show a similar trend for particulate manganese versus time at a single site. As an example, the data for the concentration of Mn in the suspended sediment versus time is shown for the Montgomery Ferry site (SR-14) in Figure IV-17. The trend is for lower particulate Mn concentration at high flow (winter-spring) and higher concentrations during times of low flow. The particulate Mn concentration reaches a maximum in August, the time of lowest flow and highest water temperature during the study period. It should be emphasized that the Conowingo site appears to be the same, even though some modification of particulate and dissolved Mn must occur in the reservoirs. Even those sections of the river which are acid (see: SR-6 in Table IV-8) show this trend considerably subdued. In fact, this trend is the same at all the sample sites, including the type region streams unaffected by mine drainages (Figures IV-8 and IV-9). The variation in particulate Mn in the type regions must be considered a natural phenomenon in the sense that the Mn is not from a man-induced source such as mine drainage.

The trends in particulate Mn below Nisbet can be understood in light of the manganese removal kinetics and sediment load. At a site there will be higher Mn concentrations in the suspended sediment in the summer because there is more Mn added per gram of suspended sediment (lower suspended sediment load) than in the winter. Similarly, in the profile samples at low flow in the summer the sediment is progressively enriched in Mn downstream for the Mn precipitates on the particles and the particles are moved downstream with the flowing river. However, at high flow and in the winter and spring the slower removal of Mn while in the river and the higher suspended sediment concentrations combine, so there is very little increase in particulate Mn downriver.

The trends for particulate Mn versus time for the type region streams, the Driftwood Branch (RV-1) and Buffalo Creek (SR-11), are similar. Since it has been demonstrated that this trend is due to precipitation of Mn at the main river sites, it is implied that the trend in the type region streams is also due to precipitation of Mn. The source of this Mn must be natural as the type streams are free from mine drainage pollution. Because the water in the streams is supplied from the generally reducing ground water, it is reasonable that it should contain some dissolved Mn. Mass balance calculations for the type streams show that the amount of dissolved Mn needed to produce the particulate Mn trend is only a couple of micrograms/ℓ; hence the precipitation will not be discernible by observing changes in dissolved Mn as it would be obscured by the error in the dissolved Mn determination. In fact, dissolved Mn is relatively constant and low in the type streams. It must be concluded that there is a continuous natural supply of Mn to streams in the ground water and that this Mn is oxidized and precipitates on stream particles, resulting in a supply of fresh Mn-oxyhydroxides at all times. There is less precipitation per unit volume of water during periods of colder water and higher flow.

The dissolved and particulate Mn data for the Marietta (SR-16) and Conowingo (SR-17) sites indicate that reducing conditions are established either in the sediment or water column in the reservoir, thereby releasing dissolved manganese. Such a process is a means of delivering soluble Mn to coastal waters. Klinkhammer (1975) has reported an excess of dissolved Mn in the salinity gradient in the Hudson River estuary. As there is abundant organic material present, it is likely that at some site reduction occurs releasing Mn from the sediment into the water column.

In the main river the bottom consists of sediment that is transported by the river at high flow. Jar experiments with sediment cores of this bottom sediment indicate a flux of manganese and iron out of the sediment. If this occurs in the river, escape of Mn from the interstitial water by physical and biological means would supply dissolved Mn to the river, where it would precipitate forming fresh Mn-oxyhydroxides. This is a process which might occur naturally in many large rivers and would provide a mechanism for continuously supplying fresh Mn-oxyhydroxides which are more efficient at scavenging trace metals than the aged Mn-oxides (Kharkar et. al., 1968) derived from erosion of soils and rocks.

Dissolved Iron in the Susquehanna River Basin

Type Regions

The data for dissolved Fe in the Driftwood Branch (RV-1) is shown in Table IV-11. There is no real trend for dissolved Fe versus time of sampling. Furthermore, concentrations observed are near the lower limit of the analytical technique used. In that light, the observed differences in concentrations between samples (e.g., November and January) may not be significant.

Similarly, the data shown in Table IV-11 for the stream draining a carbonate terrane, Buffalo Creek (SR-11), show no significant trends with time of sampling and discharge.

The data in Table IV-11 for the mine drainage-affected stream, Clearfield Creek (SR-4), show a clearly defined trend with sampling time and discharge. The concentrations are lowest in the summer (during low flow conditions) and highest during the winter and spring (during high flow, lower water temperature).

Main River: Profile

Even though some mine drainage is delivered to this section of the river, as shown by the Mn and sulfate concentrations, the uppermost reaches of the West Branch of the Susquehanna have relatively low dissolved Fe concentrations.

The section of the West Branch from Shawville (SR-3) to Lock Haven has relatively high dissolved Fe (Table IV-11). Downriver from Keating (SR-5a), the point of the last major mine drainage addition, the dissolved Fe concentrations are lower. A notable exception to this is the West Branch sample at Lock Haven (SR-6) for June 1973. The value of 844 ppb probably represents sample contamination since it is difficult to imagine a model that would allow such a concentration at this point, given the upriver and downriver concentrations at the same time. Using the same model as for Mn, it is possible to compare expected concentrations by dilution to measured concentrations.

With two exceptions, the values observed in the West Branch below the confluence with Bald Eagle Creek are relatively low (Table IV-11) and not significantly different from those observed in the type streams. The values are considerably lower than the values expected by dilution alone. During June 1973 and March 1974 there is a significant trend to the dissolved Fe data for the sites below the confluence with Bald Eagle Creek (Figures IV-26 and IV-27). Using the same model as for Mn the values expected from dilution alone can be computed (Figures IV-26 and IV-27 and Table IV-12).

For all the remaining sites in the Susquehanna River (and the Juniata River) the dissolved Fe is at a low, constant concentration and shows no significant trend, which is in sharp contrast to that trend observed for Mn.

Particulate Iron in the Susquehanna River Basin

The concentration of iron in the suspended sediment has been analyzed only for samples collected in April and June 1973. This data (Table IV-13) is representative of what is to be expected in the river. Generally the concentration of iron in the suspended sediment is between 4 and 8 percent for all river and tributary stations, with the exception of the acid streams (SR-4) and acid portions of the West Branch where the Fe content of the sediment is 16 to 18 percent. Also, there is the qualitative observation of yellow coatings on rocks and man-made structures in the West Branch and its acid tributaries.

Considering both the dissolved and particulate Fe data, it is evident that a major source of dissolved Fe is the mine drainage. Furthermore, it is apparent that even in the acid tributaries and acid section of the West Branch, Fe is precipitating. In a similar area in western Pennsylvania, Gang and Langmuir (1974) have shown that Fe is supersaturated and is precipitating in acid mine drainage streams. In addition, removal of Fe occurs rapidly below the confluence with Bald Eagle Creek. Occasionally the Fe is not completely precipitated until the mouth of the West Branch, although generally it is at background levels at Nisbet (SR-9).

Iron Removal Rate Constant

For the times when Fe is present above background levels in the sites in the West Branch, June 1973 and March 1974, a rate constant for removal can be determined just as was done for Mn. As was discussed in the Mn section, a dilution correction can be made to the observed concentration at a site. Furthermore, station distance below the confluence with Bald Eagle Creek can be converted to time as has been shown. Since the removal of Fe at constant pH and P_{O_2} is supposed to be first order, the data are plotted as ln[Fe] versus time (Figure IV-28). The data for June 1973 fall on a reasonably straight line while the data for March 1974 are somewhat less satisfactory. The slope of the June 1973 line gives a rate constant of $\sim 5 \times 10^{-4}$ min^{-1}. Stumm and Morgan (1970), reporting results of Stumm and Lee (1961), show that in laboratory experiments the removal of Fe follows the rate expression

$$-\frac{d\ \ln[\mathrm{Fe}]}{dt} = \frac{k_H[O_{2(aq)}]}{[H^+]^2}$$

where $k_H = 3 \times 10^{-12}$ min^{-1} mole^{1} liter^{-1}

The rate constant determined above is equivalent to the entire right side of the above equation. Therefore, by substituting values for pH and $[O_{2(aq)}]$ in the river, 6 and 0.25×10^{-3} mole/ℓ (8 mg/ℓ), respectively, a comparable constant can be calculated. The calculated rate constant is 7.5×10^{-4} min^{-1}, which is very nearly the same as the one determined in the river. Hence, it appears that, unlike Mn, the kinetics of removal for Fe in systems like the Susquehanna are compatible with experimentally determined laboratory rates.

Discussion

During most periods of the year there is fresh Fe-oxyhydroxide in the acid section of the river and in the West Branch below the confluence with Bald Eagle Creek. At Nisbet and below, however, the amount of Fe added to the sediment is small compared to the amount already in the sediment, so no pronounced enrichment is seen for Fe as it was for Mn.

Unfortunately, very little has been learned from this study regarding the supply of dissolved Fe to the river system from natural sources. As has been shown for the Mn supplied to streams, precipitation cannot be detected by measuring the dissolved concentration in streams. Therefore, a supply of freshly precipitated Fe can only be surmised from the observation that the stream waters are ground water and contain some dissolved Fe and that precipitation of some of the Fe is expected, as has been shown to be the case for Mn.

TABLE IV-1. DISSOLVED Mn IN FIELD FILTERED, ACIDIFIED WATER SAMPLES, µg/l

Sample	1973						1974			
	April	June	August	Oct-Nov	Nov	Dec	Jan	March	April	June
SR-1	300	370	409	366						
SR-2	400	550	688							629
SR-2a			688							
SR-3	1000	1190	1355							1252
SR-4	1100	1210	2427	2738			1200	1122		2453
SR-4a								3280		3721
SR-5 east	2000	2840	3802							
SR-5 west		2420	2775							
SR-5a		2430	2598					1436		2356
SR-5b		350	518					200		296
SR-5c		1220	1258							
SR-5d								1185		
SR-5e								2		
SR-5f								1050		
SR-5g										11
SR-6	600	1440	1535	1754				849	486	1265
SR-7 north	350	370	409	734				717		
SR-7 south			92							284
SR-8	50	17	45	88			43	37	16	72
SR-9	450	1170	1179					730		925
SR-10	200	660	428	366				476		409
SR-10a								28		
SR-11	10	24	18	47			10	17	10	24
SR-12	100	253	38	302			105	168	110	45
SR-13	250	388	229							
SR-13a			31	309			261	370	253	143
SR-14	187	173	133	100			218	207	143	90
SR-14a										58
SR-15	22	24	20	68			15	25		27

TABLE IV-1. (Continued)

	1973						1974			
Sample	April	June	August	Oct-Nov	Nov	Dec	Jan	March	April	June
SR-16	112	100	35	171			269	282		49
SR-17	127	43	118	11			201	272		144
RV-1					13	10	10	9	16	9
RV-2						0.7		0		
RV-3						0		0		0
RV-4						0	0	0		0
RV-5	0					0	1	0		0
RV-6							15			
RV-7									2	0
RV-8									0	

TABLE IV-2. MAJOR ELEMENT CONCENTRATIONS IN CLEARFIELD CREEK, SR-4 (mg/ℓ)

	April 1973	June 1973	August 1973	Oct-Nov 1973	January 1974	March 1974	June 1974
Na^+	3.21	3.54	4.75	5.55	3.21	3.83	4.60
K^+	1.16	1.44	1.57	0.58	1.03	1.07	1.07
Ca^{++}	20.6	31.2	36.4	44.7	21.1	20.6	38.8
Mg^{++}	8.60	13.30	15.50	18.35	9.35	8.75	16.62
$SO_4^=$	98	151	177	222	106	100	195
HCO_3^-					0	0	
Cl^-	4.59	3.87	4.79	4.55	3.91	4.16	6.76
Mn	1100	1210	2427	2738	1200	1122	2453
pH	4.6	4.1	3.9	4.0	4.8	4.9	4.0

TABLE IV-3. MODEL CALCULATED AND MEASURED Mn AT SR-5c AND SR-6, WEST BRANCH SUSQUEHANNA RIVER

	June 1973		August 1973		March 1974	June 1974
	SR-5c	SR-6	SR-5c	SR-6	SR-6	SR-6
Model Mn μg/ℓ	1151	1290	1142	1258	844	1209
Measured Mn μg/ℓ	1220	1440	1401	1535	849	1265

TABLE IV-4. pH AT STATIONS ON THE WEST BRANCH OF THE SUSQUEHANNA RIVER BELOW LOCK HAVEN TO NORTHUMBERLAND

	1973				1974	
Site	April	June	Aug	Oct	March	June
SR-9	7.1	6.5	6.7	-	6.4	7.0
SR-10	7.2	6.7	6.8	6.5	6.5	7.4
SR-13a	-	-	7.6	6.6	7.4	7.6
SR-13	6.9	7.1	8.2	-	-	-

TABLE IV-5. MIXING VOLUME PARAMETERS AND DISCHARGE USED TO CALCULATE THEM

	$Q_{L.H.}$	$Q_{B.E.Cr}$	$Q_{P.C.}$	ΣQ	a	b	c
April 1973	11236	1730	6060	19026	0.59	0.09	0.32
June 1973	3392	600	510	4502	0.75	0.13	0.11
August 1973	1855	233	600	2688	0.69	0.09	0.22
March 1974	8162	530	1700	10392	0.78	0.05	0.16
June 1974	3286	570	800	4656	0.70	0.12	0.17

$Q_{L.H.}$ = discharge of WBSR at Lock Haven

$Q_{B.E.Cr}$ = discharge of Bald Eagle Creek

$Q_{P.C.}$ = discharge of Pine Creek

$$\Sigma Q = Q_{L.H.} + Q_{B.E.Cr.} + Q_{P.C.}$$

$$a = \frac{Q_{L.H.}}{\Sigma Q}$$

$$b = \frac{Q_{B.E.Cr}}{\Sigma Q}$$

$$c = \frac{Q_{P.C.}}{\Sigma Q}$$

TABLE IV-6. COMPARISON OF CALCULATED CONCENTRATIONS VS MEASURED CONCENTRATIONS AT SR-9

	Mg (μg/ℓ)		SO_4 (μg/ℓ)		Mn (μg/ℓ)	
	calculated	measured	calculated	measured	calculated	measured
April 1973	3.64	4.90	33	45	401	450
June 1973	7.20	8.12	73	79	1129	1170
August 1973	7.10	7.94	75	84	1078	1179
March 1973	5.36	6.15	61	64	704	730
June 1974	7.21	8.33	75	80	932	925

TABLE IV-7. DISSOLVED $SO_4^=$ CONCENTRATION FOR THE SUSQUEHANNA RIVER ABOVE THE JUNIATA RIVER (SR-14), THE JUNIATA RIVER (SR-15) AND THE SUSQUEHANNA RIVER BELOW THE JUNIATA RIVER AT MARIETTA (SR-16)

	1973				1974		
	April	June	Aug	Oct	Jan	March	June
SR-14	29	44	61	25	33	32	44
SR-15	22	27	34	27	23	24	25
SR-16	31	86	108	109	43	51	82

TABLE IV-8. PARTICULATE Mn FOR THE SUSQUEHANNA RIVER (μg/gm SEDIMENT, DRY)

	1973					1974			
	April	June	August	Oct-Nov	Nov-Dec	January	March	April	June
SR-1	975		1812	2100					
SR-2	656		1172				390		1339
SR-2a			2711						
SR-3	549		617						388
SR-4	597		1212	982		547	459		773
SR-4a							403		378
SR-5 R.R.stat.			408						
SR-5 east	591		1445						
SR-5a			821				485		675
SR-5b			624				483		982
SR-5c			627						
SR-5e							508		
SR-5f							517		
SR-5g									1832
SR-6	671	526	915	1234			579	1018	1156
SR-7 north		2836	1670						3923
SR-8		4952	3966	1926		1390	294	1716	2887
SR-9	897	515	1520				430		2512
SR-10	1170	1437	3724	3154			498		5065
SR-10a							305		
SR-11	800	862	1781	945		714	368	874	1003
SR-12		2395	10570	2500		1019	556	893	5966
SR-13	1009	1056	2674						
SR-13a			6707	2957		697	787	1762	3502
SR-14	1993	4290	8290	1825		1879	999	2336	5088
SR-14a									2539
SR-15	1034	698	5912	1764		1411	1183		1733
SR-16		5162	8805	2358		1767			8558
SR-17	1093	7416	8407	6865		1370	1558		5360

TABLE IV-8. (Continued)

	1973					1974			
	April	June	August	Oct-Nov	Nov-Dec	January	March	April	June
RV-1				610	1320	752	759	1142	1716
RV-2							662		
RV-3									
RV-4									
RV-5									
RV-6									
RV-7									
RV-8							499		
JML Pond			1189						

TABLE IV-9. DISSOLVED MANGANESE CONCENTRATIONS USED IN THE MANGANESE RATE STUDY

		Measured Mn conc. (μg/ℓ)	Dilution corrected Mn (C_{Mn_1}) (μg/ℓ)
Three component model			
June 1973	SR-9	1170	1170
	SR-10	660	979
	SR-13	388	508
August 1973	SR-9	1179	1179
	SR-10	428	686
	SR-13a	31	50
	SR-13	229	231
March 1974	SR-9	730	730
	SR-10	476	735
	SR-13a	370	587
June 1974	SR-9	925	925
	SR-10	409	622
	SR-13a	143	248
Two component model			
April 1973	SR-9	450	450
	SR-10	200	445
	SR-13	250	384
October 1973	SR-9	966*	966
	SR-10	366	592
	SR-13a	309	485

*Calculated

TABLE IV-10. PARAMETERS USED FOR FIRST ORDER AND AUTOCATALYTIC MANGANESE PLOTS

	Mn_o SR-9 conc. (μg/ℓ)	Mn_t dilution corrected conc. (μg/ℓ)	$\frac{Mn_t}{Mn_o}$	$\frac{Mn_o}{Mn_t} - 1$	t, hr	$Mn_o \cdot t$ (10^{-5} mole ℓ^{-1} hr)
June 1973						
SR-10	1170	979	0.837	0.195	17.67	35.34
SR-13	1170	508	0.434	1.303	34.90	69.80
August 1973						
SR-10	1179	686	0.582	0.719	23.98	50.36
SR-13a	1179	50	0.042	22.580	45.45	95.44
SR-13	1179	231	0.196	4.104	45.50	99.43
June 1974						
SR-10	925	622	0.672	0.487	18.66	31.72
SR-13a	925	248	0.268	2.730	35.36	60.12
April 1973						
SR-10	450	445	0.989	0.011	14.28	
SR-13	450	384	0.853	0.172	24.33	
October 1973						
SR-10	966	592	0.613	0.632	10.63	18.07
SR-13a	966	485	0.502	0.992	20.15	34.25
March 1974						
SR-10	730	735	1.007	-0.007	13.28	
SR-13a	730	587	0.804	0.244	25.17	

TABLE IV-11. DISSOLVED (< 0.4 μm) Fe DETERMINED BY FERROZINE METHOD (μg/ℓ)

	1973						1974		
	April	June	August	October	November	December	January	March	April
SR-1		4							
SR-2		3	7					292	
SR-2a			5						
SR-3	755	90	138						
SR-4	451	382	195	762			822	1011	
SR-4a								∿8000	
SR-5 east	1656	1297	1567						
SR-5 west		562							
SR-5a		339	314					522	
SR-5b			46					394	
SR-5c		223	122						
SR-5d								473	
SR-5e								8	
SR-5f								409	
SR-6	27	844	174	85				214	117
SR-7 north	6	3	31	16				48	
center									
SR-7 south			9						
SR-8	23	15	50	24			8	9	6
SR-9	8	62	4					140	
SR-10	8	19	18	18				82	
SR-10a								31	
SR-11	19	27	11	65			13	14	14
SR-12	38	4	8	16			37	29	13S
SR-13	10	11	15						
SR-13a			11	18			8	13	6
SR-14		3	19	46			5	11	6
SR-15		14	14	36			6	5	

TABLE IV-11. (Continued)

	1973						1974		
	April	June	August	October	November	December	January	March	April
SR-16		15	25	9			10	13	
SR-17		7	5				18	12	
RV-1					37	26	12	21	12
RV-2						3			
RV-3						47		43	
RV-4						20	12	7	
RV-5						17	20	19	
RV-6									
RV-7								83	
RV-8								5	

TABLE IV-12. MEASURED AND MODEL DISSOLVED FE CONCENTRATIONS IN THE WEST BRANCH OF THE SUSQUEHANNA RIVER BETWEEN NISBET AND NORTHUMBERLAND

	Measured Fe µg/ℓ	Measured Fe corrected for dilution (µg/ℓ)
March 74		
SR-9	140	140
SR-10	82	131
SR-13a	13	21
June 73		
SR-9	62	62
SR-10	19	35
SR-13	11	14

TABLE IV-13. IRON CONCENTRATIONS IN SUSPENDED SEDIMENT, APRIL AND JUNE 1973

Site	mg sed/ 1	April 1973 suspended sed. wt% Fe (dry)	June 1973 suspended sed. wt% Fe (dry)
SR-1	25	6.56	8.41
SR-2	29	8.20	7.61
SR-3	19	8.77	6.53
SR-4	6	15.96	18.53
SR-5 (east)	12	18.51	16.10
SR-5 (west)	n.s.	n.s.	n.a.
SR-5a	n.s.	n.s.	15.55
SR-5b	n.s.	n.s.	3.90
SR-5c	n.s.	n.s.	10.31
SR-6	13	10.72	8.06
SR-7	22	4.56	3.09
SR-8	27	6.59	3.60
SR-9	30	5.80	5.56
SR-10	16	6.75	4.83
SR-11	10	4.33	4.56
SR-13	12	6.05	6.74
SR-12	180	6.01	5.21
SR-14	23	5.53	4.48
SR-15	37	4.77	4.03
SR-16	118	6.43	3.72
SR-17	49	7.12	5.06

n.s no sample taken
n.a. not analysed

FIGURES

FIGURES (Continued)

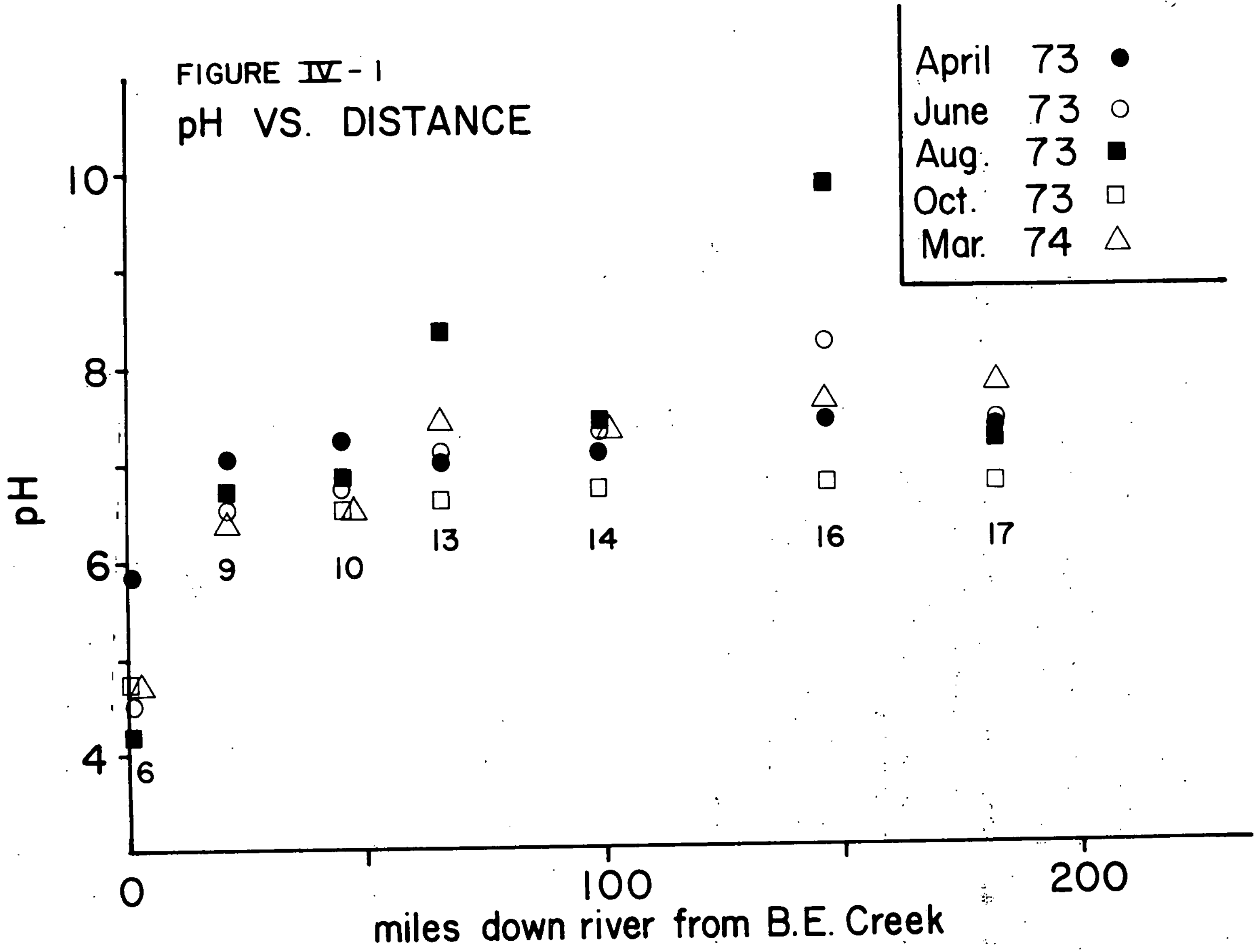


FIGURE IV - I

pH VS. DISTANCE

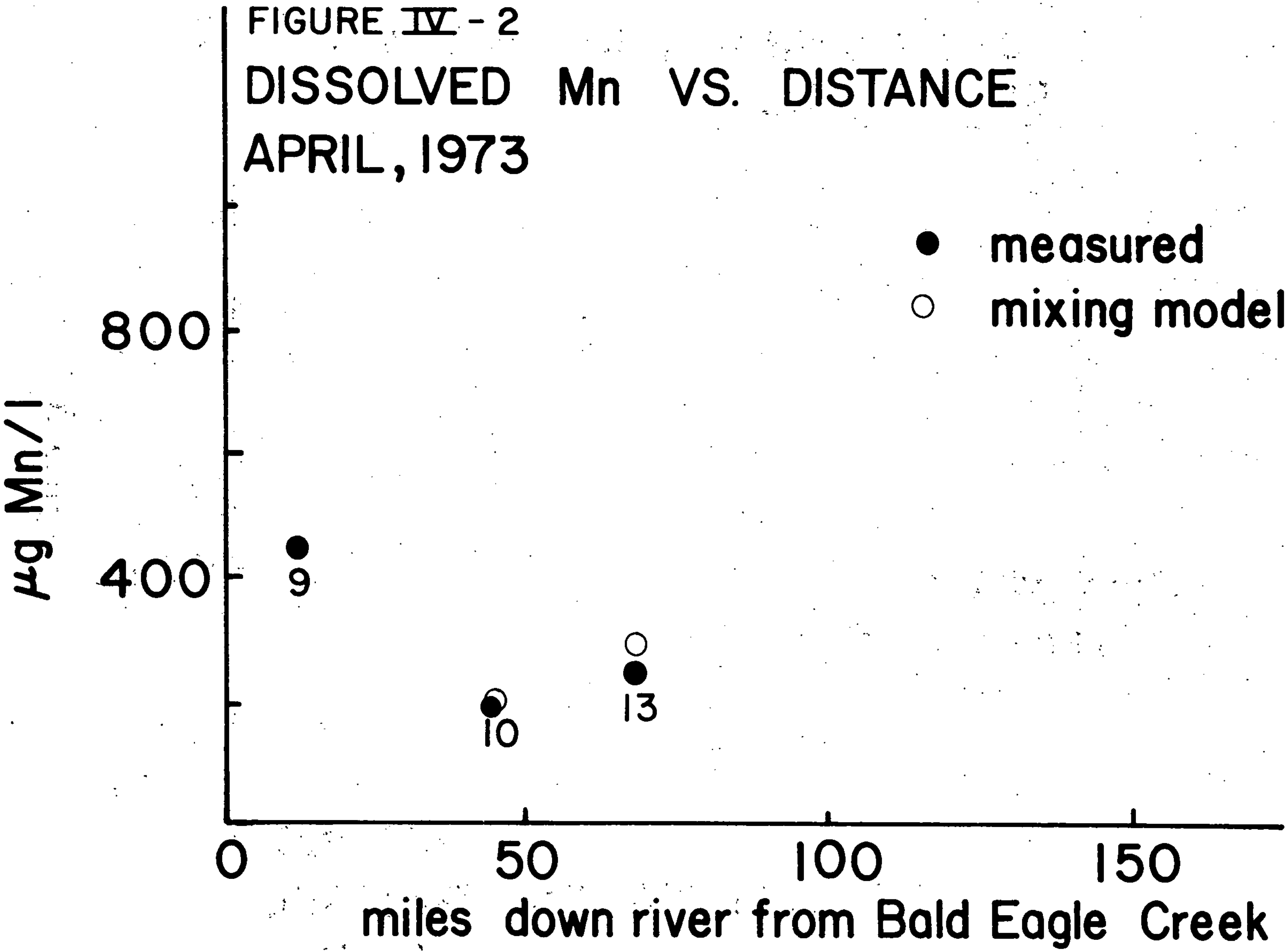
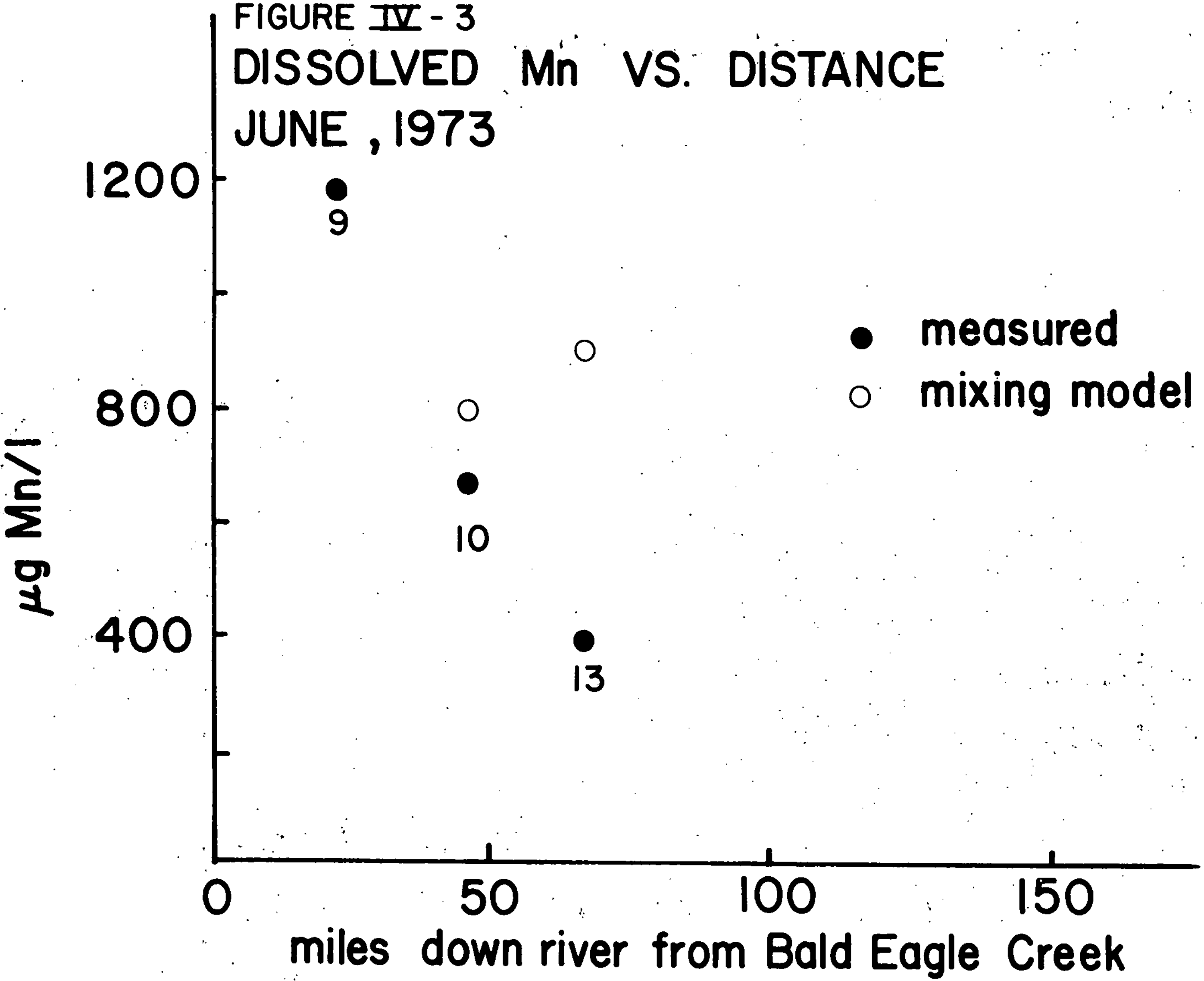


FIGURE IV - 2
DISSOLVED Mn VS. DISTANCE
APRIL, 1973

FIGURE IV - 3
DISSOLVED Mn VS. DISTANCE
JUNE, 1973



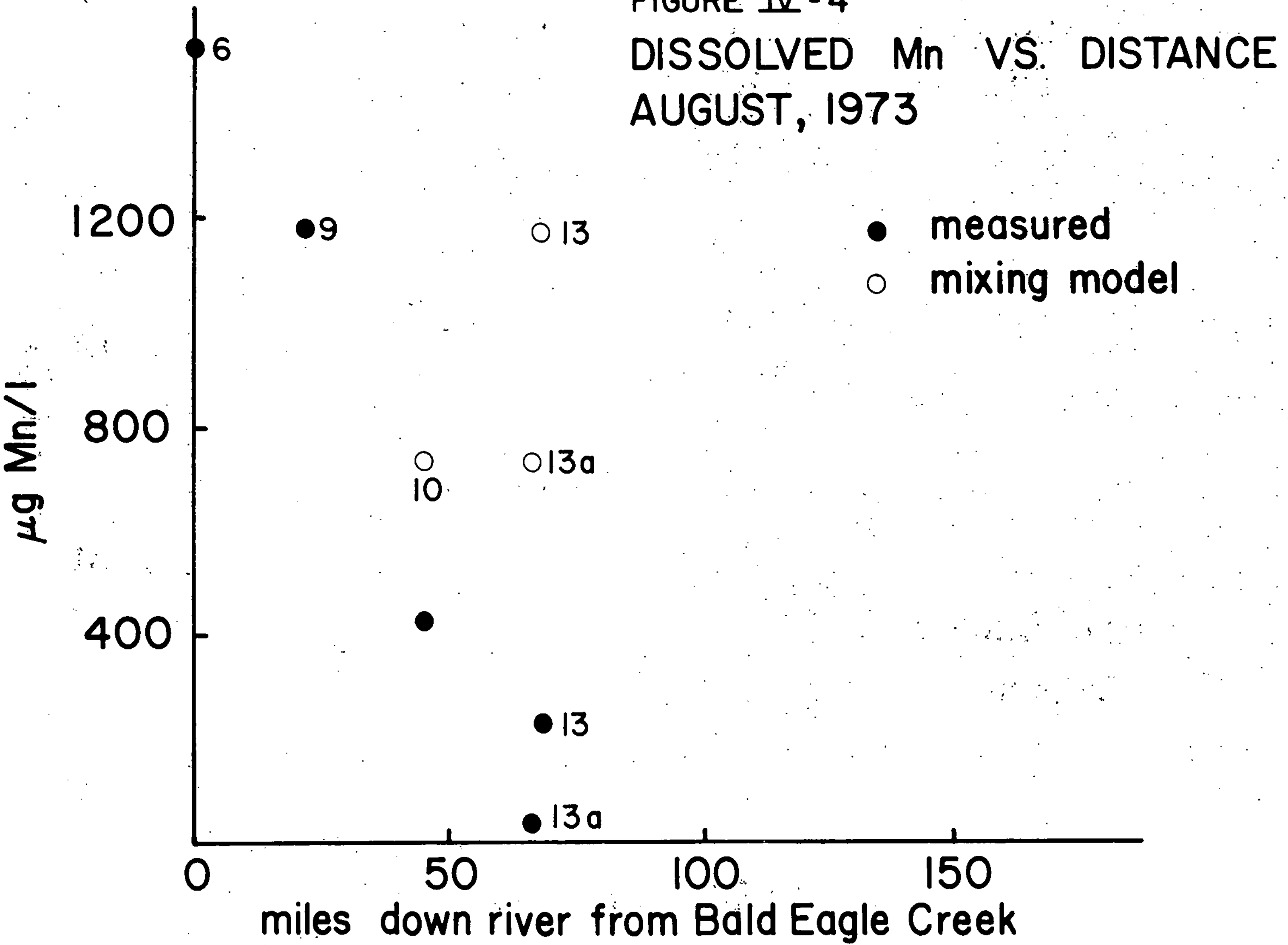
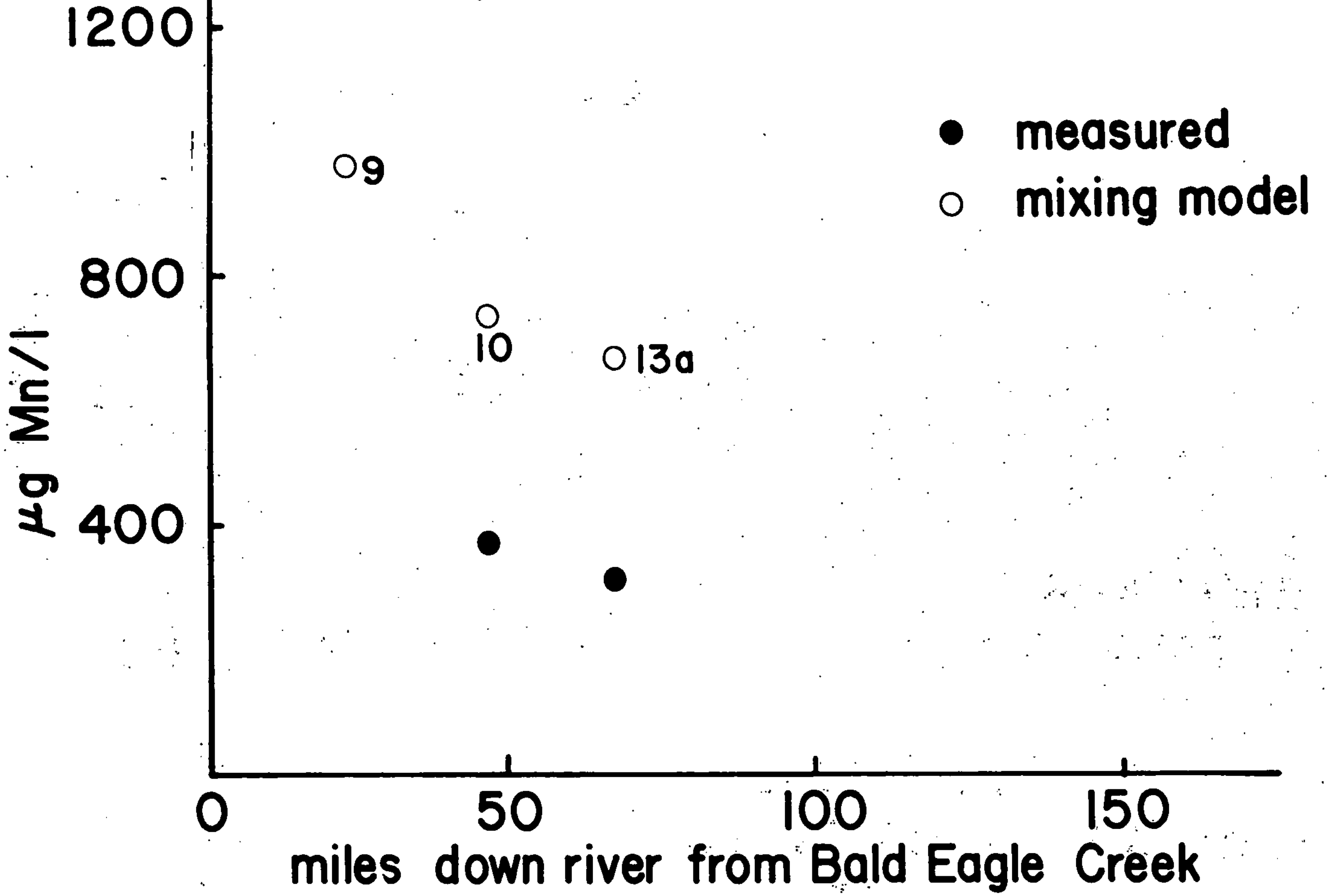


FIGURE IV - 4
DISSOLVED Mn VS. DISTANCE
AUGUST, 1973

FIGURE IV - 5

DISSOLVED Mn VS. DISTANCE
OCT.-NOV., 1973



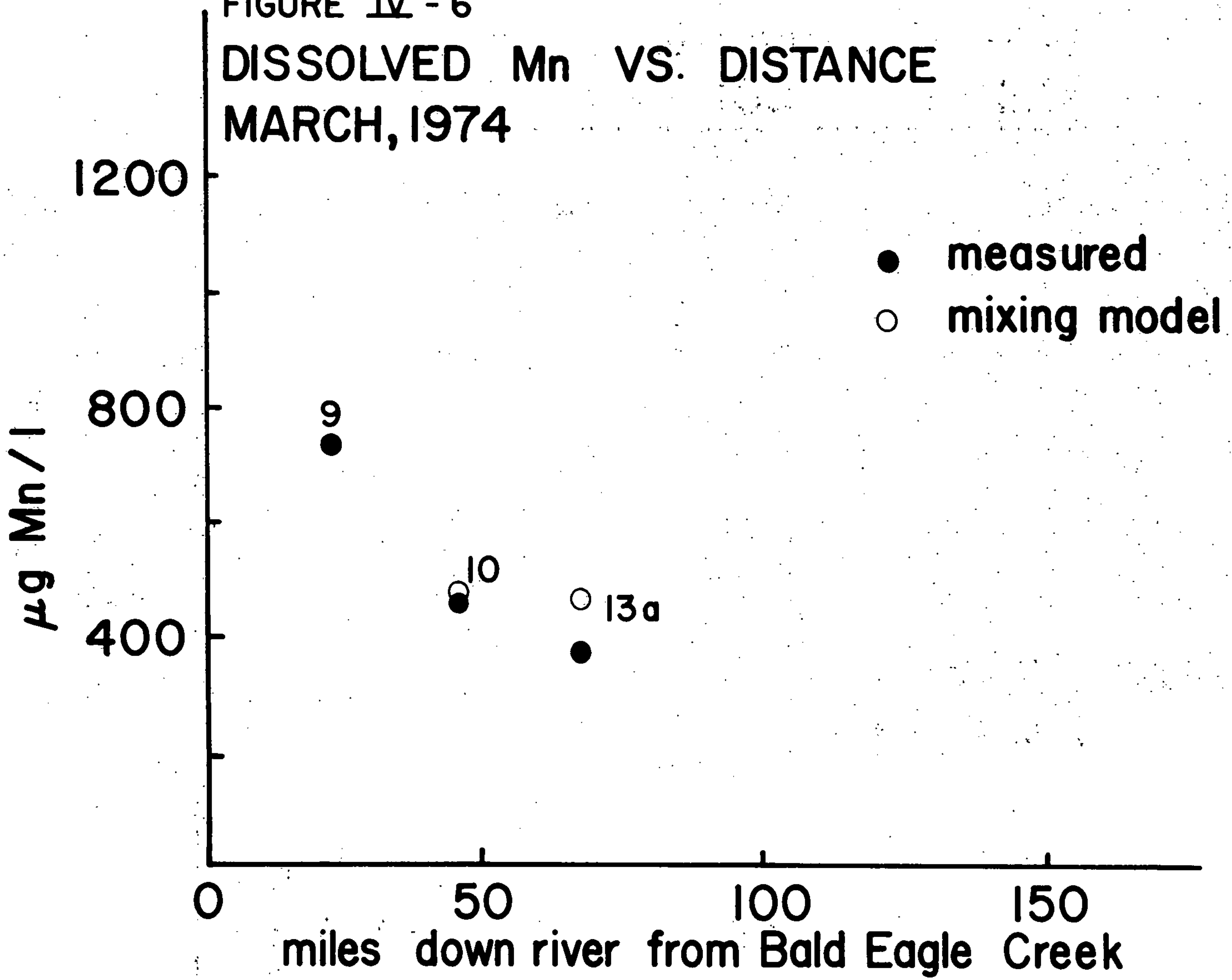
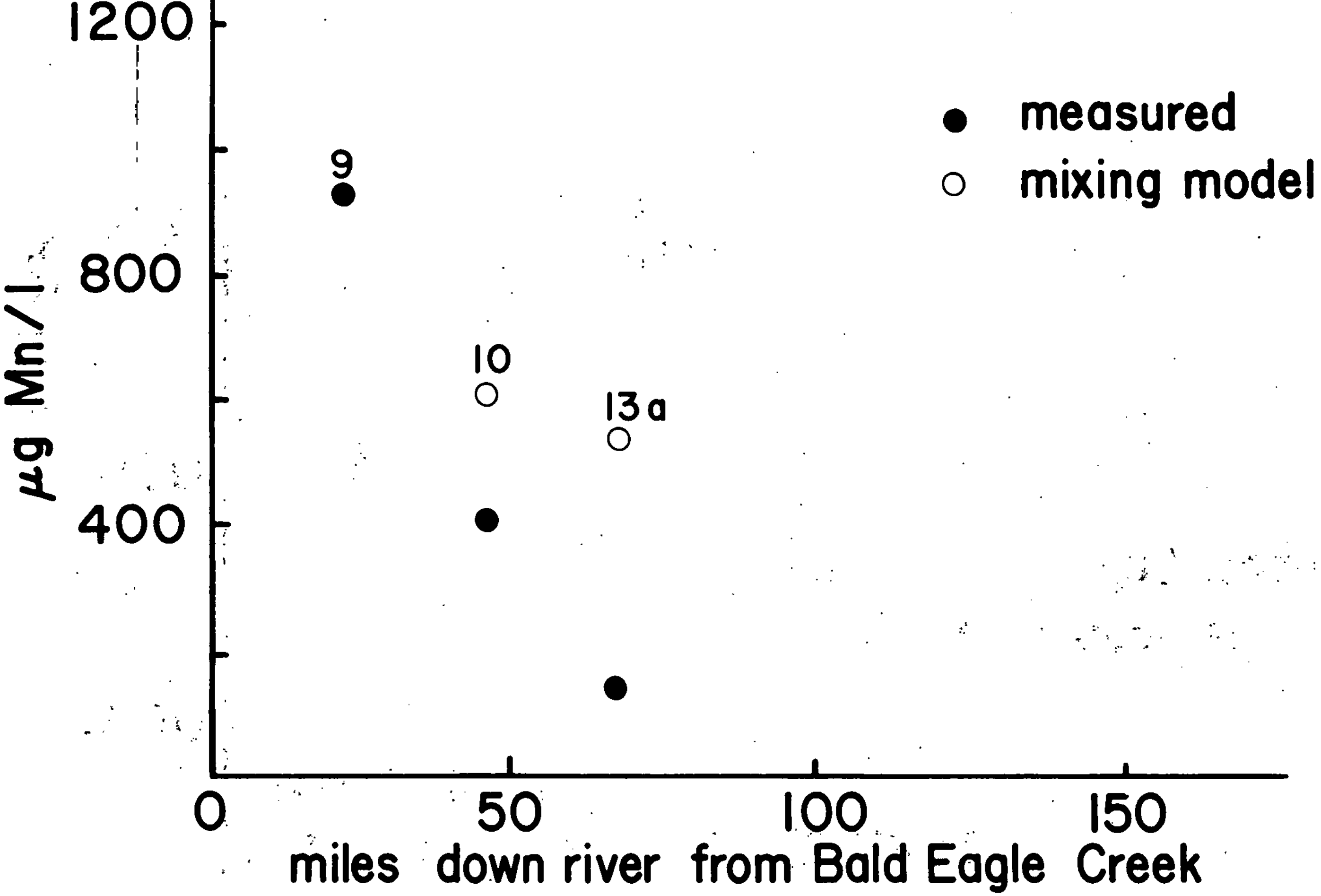


FIGURE IV - 6
DISSOLVED Mn VS. DISTANCE
MARCH, 1974

FIGURE IV-7

DISSOLVED Mn VS. DISTANCE

JUNE, 1974



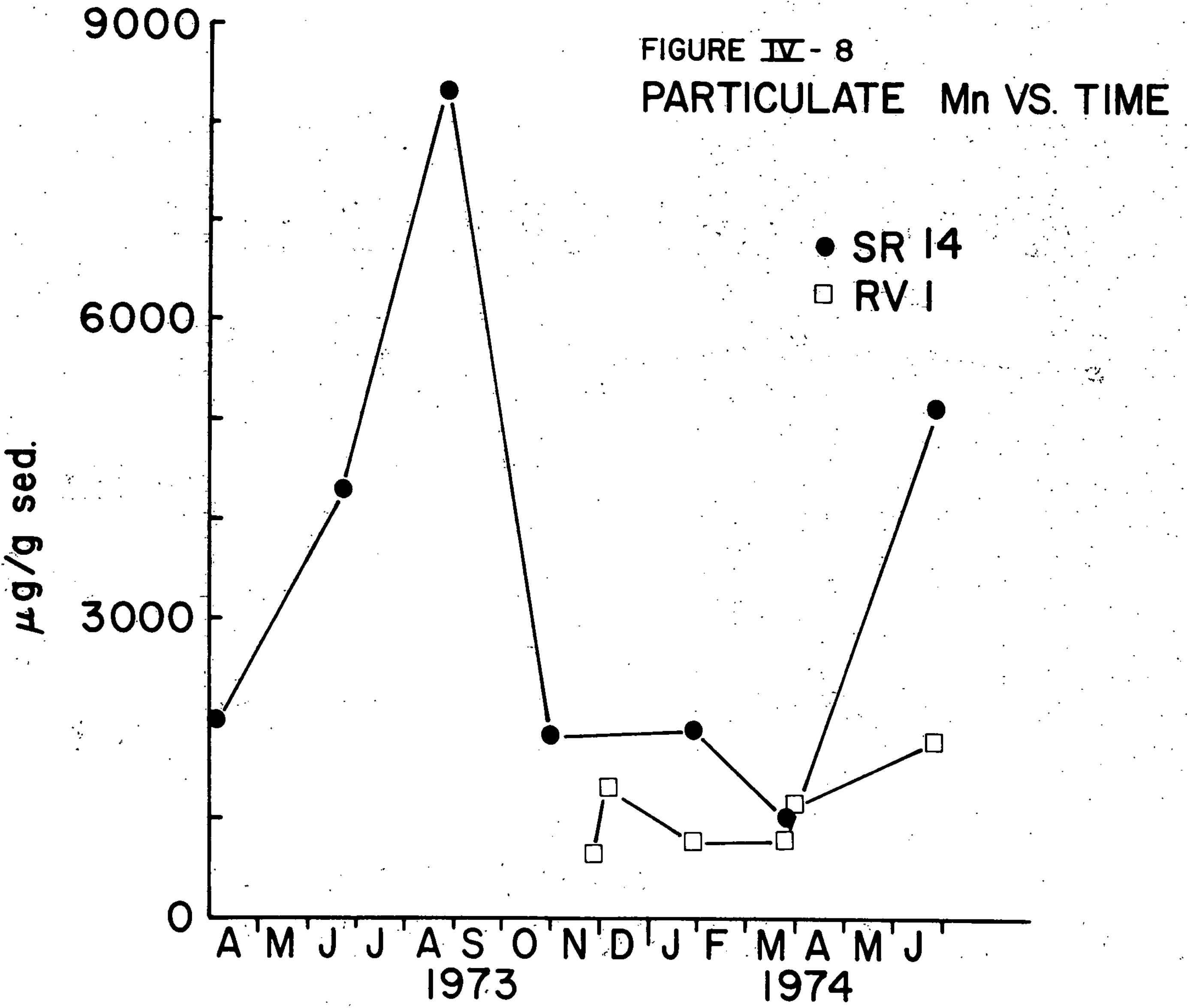


FIGURE IV - 8
PARTICULATE Mn VS. TIME

FIGURE IV - 9

PARTICULATE Mn VS. TIME AT SITE SR-11
BUFFALO CREEK

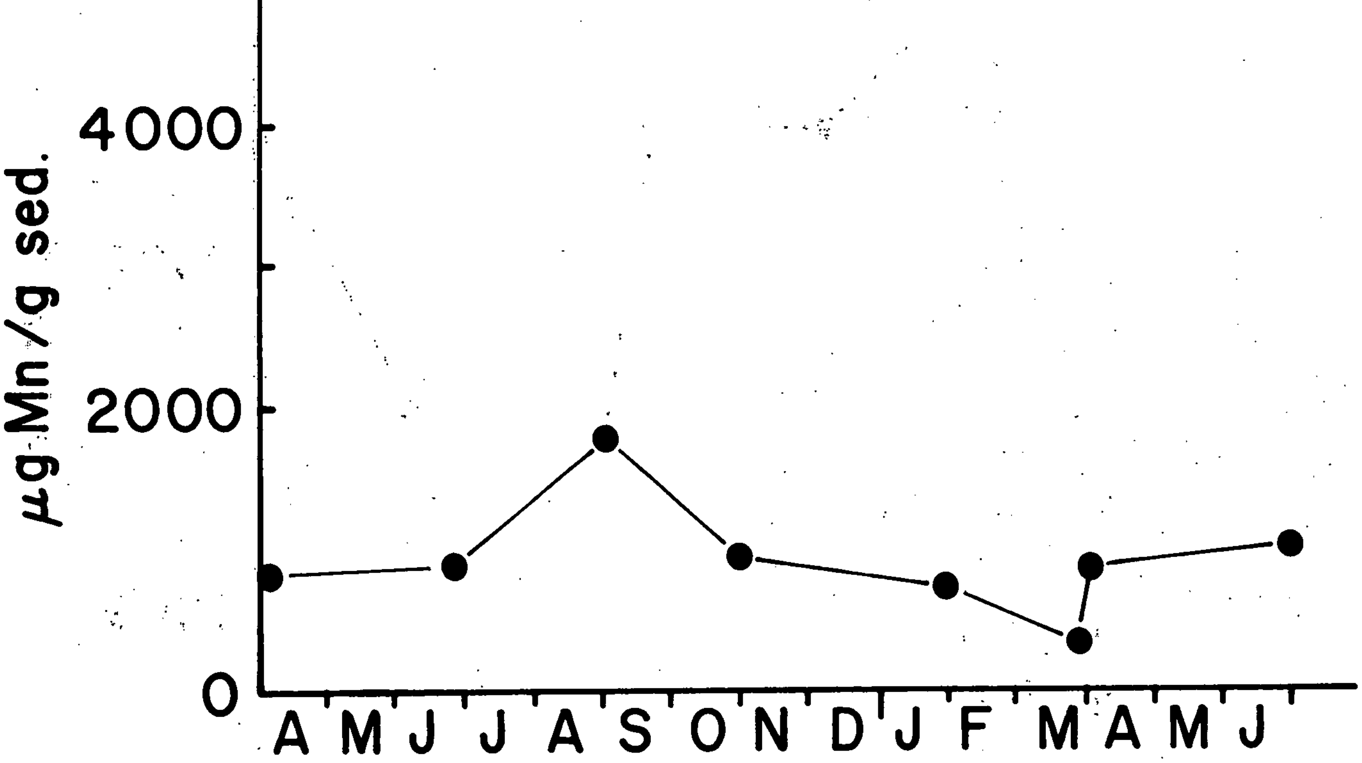
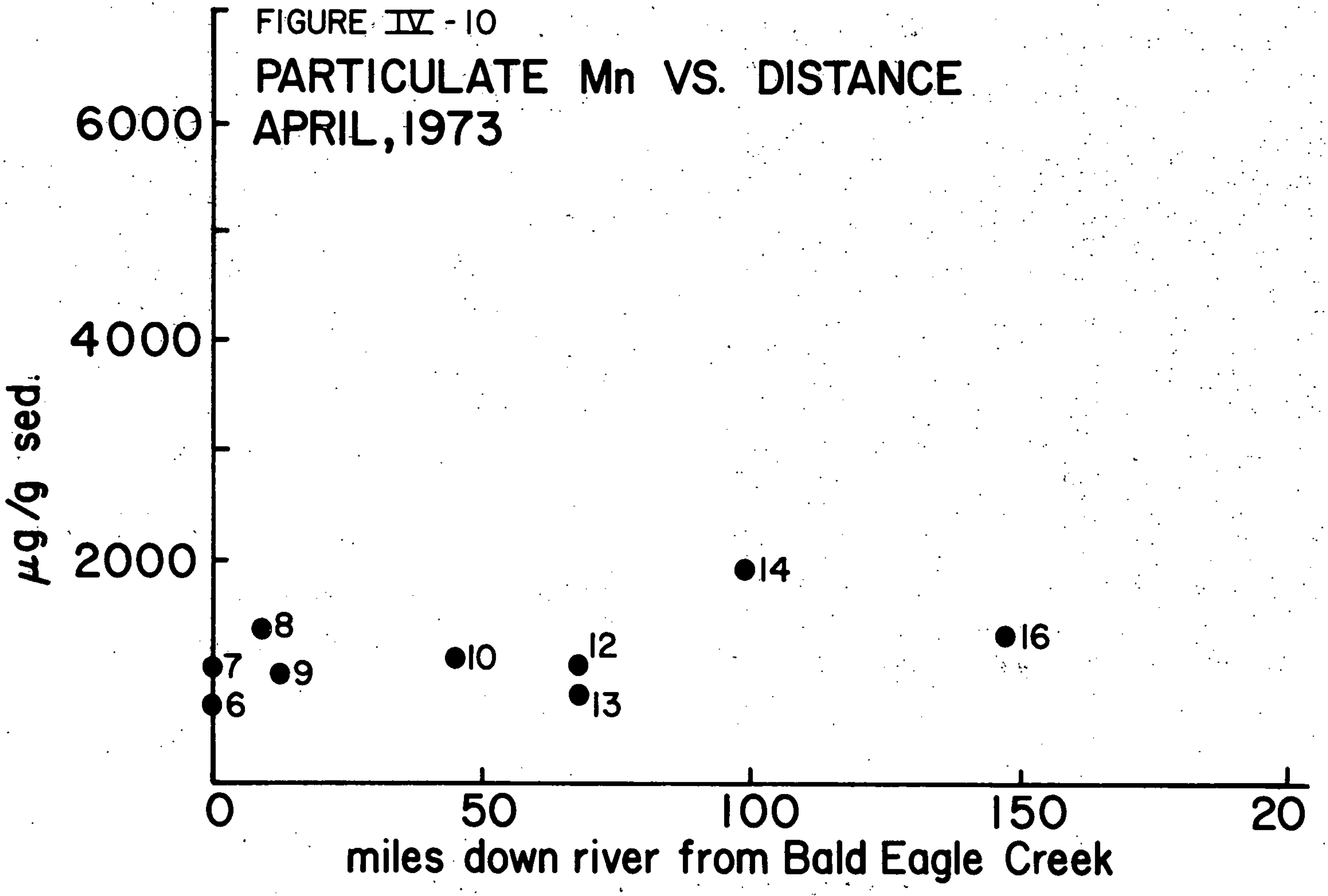


FIGURE IV - 10

PARTICULATE Mn VS. DISTANCE
APRIL, 1973



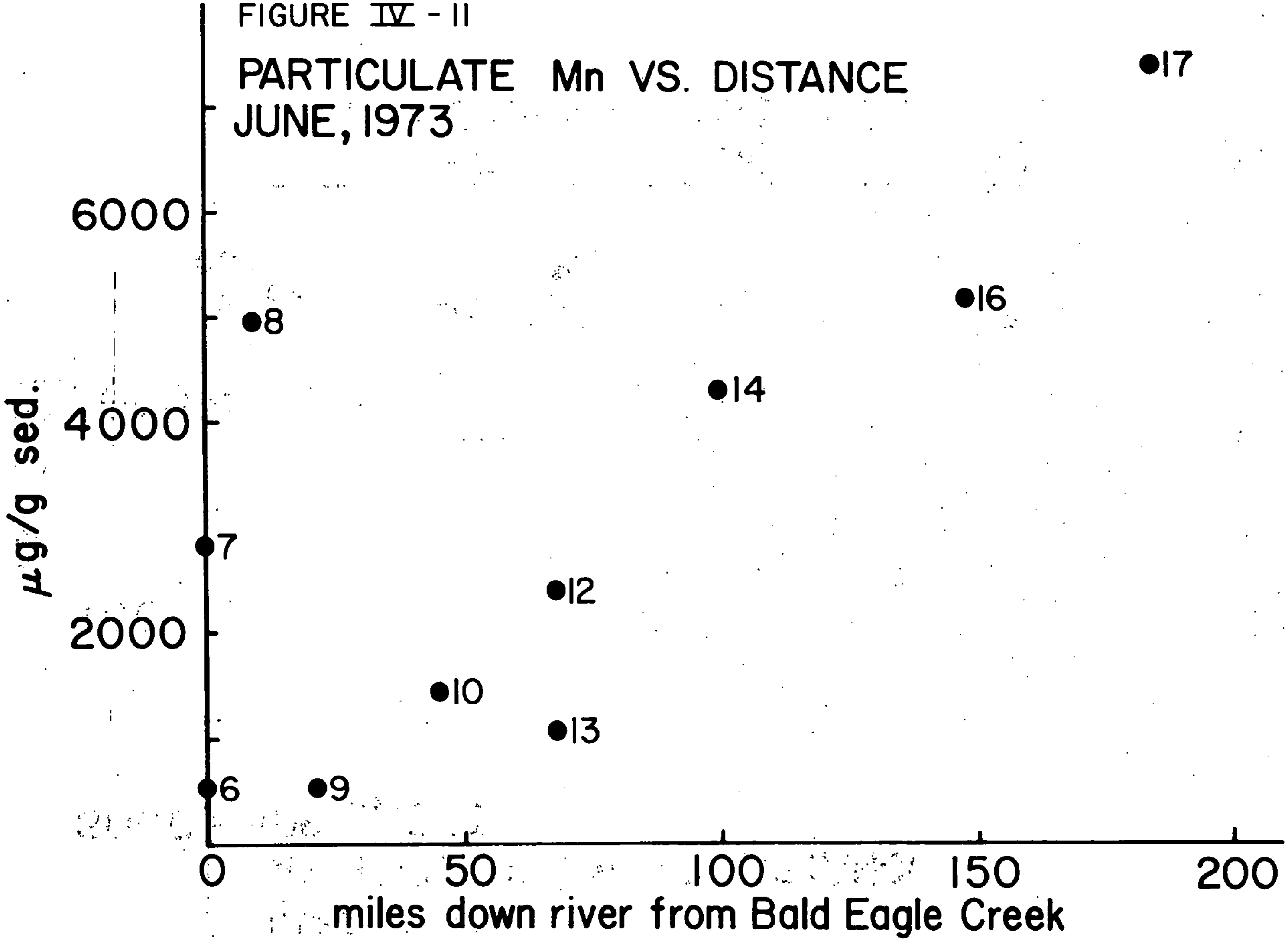


FIGURE IV - 11

PARTICULATE Mn VS. DISTANCE
JUNE, 1973

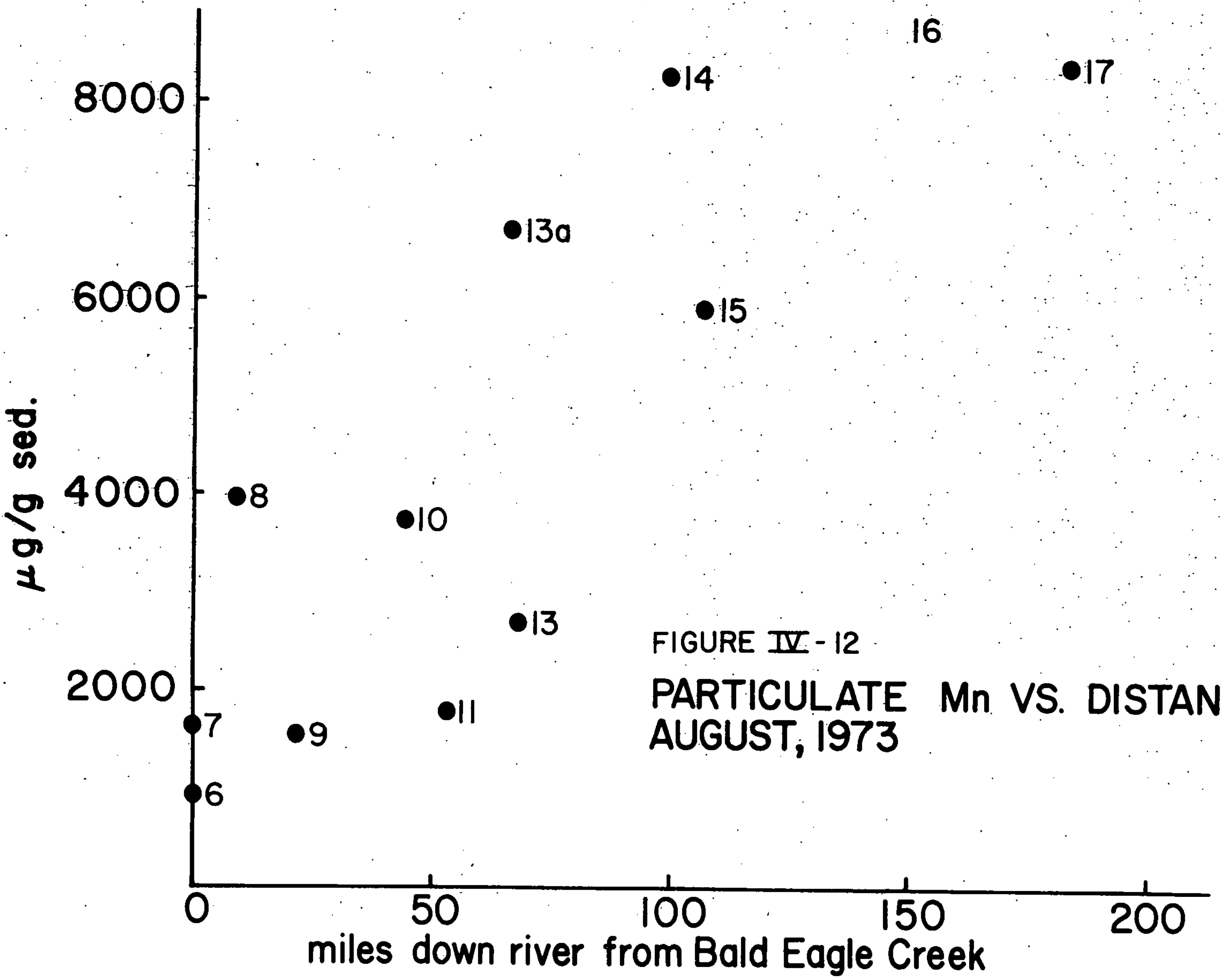


FIGURE IV - 12

PARTICULATE Mn VS. DISTANCE
AUGUST, 1973

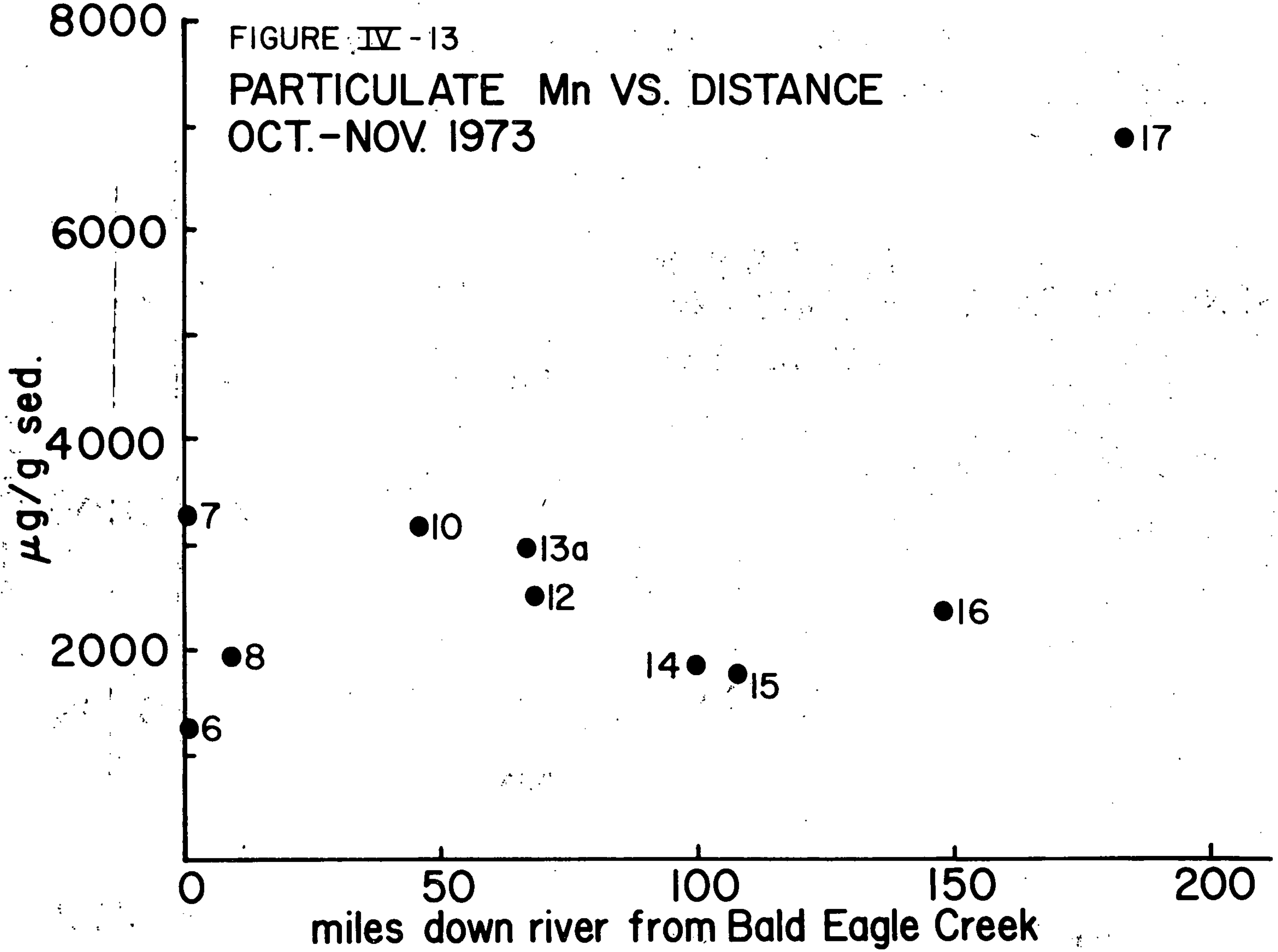


FIGURE IV - 13

PARTICULATE Mn VS. DISTANCE
OCT.-NOV. 1973

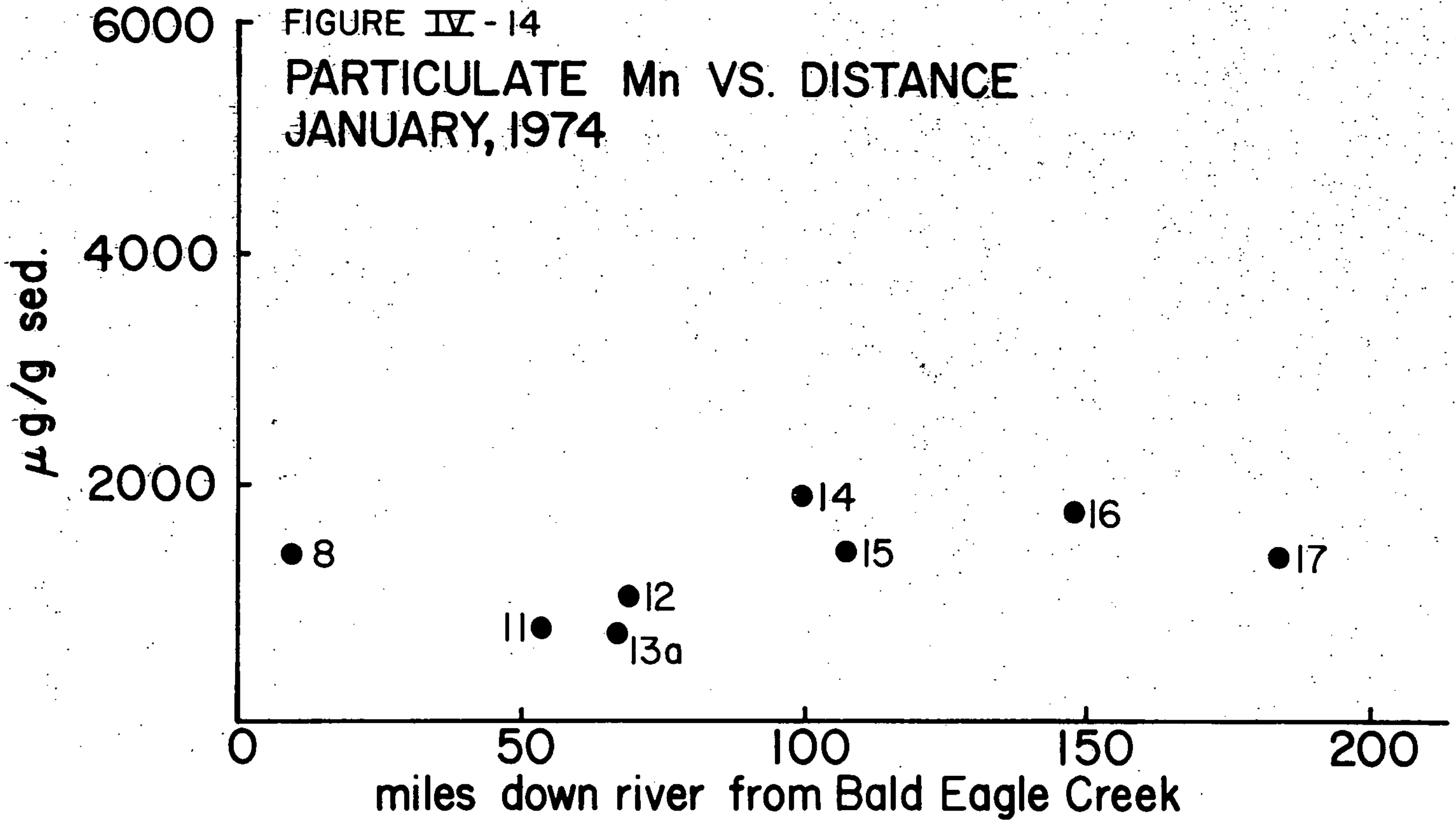


FIGURE IV - 14
PARTICULATE Mn VS. DISTANCE
JANUARY, 1974

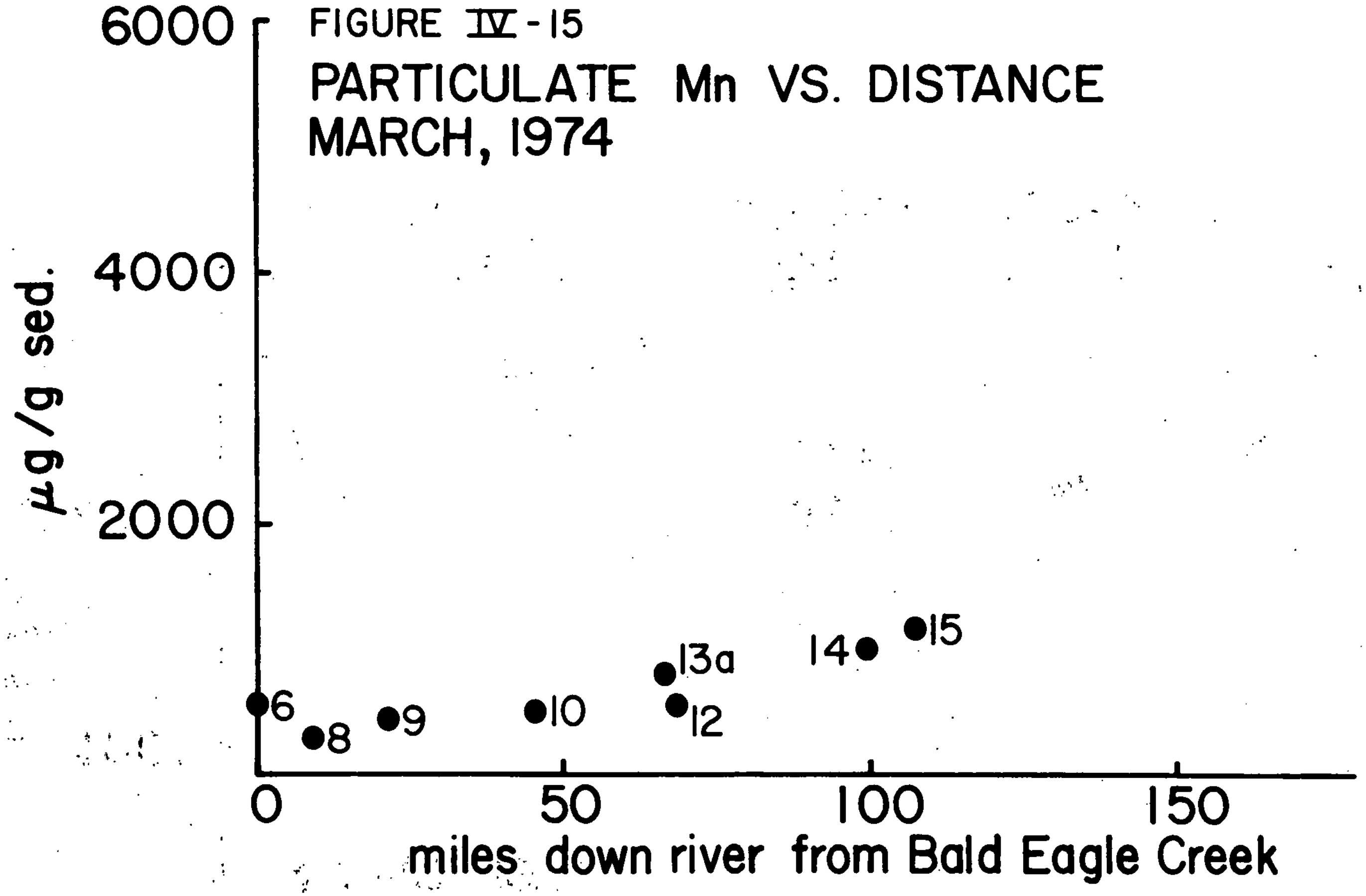


FIGURE IV-15
PARTICULATE Mn VS. DISTANCE
MARCH, 1974

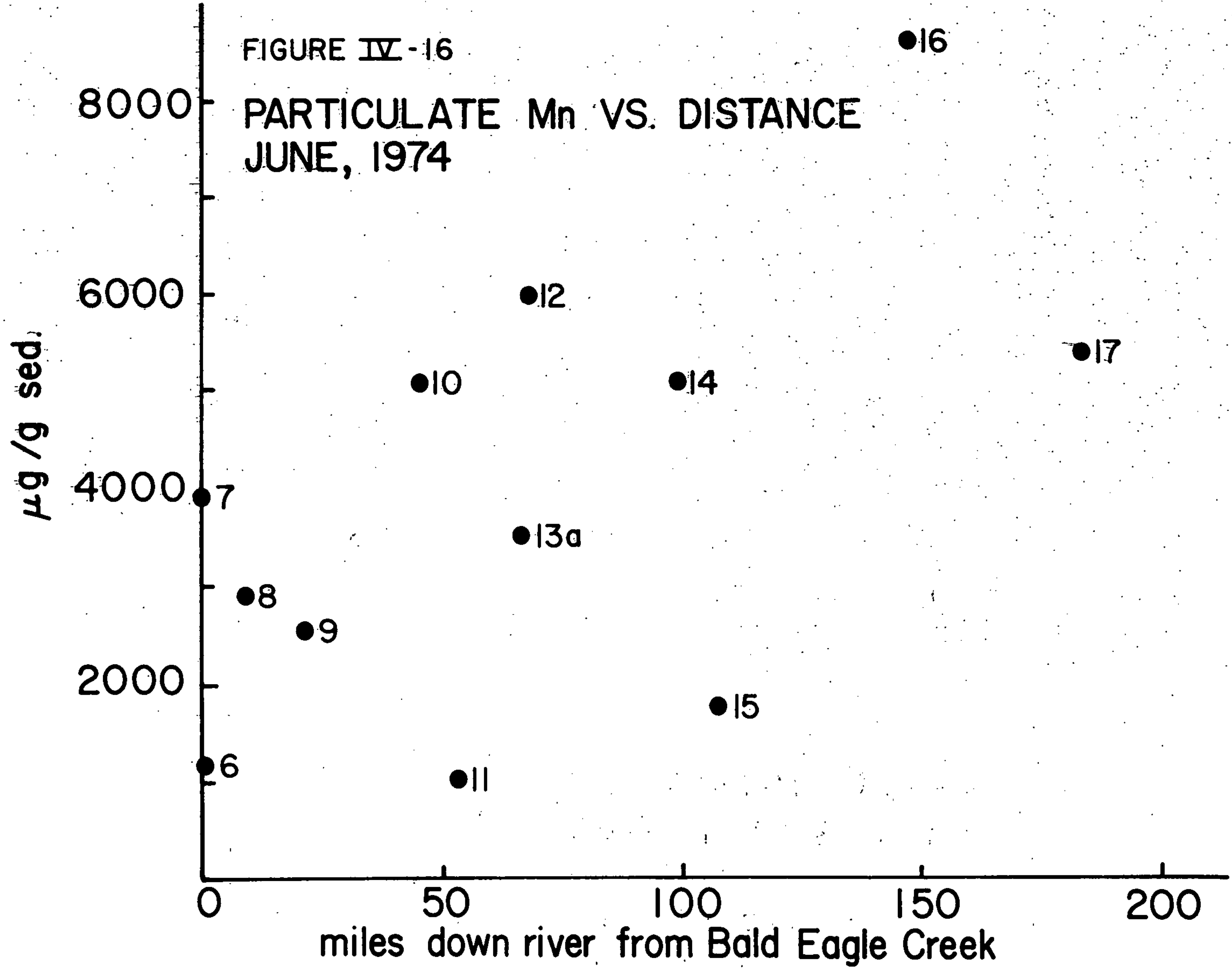


FIGURE IV-16

PARTICULATE Mn VS. DISTANCE
JUNE, 1974

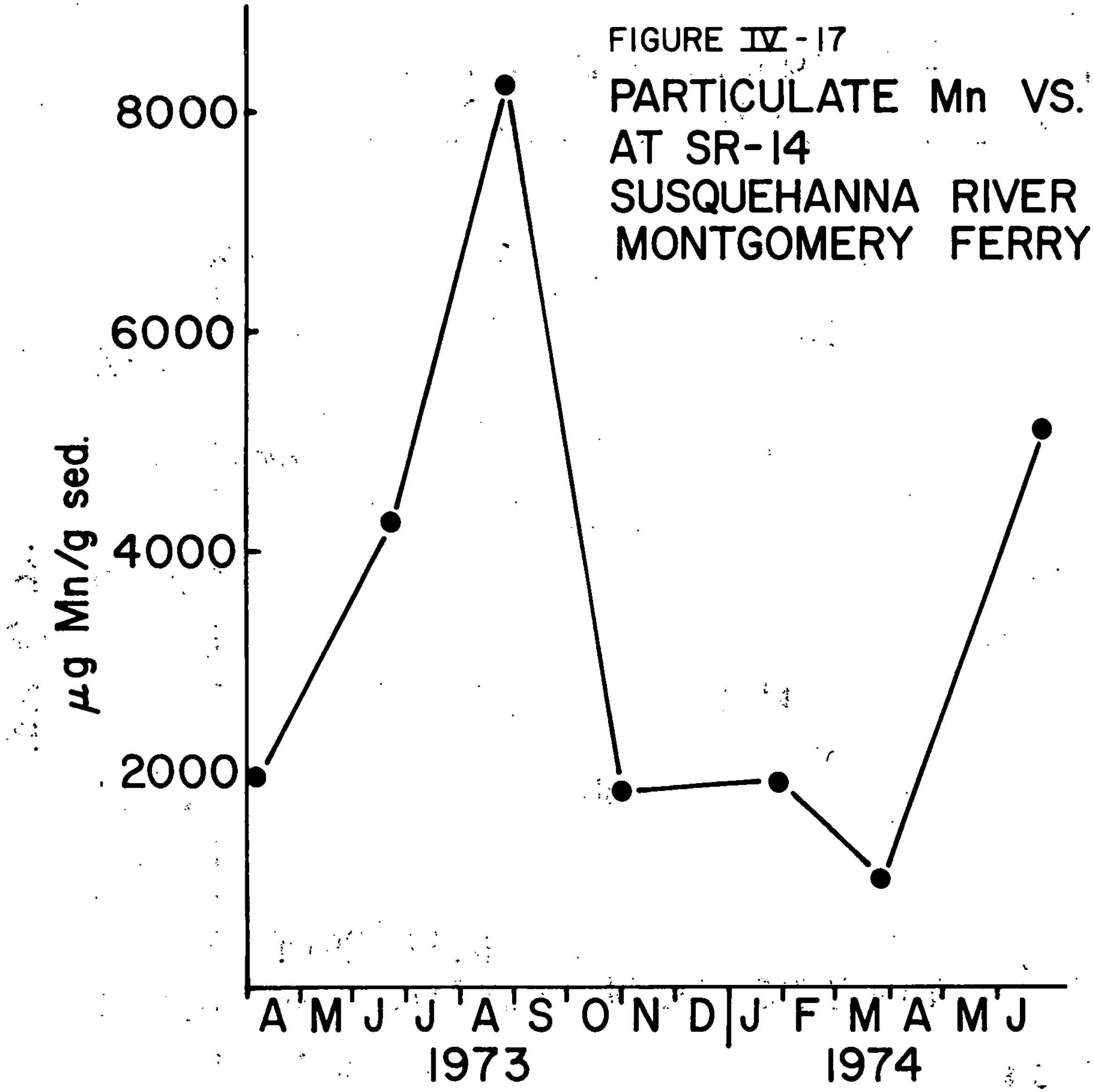


FIGURE IV-17
PARTICULATE Mn VS. TIME
AT SR-14
SUSQUEHANNA RIVER AT
MONTGOMERY FERRY

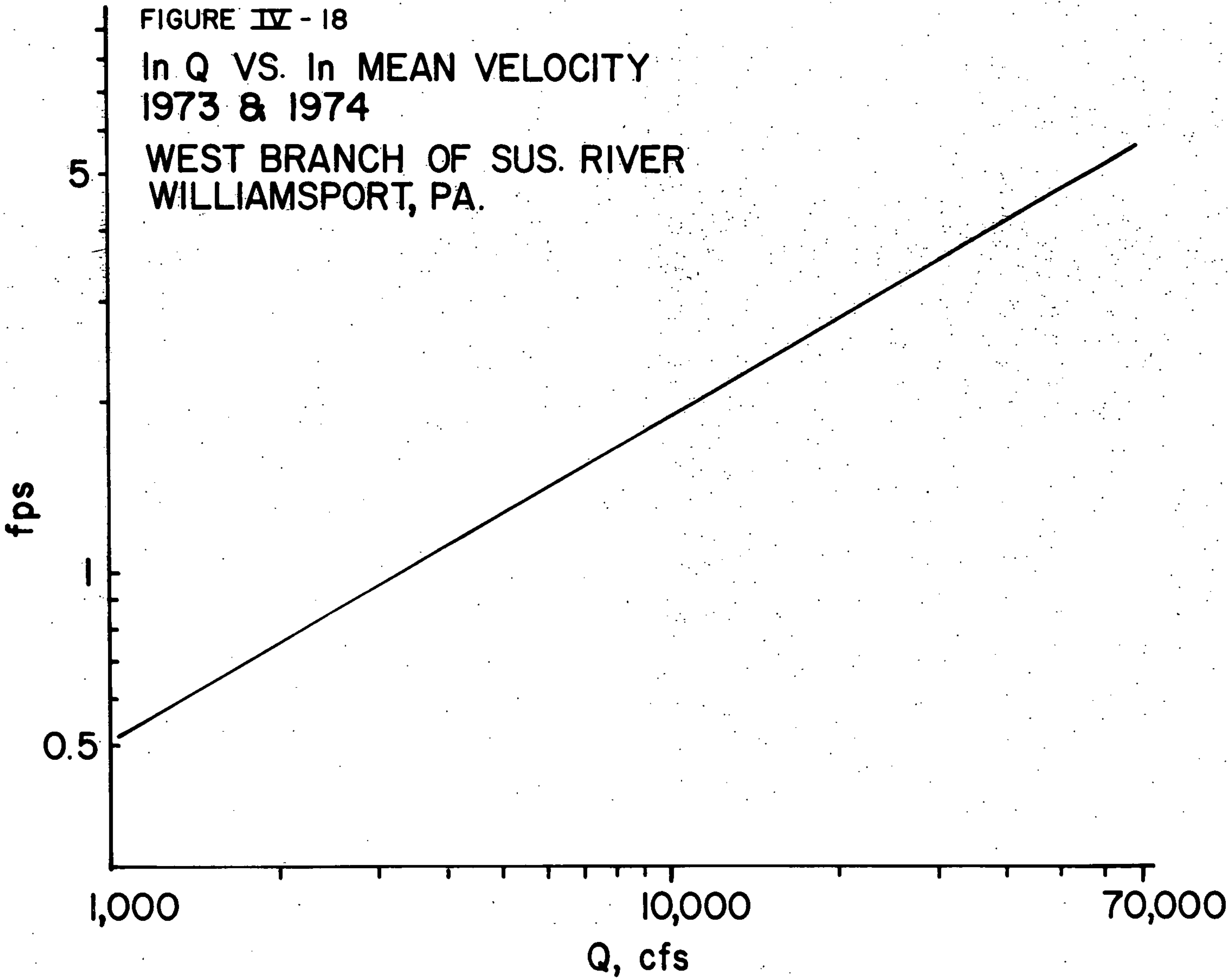


FIGURE IV - 18

ln Q VS. ln MEAN VELOCITY
1973 & 1974

WEST BRANCH OF SUS. RIVER
WILLIAMSPORT, PA.

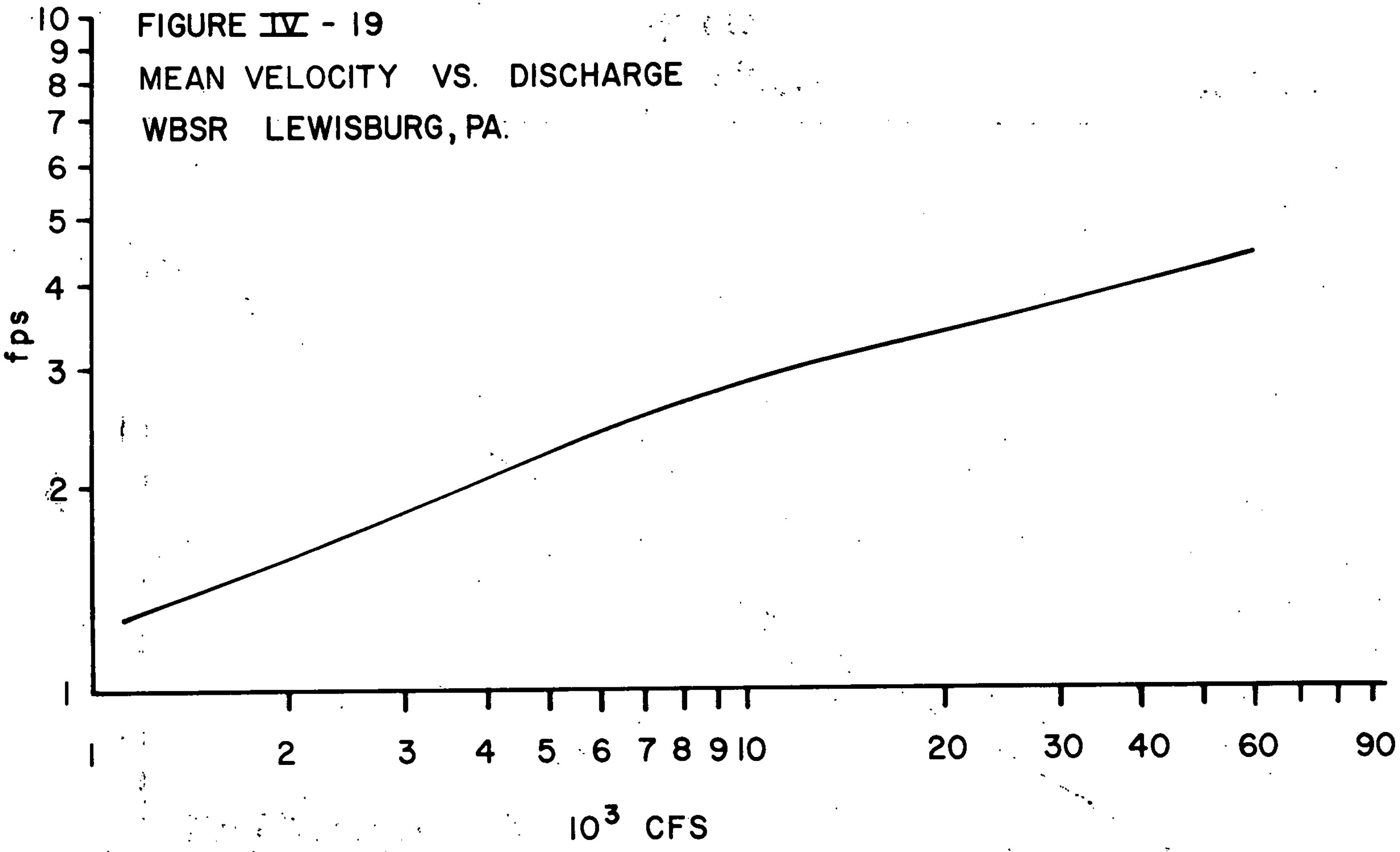


FIGURE IV - 19

MEAN VELOCITY VS. DISCHARGE

WBSR LEWISBURG, PA.

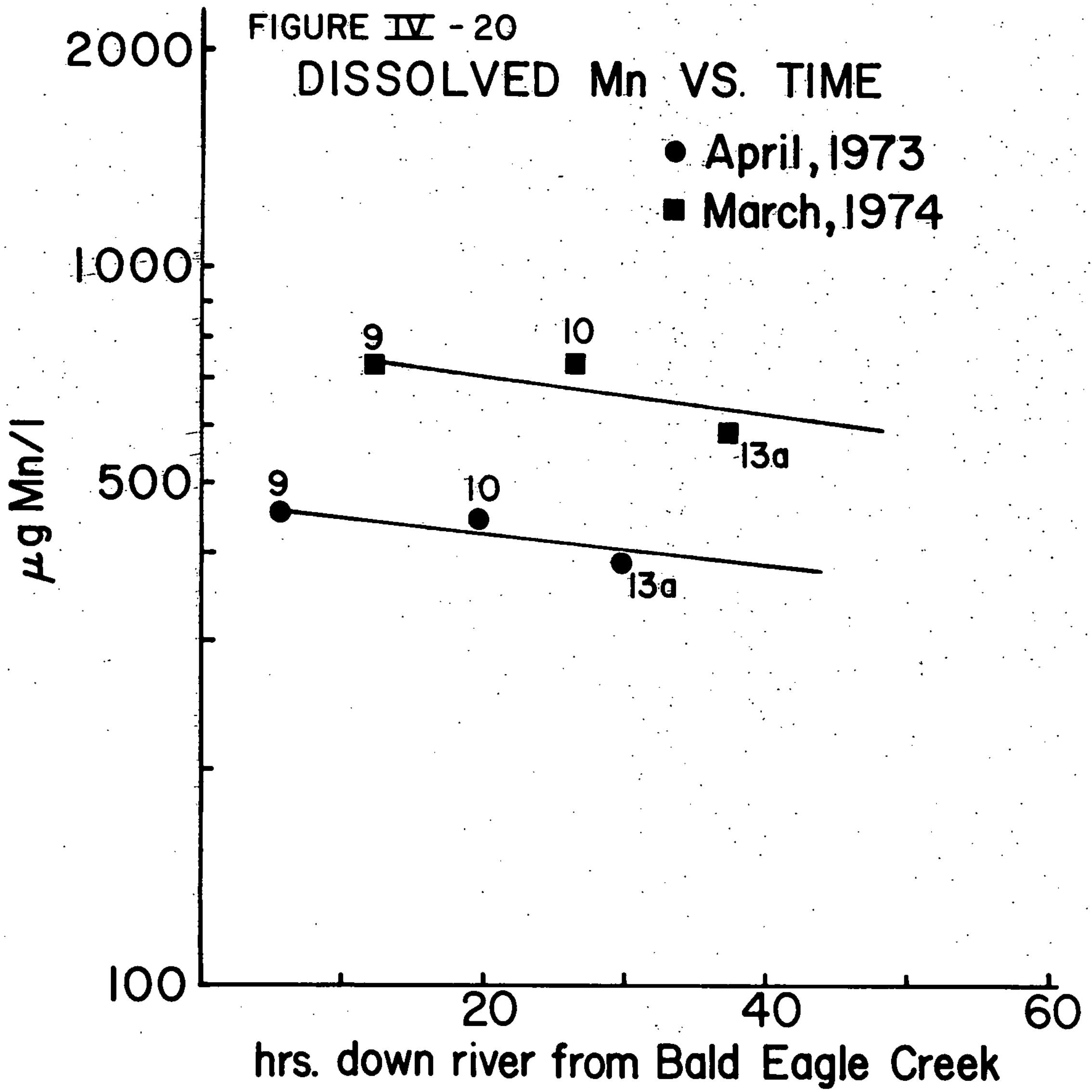


FIGURE IV - 20

DISSOLVED Mn VS. TIME

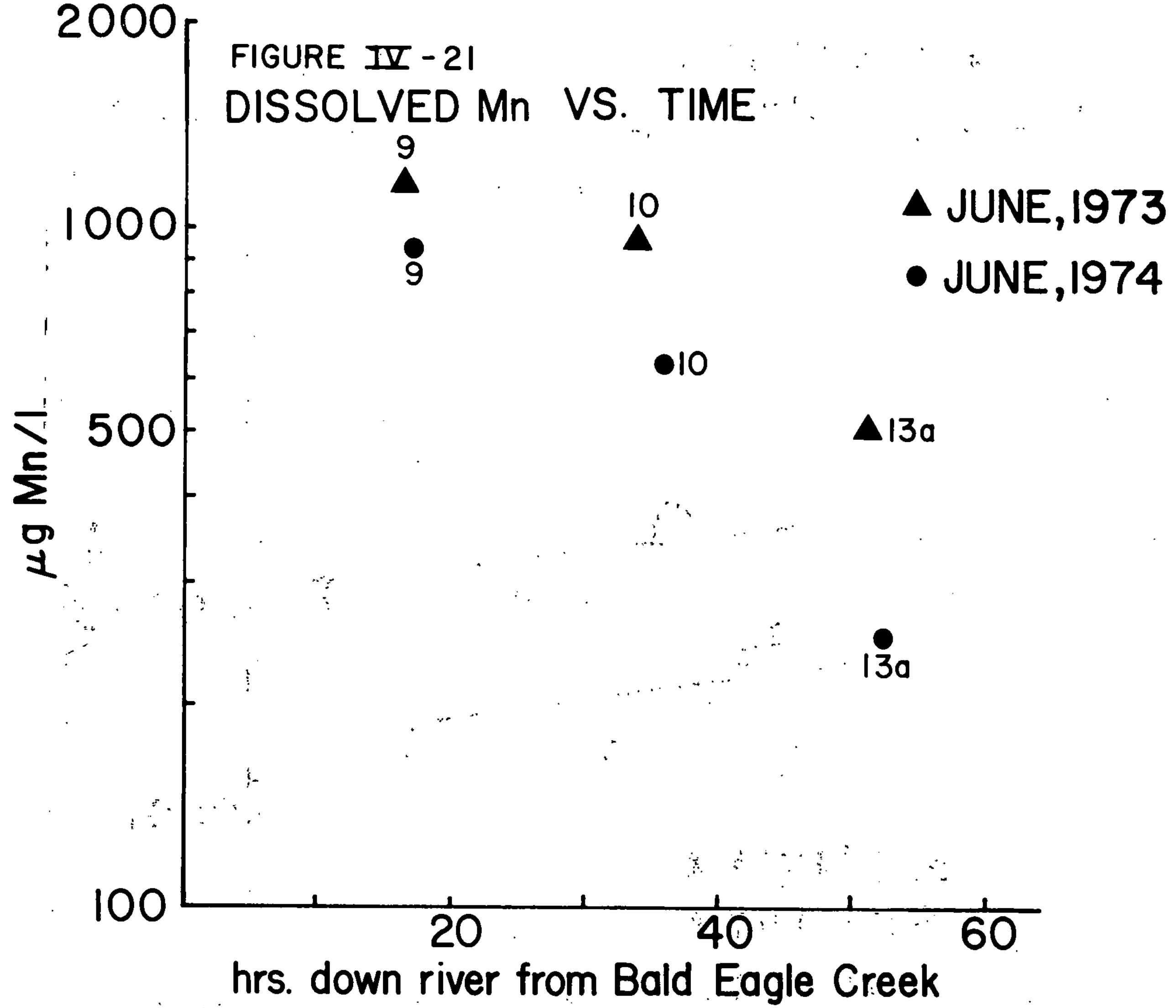


FIGURE IV - 21
DISSOLVED Mn VS. TIME
▲ JUNE, 1973
● JUNE, 1974
9
9
10
10
13a
13a
2000
1000
500
100
μg Mn/l
20
40
60
hrs. down river from Bald Eagle Creek

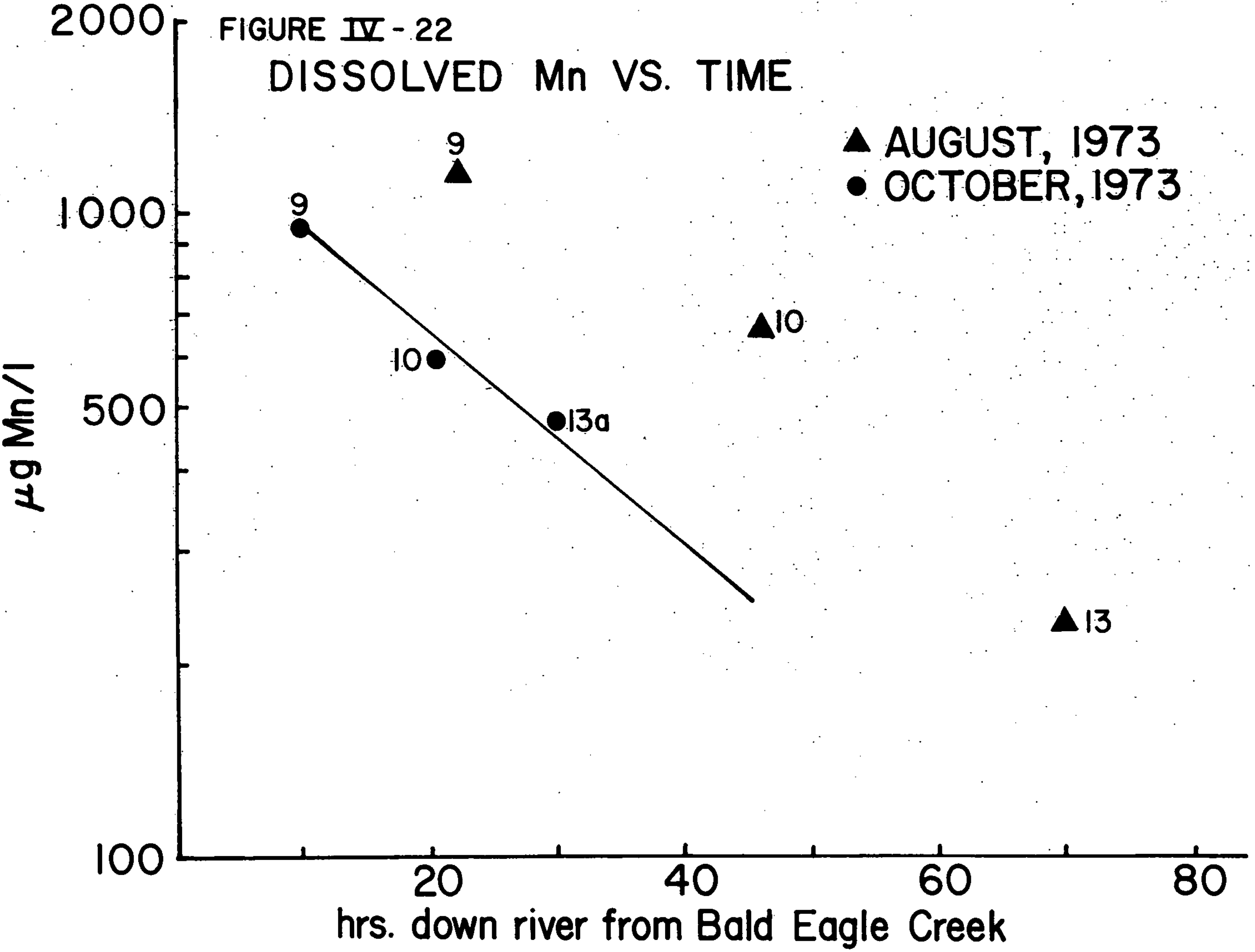
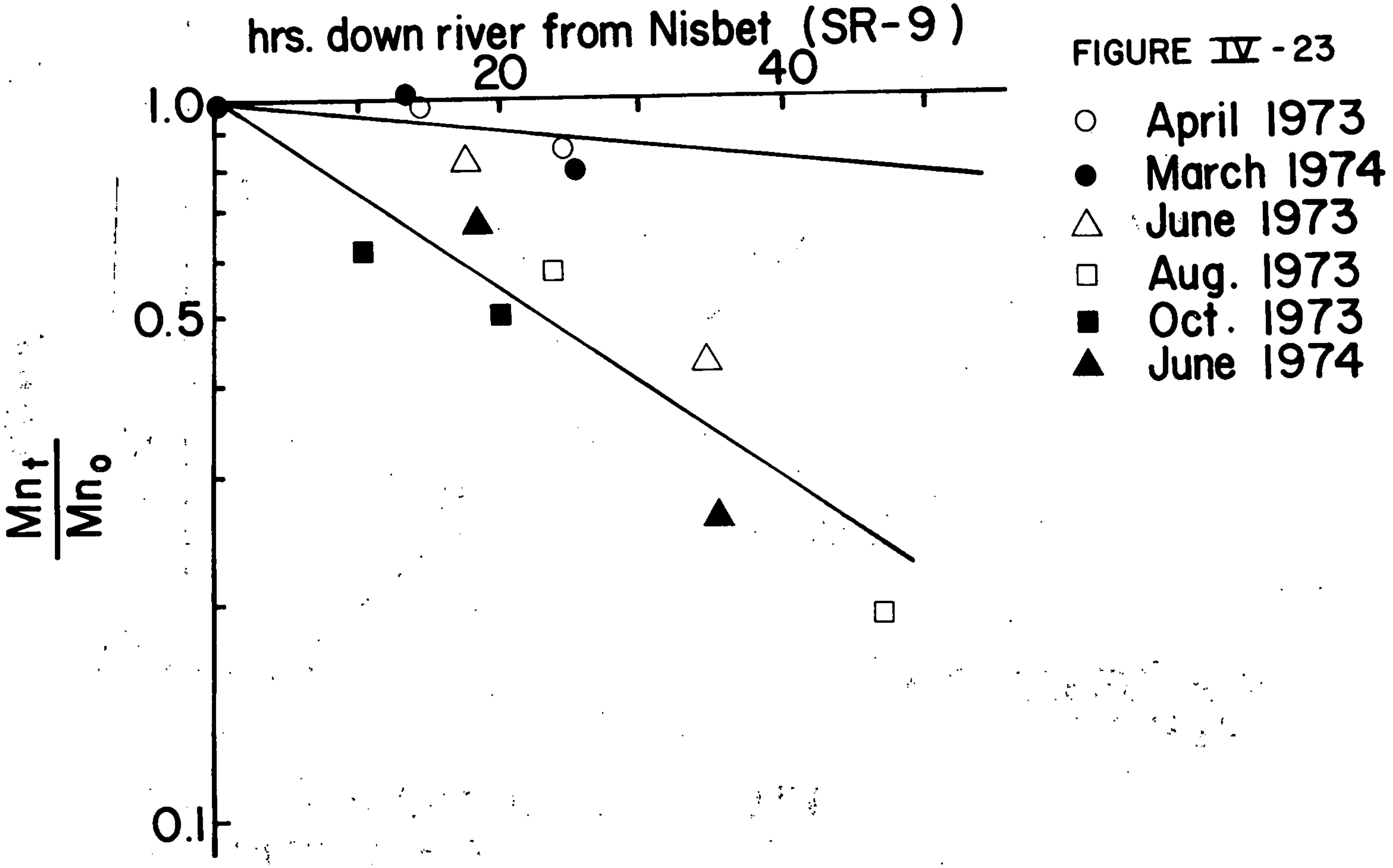


FIGURE IV - 22

DISSOLVED Mn VS. TIME

$\ln \frac{Mn_t}{Mn_0}$ VS. TIME

FIGURE IV-23



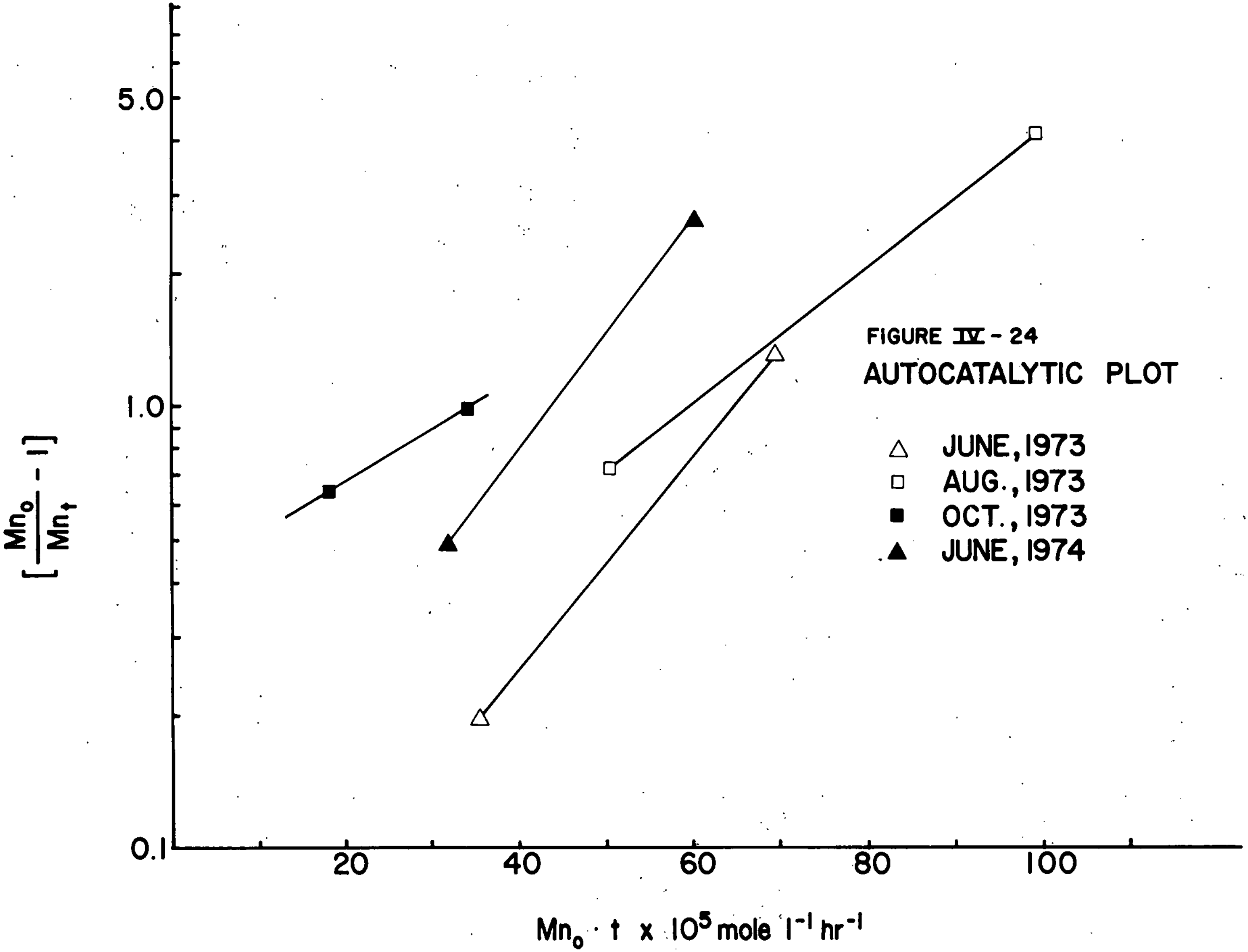


FIGURE IV - 24

AUTOCATALYTIC PLOT

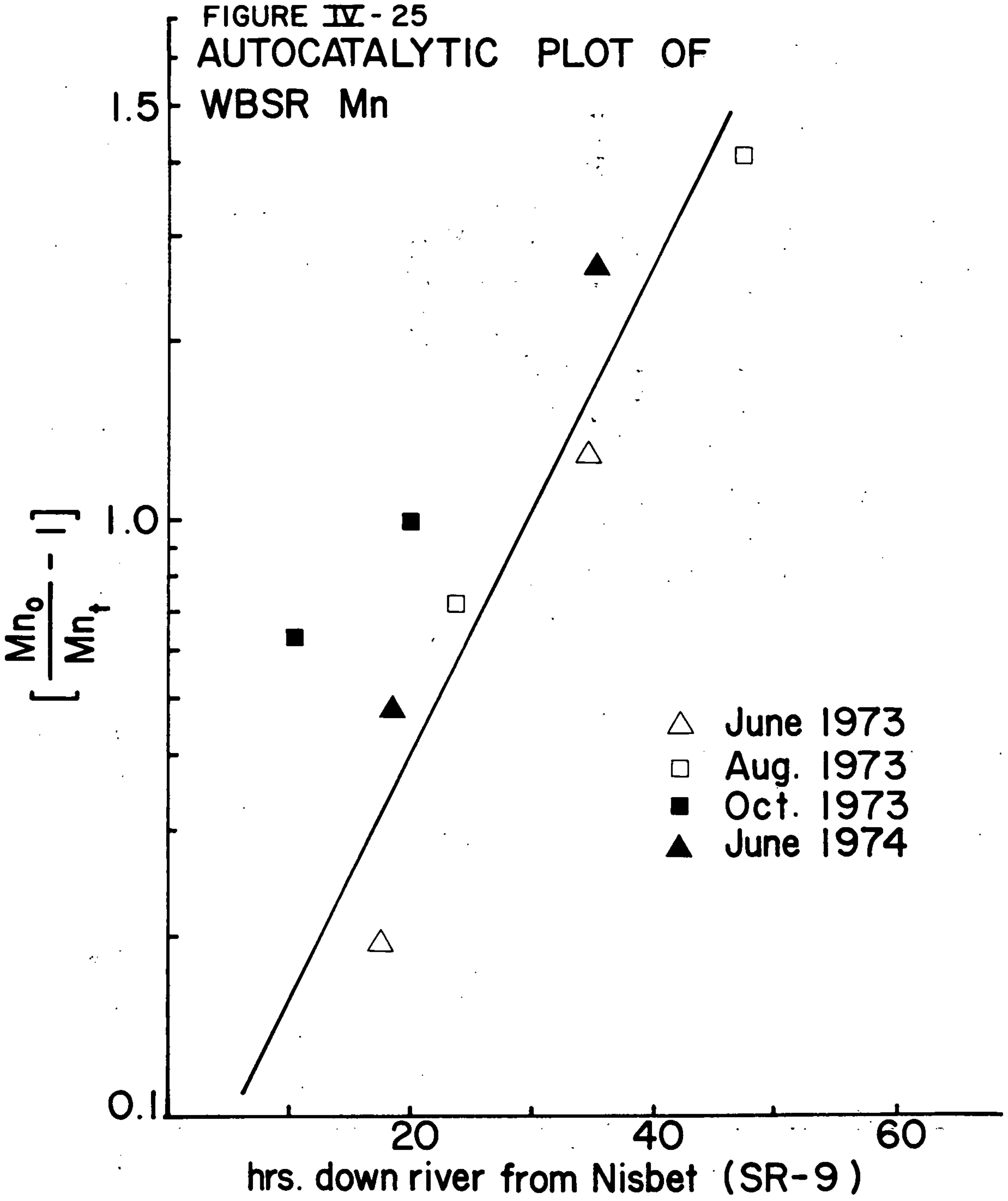


FIGURE IV-25
AUTOCATALYTIC PLOT OF
WBSR Mn

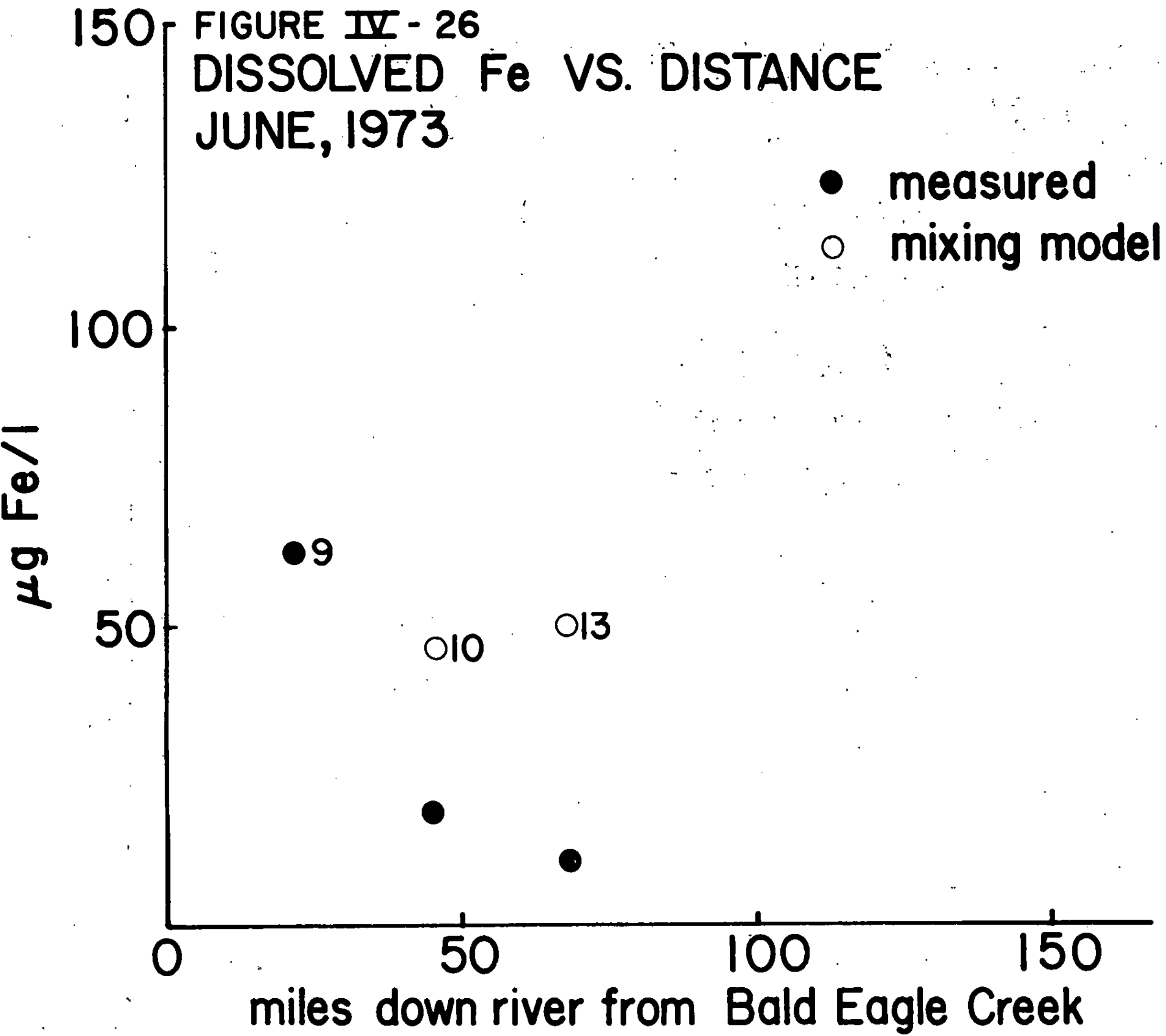


FIGURE IV - 26
DISSOLVED Fe VS. DISTANCE
JUNE, 1973

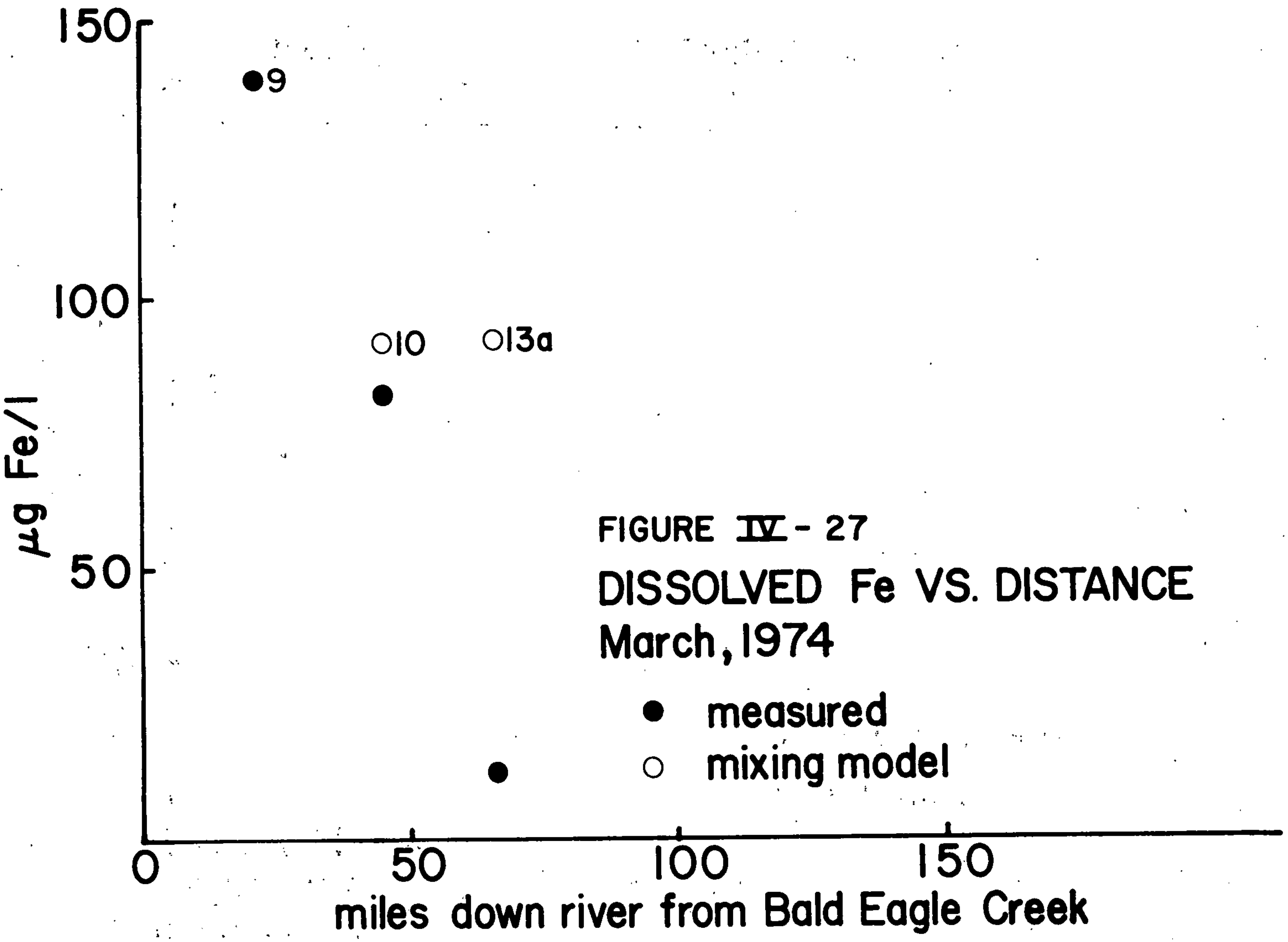


FIGURE IV - 27

DISSOLVED Fe VS. DISTANCE
March, 1974

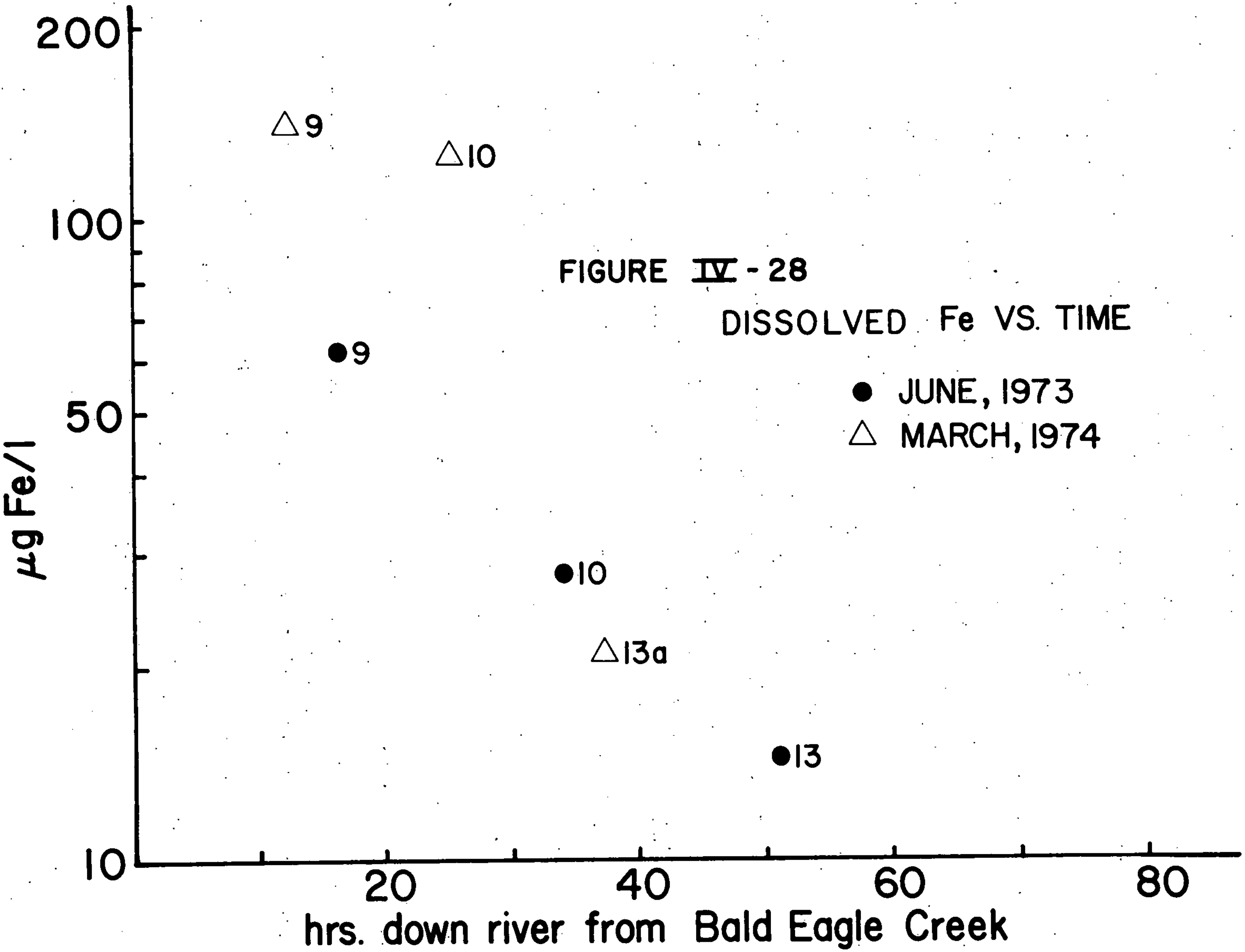


FIGURE IV - 28
DISSOLVED Fe VS. TIME

V. THE USE OF Pb^{210} AS A TRACER

The widespread introduction of heavy metals into the environment from anthropogenic sources often makes the study of the behavior of these elements ambiguous. Furthermore, contamination during sample processing and analysis, especially for stable Pb, is common, again bringing the results of such studies into question. Pb^{210}, a naturally occurring radioactive isotope of Pb, is not subject to the same problem as stable Pb.

The most abundant naturally occurring isotope of uranium, U^{238}, decays through a long chain of radioactive daughter nuclides to stable Pb^{206}. One of these, Rn^{222} ($t_{1/2}$ = 3.8 days) produced from Ra^{226} ($t_{1/2}$ = 1620 yrs), is a noble gas. The emanation of Rn^{222} from soils is a widespread, well documented phenomenon (Wilkening, 1975). Rn^{222} decays through a series of short-lived nuclides (Po^{218}, Pb^{214}, Bi^{214}, Po^{214}) to Pb^{210} ($t_{1/2}$= 22 yrs). As a non-reactive gas Rn^{222} remains in the atmosphere until it decays. Pb^{210}, on the other hand, becomes attached to aerosols and is swept out of the atmosphere by precipitation and dry fallout with an atmospheric residence time of less than a week (Poet et al., 1972). This flux of Pb^{210} provides a widespread, uniform, measurable flux to the land surface. There are other possible sources of Pb^{210} in the system. The Ra^{226} in the soil and rock decays to Pb^{210} which could be leached into the ground water that feeds streams. Also, the Ra^{226} and Rn^{222} dissolved in ground water could produce Pb^{210}.

The behavior of Pb^{210} from these sources in the soil-ground water stream systems provides the most direct information on the kinetics of processes involving trace heavy metals from natural or man-made sources.

Atmospheric Flux of Pb^{210}

The atmospheric flux of Pb^{210} in precipitation and dry fallout has been directly measured for New Haven, Connecticut, at Kline Geology Laboratory, Yale University. The results from monthly samples collected for more than a year indicate a flux of 0.9 ± 0.1 dpm Pb^{210} cm^{-2} yr^{-1} (Benninger, 1976). It can be shown that this flux is approximately the same over the Northeastern U.S. and probably from the Rockies eastward (Benninger et al., 1975; More and Poet, 1976). The methods employed to establish this are based on the analysis of soil profiles and atmospheric measurements, and, although these are less direct than the precipitation techniques, they provide more easily obtained data.

The A_1 horizon of soils, known to be rich in heavy metals and organics, can be expected to retain some, if not all, of the atmospheric flux of Pb^{210} delivered to the site. Soil profiles are also a source of Rn^{222} to the atmosphere which would appear as a deficiency of Pb^{210} relative to Ra^{226}. An analysis of the distribution of Pb^{210} and Ra^{226} down a soil profile permits the modelling of both the retained Pb^{210} flux downward and the Rn^{222} loss to the atmosphere (Moore and Poet, 1976). Soil profiles from several northeastern sites have been analyzed for Ra^{226} and Pb^{210}. McCaffrey (1976) has sampled a salt marsh soil and the soil from an adjacent upland island from the Farm River salt marsh in East Haven, Connecticut. This site is within 10 miles of the site for direct atmospheric flux sampling reported by Benninger (1976). Fisenne (1968) reports data for a soil profile from a tobacco-growing region of Maryland that is within 50 miles south of the mouth of the Susquehanna River.

A soil profile was collected in Pennsylvania for analysis to enable comparison with the other data. It was taken in the Cook Forest State Park, which lies just outside of the western boundary of the Susquehanna River basin at about its north-south mid-point. The total excess Pb^{210} in each site and the calculated steady state flux are shown in Table V-1. It can be seen that they all agree with the flux measured directly in New Haven, hence indicating no major variation in regional flux of Pb^{210} for the Northeast.

Using the average annual rainfall ($\sim$ 100 cm), the evapotranspiration rate of 50%, and the atmospheric flux of Pb^{210} (1 dpm $cm^{-2}yr^{-1}$), the concentration of Pb^{210} in waters recharging ground water systems should be $\sim$ 20 dpm/ℓ. The water from three springs were analyzed for Pb^{210}. Two of the springs, RV-5 and SM-spring, are thought to be fed by waters with shorter residence times than the well and the other springs sampled because of the significantly lower concentrations of rock-derived major ions in these two springs compared to the others (Table V-2). The Pb^{210} concentration for the springs are shown in Table V-2. SM-spring and RV-5 both have a Pb^{210} concentration of $\sim$ 1 dpm/ℓ. The spring RV-3 has less than 0.01 dpm Pb^{210}.

In Chapter II it was shown that at all times the water flowing in streams is from the ground water system. This being the case, the streams are good integrators of the composition of the ground water. The type streams contain water very recently discharged from the ground water system and therefore should be good indicators of the average Pb^{210} in the shallow ground water. The concentration of Pb^{210} in these streams is shown in Table V-2. The concentration of Pb^{210} in the Driftwood Branch and Buffalo Creek is 0.01 dpm/ℓ.

Holtzman (1964) reports Ra^{226} and Pb^{210} analyses for ground waters in Illinois. The deep aquifers are in limestone and sandstone. If it is assumed that the water in these deep aquifers have a mean residence of 100 years or greater, a residence time for Pb^{210} can be calculated from the Ra^{226} and Pb^{210} data. Using the range of concentrations he gives for these deep aquifers, the range in mean residence time is from one year to one day while the average Ra^{226}/Pb^{210} ratio yields a residence time of one month. This result is compatible with the conclusions concerning Pb^{210} concentrations in the ground water of the Susquehanna River system.

The data for excess Pb^{210} in soils compared to precipitation data indicate loss primarily through radioactive decay. The small concentration of dissolved Pb^{210} in the shallow ground water of the region compared to the expected value from precipitation also confirms this. Therefore, all the data together indicate that soils are virtually 100% efficient at suquestering the atmospherically supplied Pb^{210} to a terrain. This sequestering of Pb^{210} by the soil materials occurs despite low pH in these soil horizons and may be related to the properties of the organic material with which a correlation exists (Table V-3).

An interesting situation is presented by those areas affected by coal mining. There the acid streams are high in dissolved Pb^{210} relative to other streams. However, the concentration of Pb^{210} in the mine drainage is about 0.3 dpm/ℓ, which is only 1.5% of the expected concentration in rain-derived ground water. Surprisingly then, most of the Pb^{210} in rain falling on the mined areas is also removed from solution. In areas of strip mining the mine drainage is formed as rain water percolates through the spoil piles made of rock rubble and probably the former soils. However, the data seem to indicate that, even in the absence of organic soil material, most of the Pb^{210} will be removed from the water by contact with rock materials, even at low pH.

Fate of Pb^{210} in River Water

In the preceding discussion it is shown that all the water flowing in the river (with the exception of that falling directly on the river) under natural conditions must pass through the soil-ground water system where efficient scavenging of Pb^{210} occurs. The water flowing into the stream system is very low in dissolved Pb^{210}, and modelling its behavior downstream becomes impossible.

Mine drainage streams and sections of the river affected by mine drainage, however, are relatively high in Pb^{210} (0.3 dpm/ℓ compared to 0.01 dpm/ℓ for normal streams), and some information on the behavior of Pb^{210} during stream transport can be obtained from this source. The portion of the West Branch from Keating to Lock Haven is massively affected by mine drainage, although very little additional mine drainage is added to the river within this stretch of river. The river is at low pH (∿ 4 to 4.5) and contains relatively high dissolved Mn and Fe. In the previous chapters it was shown that Mn remains in solution in this section of the river but that Fe is probably precipitating as an oxyhydroxide throughout the region. Below Lock Haven the acid of the West Branch is neutralized and the pH rises to 6.5 to 7, resulting in the precipitation of Fe and Mn. The Fe precipitates very rapidly after neutralization and is generally completed before the first downriver station (SR-9). On the other hand, the Mn precipitates more slowly and occurs in the entire West Branch below Lock Haven. These relationships are summarized in Figure V-1. Immediately downriver from the point of acid neutralization, for a distance of about 15 miles, there is precipitation of Fe. Below the point of Fe removal precipitation of Mn occurs throughout the length of the river.

Samples for Pb^{210} analyses were collected on the acid portion of the river in June 1974 at Keating and Lock Haven. The Pb^{210} concentration for the West Branch at Keating is 0.17 dpm/ℓ. As in the cases of Mn and Fe discussed already, the expected concentration of Pb^{210} at Lock Haven by dilution alone can be calculated given a starting concentration at Keating. When this is done, it can be seen that the concentration at Lock Haven (0.12 dpm/ℓ) is due to dilution and that the Pb^{210} is not removed from the river at a pH of 4. It is interesting to note that the Pb^{210} is not sequestered by the Fe oxides at a pH of 4, whereas Pb^{210} is sequestered by organic soil material and rock debris at similar pH values.

Samples were collected for Pb^{210} analyses below Lock Haven in October 1973, March 1974 and June 1974. In June 1974 samples were collected at all river stations from Lock Haven (SR-6) to the mouth of the West Branch so that detailed information could be obtained on the removal of Pb^{210}. In October 1973 samples were collected only at Lock Haven (SR-6) and Northumberland (SR-13a). In March 1974 samples were collected at Keating and Northumberland. A starting concentration for the West Branch at Lock Haven can be calculated, however, as the June data above show that Pb^{210} is not removed in this section of river.

The most complete data are available for June 1974. The concentration of Pb^{210} versus time in hours downriver from the point of acid neutralization (taken to be the confluence with Bald Eagle Creek) is shown in Figure V-2. The Pb^{210} concentration is nearly zero by the time the first station is reached. The apparent increase downriver from Nisbet (SR-9) is consistent with addition of tributary waters containing non-zero Pb^{210} concentrations below this point or may be attributed to a steady state Pb^{210} concentration in the river below the region of Fe hydroxide coprecipitation. The higher downriver values may also be due to particles passing the 0.4 μm filter, whereas in the area of Fe precipitation filtering is more efficient. These removal data indicate a mean residence time of < 0.7 day when calculated as a first order rate process.

Similar data for October 1973 and March 1974 (Figure V-3) show that by the time the water reaches Northumberland (SR-13a) the Pb^{210} in solution at Lock Haven (SR-6) has been reduced to low levels similar to those observed at Northumberland (SR-13a) for June 1974. Also, a sample collected in January 1974 at Northumberland (SR-13a) has a a similar dissolved Pb^{210} concentration, although it must be surmised that dissolved Pb^{210} was present in the river at Lock Haven (SR-6). These data indicate a residence time for Pb^{210} in the river water of < 1.5 days based on first order removal.

The Fate of Particulate Pb^{210}

The Pb^{210} which falls on the Susquehanna River basin is lost from solution to the soils. Therefore, no Pb^{210} is lost from the terrain in solution with the exception of mine drainage. All the

Pb^{210} is retained on particles in the soil and the only way it can be lost from a terrain is by erosion.

The stream-borne particles with their associated Pb^{210} are derived mainly from soil. It can be determined how much Pb^{210} derived from atmospheric precipitation on a terrain leaves the system via streams if the sediment flux and excess Pb^{210} concentration of the particles are known. Table V-4 shows the results of the calculation for the entire Susquehanna River based on the long-term annual sediment yield of Williams and Reed (1972). This flux is equivalent to 0.05% of the soil standing crop of excess Pb^{210}.

The Pb^{210} data for soil profiles show a Pb^{210}/organic matter ratio which is nearly constant with depth in the soil (Table V-5). This implies that the Pb^{210} added to the soil surface is rapidly homogenized within the organic-rich layers. Nearly the same ratio of Pb^{210}/organic matter is observed in the suspended matter of streams (Table V-5), and this indicates that stream sediments directly reflect the metal content of soils. The removal of 0.05% of the standing crop of Pb^{210} is equivalent to a first order removal constant for Pb^{210} by erosion of $\lambda = 5 \times 10^{-4} yr^{-1}$ or a mean life of 2000 years for metals similar to Pb^{210} in soil profiles.

If Pb is analogous to stable Pb and other trace metals in the natural system (including those supplied by human purturbations), then the Pb^{210} results can be applied to these more general problems. The first question that arises is whether Pb^{210} becomes homogenized with the stable Pb in a system. The dominant source of Pb injection into the environment today is from combustion of leaded gasoline in internal combustion engines. The Pb in such exhaust is vented into the atmosphere as Pb bromo-chlorides. However, studies of Pb in soils in areas of pronounced pollution show that the Pb in soils is present as Pb oxides and Pb sulfate (Olson and Skogerboe, 1975). Furthermore, research on aerosol chemistry shows that the trend of reaction is to replace the chloride (and presumably other halogens) in the aerosols with NO_3^- and other anions (Martens, et al. 1973). Collectively this indicates that the Pb^{210} should become homogenized with stable Pb in the atmosphere and thus be an effective tracer. The nature of Pb^{210} and stable Pb in the riverine system cannot be evaluated and remains open to research; but it is likely, however, that Pb^{210} will be a useful tracer in aquatic systems.

Using their analyses for dissolved trace metals in a variety of rivers and comparing them to the particulate trace metal data reported for the same samples (Turekian and Scott, 1967), Kharkar et al. (1968) concluded that there was no relationship between dissolved trace metal concentrations and the concentration or amount of the same trace metals in the suspended sediment. Similarly, the Pb^{210} data for the Susquehanna River and tributaries at points beyond the effects of mine drainage (Table V-6) show no relationship between dissolved Pb^{210} and the concentration of Pb^{210} in the sediment or for total Pb^{210} in the suspended sediment. In fact, it appears that regardless of the sediment concentration the dissolved Pb^{210} ($< 0.4\mu m$) is at a very low concentration of ~ 0.01 dpm/ℓ.

The study of Mn and Fe in the Susquehanna River has shown that if they are introduced into the river system, precipitation will occur and Pb^{210} will be removed from solution and maintained at a very low concentration. One way that Fe and Mn are introduced into natural rivers is from the ground water that feeds the river system. However, in many rivers, as is the case for the Susquehanna, major ground water input occurs in the tributaries while the main trunk flow is merely a total of the tributary flow. Therefore, the water in the main trunk may have already precipitated all of its Fe and much of its Mn due to distance (time) from the source. From jar experiments with Susquehanna River bottom sediment there is qualitative evidence of a flux of Fe and Mn from the fine-grained river bottom sediments. Similarly, a recent study of fine-grained bottom sediment of the White Oak River, North Carolina, shows high dissolved Fe ($\sim$ 5 ppm) in the interstitial waters along with the formation of iron sulfide in zero salinity pore waters (Goldhaber and Martens, 1975--personal communications). This indicates a source for a flux of dissolved Mn and Fe into the river water where it will precipitate and become part of the suspended sediment as fresh hydroxides. The presence of sulfide in these bottom sediments would prevent the concomitant release of Pb^{210} and other trace metals. In addition to the Fe and Mn chemistry of a river, there is a supply of eroded soil organic matter which is an excellent scavenger of trace metals. Therefore, it is concluded that the continual production of Fe and Mn hydroxides which are added to the suspended sediment and the introduction of organic matter are responsible for a unidirectional removal process of dissolved trace metals onto particles, resulting in a low dissolved concentration of many trace metals in streams and rivers. The Pb^{210} rate studies show that removal is relatively fast; but if the flux of metals from pollution sources exceeds this removal term, the standing crop of dissolved trace metals could be quite high.

TABLE V-1. COMPARISON OF THE MEASURED ATMOSPHERIC Pb^{210} FLUX TO FLUXES CALCULATED FROM THE SOIL STANDING CROP OF Pb^{210}

Soil	Soil Pb^{210} Standing Crop dpm	Pb^{210} flux dpm $cm^{-2}yr^{-1}$	Source
Cook Forest	30	1.0	this study
Maryland	36	1.2	Fisenne, 1968
Salt Marsh, Conn.	30	1.0	McCaffrey, in preparation
Island, Conn.	24	0.8	McCaffrey, in preparation
Rain Collection New Haven, Conn.		1.0	Benninger, 1976

TABLE V-2. AVERAGE Ca, Mg AND Pb^{210} CONCENTRATIONS OF GROUND WATER AND STREAMS SAMPLED

	June 1974						Type Streams			
							RV-1	RV-1	SR-11	SR-11
	Spring RV-3	Spring RV-7	Spring RV-4	Well RV-6	Spring RV-5	SM-Spring	March 1974	June 1974	March 1974	June 1974
Ca	5.9	5.8	6.8	4.9	3.8	3.1	4.0	4.3	18.4	21.1
Mg	1.8	1.6	1.5	0.8	1.0	0.8	1.2	1.2	5.8	6.3
Pb^{210}dpm/ℓ	.007	-	-	-	.974	1.116	0.011	0.010	0.023	0.011

TABLE V-3. ORGANIC MATTER, Ra^{226}, AND Pb^{210} IN SOIL PROFILES

Soil*	Ra^{226}dpm/gm ash	Pb^{210}dpm/gm ash	% organic**
CF-1	3.86	340	87.7
CF-2	1.63	62.8	57.8
CF-3	1.01	9.50	17.5
CF-4	1.05	2.00	3.79
SM-1	5.45	271	86.5
SM-2	2.22	55.7	45.2
SM-3	1.29	3.58	7.5
SM-4	1.25	1.62	2.82
SM-5	1.46	1.52	3.94

*CF: Cook Forest State Park soil profile

SM: a soil profile collected in a deciduous forest near an oak tree that was 104 years old. The site ∿ 5 miles southeast of Emporium, Penna., on a flat hill top

**Weight loss on ignition at ∿ 500°C

TABLE V-4. Pb^{210} PARTICLE MASS BALANCE CALCULATED FOR THE SUSQUEHANNA RIVER AT HARRISBURG, PENNSYLVANIA

Ra^{226} dpm/gm	Pb^{210} dpm/gm	Pb^{210} excess	Sed. Flux*	Pb^{210} flux	Soil Standing Crop	Soil Metal Removal
3.5 - 4.0	7.5 - 8.0	4	3.78×10^3 gm $cm^{-2} yr^{-1}$	0.015 dpm cm^{-2} yr^{-1}	30 dpm cm^{-2}	0.05%/yr

*Based on Williams and Reed, 1972.

TABLE V-5. Pb^{210}_{excess}/ORGANIC MATTER RATIO IN SOIL PROFILES

Site	Pb^{210}/gm organic	Site	Pb^{210} dpm/gm organic
CF-1	48	SM-1	41
CF-2	45	SM-2	65
CF-3	40	SM-3	28
CF-4	24	SM-4	13

Stream sediment 30 Pb^{210}_{excess} dpm/gm organic

TABLE V-6. DISSOLVED AND PARTICULATE Pb^{210} CONCENTRATIONS IN SUSQUEHANNA RIVER SAMPLES

Site	Dissolved (< 0.4μm) dpm/l	Particulate Pb^{210} dpm/gm	dpm/l
October 73			
SR-8	0.003	6.47	1.07
SR-11	0.025	6.54	0.16
SR-13a	0.010	7.43	0.42
SR-17	0.005	7.58	0.06
January 74			
SR-13a	0.014	11.24	0.21
SR-17	0.005	8.76	0.15

FIGURES

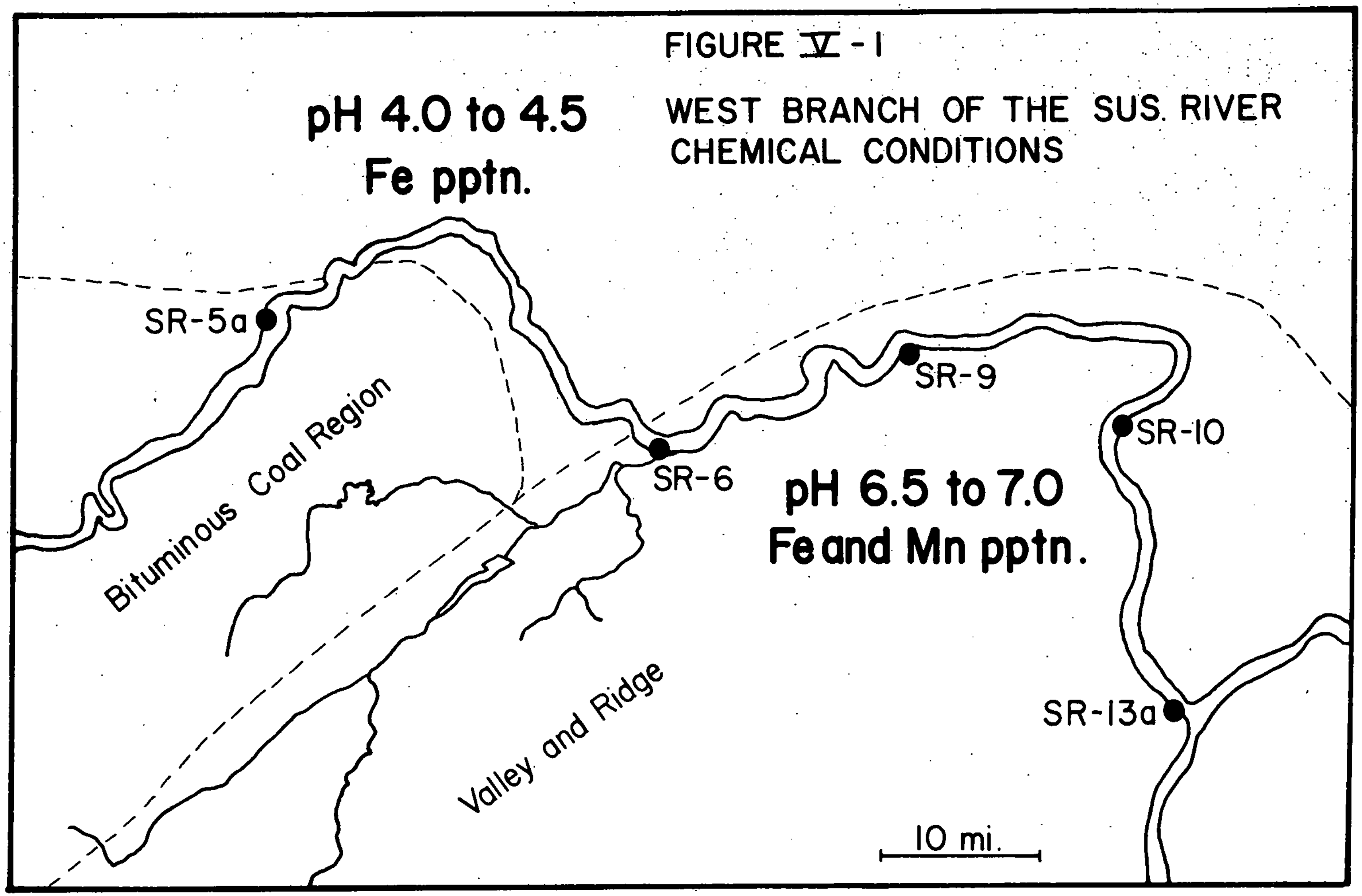


FIGURE V - 1

WEST BRANCH OF THE SUS. RIVER CHEMICAL CONDITIONS

FIGURE V - 2

Pb^{210}, West Br. Sus. River: Lock Haven to Northumberland, Pa.

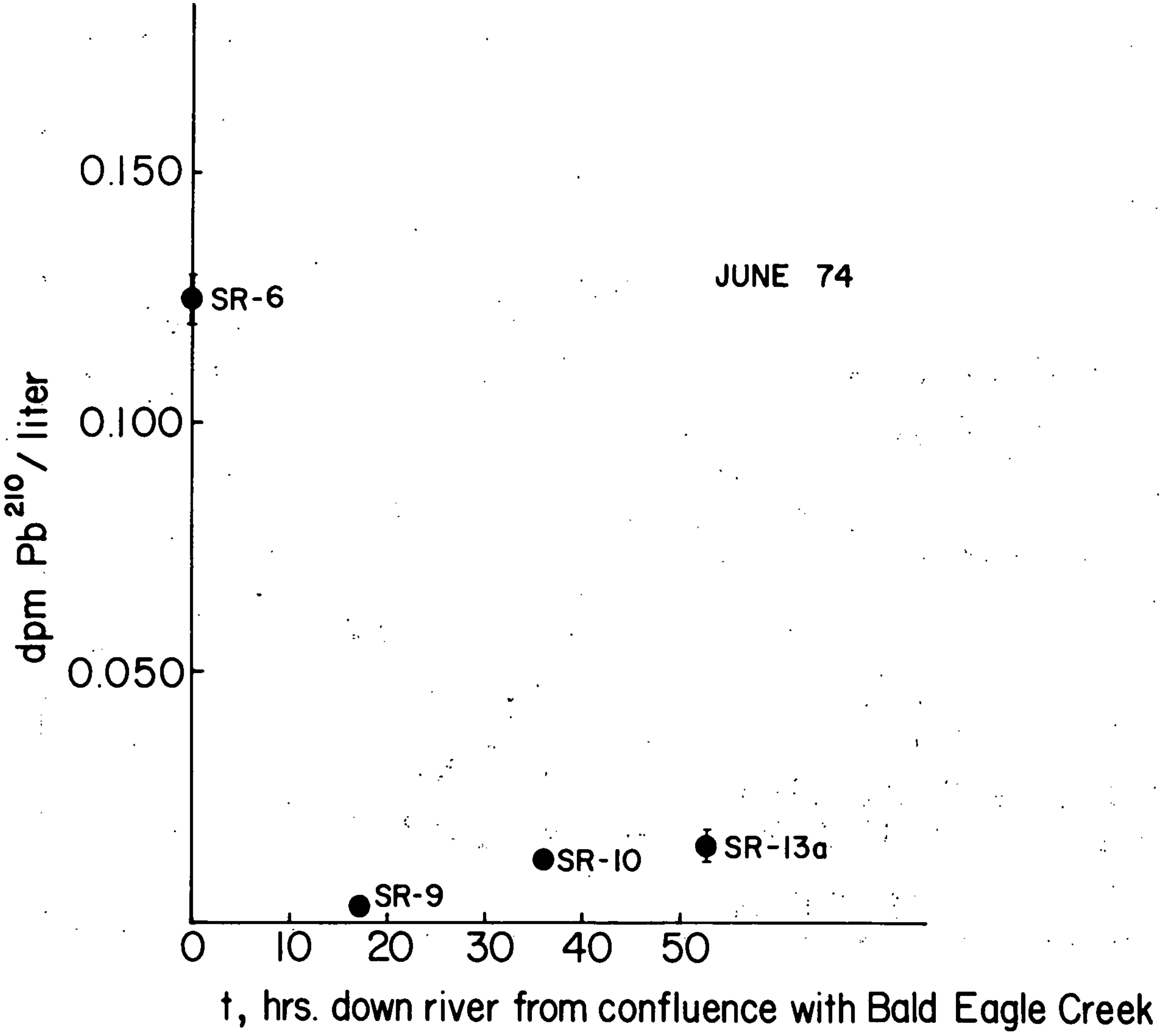
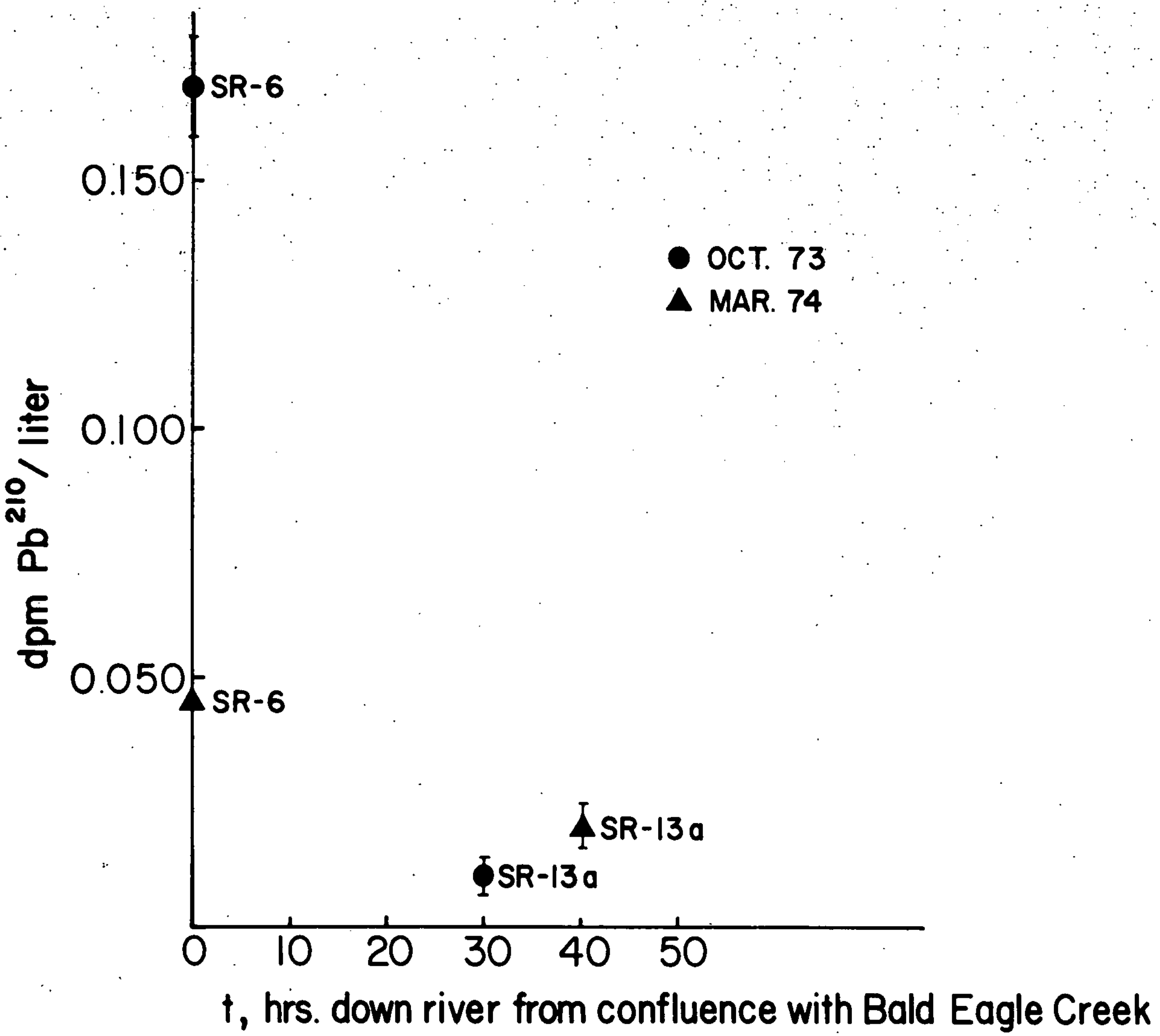


FIGURE V - 3

Pb^{210}, West Br. Sus. River: Lock Haven to Northumberland, Pa.



VI. URANIUM

Radioactive disequilibrium has been reported numerous times for dissolved uranium (U^{238} and U^{234}) in fresh water (Osmond et al., 1968; Cherdyntsev, 1971; Kronfeld, 1974) and sea water (Koide and Goldberg, 1965; Somayajulu and Goldberg, 1966; and Blanchard, 1965). This disequilibrium probably arises from the recoil of Th^{234} produced by α decay of U^{238} which subsequently decays to U^{234} (Cherdyntsev et al., 1955; Chalov, 1959; Rosholt et al., 1963; Dooley et al., 1966; and Kigoshi, 1971).

Susquehanna River U^{234}/U^{238} Activity Ratios and Dissolved U

Seven sites were sampled for analysis of dissolved and particulate uranium. These were chosen to determine if there was a relationship between rock types being weathered and the activity of U^{234}/U^{238} and dissolved U concentration. The sites sampled therefore included the silicate and carbonate type streams (RV-1 and SR-11) and the West Branch of the Susquehanna River where it is massively affected by mine drainage (SR-5a). Also sampled were Pine Creek (SR-8), the West Branch of the Susquehanna River at its mouth (SR-13a), the Juniata River (SR-15) and the Susquehanna River near the mouth (SR-17). Samples were collected in January 1974, March 1974 and June 1974. The data for dissolved uranium concentration and the U^{234}/U^{238} activity ratio are shown in Table VI-1. The data for the type streams show an activity ratio of 1.45 ± 0.25 and 0.004 dpm U^{238}/ℓ for the Driftwood Branch (RV-1), an activity ratio of 2.05 ± 0.11 and ∿ 0.080 dpm U^{238}/ℓ for Buffalo Creek (SR-11) and an activity ratio of 1.27 ± 0.04 and 0.115 dpm U^{238}/ℓ for mine drainage (SR-5a).

The concentration of dissolved uranium appears to be related indirectly to the rock type weathered since it is related to the total dissolved solids content of the streams analyzed. The data for total dissolved solids (tds) for the sites sampled is included in Table VI-1. It appears that in the surface water and ground water of the Susquehanna the uranium concentration is dependent on the amount of rock dissolved.

The U^{234}/U^{238} activity ratios for the SR-11 data (Table VI-1) are distinctly different from the other two type streams. The recoil mechanism for generating excess U^{234} in solution predicts that the amount of excess U^{234} in solution is dependent on the length of time the water is in contact with the rock as Kigoshi (1971) has shown that the build-up of Th^{234} in the interstitial fluid between the U^{238} containing mineral grains is time dependent. Therefore, the longer the residence time of a ground water, the higher its excess U^{234} concentration should be. Kronfeld (1974) has presented substantial evidence to support the recoil hypothesis in natural systems. His data for deep wells in a sandstone aquifer show that the uranium activity ratio increases dramatically down dip as the age of the water increases. On this basis the ground water source of Buffalo Creek (SR-11) has a longer residence time than the others.

The streams sampled for uranium have previously been ranked in terms of residence time of the ground water comprising the stream flow (Chapter III; Type Streams, flow duration curves). The Driftwood Branch, which drains the silicate sedimentary rocks of the Appalachian High Plateau, contains water with the shortest residence time for ground water. On the other hand, Buffalo Creek and other streams draining carbonate terranes contain water with the longest mean residence time as ground water. The mine drainage water has an intermediate residence time by comparison.

The uranium concentration plotted against the Ca concentration (as an index of total dissolved solids and rock weathering) (Figure VI-1) shows a very interesting trend. The type water samples (RV-1, SR-11 and SR-5a) lie along a straight line. This indicates that the uranium-238 concentration in the ground water is directly related to the amount of rock material dissolved. It was shown in a previous chapter (III) that the water flowing in the river or a major tributary has a composition that is a linear combination of the type waters represented above (Figure VI-1) having different uranium concentrations. Consequently, the water collected from the Susquehanna river and tributaries should also lie on the mixing line defined by the type waters.

The data for site SR-13a (at the mouth of the West Branch) and SR-17 (at the mouth of the Susquehanna River) lie well below the mixing line in Figure VI-1, which implies that uranium has been removed from solution in these samples.

Particulate Uranium

The source of the suspended sediments in the river and its tributaries is the soil and rock of the drainage basin. Data for uranium in numerous soil profiles reported by Rosholt et al. (1966) show that while U concentrations are greater in the upper part of the profiles, there is no pronounced enrichment of U^{234} relative to U^{238}. Therefore, the U^{234}/U^{238} activity ratio for soil material is 1 or less but generally not less than 0.90. Similarly, Kharkar et al. (1974) report on the uranium content of a forest soil from the Hubbard Brook Experimental Forest of New Hampshire and show that while there is enrichment of uranium in the organic layers of the soil, the U^{234}/U^{238} activity ratios are essentially unaltered. The uppermost horizon of two of the soil profiles collected for this study were analyzed to determine whether U^{234}/U^{238} activity ratios of > 1 were associated with the organic matter of soils. The data (Table VI-2) show that the U^{234}/U^{238} activity ratios are not significantly different from 1.

Since the source materials for sediment have U^{234}/U^{238} activity ratios of 1 or less, the river sediment should have similar ratios. In fact, when the river has a high sediment load, the activity ratio of U^{234}/U^{238} in the suspended matter is somewhat less than 1 as the data for the Susquehanna River at Northumberland for March 1974 indicate (Table VI-3).

The remaining sediment data represent samples collected at periods of low suspended sediment compared to flood flow. In these samples the U^{234}/U^{238} activity ratio is $\sim$ 1.2 to 1.3 (Table VI-4).

Because there is no source of primary sediment with activity ratios greater than 1, the ratio must be due to the removal of uranium from solution onto the particles. Enough of the dissolved uranium enriched in U^{234} must be added to increase the ratio of the observed value. The concentrations of uranium in the suspended sediment seem to be compatible with this hypothesis.

The dissolved uranium data shown in Figure VI-1 together with the particulate uranium data discussed above strongly imply that removal of uranium from solution onto the suspended sediment occurs. The particulate data indicate that removal occurs to some degree even in the type streams, although this cannot be very efficient since the dissolved data lie on the mixing line. On the other hand, the process is much more efficient in the main river. These samples which show removal were taken at points where the processes of Fe and Mn precipitation have occurred upriver. As discussed previously, Mn precipitation probably occurs throughout the Susquehanna River below the confluence of the two main branches at Northumberland. The Juniata River site (SR-15) was sampled only in June 1974 and is included in Figure VI-1. From previous arguments it is clear that the Juniata River is much like the Susquehanna River except that it is much less affected by coal mine drainage which injects large amounts of Fe and Mn into the system. Therefore, the comparison of the Juniata River site (SR-15) to the site at the mouth of the Susquehanna River (SR-17) should indicate whether the removal of uranium is related to the higher flux of Mn in the Susquehanna or can occur in rivers like the Juniata without major mine drainage injection. Unfortunately, the data for both sites in June 1974 fall only slightly below the mixing line of uranium from type waters. The particulate data are not of much use in posing a solution in this case. The activity ratio of U^{234}/U^{238} in the suspended sediment in the Susquehanna River (SR-17) is 1.24 ± 0.06 while that in the Juniata River (SR-16) is 0.98 ± 0.04. In June 1974 the suspended load of the Juniata River was higher than that of the Susquehanna as the result of a storm in this sub-basin. As was shown above, with higher sediment loads the activity ratio of U^{234}/U^{238} tends towards 1 or less, making direct comparison of data at different sediment loads impossible.

It is not possible to tell whether removal of uranium at the mouth of the Susquehanna is more efficient than removal of uranium at the mouth of the less-processed Juniata River. A definitive test should be provided by analysis of Juniata River water collected at the same time (January and March, 1974) as when the samples of the Susquehanna River at the mouth show pronounced removal.

Thomson et al. (1975) have shown that uranium is lost from the surface sediment of central Long Island Sound relative to sediment deeper in the core. They attribute this uranium mobility out of the sediment to oxidative processes which occur in the upper 10 cm as the result of bioturbation. Benninger (1976) has shown that the sediment being supplied to Long Island Sound is higher in uranium than the sediment accumulating there. This implies a loss of uranium in the water column or perhaps as a very near surface sediment. Furthermore, deep-sea sediments (Bertine et al., 1970) are depleted in uranium relative to the stream-supplied material. The near shore and deep-sea particulate uranium data all imply a loss of uranium from stream-borne particles at some time after their encountering sea water.

Part of the uranium in river sediment may be in relatively labile sites. The data presented for the Susquehanna River show that the uranium is removed from solution into the sediment, probably by Mn and Fe hydroxides. The enrichment of uranium in the organic layers of the soil and the erosion of this material as suggested by the Pb^{210} data indicate that 25% or more of the uranium in stream sediments is tied up in the organic matter. Estaurine processes that act to destroy or alter either the Fe and Mn oxides or the terrestrial organic matter could release uranium from the sediment.

Sea water is much higher in carbonate alkalinity than are fresh water rivers. Kolyadin et al.(1960) have shown that the uranium carbonyl complex is the stable form of uranium in sea water. The profound change in alkalinity, as well as the increase in ionic strength when stream sediments encounter sea water, would favor the release of labile uranium. It is also possible that plankton feeding on river-borne organic matter would help release uranium.

In addition to the dissolved uranium delivered to the oceans by streams, the evidence indicates that part of the particulate uranium load is also contributed to the soluble uranium in sea water. If this is, in part at least, uranium absorbed during stream transport, the uranium released should have a U^{234}/U^{238} activity ratio similar to the ratio of stream water dissolved uranium.

The cycle of removal of uranium in streams and release from the sediment in estuaries suggested by this work and others may also apply to metals such as chromium and molybdenum. This cycle should be considered both in relation to the supply of these metals to the oceans by streams and in relation to environmental questions in regards to disposal of these metals.

TABLE VI-1. DISSOLVED URANIUM, CALCIUM AND TOTAL DISSOLVED SOLIDS (tds)

	January 1974				March 1974				June 1974			
	$\left(\frac{U^{234}}{U^{238}}\right)_{AR}$	U^{238} dpm/ℓ	Ca^{++} mg/ℓ	tds mg/ℓ	$\left(\frac{U^{234}}{U^{238}}\right)_{AR}$	U^{238} dpm/ℓ	Ca^{++} mg/ℓ	tds mg/ℓ	$\left(\frac{U^{234}}{U^{238}}\right)_{AR}$	U^{238} dpm/ℓ	Ca^{++} mg/ℓ	tds mg/ℓ
RV-1					1.37±0.17	0.004	4.0	29	1.54±0.26	0.004	4.3	21
SR-5a					1.26±0.04	0.090±0.004	20.8	155	1.28±0.04	0.135±0.006	32.1	245
SR-8					1.43±0.10	0.013±0.001	6.4	46	1.22±0.11	0.016	8.6	59
SR-11					2.09±0.11	0.061±0.004	18.4	119	2.01±0.11	0.107±0.008	21.1	141
SR-13a	1.79±0.21	0.016±0.002	13.3	89	1.53±0.09	0.018±0.001	16.5	110	1.68±0.12	0.033±0.002	20.4	136
SR-15					-	-	-	-	1.66±0.08	0.072±0.004	20.0	137
SR-17	1.31±0.09	0.032±0.002	16.1	105	1.74±0.10	0.024±0.001	17.1	114	1.32±0.07	0.094±0.006	25.8	174

TABLE VI-2. URANIUM IN SOIL TOPS

	$\left(\frac{U^{234}}{U^{238}}\right)_{AR}$	U dpm/gm ash
CF-1	1.01 ± 0.04	2.89 ± 0.11
SM-1	1.04 ± 0.07	1.49 ± 0.08
Oak tree wood	1.03 ± 0.19	-

TABLE VI-3. URANIUM IN SUSPENDED SEDIMENT AT HIGH SEDIMENT LOADS

	$\left(\frac{U^{234}}{U^{238}}\right)_{AR}$	U^{238} dpm/gm
SR-17 October 1973	0.81 ± 0.09	
SR-13a March 1974	0.92 ± 0.02	4.14 ± 0.17

TABLE VI-4. URANIUM IN SUSPENDED SEDIMENT AT LOW SUSPENDED SEDIMENT LOADS

Site	January		March		June	
	$\left(\frac{U^{234}}{U^{238}}\right)_{AR}$	U^{238} dpm/gm	$\left(\frac{U^{234}}{U^{238}}\right)_{AR}$	U^{238} dpm/gm	$\left(\frac{U^{234}}{U^{238}}\right)_{AR}$	U^{238} dpm/gm
RV-1			1.07 ± 0.08	3.37 ± 0.23		
SR-5a			1.05 ± 0.07	3.16 ± 0.22	1.81 ± 0.42	5.78 ± 1.20
SR-8			1.26 ± 0.10	5.92 ± 0.46	1.27 ± 0.10	6.10 ± 0.47
SR-11			1.18 ± 0.04	2.89 ± 0.12	1.06 ± 0.04	2.69 ± 0.15
SR-13a	1.07 ± 0.03	5.33 ± 0.21			1.27 ± 0.07	3.49 ± 0.25
SR-15					0.98 ± 0.04	2.92 ± 0.02
SR-17	1.06 ± 0.08	3.55 ± 0.26	1.22 ± 0.05	4.60 ± 0.28	1.24 ± 0.06	4.26 ± 0.27

FIGURES

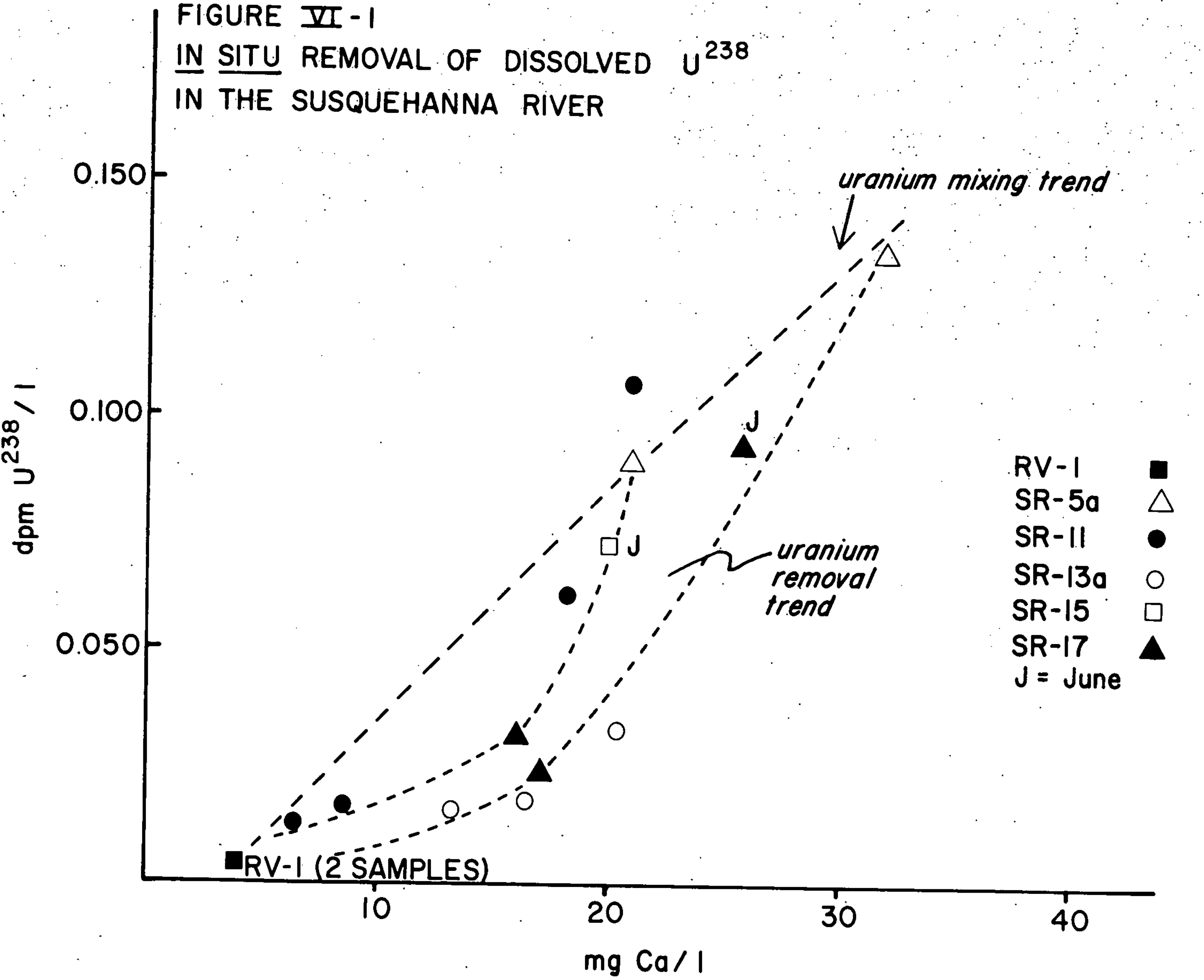


FIGURE VI-1

IN SITU REMOVAL OF DISSOLVED U^{238} IN THE SUSQUEHANNA RIVER

VII: SUMMARY AND CONCLUSIONS

The composition of a stream is closely related to the geology of the area drained by the stream. In fact, streams which drain a single general rock type such as silicate sedimentary rocks or carbonate rocks have a constant concentration (within a 10% range) of ions, while discharge ranges by two orders of magnitude. The conclusion drawn from this data is that at all times (with the possible exception of extraordinary floods such as Agnes 1972 which were not included in this study) the water flowing in a stream is from the ground water system. The increased discharge during flood flow is from increased flow of ground water into the stream and is not from overland flow or a shallow, near-surface, horizontal, subsurface flow.

The changing composition of large streams and the Susquehanna River with variations in discharge is the result of differences in the unit hydrographs of the streams draining areas of different rock types. Silicate terranes are characterized by unit hydrographs with relatively narrow basal widths and large peak discharge for a given storm, while streams draining carbonate terranes and mine drainage areas have unit hydrographs with larger basal widths and smaller peak discharge for the same storm. Consequently, with the onset of flood flow the increase in discharge is dominated by drainage from silicate streams, which results in a dilution of most dissolved species since the silicate streams are the most dilute type water. This dilution is not due to direct rain water addition.

Because the source of water to streams is from ground water sources, the elements most likely to be affected by reactions in the streams are those susceptible to a change in oxidation state. Ground waters are generally more reducing than surface water, so elements such as iron and manganese can be supplied to streams in the soluble form and then precipitate to hydroxides.

The major ions were also used in a discussion of total denudation rates. It was concluded that the ratio of chemical weathering rates of silicate:carbonate:mine drainage areas was 1:21:46. However, it was also seen that present day erosion rates for silicate and carbonate areas were about the same. With increasing elevation above sea level the rate of erosion increases, so in the past a somewhat higher elevation would increase erosion rates of all areas to the point where chemical weathering would be a small part of the total denudation rate and the total denudation rates of silicate and carbonate areas would be comparable. It was also concluded that present day erosion rates can be considered to represent geological processes if care is exercised to eliminate the sometimes huge local perturbations of man on the sediment load of streams.

The study of manganese and iron in the Susquehanna River system has been very useful. It was possible to study the rate of removal from solution (< 0.4 μm) of these elements introduced by mine drainage after neutralization of the sulfuric acid and adjustment of the pH to 6.5 to 7.0 by natural processes had occurred within the river. The study of manganese precipitation kinetics shows that the rate constant in the field is about 10^3 times greater than predicted from Morgan's (1964) laboratory work. In addition, the removal mechanism can be represented as a first order process in the river study. These findings can be explained in terms of Morgan's (1964) proposed autocatalytic rate law by imposing a large initial catalytic term due to surface other than the precipitation-produced manganese oxide. These other catalytic surfaces are probably iron and manganese oxides in the suspended sediment, organic matter, inorganic minerals and manganese-oxidizing bacteria.

The kinetic experiments for iron at the above pH values yield a first order rate constant consistent with laboratory experiments of Stumm and Lee (1961).

From data in streams unaffected by mine drainage it is shown that there is a flux of dissolved manganese into the streams in the ground water which then precipitates. While the data for iron in this system does not prove a supply for it, a similar supply of iron and precipitation in the stream can be expected.

Jar experiments with bottom sediment from several sites in the Susquehanna River system provide qualitative evidence for a flux of iron and manganese from the bottom sediment of the river into the water column above. A recent study of interstitial waters in river bottom sediments of the White Oak River, North Carolina, shows high ($\sim$ 5 ppm) iron in the pore waters (Goldhaber and Martens, 1975--personal communication). The same study also shows the formation of iron sulfide in sediments with zero salinity pore waters. These data indicate that the interstitial waters of river bottom sediment may be an important source of dissolved iron and manganese to the river water by diffusion, bioturbation or current mixing, while the presence of sulfide should suppress the movement of trace metals.

The manganese data indicate that mine drainage dominates the variation of manganese seen at the river mouth. While natural supply seems to mimic the reaction seen with the mine drainage-introduced manganese, it is on a much more subdued level.

Lead-210 has been used as a tracer to study the fate of trace metals delivered to soils and trace metals in ground water and streams. The study of soils shows that they are virtually 100% efficient for Pb^{210} scavenging. Furthermore, it is probably soil organic matter which is responsible. Therefore, the Pb^{210} in soils can only be removed from the system by erosion of the soil material. From a mass balance calculation of the amount of the standing crop of excess Pb^{210} transported out of the basin, a mean life of 2000 years has been calculated for metals similar to Pb^{210} in soil profiles.

The low concentration of Pb^{210} in ground waters, and consequently in the streams of the region, provides a low background framework within which a spike of Pb^{210} in mine drainage can be studied. From these studies it was concluded that at pH 4 Pb^{210} is not removed from solution by ferric hydroxides relative to the river flow rate. However, at pH of 6.5 to 7 it was shown that the removal of Pb^{210} from solution has a half time of < 1 day when calculated as a first order process and that removal occurs at rates consistent with this finding during all seasons of the year studied.

The amount of dissolved U^{238} in streams is related to the amount of rock weathered since the U^{238} concentration correlates with total dissolved solids or an index of rock weathering such as calcium. On the other hand, the U^{234} in solution is dependent on the residence time of the stream water as ground water because the mechanism responsible for U^{234} mobility in rocks, recoil from U^{238} decay, is a time dependent function. The $\frac{U^{234}}{U^{238}}$ activity ratio of dissolved uranium is due to a combination of the above phenomena, with the ratio of the uranium in the water resulting from both U^{238} dissolved from the rock and U^{234} ejected in part by a recoil related mechanism.

The dissolved and particulate uranium data show that in the Susquehanna uranium is removed from solution onto the suspended sediment. The data for the Juniata River indicate that removal may also occur in a river without the mine drainage inputs that the Susquehanna receives. Therefore, uptake of uranium in stream sediments may be a natural phenomenon and would contribute to the soluble uranium delivered to the oceans.

All the sections of this study combine to provide a model for trace metal behavior in rivers. Tributaries receive their water from the ground water system and contain some dissolved iron and manganese which precipitate in the streams. Due to the rates of reaction demonstrated for manganese as well as for iron, most of these metals may be precipitated by the time the water flows into the main river which has only minimal ground water input compared to the tributary flow. But it was demonstrated that fine-grained bottom sediments in the river are probably a source of dissolved iron and manganese which move into the river water and precipitate. The flux of manganese in the Susquehanna is greatly influenced by mine drainage and can be detected from manganese concentrations in suspended sediment alone. Data for numerous east coast rivers show high manganese concentrations in suspended sediment (Turekian and Scott, 1967) even for rivers not affected by mine drainage. Therefore, the production of fresh manganese hydroxides in some of these rivers may be a natural phenomenon on a very pronounced level. This, however, requires further study.

The biological activity within the river results in constant production of organic matter, which undoubtedly has some capacity for sequestering trace metals. In addition, the erosion of soil profiles introduces solid organic materials demonstrated to be excellent trace metal scavengers into the river.

The system envisioned is a dynamic one within which there is constant production of materials (iron and manganese hydroxides and organic matter) capable of sequestering trace metals. Therefore, if they are not saturated with metals, the metal concentrations in solution will show no relationship to the particulate trace metals. In fact, Kharkar et al. (1968) concluded that there was no relationship between dissolved trace metals in several rivers and either the concentration of the same metals in the suspended sediment or the total sediment load of the metals reported on the same sediments (Turekian and Scott, 1967). Consequently, while laboratory experiments defining trace metal absorption isotherms may show which phase the metals favor, the dynamic system with abundant fresh surfaces will prevent the type of equilibrium distribution envisioned by these studies. It also demonstrates why an isotope such as Pb^{210} may indeed be a tracer of a whole group of elements in the natural system even though the <u>in vitro</u> chemistry of lead is different in detail from the other heavy metals.

This study serves as the basis to discuss two other general problems related to trace metals in rivers and their supply to the oceans. Schubel (1972) suggested that the seasonal variation in dissolved iron and manganese and particulate manganese, copper, nickel and zinc was due to the natural process of annual vegetative decay. In the manganese section of this thesis it was shown conclusively that the manganese variation at the mouth of the river is an interplay of the source of supply, rate of manganese precipitation and river flow velocity. And the source for manganese causing these variations is clearly acid mine drainage from coal mining. It is also clear that mine drainage is high in most trace metals (Hollyday and McKenzie, 1973; Gang and Langmuir, 1974) which must be removed from solution in the same manner as the Pb^{210} and some of the uranium, thereby explaining, in part, the high trace metal concentrations observed for Susquehanna River suspended sediment (Turekian and Scott, 1967; Schubel, 1972). The seasonal variation observed below Conowingo for total particulate trace metals is due mostly to increasing sediment concentration with increased discharge.

The study of natural areas unaffected by mining shows that the soils are very efficient trace metal traps. The stream water must first pass through the ground water system and is consequently low in metals. The only way in which metals are moved from the terrestrial environment to the oceans is by erosion in rivers like the Susquehanna. There is then no natural pulse of metals from decaying vegetation.

Schubel (1972) and, more recently, Troup (1975) have criticized estimating the flux of trace metals from rivers by using a single sample. However, it is possible to make an adequate estimate if a proper sample is taken. The trace metal load of a stream is almost completely in the sediment. The Pb^{210} and uranium data indicate that a sample collected during high flow best represents the sediment being transported by the river without major in-river modification. Also, the sediment transported at high flow generally accounts for more than 80% of the sediment transported by a stream due to the discharge-sediment concentration relationship (Leopold and Maddock, 1953). Therefore, to estimate the flux of a trace metal the concentration of that metal in the sediment at high flow multiplied by the total sediment flux gives the trace metal flux.

APPENDIX I. SAMPLE IDENTIFICATION

MARKERS:SAMPLE SITE AND TIME OF SAMPLING

The sample identification markers for identifying the sample sites are unambiguous. The first prefix indicates the sample region (or primary locator symbol).

1. SR = Susquehanna River basin; the SR is the first part of the sample number and is the primary locator.
2. RV = Rich Valley sample area; this is a primary locator symbol of equal meaning as the SR above. The Rich Valley drainage is in the Susquehanna drainage basin, but the sampling was started after the river stations had been numbered so it was thought to be more logical to establish this new identifier for these samples.

The second part of the identification marker consists of the sample site number. However, this is somewhat confusing because the usage of the third indicator (time of sampling) was changed mid-way in the sampling from a prefix to the sample site number to a hyphenated third part of the identification marker. The sample site numbers were assigned originally to the first seventeen sites sampled in April 1973, starting near the headwaters of the West Branch of the Susquehanna River (WBSR) and proceeding down river to Conowingo near the mouth of the river. Subsequently it was found that new sample sites had to be occupied. Rather than continue on with consecutive numbers for what would be scattered sample site locations, the new sample sites were identified by adding a lower case letter suffix to the site number nearest to the new site or to the site number which was of a similar type:

Example -

Original Site Location	Site #	Sited Added Later	Site #
WBSR Karthaus	SR-5	WBSR, Keating	SR-5a
		Sinnemahoning Cr., Keating	SR-5b
Clearfield Creek	SR-4	Moshannon Cr.	SR-4a

The third part of the sample identification marker indicates the time of the field trip on which the sample was collected. As indicated above, this usage is somewhat confusing because the most logical placement of this indicator became apparent mid-way in the sampling. These time indicators are letter (or letter plus number) abbreviations for the month (and year) during which sampling occurred. For four months, June, August, and October-November, 1973, January 1974 the time indicator is prefixed to the site number (e.g., SR-J1 for SR-1, in June 1973). Later it became apparent that it would be better if the primary locator and sample site # (e.g., SR-1) were left the same each time, and the time indicator was added as a third part of the number (e.g., SR-2-Mr). There are two problems with using the time indicators as a prefix to the sample site #.

1. It would appear that SR-J8 was a different site than SR-8-Mr when in fact they differ only in time of collection.
2. For the sampling period of October-November 1973 the time abbreviation, 0, prefixed to the site number can be

misinterpreted to be a number rather than a monthly indicator (e.g., SR-08 is not SR-zero-eight but is SR-8 collected on the October-November 1973 trip).

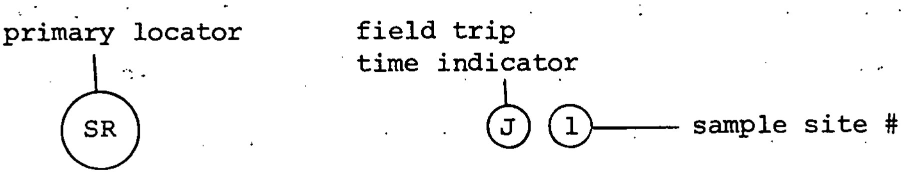
The field trip time of collection indicators are shown in the following table with examples of each.

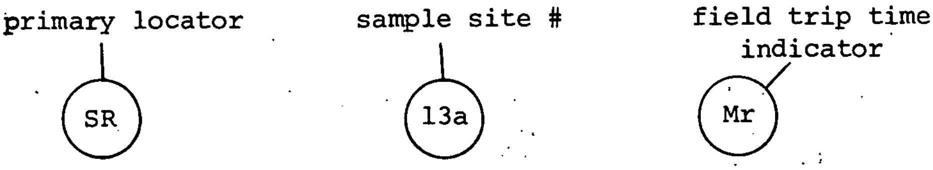
Month of sampling field trip	time indicator abbreivation	example
April 1973	no indicator**	SR-1
June 1973	J	SR-J1
Aug 1973	A	SR-A7
Oct-Nov 1973	O	SR-O8
Nov 1973	N	RV-1-N
Dec 1973	D	RV-1-D
Jan 1974	Ja(JA)*	SR-Ja*
March 1974	Mr	SR-2-Mr
April 1974	Ap	SR-13a-Ap
June 1974	Jn74	SR-8-Jn74

* In January 1974 both Ja and JA were used as a time indicator; they are equilvalent.

**In April 1973, the first trip, the need for time indicators was not yet apparent.

An actual example of the sample identification markers are the following:





APPENDIX II. SAMPLE FRACTION IDENTIFICATION:
47 mm NUCLEPORE AND 47 mm GELMAN FILTERS

At each sample site (excluding spring sites for which only unfiltered water was collected) samples for sediment mass and chemical composition were collected on 47 mm, 0.4 μm pore diameter Nuclepore membrane filters and 47 mm Gelman glass fiber filters (not bonded, pre-ashed in the lab) rated at a nominal pore size of 0.45 μm diameter.

Initially there was one Millipore, in line 47 mm filter holder for sample collection with the 47 mm Nuclepore membrane filters. This holder was used only for the membrane filters. At most sites two filters were used to collect sediment samples. Later, in the lab, samples collected this way were arbitrarily marked S1 and S2. However, each filter container is marked with the volume of water filtered so that their relative spacing and time of collection can be determined from the field notes.

Subsequent to the early sampling two 47 mm in line filter holders were obtained for use with the membrane filters. Each holder was used for one filter at each station. The filter holders were numbered B-1 and B-2. Starting in October 1973, this setup was used and the 47 mm Nuclepore membrane filters were marked BF-1 and BF-2 in accordance to which holder they were used in and not according to their relative spacing in time, although generally 1 was taken before 2. The F in the indicator BF-1 or BF-2 was used only in October 1973. Later samples were designated as B-1 or B-2 according to which filter holder they were used in. Therefore, in terms of collection procedure and identification BF-1 = B-1 as they were collected in the same holder, and similarly BF-2 = B-2.

In use, these identifiers were added to the previously discussed (A-I) sample identification marker (e.g., SR-8-Mr B-1 is a 47 mm Nuclepore membrane filter sample collected at Pine Creek in March 1974).

The identification marker for the 47 mm glass fiber filters is quite similar to the above. Initially there was only one holder and two samples were collected. Therefore, they are arbitrarily marked 1 and 2 for lab analytical purposes. As above, their relative spacing and time of sampling can be retrieved from the field notes by the volume filtered marked on the filter container (60 mm plastic petri dish). Then two filter holders for collecting with only 47 mm Gelman glass fiber filters were obtained so that each holder was used for one filter at a site. The holders were marked G-1 and G-2. Therefore, each 47 mm glass fiber filter used in a holder was marked with the number of that holder. As with the membrane filters, G-1 was usually taken before G-2, but the number refers only to the holder which held the filter at a site and not the time relative to other samples that the filter was used. An example of this usage is:

SR-8-Mr G-1 — sample fraction identifier which is a 47 mm Gelman glass fiber filter used to collect sediment on Pine Creek in March 1974.

APPENDIX III. SAMPLE FRACTION IDENTIFICATION: FILTERED WATER, 142 mm MEMBRANE FILTER AND UNFILTERED WATER

The samples collected can be divided according to the original reason for their collection. The first broad category would be those intended for use in the analyses of stable elements or parameters such as Fe, Mn, Al, C, Na, K, Ca, Mg, Cl^-, $SO_4^=$ and alkalinity. The second category consists of those samples whose primary purpose is the analysis of radionuclides such as U^{238}, U^{234}, Ra^{226}, Pb^{210} and Po^{210}.

The stable element sample set includes the 47 mm membrane filters and the 47 mm glass fiber filters described in Appendix II. The set consists of water filtered through 142 mm membrane filters and of the 142 mm membrane filters. For April 1973, 142 mm, 0.45 μm pore diameter Millipore membrane filters were used but were found less suited to gravimetric determination of the sediment than were Nuclepore membrane filters. Therefore, on all subsequent trips only Nuclepore 142 mm, 0.4 μm pore diameter membrane filters were used to collect filtered water. Usually one filter was used to filter both the unacidified and acidified fractions discussed below and the filter container was marked with the approximate volume filtered (usually 3ℓ). During weighing each filter was given a number which was recorded on the filter container (a 150 mm plastic petri dish). This number was recorded in the field notebook during sampling and on the water sample bottles for which the filter was used to filter the water. These filters are not designated in any special way. They have the primary locator id., the sample site number, and the field trip indicator marked on the container. Also, the stream or river name and the geographical location is included on the sample container.

The water filtered through the 142 mm filters was collected in 1ℓ (usually) and 2ℓ sample bottles. The first water filtered was collected in a bottle and was not acidified. The rest of the water filtered was then collected in another bottle containing acid or was collected and then acid was immediately added to the bottle. In April and June 1973 two liter bottles were used for both the unacidified and acidified water fractions, but subsequent to that one liter bottles were used for the unacidified fractions and two liter bottles were used for the acidified water.

The bottles were marked with the primary locator id., sample site number, and the field trip time indicator. In addition, the number of the filter used to filter the water was sometimes written on the bottle. The acidified fraction was marked in a similar fashion, but in addition they are marked acidified and/or with the volume of HCl added. Also, the stream or river geographical location was written on the bottle. As with the 142 mm filters above, no further identification marker has been used.

Radionuclide Set

The radionuclide set includes three basic types of samples. These are:

1. filtered, acidified water and the 142 mm filters used to filter them
2. unfiltered, acidified water
3. unfiltered, unacidified water

The first type of sample was filtered in the field and acidified immediately after filtration (the filtered water was collected in a bottle or bottles containing acid). The filters used were 142 mm, 0.4 μm pore diameter Nuclepore membrane filters, and usually more than one was required at each site sampled. The 142 mm filters were marked with the approximate volume filtered and were marked in the field as a Pb^{210} sample. Therefore, a filter container would be marked:

SR-8-Jn74 Pb^{210}

Also the geographical information for the sample site was written on the filter container. (All of the sediment samples taken specifically for Pb^{210} analyses have been dissolved.)

Unfiltered, acidified samples were collected at most sites for which the above samples were taken. They were either approximately 4ℓ samples or approximately 6ℓ. The ∿4ℓ samples were collected in a 1-gallon polyethylene jug. The ∿ 6ℓ samples were collected in either a 1-gallon jug and a 2ℓ bottle or in three 2ℓ bottles. These samples were labeled in the field with the primary site number and time indicator and as unfiltered. In addition, they were marked as a Pb^{210} sample (e.g., SR-8-Jn 74 unfiltered, Pb^{210}).

For the determination of U, large volume samples were collected. Surface bucket samples of water were dumped into large polyethylene carboys (13 gal.) without filtering or acidifying. The volume of water collected was between 20 and 40ℓ. The carboys were labeled in the field with the primary locator-site number and the time indicator (sample site-time indicator).

While these samples were distinctive as collected, it became obvious that to avoid confusion during analysis and storage of partially analysed sample fractions for future analysis, a further set of modifiers had to be added to identify sample fractions in the lab.

For samples collected in January, March and June 1974, a four-part sample fraction identification code was devised. These are 1) the phase identification to distinguish water and particulate fractions, 2) the volume identification which is the approximate volume of water involved in the original sample, 3) the filtration identification which indicates whether the sample was filtered in the field (ff) or in the lab (lf), 4) the acidification identification. The following table shows the symbols used for each identifier and relates them to the samples collected:

phase id.	volume id.
P = the particulate fraction of the sample	4, 6, 8 used for the samples previously described as sample types 1 and 2 of the radionuclide set

w = the filtered water fraction of the sample	50 used for the large volume samples whose actual volumes ranged from 17 to 40 ℓ but the sample carboy volume was ∿ 50 ℓ

filtration id.	acidification id.
ff = field filtered	fa = field acidified (which was always after filtration for filtered samples)
lf = lab filtered	la = lab acidified (after lab filtration)

Therefore, the sympbols:

phase	vol.	filtration	acidification
P	8	ff	fa

would mean the particulate fraction of an original 8ℓ, field filtered, field acidified sample.

Samples collected in October 1973 were marked with different lab identifiers for analysis. These samples were only of types 1 and 2 and the field acidified, unfiltered samples were analysed without being lab filtered. Therefore there were only three sample fractions; i.e., field filtered water, the particles from the field filtration, and the unfiltered water samples. Therefore, the fractions during analysis were marked as water, sediment (sed.), or unfiltered (unfil.), respectively. While this type of identification could be ambiguous, no other sample fractions (of other sample sets) have been labeled with these identifiers so they are unique.

During laboratory analysis the different fractions of the sample were further identified by the elements contained in the fraction; e.g., SR-8-Mr P8 fffa U is the uranium containing fraction of the particles from the ∿ 8ℓ sample collected at the Pine Creek station in March 1974.

APPENDIX IV. PARTICULATE INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA) ANALYTICAL TECHNIQUE

The activity of the product nuclide resulting from exposing a target nuclide to a neutron flux is expressed by

$$A = N \sigma \phi (1-e^{-\lambda t})$$

where A = activity (disintegrations/time)

N = number of target atoms

σ = neutron capture cross section of target nuclide

ϕ = the neutron flux, #/time

λ = decay constant of the product nuclide

t = time of the irradiation

The count rate obtained from a sample containing the product nuclide is determined by the efficiency of the detecting system, ε, so that

$$C = A \varepsilon$$

where ε will be a function of the counting geometry.

The ratio of the count rates of two nuclides in an irradiated sample is

$$\frac{C_1}{C_2} = \frac{N_1 \sigma_1 \phi (1-e^{-\lambda_1 t}) \varepsilon_1}{N_2 \sigma_2 \phi (1-e^{-\lambda_2 t}) \varepsilon_2}$$

when the isotopes are designated by 1 and 2.

For a given time of irradiation t

$$1-e^{-\lambda_1 t} = k_1 \quad \text{and} \quad 1-e^{-\lambda_2 t} = k_2$$

therefore

$$\frac{C_1}{C_2} = \frac{N_1\ \sigma_1\ \phi\ k_1\ \varepsilon_1}{N_2\ \sigma_2\ \phi\ k_2\ \varepsilon_2}$$

since the neutron flux ϕ is equal for both nuclides

$$\frac{C_1}{C_2} = \frac{N_1\ \sigma_1\ k_1\ \varepsilon_1}{N_2\ \sigma_2\ k_2\ \varepsilon_2} = \frac{N_1}{N_2} K$$

where $K = \dfrac{\sigma_1\ k_1\ \varepsilon_1}{\sigma_2\ k_2\ \varepsilon_2}$

The constant K can be determined experimentally by irradiating standards containing nuclides 1 and 2 and counting them. Since ε is function of counting geometry and k is a function of length of irradiation, a K must be determined for each difference circumstance of irradiation and counting. Once the constant K is determined for an element pair, if the amount of one element is known, the amount of the other element can be caluclated after irradiation and counting under the exact conditions as the standards from the expression

$$N_1 = \frac{C_1}{C_2}\frac{N_2}{K}$$

Therefore if one element in a sample is known, other elements of interest can be determined by using standards to determine K for each element of interest relative to the known element. Hoffman et al. (1974) have shown this to be the case and determine one element by other analytical techniques. In the case of this technique an internal standard is added to each sample as will be discussed below.

Analytical Procedure

The samples analyzed were sediment on 47 mm, 0.4μm pore diameter Nuclepore membrane filters or, in a few cases, on 142 mm, 0.4μm Nuclepore membrane filters. The internal standard was added by pipetting 0.1 ml of an appropriate Yb solution (in dilute HNO_3) onto the center of a 13 mm, 0.4μm pore diameter Nuclepore membrane filter supported on short pieces of glass tubing ∿ 13 mm in outside diameter. The inside diameter was large enough that the drop of Yb solution was free from contact with the tubing. Several filters on the glass tubing were put in a covered glass dish and dried at 105°C in an oven. When dried the 13 mm filters were placed on the sediment-bearing filters to be analyzed. The 47 mm filters were then carefully folded using tweezers so that the sediment side was in and the 13 mm filter was completely enclosed within. Then the filter was pellitized using a stainless steel die with 5 mm bore diameter (Beckman). The resulting pellet was 5 mm in diameter and about 2 mm high, and only rarely did the resiliency of the 47 mm filter result in some "unraveling" of the pellet. The pellets provide very consistent internal sample geometry for counting.

Standards were prepared in an analogous manner. A single aqueous standard solution containing the elements to be analyzed was prepared from commercially available atomic absorption standards. An aliquot of the standard was diluted to provide a choice of standard to duplicate element masses expected in samples. The standard solution was pipetted onto a 13 mm filter on a 13 mm glass tube and dried in an oven at 105°C as described above for the Yb internal standard. A standard pellet was prepared by taking a new, unused 47 mm, 0.4μm

Nuclepore membrane filter and placing a Yb internal standard 13 mm filter and a metal standard 13 mm filter on the 47 mm filter. Then as described for the sediment samples, the 47 mm filter was folded and pelletized in the 5 mm die. The resulting pellet has nearly identical geometry, for counting purposes, as the sample pellets.

After each pellet was made, the die was wiped inside with a cotton swab to reduce cross contamination. Blanks of new 47 mm filters with and without Yb internal standards showed that cross contamination was not a problem for Yb or the other metals when the above procedure was used. The irradiation, counting and data reduction was carried out at the Rhode Island Nuclear Science Center, Narrangansett, R.I. Samples and standards were irradiated for exactly the same length of time utilizing a pneumatic rabbit system, cooled for the same amount of time, and then counted for 13 minutes on a Ge(Li) detector on a Nuclear Data 2200 multichannel analyzer with 4096 channels. The most typical analysis was a ten minute irradiation, 2 minute cooling and 13 minute count. Only one sample was irradiated at a time as only one could be counted within the short period following irradiation due to the short half life of Al^{28} (2.24 min).

The spectra for counts per channel collected by the multichannel analyzer were transferred to magnetic tape at the completion of each count. Utilizing a data reduction program for neutron activation spectra made available to me through the Rhode Island Nuclear Science Center, the peaks and their total counts were obtained.

Using the ratios of the counts in the metal peak of interest to the Yb standard and the experimentally determined K, the amount of that metal can be calculated in the sample. Then from the mass of total sediment, the concentration of the metal can be calculated.

APPENDIX V. MIXING MODEL: WEST BRANCH OF THE SUSQUEHANNA RIVER, KEATING TO LOCK HAVEN

A composition after mixing of the WBSR and Sinnemahoning Creek is calculated as a starting point for dilution of downriver sites.

Mixing of WBSR with Sinnemahoning Creek to get the starting composition

1) $Q_T C_T = Q_1 C_1 + Q_2 C_2$

2) $Q_T = Q_1 + Q_2$

Q_T = mixture below Sinnemahoning Creek

Q_1 = WBSR at Karthaus

Q_2 = Sinnemahoning Creek at Sinnemahoning and First Fork at G. B. Stevenson Dam

dividing 1) by Q_T

$$C_T = \frac{Q_1}{Q_T} C_1 + \frac{Q_2}{Q_T} C_2$$

and dividing 2) by Q_T

$$1 = \frac{Q_1}{Q_T} + \frac{Q_2}{Q_T}$$

1st. $a = \frac{Q_1}{Q_T}$ and $b = \frac{Q_2}{Q_T}$

3) $C_T = a\ C_1 + b\ C_2$

$1 = a + b$

The only unknown is C_T so it can be calculated.

For mixing below Sinnemahoning Creek:

5) $Q_T\, C_{T,Ca} = Q_3\, C_{3,Ca} + Q_4\, C_{4,Ca} + Q_5\, C_{5,Ca}$

6) $Q_T\, C_{T,SO_4^=} = Q_3\, C_{3,SO_4^=} + Q_4\, C_{4,SO_4^=} + Q_5\, C_{5,SO_4^=}$

7) $Q_T = Q_3 + Q_4 + Q_5$

Q_T = total discharge of West Branch at sample site

Q_3 = discharge of the West Branch of The Susquehanna River after the addition of Sinnemahoning Creek

Q_4 = discharge of silicate type water (RV-1) added

Q_5 = discharge of mine drainage (Moshannon Creek comp.) added

$C_{T,Ca}$ = concentration of Ca in the sample at the point of interest

$C_{3,Ca}$ = concentration of Ca in West Branch-Sinnemahoning Creek mixture

$C_{4,Ca}$ = concentration of Ca in silicate type water

$C_{5,Ca}$ = concentration of Ca in mine drainage type water

C_{T,SO_4} = concentration of SO_4 in the sample at the point of interest

C_{3,SO_4} = concentration of SO_4 in the West Branch-Sinnemahoning Creek mixture

C_{4,SO_4} = concentration of SO_4 in silicate type water

C_{5,SO_4} = concentration of SO_4 in mine drainage type water dividing equations 5), 6) and 7) by Q_T and substituting

$c = \frac{Q_3}{Q_T}$, $d + \frac{Q_4}{Q_T}$ and $e = \frac{Q_5}{Q_T}$ results in equations 8), 9) and 10):

$$C_{T,Ca} = c\,C_{3,Ca} + d\,C_{4,Ca} + e\,C_{5,Ca} \tag{8}$$

$$C_{T,SO_4} = c\,C_{3,SO_4} + d\,C_{4,SO_4} + e\,C_{5,SO_4} \tag{9}$$

$$1 = c + d + e \tag{10}$$

Using the measured concentrations of Ca and SO_4 the unknown properties of flow (c, d and e) may be calculated.

APPENDIX VI. MIXING MODEL: WEST BRANCH OF THE SUSQUEHANNA RIVER, LOCK HAVEN TO NORTHUMBERLAND

The starting composition is taken as the West Branch of the Susquehanna at Nisbet (SR-9). The inputs along the river are taken to have the composition of Pine Creek (SR-8) and Buffalo Creek (SR-11). The appropriate equations and definitions are as follows:

1) $Q_T C_{T,Mg} = Q_1 C_{1,Mg} + Q_2 C_{2,Mg} + Q_3 C_{3,Mg}$

2) $Q_T C_{T,SO_4} = Q_1 C_{1,SO_4} + Q_2 C_{2,SO_4} + Q_3 C_{3,SO_4}$

3) $Q_T = Q_1 + Q_2 + Q_3$

where

Q_T = total discharge of sample site

Q_1 = the combined discharge of Bald Eagle Creek, Pine Creek, and the West Branch at Lock Haven

Q_2 = discharge of water added with Pine Creek concentration

Q_3 = discharge of water added with Buffalo Creek concentration

$C_{1,Mg}$ = Mg concentration of WBSR at Nisbet

$C_{2,Mg}$ = Mg concentration of Pine Creek

$C_{3,Mg}$ = Mg concentration of Buffalo Creek

$C_{T,Mg}$ = Mg concentration of WBSR at sample site of interest

C_{1,SO_4} = SO_4 concentration of WBSR at Nisbet

C_{2,SO_4} = SO_4 concentration of Pine Creek

C_{3,SO_4} = SO_4 concentration of Buffalo Creek

C_{T,SO_4} = SO_4 concentration of WBSR at sample site of interest

Dividing equations 1), 2), and 3) each by Q_T and substituting $a = \frac{Q_1}{Q_T}$, $b = \frac{Q_2}{Q_T}$ and $c = \frac{Q_3}{Q_T}$ yields equation 4), 5) and 6):

4) $C_{T,Mg} = a\,C_{1,Mg} + b\,C_{2,Mg} + c\,C_{3,Mg}$

5) $C_{T,SO_4} = a\,C_{1,SO_4} + b\,C_{2,SO_4} + c\,C_{3,SO_4}$

6) $1 = a + b + c$

The unknown parameters are a, b and c.

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