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EFFECTS OF PHOSPHATE FERTILIZER APPLICATIONS AND CHEMISTRY-MINERALOGY OF THE IRON OXIDE SYSTEM ON PHOSPHATE ADSORPTION-DESORPTION BY STREAM SEDIMENTS

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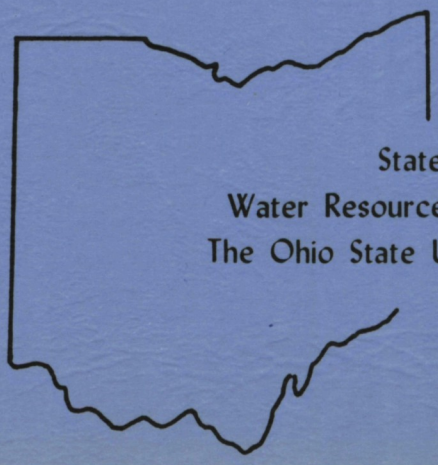

State of Ohio
Water Resources Center
The Ohio State University

FINAL REPORT

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by

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ABSTRACT

Despite geologic, geomorphic, and land use differences, suspended sediments collected from the Muskingum River and its tributaries during spring flooding were remarkably uniform in mineralogy and size distribution. The greatest evidence of regional differences came from Moxahala Creek, which receives acid drainage from abandoned coal mines. As a result, Black Fork Creek, a tributary to Moxahala Creek, was chosen for detailed water quality and bottom sediment studies. Marked increases in dissolved SO_4, Fe, and Al, and decreased. pH were observed in sections of the stream affected by acid mine drainage. In addition, a gelatinous yellow precipitate of iron was abundant in the bottom sediments below sources of pollution. This Fe-oxide or oxyhydroxide precipitate greatly increased surface area and reactivity of bottom sediments and added to the overall sediment load.

A standard P adsorption procedure was proposed and the ability of four laboratories to produce consistent results over a wide range of soils was determined. Soil (0.5 or 1.0 g) was shaken in 0.01 mol L^{-1} $CaCl_2$ at a soil: solution ratio of 1:25 in containers allowing a 50% head space for 24 hours at 24 to 26°C on an end-over-end shaker. Initial dissolved inorganic P concentrations of 0 to 323 μ mol P L^{-1} (as KH_2PO_4 or NaH_2PO_4) were used and microbial activity inhibited by 20 g L^{-1} chloroform. Excellent agreement between the four laboratories was obtained for P adsorbed by the 12 soils studied, with a mean coefficient of variation over all P levels and soils of 0.91%. The laboratories also exhibited a high degree of replication of individual treatments with no laboratory showing a strong consistent bias across all soils and P levels in terms of P adsorption. Langmuir, Freundlich and Tempkin adsorption models were highly correlated with the adsorption data. Respective mean correlations

for the 12 soils were 0.98, 0.97 and 0.95. The proposed method has the potential to produce consistent results which can be used to predict partitioning of dissolved inorganic P between solid and solution phases in the environment.

CHAPTER 1

SUSPENDED SEDIMENTS OF THE MUSKINGUM RIVER BASIN

1.1 Introduction

The Muskingum River Basin of southeastern Ohio occupies approximately 1,753,800 ha and encompasses all or part of 27 counties (Figure 1.1, Table 1.1). It is the largest drainage basin in the state, and it is subjected to a variety of land uses. Currently, agriculture and forestry account for 78% of the land use in the basin, but other forms of regional activity are also economically and ecologically important. For example, localized sandstone deposits are used for glass, foundry, and surface sand, and also account for 53% of the dimension stone used in the state. Since 1802, the ceramics industry has been a profitable business in Ohio, and nearly half the state's clay and 69% of the shale deposits are found in the Muskingum Basin. In addition to ceramics, clay and shale are also used in refractories and cement. Small amounts of limestone are mined within the basin and are used in agriculture, ceramics, construction, and steel making. Finally, the Muskingum River Basin is currently the source of 80% of the coal mined in Ohio, and surface mining accounts for 90% of total production.

1.2 Purpose of the Study

Soil and water management problems within the Muskingum Basin have been recognized for several decades. Excess surface runoff and accompanying soil erosion, sedimentation and flooding have resulted in the development of numerous flood-retarding reservoirs throughout the basin. In addition, land treatment measures such as contour and strip farming, terraces, diversions and

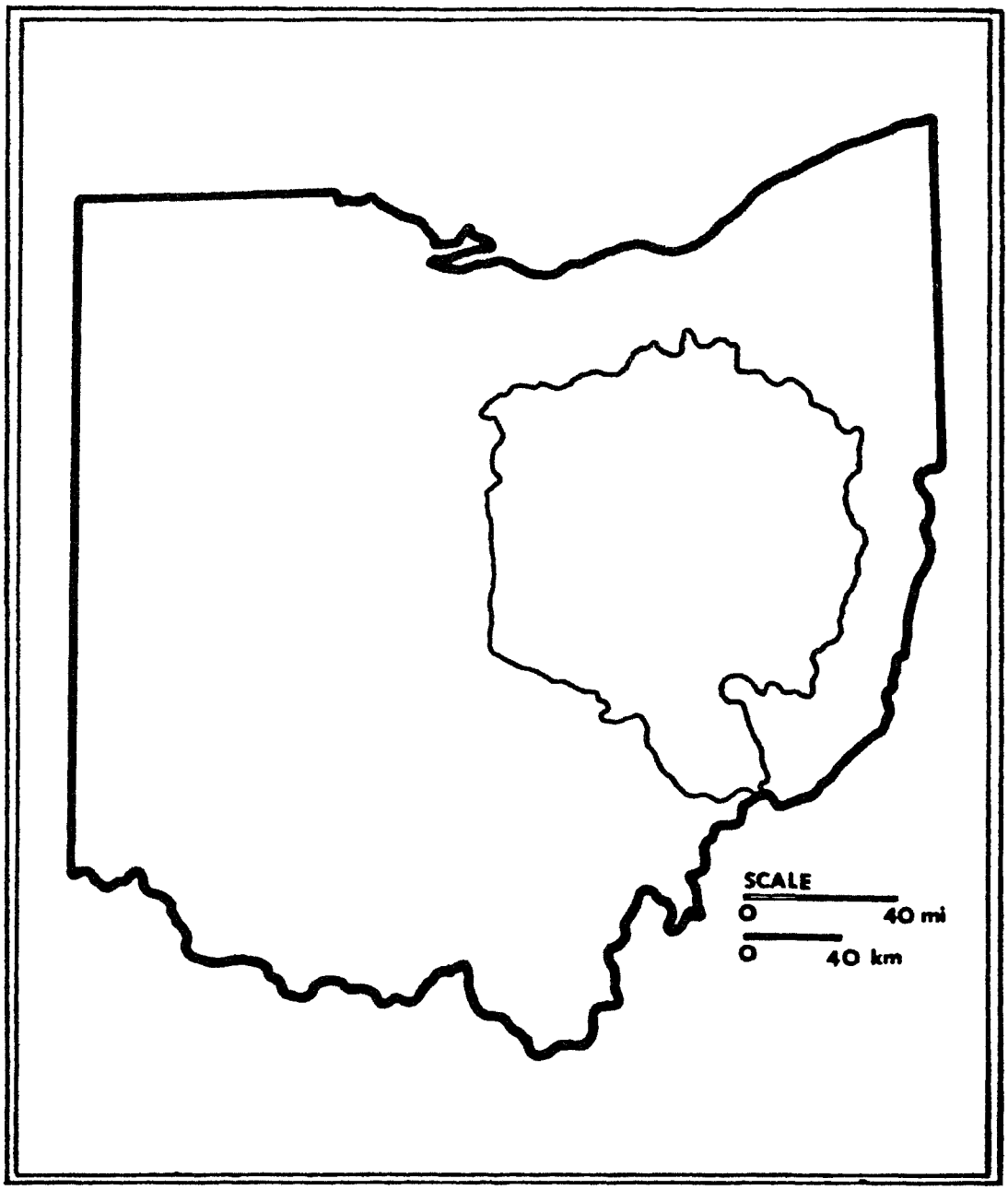

Figure 1.1 Location of the Muskingum River Basin.

Table 1.1 Counties in the Muskingum River Basin (From O.D.N.R., 1968)

County	Square miles in basin	Percent in basin
Ashland	350	82.2
Athens	3	0.6
Belmont	117	21.7
Carroll	314	79.3
Columbiana	52	9.7
Coshocton	563	100.0
Crawford	6	1.5
Fairfield	21	4.1
Guernsey	525	99.2
Harrison	301	73.2
Holmes	424	100.0
Knox	526	98.9
Licking	644	93.7
Medina	144	33.9
Monroe	39	8.6
Morgan	350	83.1
Morrow	140	34.6
Muskingum	670	100.0
Noble	211	52.2
Perry	177	43.2
Portage	2	0.4
Richland	440	88.2
Stark	509	87.6
Summit	156	37.5
Tuscarawas	571	100.0
Washington	222	34.6
Wayne	561	100.0

rotation farming have been actively promoted. Despite these improvements, pollution from municipal, agricultural and industrial sources is still a major problem.

Pollutants originating from municipal and factory wastes are monitored by the Water Control Board of the Ohio Department of Health, and abatement measures are in force. In most cases, time tables for elimination of point-source pollution were established as early as 1970 (O.D.N.R., 1968).

A more extensive problem in the Muskingum Basin is erosion of agricultural lands. It is estimated that 622,965 tons of sediment reach the mouth of the Muskingum annually; however, this accounts for only 2-3% of the average annual gross erosion in the basin (USDA, 1975). The other 97-98% of the sediment causes damage directly by filling lakes, ponds, and channels. This reduces reservoir capacities and also acts to reduce the water carrying capacities of streams. Sediments removed by soil erosion are usually composed of silt, clay, or organic colloids, which can carry nutrients such as phosphorus and potassium, or organic chemicals such as pesticides, adsorbed to their surfaces. These materials may act as pollutants or as nutrients for algae and aquatic plants. Also, sediment and phosphorus are an important cause of accelerated eutrophication of lakes.

A third and very important source of pollution in the Muskingum Basin results from acid coal mine drainage. The Pennsylvanian coals that are mined throughout the basin are generally high in sulfur impurities, such as pyrite (FeS_2). When tailings from surface or deep mines are exposed to air and water, these sulfur compounds are oxidized to form sulfuric acid (H_2SO_4) and dissolved Fe(II). The sulfuric acid may further react with other minerals in the soil or in adjacent spoil banks to dissolve large quantities of calcium, magnesium,

aluminum and manganese which subsequently enter stream systems or groundwaters along with the sulfate and iron.

The purpose of this study was to produce a single, broad inventory of suspended sediments from sites throughout the Muskingum River Basin to determine if sediment properties could be related to differences in geology, land use, or pollution on a regional basis.

1.3 Literature Review

The amounts of sediment, or chemical pollutants that occur in rivers may vary considerably due to such factors as geology, the geomorphology and slope of the land, soil mineralogy, and agricultural, urban, and industrial activities within a drainage basin.

1.3.1 Terrain, Geology, and Soils of the Muskingum River Basin

The Muskingum River Basin lies entirely within the Appalachian Plateau Province, which is characterized by mature, hilly topography (Williams, 1973). A number of geomorphic cycles of uplift and erosion have resulted in a series of erosional surfaces. During the Cretaceous the entire Appalachian area was supposed to have been eroded to base level; however, no evidence of this surface is now found in the Muskingum Basin. During the Tertiary, there were three such uplift and erosion cycles that are still expressed on the landscape, particularly in the non-glaciated portions of the basin.

Bedrock outcrops occur primarily in the eastern and southern parts of the basin and are dominated by shale and sandstone; however, clay, limestone, coal, and conglomerate are also common. These rocks are from the Mississippian, Pennsylvanian, and Permian systems. Pleistocene glacial drift has obscured much of the bedrock in the northern and western parts (Figure 1.2), and glacial outwash is present in many of the major valleys throughout the basin. Most of

Figure 1.2 Wisconsinan and Illinoian glacial boundaries in Ohio.

the existing glacial till in the Muskingum River Basin was deposited during Wisconsinan glaciation. Two principal till sources are identified; one is found in the northwest, is primarily calcareous, and is part of the Indiana and Ohio Till Plain. The other, north-central in location, is non-calcareous, and is part of the Eastern Ohio Till Plain. The two types of till are characteristic of source areas and the underlying bedrock. Illinoian drift, which lies southeast of the boundary of Wisconsinan drift is characteristically a thin, weathered, discontinuous deposit that only slightly modifies the bedrock topography. Outwash and loess deposits, mostly Wisconsinan in age, occur beyond the drift borders.

The basin has also experienced a number of drainage changes as a result of glaciation. The latest preglacial drainage was the Teays River System, which flowed northwestward across Ohio from the vicinity of Portsmouth and into Indiana south of Fort Wayne. Pre-Illinoian glacial advances blocked this westward flowing stream causing ponding and stream reversals. The Wisconsinan glacier caused additional ponding and further modified the drainage to its present form. Evidence for drainage reversals consists of numerous barbed and underfit streams and narrowing of valleys downstream. The Muskingum River itself shows the most dramatic reversal. At Dresden, the valley is 3.2 km wide, but it is only 0.4 km wide near the Muskingum-Morgan County border.

The soils of the basin reflect geologic-geomorphic influences, and a noticeable spacial distribution with respect to soil order exists. Soils on the glaciated surfaces are predominantly Alfisols. Soils in the unglaciated portion of the basin are Alfisols, Ultisols, and Inceptisols.

1.3.2 Erosion and Sedimentation within the Muskingum River Basin

Sediment is defined as solid material which originates mostly from soil or disintegrated rock and is transported by, suspended in, or deposited from water. It can, but does not always include chemical and biochemical precipitates and decomposed organic material, such as humus. Suspended sediment is the sediment that at any given time is maintained in suspension by the upward components of turbulent currents or that exists in suspension as a colloid. The quantity, characteristics, and cause of suspended sediment in streams are influenced by environmental factors as well as man's activity. Some major factors are degree of slope, length of slope, soil characteristics, land use, and quantity and intensity of precipitation.

Previous studies in the Maumee River Basin (Jones et al., 1977) have shown that significant sediment losses occur even in nearly level farmland as a result of surface runoff and subsurface tile flow. The range in topographic relief in the Muskingum River Basin is about 280 m. The highest point within the basin, about 457 m above sea level, and the lowest, about 177 m above sea level, provide ample opportunity for erosion. The U. S. Geologic Survey reported the average suspended sediment load of the Muskingum River at McConnelsville to be 134 mg/l for the 12-month period October, 1977-September, 1978 (U. S Geological Survey, 1978). However, suspended sediments can be as high as 700 mg/l or more during periods of storm flow.

A major factor in sediment production is the entrainment and transport of clay minerals by fluvial action. The size, shape, and chemical properties of clay minerals determine not only their resistance to erosion but also their activity in suspension, and eventually the mineral character of sediments in the suspended or the bed load. When specific minerals are identified in determining the

character of sediments, the possibility of using these same minerals as guides to provenance exists.

1.3.3 Sediment Mineralogy and its Relation to Provenance

Provenance is concerned with origin of sediments. Frequently, a mineral or particular suite of minerals occurring in sediment may be characteristic of a certain source area. Knowledge of the bedrock, recent geologic history, and soil weathering products within the source areas can, in turn, aid in determining the origin of a mineral or suite of minerals many kilometers from the point of entrainment.

Ehlman (1968) indicated that clay mineral assemblages which make up the stream load can originate from three possible sources within a watershed: sheet erosion from the land surface, streambank erosion, and resuspension of materials composing the streambed. It is possible for the stream load to mirror these sources, but the relative contribution of any one of them may vary greatly depending upon such factors as topography of the watershed, history of disturbance, and stream flow.

Schneider and Angino (1980) analyzed suspended sediments from selected rivers in eastern Kansas, and observed that vermiculite was a significant component of samples from rivers draining Pleistocene glacial deposits. Walling et al. (1979) reported that measurements of the magnetic properties of suspended sediments in transit can provide a general indication of the relative importance of slope and channel sources to the sediment yield of a drainage basin, and often can yield specific information on the relative contributions of individual sources during a storm event and on contrasts in the pattern of sediment generation between particular events. Klages and Hsieh (1975), in their examination of sediments transported by the Gallatin River of southwestern

Montana, noted that differences in clay mineralogy due to source area variations could be detected only among smaller tributaries. Knebel et al. (1968) noted that clay mineralogy was a function of distance downstream in their study of tributaries of the Columbia River: montmorillonite was observed to increase while the amount of illite decreased. This trend, however, was attributed to differing mineralogies of soils forming in the source areas of the tributaries. Jones et al. (1977) indicated that illite and quartz were the two most abundant minerals leaving watersheds in the Maumee River Basin of Ohio. They reasoned that the preferential removal of these minerals was related to their relatively low plasticities and low surface charge. Imeson and Verstraten (1981) noted a relationship between electrolyte concentration, exchangeable sodium percentage of soils in source areas, and suspended solid concentrations for drainage basins of a small river in Eastern Australia. Changes in the electrolyte concentrations resulted in an alternation between conditions favoring dispersion and flocculation of the suspended load.

Provenance is also a determining factor in the clay mineralogy of bottom sediments. Sartori et al. (1979) related chloritic intergrades occurring in bottom sediments near the estuary of the Arno River of Italy to chloritic intergrades found in suspended samples of the Arno River and one of its tributaries, and, finally, to the soils and underlying rocks in the tributary basin. Stober and Thompson (1979) reported that magnetite concentrated in the sediments of some Finnish lakes could be related to glacial drift, and that the hematite/magnetite ratio was found to decrease in the progression drift-stream bedload-lake sediment.

Knebel et al. (1968) found that differences in the clay mineralogy of bottom sediments were related to source areas by a number of factors, among

them: size segregation of particles due to preferential erosion and settling, and natural particle size. Pinet and Morgan (1979) indicated that amount of freshwater discharge played an important role in determining the composition of bottom sediments in two Georgia estuaries. For one, associated with a large river, bottom sediments of the river and estuary were similar. The other, with low discharge, seemed to derive much of its sediment from erosion of coastal outcrops. Knebel et al. (1968) found that chlorite and kaolinite components were most concentrated in the sediment near the source river and illite predominated at greater distances from the river. This distribution was attributed to particle size differences. In addition, there seems to be a positive correlation between water velocity and expandable clay mineral content (Berry et al., 1970). Three possible causes for this correlation are: resuspension of the expandable clay components from bottom sediments due to increased shear velocities, greater rainfall intensities which detach and entrain the expandable clay minerals from soil surfaces, and the ability of high velocity water to carry aggregates of expandable minerals.

Finally, chemical weathering of iron, manganese, and aluminum containing minerals can result in the widespread appearance of various metal oxides in the secondary environment (Oades, 1963), of which soils and sediment are a part. These oxides may occur as discrete crystalline precipitates, as near-amorphous coatings on other, larger sediment grains, or as complexes with organic matter. Their surfaces are highly reactive, and they are important scavengers of charged species from solution. Chemical fractionation of secondary oxides into mineral phases and chemical forms is possible through the use of selective chemical extractants (Chao and Theobald, 1976). Consequently, the distribution, type and composition of these oxides in stream sediments can be significant indicators of

both origin and environment of deposition. The value of the iron and manganese oxides to geochemical exploration has, in particular, been recognized (Chao and Theobald, 1976).

1.3.4 Phosphorus and Nitrogen in Soils and Sediments

Critical levels of nitrogen and phosphorus are used to indicate the trophic state of natural waters. These levels are 0.3 μg/ml soluble inorganic nitrogen and 0.003-0.015 μg/ml soluble inorganic phosphorus (Stewart and Rohlich, 1967). The literature suggests that despite an overall greater input of nitrogen into most watersheds, phosphorus is frequently the limiting factor for the growth of biomass in a body of water (Hooper, 1969). For this reason, the greatest emphasis in this discussion of nutrient additions is given to phosphorus.

Until recently, the major source of phosphorus entering most streams and lakes was thought to be phosphates from urban sources, especially laundry detergents. Although urban centers still represent important point sources for phosphorus accumulation in sediments, runoff from agricultural land is receiving increasing attention. The US Army Corps of Engineers (1982) has documented that erosion from agricultural lands is the primary source of sediment into Lake Erie, and that land use activities contribute from a third to a half the total phosphorus load in the Great Lakes. Other researchers (Johnson et al., 1976) indicate that phosphorus increases are due primarily to sewage from urban areas and non-functioning single dwelling septic tanks. In any case, the Muskingum River Basin is largely a rural watershed, and the primary concern is the effect phosphorus as a nutrient addition to agricultural soils will have on the sediments entering lakes and streams.

The more important forms of total P in sediments are determined by both organic and inorganic sources. The two forms are controlled by independent

factors. Organic P is a constituent of organic matter, and the decomposition of organic matter is one way that soluble orthophosphates are released into streams and lakes (Black, 1968; Williams, et al., 1976). However, inorganic P frequently constitutes the major portion of the total P, and is usually in the form of the orthophosphate (PO_4^{3-}) ion. While much orthophosphate enters waterways as adsorbed ions on oxides and hydrous oxides of Fe and Al, and $CaCO_3$, P may also be added in subsurface waters. Johnson et al. (1976), for example, showed that 44% of the total phosphate load in a small stream of central New York was derived from percolating water. Factors which determine the entry of orthophosphate into streams from subsurface flow are volume and intensity of precipitation, rate and type of fertilizer additions, permeability of the soil, and phosphate adsorption properties of the soil.

During the process of erosion and transport of sediment across a land surface, the finer clay is selectively transported (Logan, 1977). Since clay contains a higher concentration of total P than the soil as a whole, the sediment in streams will have an enriched P content compared to the soil from which the clay was removed. This is consistent with observations made by Singer and Rust (1975) that a primary loss of agricultural P comes from erosion of tilled lands. In addition, Sharpley and Syers (1979), in a study of an agricultural watershed in New Zealand, report that surface runoff produced a minor portion of the total stream flow, but it contributed a major portion of both soluble and particulate P compared to other sources. For the small agricultural watershed studied, total P load was 1.48 kg/ha/yr in the suspended sediments. Total P values ranging from 900-2000 μg/g in sediments from the Maumee River have been reported by Green et al. (1978).

Total P has also been associated with the mineral character of sediments. Oloya (1979) stated that higher amounts of total P were generally found in non-calcareous versus calcarous sediments, despite the possibility that native apatite could be present locally as a constituent of the total P eroded from a landscape. Thus, differences in total P may arise in tributaries of a large drainage basin based on the calcareous or non-calcareous character of the soils or geologic materials, such as glacial drift, in a watershed.

Nitrogen losses by soil erosion, like phosphorus, is generally related to organic matter removal. Organic nitrogen removal, or the entrainment of organic matter, is usually significant only during higher soil loss periods (Logan and Stiefel, 1979). Total nitrogen in a stream system is a measure of both dissolved and solid-phase organic and inorganic N. Sediment nitrogen, because it is so closely associated with detrital organic matter, is usually equated with organic nitrogen.

The two most common forms of dissolved inorganic nitrogen in stream waters are NO_3 and NH_4. As a pollutant, NH_4-N is generally insignificant in soil and groundwaters (Terry et al., 1981). However, NO_3-N is found in measurable quantities, and has been used as a primary indicator of nitrogen pollution. Nitrate is naturally formed in soils as a product of the nitrogen cycle, and because of its mobility, is found in groundwater. One of the greatest concerns is the ease with which this ion may be reduced to nitrite and cause methemoglobinemia in babies or nitrite poisoning in ruminants. Considerable controversy reigns as to whether the source of nitrate can be directly related to fertilizers applied to fields. Logan and Stiefel (1979) in a study of the Maumee River Basin, indicated that NO_3-N losses from soil were similar to amounts added by precipitation. However, none of their study sites had received

fertilizer nitrogen, soybeans having been grown on all test sites. Nightingale (1972) noted that NO_3-N contents of both soil water and groundwater were a function of crop type and soil depth, and found that orchards and truck crops were major contributors of NO_3-N. Maximum NO_3-N from these sources was found to be in the range of 46 mg/l in the groundwater. This value exceeds the maximum permissible NO_3-N level of 10 mg/l established by the U.S. Public Health Service for public drinking water. Often of greater concern is the NO_3-N losses from feedlot areas which clearly contaminate groundwaters, and which have been monitored at levels as high as 46 mg/l (Terry et al., 1981).

Thus, P and N can vary greatly in their origins within a watershed. Soluble inorganic P (orthophosphates) is usually the greatest constituent of total P, and total P is generally found in greatest amounts in non-calcareous sediments. Nitrate-N, on the other hand, is closely correlated with agricultural fertilization and feedlot activities. While both P and N may be agricultural in origin, total P in sediments is frequently related to areas of major soil erosion while NO_3-N levels may more readily provide evidence of fertilizer and feedlot (farming) differences within a watershed.

1.3.5 Acid Mine Drainage

Abandoned spoil banks from both surface and deep mines can produce serious water quality problems due to erosion and acid mine drainage. As indicated earlier, many eastern U. S. coal deposits are characterized by high-sulfur contents. Sulfide oxidation produces large concentrations of sulfuric acid and dissolved iron. While spoil banks are not homogeneous in character, it is generally considered that a significant portion of spoil within the eastern coal province has a pH of less than 4 (Berg and Vogel, 1969). Further disintegration and decomposition of minerals is accentuated by low pH (acid attack) (Berner,

1971), and adequate rainfall combined with the general good permeability of spoil materials provide optimal conditions for rapid weathering and leaching. Geologic strata associated with coal seams are of sedimentary origin and may consist of shale, siltstone, sandstone, mudstone, and limestone (Chadwick, 1969). Carbonaceous material is abundant in spoils and makes up the bulk of weight loss when spoil is heated to 600[C (loss-on-ignition). Spoil material is generally slow to decompose and supplies few nutrients for plant growth. Usually more than 90% of the inorganic matter in a strip-mine spoil bank is composed of quartz and clay minerals derived from mudstones and shales. Wiram (1976) observed that clay minerals present in spoil near Latta, Indiana consisted of varying proportions of illite and kaolinite. Also commonly present in the spoils are small amounts of iron and aluminum hydroxides, sulfates, and carbonates. The release of ions in weathering is then a function of congruent dissolution of all the above mentioned components. Subsequent leaching of weathering products results in high amounts of Fe, Al, Mn, Mg, K, Na, H, and SO_4 in receiving streams and groundwaters.

Since hydrogen, carbon, iron, aluminum, and manganese are among the most abundant elements released in acid mine drainage, this inventory of suspended sediments in the Muskingum River Basin included direct or indirect measures of all these parameters to determine if they could be related to regional influences of acid mine drainage.

1.4 Materials and Analytical Procedures

1.4.1 Selection of Field Sites

The headwaters of the Muskingum River originate near the city of Akron, within 40 km of Lake Erie. The river flows south to its junction with the Ohio River at Marietta, Ohio. The total basin is 192 km long and 152 km wide at its

widest point and includes 11 major tributaries. In the late fall of 1979 and winter of 1980, extensive field reconnaissance was done in an attempt to establish sample sites for all the major drainage sub-basins. In most cases, sampling sites were selected near the mouth of each major tributary. Larger watersheds such as the Tuscarawas and the Muskingum were assigned two or more sites (Figure 1.3, Table 1.2). As a result, 16 sites in the basin were chosen as points of collection.

1.4.2 Sample Collection and Preservation

All the suspended sediments were collected over a 12-hr period in March of 1980 during a time of high flow resulting from the spring snow melt and widespread precipitation. High flow was preferred because mixing of sediments is optimal, and it was easier to obtain sediment samples that were representative of eroded materials throughout the basin.

Approximately 57 l of suspended sediment were collected at each site using a 9.5 l bucket suspended by rope over the central part of a bridge. The fastest flow free from stream-bank eddy effects and possible problems with channel erosion is in the center of the stream and, since velocity and discharge data were not a goal of the study, more sophisticated sampling devices were not considered necessary. This reasoning may only be applicable to low-gradient streams and rivers where sediment is mostly a mixture of silt and clay. Once entrained, these materials stay in transport with very small energy input, and mixing of the sediment is optimal at high flow periods.

Upon returning to the laboratory, aliquots of the suspended material were immediately removed for determining total sediment, phosphorus, and nitrogen contents. Then, phenol (0.2 g/l) was added to the bulk sample to control microbial activity, and the sediment was placed in a walk-in refrigerator and

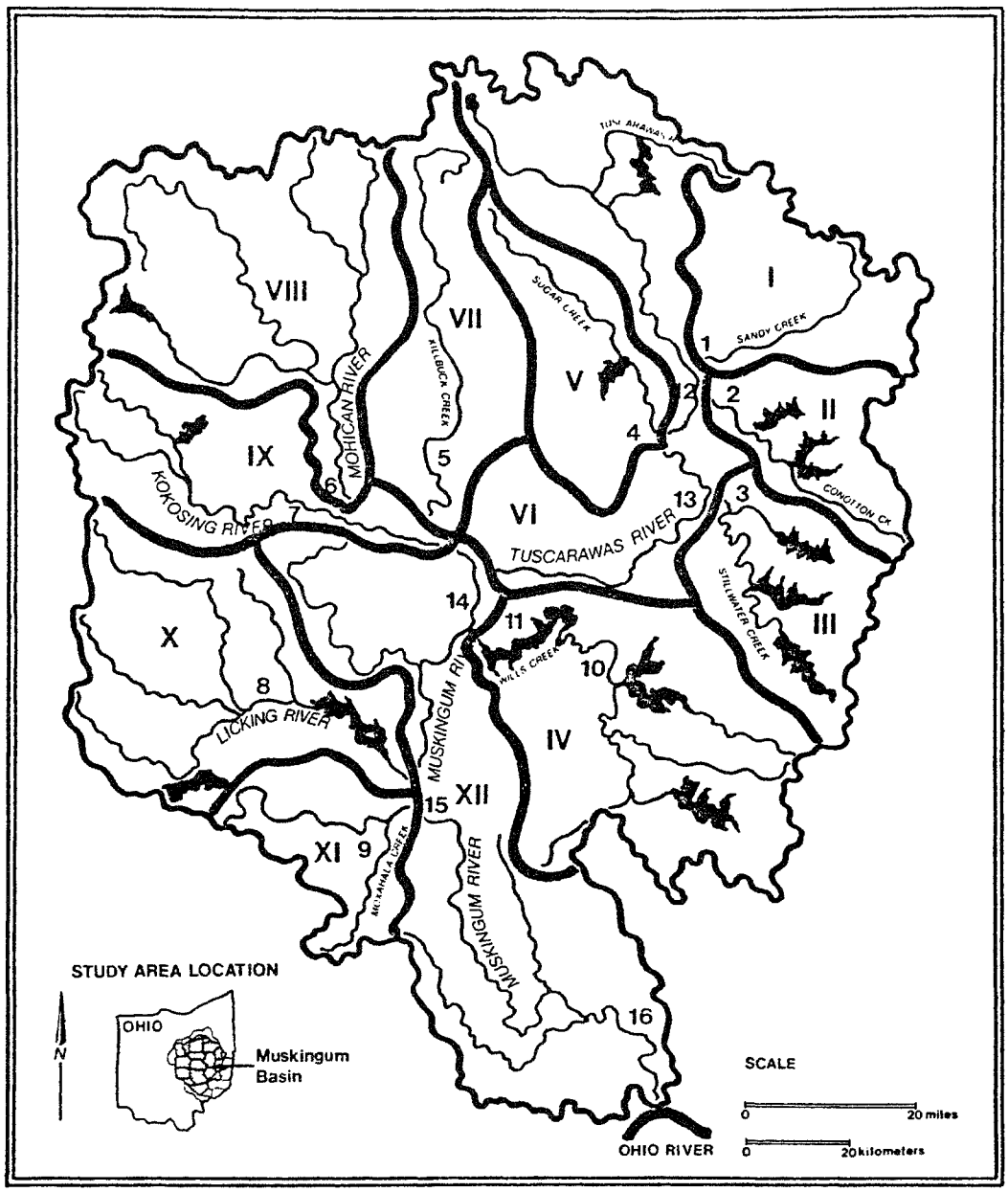

Figure 1.3 Hydrologic sub-basins and sampling locations within the Muskingum River Basin.

Table 1.2 Hydrologic Study Areas of the Muskingum River

Hydrologic Sub-Basin	River or Stream	Approx. Sample Site Town/Location	No.	Drainage Area (sq. ha)
I	Sandy Creek	Sandyville	1	109,800
II	Conotton Creek	Zoarville	2	77,700
III	Stillwater Creek	Midvale	3	122,500
V	Sugar Creek	Strasburg	4	89,400
VII	Killbuck Creek	Killbuck	5	169,400
VIII	Mohican River	Brinkhaven	6	225,800
IX	Kokosing River	Millwood	7	163,200
X	Licking River	Newark	8	196,800
XI	Moxahala Creek	Roseville	9	119,100
VI	Wills Creek	Kimbolton	10	234,100
		Wills Creek	11	
IV	Tuscarawas River	Bolivar	12	246,000
		Gnadenhutten	13	
XII	Muskingum River	Tyndall	14	300,000
		Philo	15	
		Lowell	16	

allowed to settle. Excess water was removed by siphoning, and the sediments were further concentrated by centrifugation at 1500 rpm for 10 min using a Beckman J21B centrifuge and an angle-head rotor. The samples were then frozen in 400-ml polyethylene beakers using a slurry of trichloroethylene and dry ice and freeze-dried in a Virtis lyophilizer. This procedure allowed for estimates of total sediment available for analysis and provided easy storage of dried samples.

1.4.3 Analytical Procedures

The analytical procedures used in this general study of the regional character of suspended sediments in the Muskingum Basin include various physical, chemical, and mineralogical analyses. These procedures are described in detail in the following sections.

1.4.3.1 pH. Measurements of hydrogen ion activity in the stream waters from which the sediments were collected were performed according to standard methods (APHA et al., 1980). Measurements were made using a Corning Research Model 12 pH meter with a combination electrode.

1.4.3.2 Total Sediment Contents. Concentrations of suspended sediment were measured by withdrawing a 50-ml aliquot from the dispersed field sample prior to phenol addition. This 50-ml aliquot was then filtered using a pre-weighed Nucleopore membrane with a pore diameter of 1.0 μm. The sediment retained on the filter was dried at 105° C, and the weight of sediment was determined by difference in weight of the filter before and after filtration.

1.4.3.3 Phosphorus Analysis. Dissolved inorganic phosphorus (DIP) and total phosphorus were determined by separate methods. DIP was determined by passing duplicate 25-ml aliquots of suspended sediment through a 0.45 μm Nucleopore filter. Eight ml of a mixture of L-ascorbic acid and Murphy-Riley

solution (John, 1970) were then added to a suitable aliquot of the filtrate and the samples were brought to a 50-ml volume, stoppered, shaken, and set aside for 30 min for color development. The phosphate levels were measured by photon absorption at 730 nm using a Beckman 24 spectrophotometer equipped with a 1 cm cell and a vacuum sipper.

Total phosphorus was determined using the perchloric acid method of Sommers and Nelson (1972). Aliquots (25-ml) of unfiltered sediment were pipetted into 50-ml digestion tubes. Five drops of concentrated H_2SO_4 were added to each suspension and the samples were evaporated in an oven at 105° C overnight. On cooling, 3 ml of 70% perchloric acid were added, and pyrex funnels were placed atop the tubes to ensure complete digestion. The samples were digested at 203° C for 75 minutes, allowed to cool, and then diluted to 50 ml with distilled water. The tubes were then shaken to mix the contents and left to settle overnight or centrifuged to separate solid residues. Ten-ml aliquots from the clear supernatant solutions were then pipetted into 50-ml tubes and neutralized with 5N NaOH using p-nitrophenol as an indicator. Five ml of L-ascorbic acid solution (previously described) were added, and the solution brought to a final volume of 25 ml. Absorbance readings were taken after 1 hr with a Beckman 24 spectrophotometer at 730 nm wavelength.

1.4.3.4 Nitrogen Analysis. Duplicate, 10-ml aliquots of each sample were passed through 0.45 μm Nucleopore filters, and the filtrates were transferred to micro-kjeldahl flasks. For total inorganic N, 1 g MgO + 1 g Devarda's alloy were then added. The flasks were immediately transferred to a distillation apparatus, and the samples were distilled into 50-ml flasks containing 5 ml of 2% boric acid until approximately 30 ml of distillate were collected. The distillates were then titrated with 0.01N HCl solution to a blue-green end point. Ammonia-nitrogen

was determined using the same method but without Devarda's alloy. Nitrate-N was determined by subtraction of the NH_4-N from the total inorganic N. Results were reported as NO_3-N and NH_4-N in μg/ml.

1.4.3.5 Organic Carbon. Total organic carbon was determined on the whole, freeze-dried sediment prior to any treatment with H_2O_2 for removal of organic matter. The method used was modified from those given by the Soil Survey Staff (1972) and Post (1956). Duplicate 0.5 g samples were placed in small, heat resistant ceramic boats containing powdered MnO_2 as a catalyst. The boats were transferred to a Lindberg oven and heated at 1000° C for 10-12 min. Dry combustion resulted in the volatilization of CO_2 which was trapped in ascarite treated with NaOH. Carbon dioxide was then determined gravimetrically, and organic carbon was calculated from a standard curve prepared by combustion of known amounts of oven dried (110° C) $CaCO_3$.

1.4.3.6 Fractionation and Particle Size Analysis. The freeze-dried whole sediment was fractionated after total organic carbon analysis had been completed (see section 1.4.3.5). In most cases, the total sediment yield was limited, so the entire sample was fractionated. This was accomplished by transferring the sediment to a 250-ml centrifuge bottle after which approximately 60 ml of distilled water were added. The sample was then washed once with 100 ml of 1N NaCl and twice with 100 ml of 60% methanol, using centrifugation after each washing. The washings were discarded, and the sample was transferred to a 400-ml plastic beaker. Thirty ml of 0.5N Na_2CO_3 were added, and distilled water was used to adjust the final volume to 200 ml. An ultrasonic probe (Branson Sonifier Cell Disruptor Model W 185) was immersed into the suspension and the sample was dispersed for 5 min at 100 watts. The suspension was allowed to stand 4 sec for each cm of suspension depth. The

supernatant suspension was then decanted onto a 300-mesh sieve, and the fines were washed through the sieve with distilled water directly into the sample holder of an automatic clay separator (Rutledge et al., 1967). Wet sieving was continued until the material on the 300-mesh sieve was washed free of silt and clay. Retained sands were transferred to a beaker, dried at 60° C, and weighed. The clay (<2 μm) was separated from the silt by repeated siphoning (up to seven cycles) at a convenient depth and time interval calculated according to Stoke's Law (Jackson, 1975). Volume of the siphoned, suspended clay was controlled by flocculation with 1N $MgCl_2$ and subsequent decantation of the supernatant liquid. The sedimented silts were transferred to a beaker, dried at 60° C, and weighed; the clay content was then determined by difference from the original sample weight.

The flocculated clays were washed free of excess salts using sequential, 100 ml distilled water washes. Occasionally, dispersion occurred before salts were completely removed. Dispersion was then controlled by washing with 60% methanol and/or acidification with 1 or 2 drops of 0.1N HCl. The washed clays were quick-frozen and freeze-dried as stated above. It should be noted that care was taken to treat all sediments in as gentle a manner as possible. Clay minerals, especially the iron oxides, can be altered by harsh treatments involving elevated temperatures. For this reason, most of the original whole sediment samples were not exposed to the usual H_2O_2 treatment for removal of organic matter, and the temperature was not elevated above 60° C during freeze-drying. The freeze-dried clays were used for nearly all the chemical and mineralogical analyses in this study. The moisture content of each freeze-dried clay was determined gravimetrically and sample weights were adjusted when necessary to their oven-dry (110° C) equivalents.

1.4.3.7 Sodium Pyrophosphate Extractions. A 0.1 M solution of sodium pyrophosphate ($Na_4P_2O_7$) was prepared as directed by Bascomb (1968). Fifty ml of the solution were then added to 0.25 g of clay material in a 100-ml polypropylene test tube. The tube was stoppered and placed on an oscillating shaker, and shaken overnight. After shaking, 1 drop of 0.4% superfloc solution was added to the sample, and the suspension was centrifuged at 1500 rpm for 6 min. The resulting supernatant liquid was decanted into a 50-ml Erlenmeyer flask and analyzed for Fe and Al using a Varian AA-6 atomic absorption spectrophotometer.

Samples were analyzed directly for Al using the original extracts but Fe was determined after dilution by a factor of 10. Concentrations of Fe in the sample extracts were compared to standard solutions ranging from 0 to 20 μg/ml; Al standards ranged from 0-100 μg/ml. All standards were prepared from Fisher certified atomic absorption reference materials and appropriate quantities of blank solution. The samples were extracted and analyzed in duplicate.

1.4.3.8. Acid Ammonium Oxalate Extractions. Tamm's Reagent, a buffered solution of ammonium oxalate and oxalic acid was prepared as directed by McKeague et al. (1971). The pH was adjusted to 3.0 with concentrated NH_4OH, and the solution was stored in the dark. A 0.25 g sample of clay material was placed into a 100-ml polypropylene test tube, and, in near darkness, 50 ml of the ammonium oxalate buffer was added. The test tubes were stoppered and shaken in an oscillating shaker for 4 hr in complete darkness. Following extraction, superfloc was added, the samples were centrifuged, and the extract was transferred to a 50-ml Erlenmeyer flask. The extracts were then stored in the dark until ready for analysis.

Samples were analyzed for Al and Mn with no further dilution of the original extracts. Concentrations of Al and Mn were compared to standard solutions ranging from 0-100 μg/ml and 0-2 μg/ml for Al and Mn, respectively. Iron was determined from a 1 to 10 dilution of the original extract by comparison with standard solutions containing 0-20 μg/ ml Fe. Duplicate analyses for all three elements were made with a Varian AA-6 spectrophotometer.

1.4.3.9 Sodium Citrate-Bicarbonate-Dithionite Extractions. Sodium citrate-bicarbonate-dithionite (CBD) extractions were done on 0.5 g of clay using a procedure adapted from that of Mehra and Jackson (1960). The clay was placed in a 100-ml polypropylene test tube, and 40 ml of sodium citrate-bicarbonate buffer were added. The sample was placed in a water bath and the temperature elevated to 75-80° C. One g of $Na_2S_2O_4$ was then added and the sample was stirred occasionally for 5 min. Then a second 1 g portion of $Na_2S_2O_4$ was added. After an additional 5 min, the sample was removed from the water bath and centrifuged for 5 min at 1500 rpm. The supernatant liquid was then decanted into a 250-ml volumetric flask and brought to volume with distilled water. A 1 to 20 dilution of this solution was used for analysis of Fe; Al and Mn were determined with no further dilution.

All samples were analysed using a Varian AA-6 atomic absorption spectrophotometer with standards made from 1000 μg/ml stock solutions of Fisher atomic absorption standards and CBD reagent. Standard solutions ranged from 0-20 μg/ml for Fe, 0-100 μg/ml for Al, and 0-2 μg/ml for Mn.

1.4.3.10 Total Chemical Analysis. Total dissolution of clay materials was achieved using a Parr acid digestion bomb and the method of Bernas (1968). All samples were prepared in duplicate and stored in polyethylene bottles after digestion. Fe and K were determined by a Varian AA-6 atomic absorption

spectrophotometer. Iron was analyzed using a 1 to 10 dilution and K was determined directly from the original 100-ml digests. Again, standard solutions of these elements were prepared using Fisher certified reference materials and appropriate quantities of blank solution. The standard range employed was 0-20 μg/ml for both Fe and K.

1.4.3.11 X-ray Diffraction Analysis. Clay samples from the sediments were K- and Mg-saturated and prepared for analysis using the oriented slide procedure described by Whittig (1965). Potassium saturation was achieved by placing approximately 0.5 g of air-dried clay into a 50-ml centrifuge tube. Twenty ml of 1N KCl were added, the tube was stoppered, and the sample was dispersed by shaking. The tubes were then centrifuged at 1500 rpm for 5 min and the clear liquid decanted. This salt wash was repeated twice, after which the clay was washed free of excess salts using one 20-ml distilled water wash and subsequent 20-ml, 60% methanol washes as needed. When washing was completed, 30 ml of distilled water plus 1 or 2 drops of 0.5N KOH were added, and the sample was dispersed for one minute using a Branson Sonifier Cell Disruptor (Model W 185). Two ml of the resulting suspension were pipetted onto a 27 x 46 mm petrographic microscope slide and allowed to air dry. The K-saturated clays were subsequently analyzed at room temperature, after heating to 350° C, and after heating to 550° C.

All clays were Mg-saturated prior to freeze-drying; therefore, 0.5 g of clay was placed in a 50-ml plastic beaker, 30 ml of water plus 1-2 drops of 0.5N KOH were added and the sample was dispersed with an ultrasonic probe without additional washing. Duplicate two-ml aliquots of suspension were transferred to glass slides and allowed to air dry. When dry, one was analyzed directly and the

other was placed in a covered vessel over ethylene glycol and held at 60° C for 12 hr prior to analysis.

X-ray diffraction analyses were conducted using a Philips PW 1316/90 wide range goniometer equipped with a theta compensating slit, a curved crystal monochrometer, and a scintillation detector. The diffraction tube was operated at 35 kV with a current of 15 mA, and provided CuKα radiation. A one-sec time constant and a 1000-count per sec range factor were used for most analyses. Diffractograms were normally obtained over an angular range of 2-30° 2θ with a scanning speed of 2° 2θ per min and a recorder speed of 1 in per min.

1.5 Results and Discussion

1.5.1 pH, Nitrogen, and Phosphorus Analyses

Analytical results for pH, nitrogen and phosphorus are given in Table 1.3. The pH's of the water samples from most of the Muskingum Basin are very uniform and are at or slightly below neutrality. A noticeable difference is seen only in water taken from Moxahala Creek which has a pH of 4.2 and which is probably indicative of high levels of acid coal mine drainage within the small Moxahala watershed (BUSML, 1974).

Total nitrogen contents are generally low, and NH_4-N levels are likewise low to non-detectable (detection limit was 0.001 μg/ml) in a majority of the waters. In addition to being in greater concentrations compared to NH_4-N, NO_3-N appears to reflect regional differences within the watershed. Undetectable to low concentrations of NO_3-N are found in samples from Conotton, Stillwater, Moxahala, and Wills Creeks, all watersheds left unglaciated during the Pleistocene. There is as much as a seven-fold increase in NO_3-N in samples from sub-basins affected by glaciation and, presumably, greater agricultural activity.

Table 1.3 Nitrogen and Phosphorus Contents and pH of Waters in the Muskingum River Basin

River or Stream	Site	pH	Nitrogen		Phosphorus	
			NH_4-N	NO_3-N	DIP**	Total P
			μg/ml			
Sandy Creek	1	6.3	0.24	1.75	--	0.37
Conotton Creek	2	6.5	--	--	0.01	0.16
Stillwater Creek	3	6.7	--	0.46	0.01	0.11
Sugar Creek	4	7.2	--	3.15	0.01	0.37
Killbuck Creek	5	6.4	--	1.56	0.02	0.36
Mohican River	6	6.6	--	1.40	0.02	0.58
Kokosing River	7	6.8	--	1.33	0.07	0.26
Licking River	8	6.8	--	--	0.02	0.21
Moxahala Creek	9	4.2	0.11	--	0.01	0.16
Wills Creek						
Kimbolten	10	6.8	0.24	0.46	0.01	0.16
Wills Creek	11	6.7	0.25	0.46	0.01	0.16
Tuscarawas River						
Bolivar	12	6.5	0.24	2.87	0.08	0.42
Gnadenhutten	13	6.6	--	2.67	0.01	0.32
Muskingum River						
Tyndall	14	6.5	0.53	2.38	0.15	0.42
Philo	15	6.5	*	*	*	*
Lowell	16	6.4	--	1.54	0.01	0.26

* Sample missing
** DIP = dissolved inorganic phosphorus
— Not detectable at 0.001 μg/ml

Dissolved inorganic phosphorus (DIP) is much lower than total P, and is uniform throughout the basin. The highest values come from two glaciated areas, the Kokosing and the upper Tuscarawas, but the sources of glacial drift for these two sub-basins are different. Glacial drift in the area drained by the Kokosing is predominantly calcareous, while that drained by the Tuscarawas is not. Variation in dissolved P, therefore, does not seem to be attributable to geologic provenance. This observation does not prohibit the possibility of an agricultural origin for the DIP. Under usual conditions, fertilizer phosphorus is readily immobilized by soil (Tisdale and Nelson, 1975). Increased quantities of dissolved P in runoff may indicate direct loss of this fraction as might occur if manure or other fertilizers were applied to frozen soil. Both the Tuscarawas and Kokosing sub-basins have high agricultural activity. However, samples from the other sub-basins draining glacial areas are low in DIP, despite similar agricultural activity.

Total P concentrations generally increase with increases in suspended sediment within the basin (Tables 1.3 and 1.4), which indicates that most P lost in surface runoff occurs as sediment-P. This observation is supported by Sharpley and Syers (1979) in their study of sources of P from agricultural soils in New Zealand. As with NO_3-N, geologic or land use differences seem to influence total P. Values for total P from unglaciated areas average 0.15 μg/ml; whereas, total P contents average 0.36 μg/ml in the sediments from glaciated areas.

1.5.2 Whole Sediment Analyses

The results of analyses performed on the bulk sediment (<2 mm) are given in Table 1.4, and indicate that most of the sediment is a combination of silt and clay. This size distribution reflects the geology of the basin and the low gradient

Table 1.4 Particle Size Distribution, Organic Carbon Content, and Concentration of Suspended Sediments in the Muskingum River Basin

River or Stream	Site	Sand	Silt	Clay	O.C.	Suspended Sediment Load
		%				mg/l
Sandy Creek	1	1.3	50.5	48.2	4.5	280
Conotton Creek	2	1.4	53.2	45.4	3.6	128
Stillwater Creek	3	1.4	43.1	55.5	4.9	120
Sugar Creek	4	1.8	36.3	61.9	4.6	228
Killbuck Creek	5	5.1	47.9	47.0	2.5	264
Mohican River	6	4.4	57.3	38.3	3.2	428
Kokosing River	7	2.7	48.7	48.6	3.9	224
Licking River	8	3.9	51.5	44.6	3.9	908
Moxahala	9	6.0	52.4	41.6	4.2	188
Wills Creek						
Kimbolton	10	1.1	37.9	61.0	4.4	132
Wills Creek	11	--	--	--	8.7	64
Tuscarawas						
Bolivar	12	1.6	52.2	46.2	4.1	256
Gnadenhutten	13	1.4	54.1	44.5	3.6	212
Muskingum						
Tyndall	14	2.6	57.2	40.2	3.6	356
Philo	15	1.9	49.8	48.3	3.7	166
Lowell	16	2.3	52.7	45.0	3.1	328

of the Muskingum River. Much of the till in the glaciated portions of the basin has a high silt + clay content in the <2 mm portion, and the surface geology of the unglaciated portion of the basin is predominantly represented by siltstone and shale members. Size fractionation data from Wills Creek at Wills Creek hamlet are missing. This is because the total sediment yield was too small for analysis. Only suspended sediment concentration and organic carbon data are available for this site.

Suspended sediment concentrations (Table 1.4) are highly variable throughout the basin. As described in section 1.4.2, an effort was made to collect all samples during high flow. However, it was not possible to know if the samples were taken at the time of maximum flow in each watershed. Effective drainage area of the sub-basins (Table 1.2) also does not seem to provide a consistent explanation for the variation in suspended sediment concentrations. Sub-basins with reservoirs above sampling sites are Sugar, Conotton, Stillwater, and Wills Creeks, and the South Fork of the Licking River (Figure 1.3). The suspended sediment concentrations of Conotton, Stillwater, and Wills Creeks are among the lowest reported (128, 120, and 64 mg/l, respectively). However, Sugar Creek, and especially the Licking River, have much greater sediment concentrations (228 and 908 mg/l, respectively).

A better explanation of load variability is permitted when sub-basins are again grouped according to surface geology and land use. In this case, all of the sub-basins yielding <200 mg/l suspended sediment can be identified with the unglaciated portion of the basin. This portion accounts not only for Wills, Conotton, and Stillwater Creeks, but the Moxahala watershed as well. All those watersheds with concentrations >200 mg/l, including the Tuscarawas above Bolivar, drain glaciated areas of the basin. However, amongst these watersheds,

there is still great variability in sediment concentrations. The lowest concentration is from the Kokosing River, while the highest is found in the Licking River (224 and 908 mg/l, respectively). This difference may reflect greater farming activity, especially in the Licking watershed, where row and field cropping practices may increase soil losses and, hence, suspended sediment loads in the streams and rivers. With respect to this observation, it may also be that an apparent division of the watersheds along a glaciated and an unglaciated line of demarcation actually reflects the importance of farming as an economic activity associated with the more fertile soils found in glaciated areas.

A comparison of the organic carbon values does not reveal any significant trends within the Muskingum Basin, and comparisons with sediment size data do not permit association with any one sediment size fraction. The highest value for organic carbon was yielded by sediment from Wills Creek just below the Wills Creek Reservoir (site 11). This value is 2-3 times greater than those from all other sites sampled and may reflect the flushing of detrital matter accumulated in the reservoir during the winter months.

Limited organic carbon data is available for the Muskingum River. The yearly average organic carbon concentrations at McConnelsville (a city along the Muskingum River between Philo and Lowell) was reported by the U.S.G.S. (1974 and 1978) as 5.8 and 8.2 mg/l during 1974 and 1978, respectively. Multiplication of per cent organic carbon by sediment concentration measured at the Philo and Lowell sites in this study gives 6.1 mg/l and 7.7 mg/l organic carbon, respectively.

1.5.3 Clay Mineralogy by X-ray Diffraction.

The clay fraction was considered to be of primary importance for analysis as several studies (e.g., Klages and Hsieh, 1975; Jones et al., 1977) have

indicated that clay mineralogy of suspended sediments may indicate differences in source areas. Table 1.5 gives relative quantities of clay minerals detected in the Muskingum River Basin by X-ray diffraction techniques. Total K (Table 1.6) was also used to estimate the relative amounts of clay mica present in the suspended sediments. This analysis is based on the work of Jackson (1975), who estimated clay mica using the relationship 1% K_2O = 10% clay mica.

The results are considerably different from observations made by Jones et al. (1977) in a study of sediments in tributaries to the Maumee River. The Maumee drains an area where the surface geology is exclusively glacial in origin, and illite and quartz were the two most abundant minerals leaving the watersheds. Illite, or clay mica as shown here, is abundant, but it is not the dominant clay mineral in any of the sediments. However, note that in three of the four cases in which it is estimated to range in the 35-50 percentile, the watersheds (Mohican, Licking, and Killbuck) drain Wiscinsinan glacial materials. Note also, that the two lowest estimates for kaolinite are from watersheds (Kokosing and Killbuck) which drain glacial areas. All the watersheds have small amounts of clay-sized quartz (<5%) and traces of clay-sized feldspar moving downstream, and 60% of the samples showed traces of (<5%) goethite. Only one watershed, the Licking, gave evidence of chlorite, and then only a trace. Chloritized (Al-interlayered) vermiculite, on the other hand, is abundant in all the clays, especially those derived from glaciated watersheds.

Despite the above mentioned differences, and despite great differences in terrain, geology, and parent material within the Muskingum River Basin, the suspended sediments from the different watersheds seem to be relatively uniform. The typical clay fraction of the average suspended sediment would contain 20-35% kaolinite; 20-35% clay mica; 5-20% interstratified smectite-clay

Table 1.5 Estimated Clay Mineralogy[+] of Suspended Sediments in the Muskingum River Basin

River or Stream	Site	[ξ]K	M	I	AV	Q	C	G	F
Sandy Creek	1	XXX	XXX	XX	XXXX	X	--	--	t
Conotton Creek	2	XXX	XXX	XXX	XX	X	--	t*	t
Stillwater	3	XXXX	XXXX	X	XXX	X	--	--	t
Sugar Creek	4	XXX	XXX	XX	XXXX	X	--	t	t
Killbuck	5	XX	XXXX	XX	XXX	X	--	t	t
Mohican	6	XXX	XXXX	XX	XXX	X	--	--	t
Kokosing	7	XX	XXX	XX	XXXXX	X	--	t	t
Moxahala Creek	9	XXXX	XXX	XX	XXX	X	--	t	t
Wills Creek									
Kimbolten	10	XXXX	XXX	XXX	XX	X	--	--	t
Tuscarawas River									
Bolivar	12	XXX	XXX	XX	XXXX	X	--	t	t
Gnadenhutten	13	XXXX	XXX	XX	XXX	X	--	--	t
Muskingum River									
Tyndall	14	XXX	XXX	XX	XXXX	X	--	t	t
Philo	15	XXXX	XXX	XX	XXX	X	--	t	t
Lowell	16	XXX	XXX	XXX	XX	X	--	--	t

[+] Relative quantities XXXXX = >50%, XXXX = 35-50%, XXX = 20-35%, XX = 5-20%, X = <5%.

[ξ] K = Kaolinite, M = Clay Mica, I = Interstratified Smectite-Clay Mica, AV = Al-interlayered Vermiculite, Q = Quartz, C = Chlorite, G = Goethite, F = Feldspar.

* t = trace.

Table 1.6 Extractable Manganese* and Total Potassium Contents of the <2 μm Fractions from the Muskingum River Sediments

Stream or River	Site	Mn_o	Mn_d	K	K_2O
		%			
Sandy Creek	1	0.004	0.030	2.20	2.65
Conotton Creek	2	--	0.020	2.54	3.06
Stillwater Creek	3	--	0.020	2.34	2.82
Sugar Creek	4	0.004	0.035	2.02	2.43
Killbuck Creek	5	0.004	0.035	2.54	3.06
Mohican River	6	0.004	0.020	2.54	3.06
Kokosing River	7	0.008	0.030	2.64	3.18
Licking River	8	0.004	0.020	2.70	3.25
Moxahala Creek	9	0.006	0.020	2.04	2.46
Wills Creek					
Kimbolton	10	--	0.020	2.28	2.75
Tuscarawas River					
Bolivar	12	--	0.025	2.28	2.75
Gnadenhutten	13	0.004	0.025	2.60	3.13
Muskingum River					
Tyndall	14	0.004	0.035	2.12	2.55
Philo	15	0.004	0.040	2.46	2.96
Lowell	16	0.004	0.040	2.42	2.92

* Mn_o and Mn_d are ammonium oxalate and CBD extractable Mn, respectively.
— Not detectable

mica; 20-35% Al-interlayered vermiculite, less than 5% quartz, and traces of feldspar and possibly some goethite. In general, the unglaciated watersheds of Conotton, Stillwater, Wills, and Moxahala Creeks seem to have higher kaolinite, lower mica, and lower Al-vermiculite contents than the glaciated watersheds.

1.5.4 Chemical Dissolution Data

The chemical dissolution data described in this discussion are from the selective extraction of secondary Mn, Al, and Fe compounds using pyrophosphate, oxalate, and CBD reagents. Total Fe content was also measured.

Manganese, as indicated by Cummins et al. (1965), is one of the more important elemental products of acid mine drainage. The partitioning of Mn into "amorphous" and crystalline oxide fractions can be achieved through acid ammonium oxalate and CBD extraction, respectively. The results of analysis for Mn are given in Table 1.6, and indicate remarkably little oxalate extractable Mn throughout the Muskingum Basin; the range is from non-detectable to 0.008% Mn. Oxalate-Mn to CBD-Mn ratios (Mn_o)/Mn_d) range from 0.1 to 0.3 and indicate that crystalline oxides of Mn are the dominant forms of Mn in the suspended sediments. However, there does not seem to be any noticeable trend within the basin concerning the distribution of either amorphous or crystalline manganese oxides with respect to glacial history; nor does manganese seem to be a useful indicator of the effects of acid mine drainage on a regional basis.

Except for the Moxahala Creek site, (Table 1.7), lower amounts of all forms of extractable aluminum occur in watersheds draining unglaciated areas of the basin compared to sediments in waterways draining glaciated portions of the basin. Likewise, the ratios of oxalate extractable to CBD extractable Al (Al_o/Al_d) are generally lower in the sediments of watersheds draining

Table 1.7 Extractable Aluminum Data (<2 μm) in the Muskingum River Basin

River or Stream	Site	Al_p	Al_o	Al_d	Al_p/Al_d	Al_o/Al_d
		%				
Sandy Creek	1	0.28	0.39	0.44	0.64	0.89
Conotton Creek	2	0.10	0.21	0.35	0.29	0.60
Stillwater Creek	3	0.08	0.22	0.35	0.23	0.63
Sugar Creek	4	0.12	0.23	0.30	0.40	0.77
Killbuck Creek	5	0.18	0.32	0.48	0.38	0.67
Mohican River	6	0.12	0.35	0.42	0.28	0.83
Kokosing River	7	0.14	0.33	0.38	0.37	0.87
Licking River	8	0.25	0.29	0.38	0.66	0.76
Moxahala Creek	9	0.43	0.54	0.63	0.68	0.86
Wills Creek						
Kimbolton	10	0.08	0.19	0.25	0.32	0.76
Tuscarawas River						
Bolivar	12	0.18	0.29	0.44	0.41	0.66
Gnadenhutten	13	0.14	0.27	0.38	0.37	0.71
Muskingum River						
Tyndall	14	0.16	0.30	0.36	0.44	0.83
Philo	15	0.14	0.29	0.38	0.37	0.76
Lowell	16	0.24	0.29	0.30	0.80	0.97

* Al_p, Al_o, and Al_d are sodium pyrophosphate, ammonium oxalate and CBD extractable aluminum, respectively.

unglaciated areas and suggest that the Al oxides are more crystalline in those clays.

The highest values for all forms of extractable Al are from the Moxahala Creek watershed with the pyrophosphate, oxalate and CBD extractions accounting for 0.43, 0.54, and 0.63%, respectively, of the total clay. These values, though low, represent 1.5-3 fold increases over other sites in the Muskingum River Basin. Overall increases, especially of poorly crystallized aluminum oxide materials can be expected in areas affected by acid mine drainage, and it is possible that the increases in Al detected in the suspended sediments are a result of mining disturbance.

Extractable Fe data are given in Table 1.8 and show many of the same trends as described for extractable Al. Excluding the Moxahala creek sites, data for all forms of extractable Fe are lowest in clays derived from unglaciated portions of the basin. The Fe data from the Moxahala sediments stand out by comparison. Pyrophosphate, oxalate, and CBD Fe are between 2-6; 2-7; and 1-3 times greater than respective values for the same type of extractable Fe in other areas of the Muskingum Basin. Also, Fe_o/Fe_d ratios indicate that amorphous and organically-held Fe account for 97% of the extractable Fe in the Moxahala sediment. This is the highest value for the entire Muskingum Basin, and is consistent with the work of Cummins et al. (1965), who indicate that Fe concentrations will be greatly increased in waters draining spoil materials which contain pyrite as an impurity. Observations concerning Fe in the Moxahala sediment are also supported by Nordstrom (1982) in his review of pyrite oxidation and "amorphous" iron oxide precipitation in acid mine drainage water.

Table 1.8 Extractable and Total Iron Contents* of the <2 μm Fractions from the River Sediments

River or Stream	Site	Fe_p	Fe_o	Fe_d	Fe_t	Fe_p/Fe_d	Fe_o/Fe_d
		%					
Sandy Creek	1	1.00	2.17	3.00	6.20	0.33	0.72
Conotton Creek	2	0.50	1.15	2.20	5.60	0.23	0.52
Stillwater Creek	3	0.45	1.03	2.00	4.50	0.22	0.51
Sugar Creek	4	0.63	1.20	2.50	4.25	0.25	0.48
Killbuck Creek	5	0.78	2.22	3.40	6.50	0.23	0.65
Mohican River	6	0.63	2.05	3.15	6.10	0.20	0.65
Kokosing River	7	0.74	2.18	3.10	6.60	0.24	0.70
Licking River	8	0.78	1.61	2.90	6.20	0.27	0.56
Moxahala Creek	9	2.46	5.89	6.10	9.90	0.40	0.97
Wills Creek							
Kimbolton	10	0.39	0.85	2.20	4.45	0.18	0.39
Tuscarawas River							
Bolivar	12	0.66	1.47	2.60	5.40	0.25	0.57
Gnadenhutten	13	0.54	1.45	2.60	6.00	0.21	0.56
Muskingum River							
Tyndall	14	0.68	1.36	2.70	5.80	0.25	0.50
Philo	15	0.58	1.38	2.35	5.50	0.24	0.59
Lowell	16	0.99	1.86	4.85	5.30	0.21	0.38

* Fe_p, Fe_o, and Fe_d are sodium pyrophosphate, ammonium oxalate, and CBD extractable iron, respectively. Fe_t = total iron content.

Total Fe, which includes Fe held in alumino-silicate structures, ranges between 1.1 and 2.5 times greater than CBD-extractable Fe at all sites. For the Moxahala watershed, total Fe is 1.6 times that obtained by CBD extraction.

1.6 Summary and Conclusisons

With little exception, DIP, NH_4-N, sediment size fractions, organic carbon and clay mineralogy did not yield definitive information concerning source areas for suspended sediments within the Muskingum River Basin. On the other hand, extractable oxides, especially those of Al and Fe, do seem to be related to geologic source areas, and are generally higher in sediments from areas affected by glaciation. Also, total P, which generally reflects sediment P, and NO_3-N show some correlation with geology and/or land use.

The most convincing evidence of regional differences within the Muskingum Basin came from Moxahala Creek. The low pH of its water and the high extractable Al and Fe contents of its sediment all reflect problems with acid coal mine drainage. As a result, the Moxahala Creek watershed was chosen for further study.

CHAPTER 2

WATER AND BOTTOM SEDIMENT QUALITY IN STREAMS AFFECTED BY ACID COAL MINE DRAINAGE - A STUDY OF THE BLACK FORK CREEK WATERSHED, OHIO

2.1 Introduction

The coal beds in Ohio comprise one of the four largest coal deposits in the continental United States. This deposit, known as the Main Bituminous Coal Basin, is associated with the Appalachian Plateau, and occurs in a northeast - southwest trending band which extends from north-central Pennsylvania through eastern Ohio, West Virginia, Western Maryland and Virginia, and southward into Kentucky, Tennessee and Alabama. The coal-bearing rocks in the basin were formed from alternating sea and swamp deposits of detrital inorganic and organic constituents of Pennsylvanian Age (280 to 320 million years B.P.). The sedimentary units within the Ohio coal field gradually slope to the southeast, toward the center of the basin in northern West Virginia. As a result, coal-bearing seams are nearer the surface in the western part of the field, and are more deeply buried near the Ohio River.

Pennsylvanian coal seams average 1 to 2 feet in thickness and occur interbedded with common sedimentary rocks. In Ohio, there are over 40 coal seams, only 13 of which have been mined commercially. The cyclical character of the Pennsylvanian system resulted from the recurrence of a geologic environmental sequence involving swamps associated with the shoreline of an ancient sea. The prevailing view of coal formation is one of accumulation and compaction of organic matter in freshwater swamps according to the following

sequence of events: primary formation of a swamp; rise in sea level and flooding of the swamp; accumulation of inorganic sediments on top of the swamp; and finally a drop in sea level and formation of a new swamp.

Portions of thirty counties in the bituminous basin in Ohio have been mined for coal since the early 1800's. Early operations involved primarily deep mines, but now more than 70% of the state's coal production is from surface mining. The recent expansion of surface mining activity has resulted in comprehensive state legislation which requires the complete reclamation of areas currently being mined. However, it does not provide for reclamation of land mined prior to 1972. As a result, the utility of at least 72,800 ha of land has been lost due primarily to toxic spoils from abandoned surface and deep mines (BUSML, 1974). While loss of productive land is a major concern, a more serious and pervasive problem is the environmental damage caused by pollution of streams, rivers and groundwaters with acid mine drainage. According to the Board on Unreclaimed Strip Mine Lands (BUSML, 1974), over 454,000 kg of acid are discharged into Ohio streams every day.

Acid mine drainage arises from the microbially catalyzed oxidation of iron sulfides, principally pyrite and marcasite, which occur as impurities in coal and associated rocks, particularly roof shales. These iron sulfides not only create phytotoxic conditions in spoils and polluted waterways, but also lower the coking quality of coal, accelerate the corrosion of boilers firing the coal, and contribute to air pollution. In southeastern Ohio, mine effluents release copious amounts of both acid and iron to surface and ground waters where they cause severe stress to aquatic organisms and a general deterioration of the regional water supply. Much of the iron is ultimately transformed to gelatinous precipitates that increase the sediment load in receiving streams. In addition, these precipitates

may have a significant impact on chemical reactions which occur at the sediment/water interface. The primary objectives of this study were to evaluate the impact of acid mine drainage on water quality in a representative stream system, and to evaluate the mineralogy and surface chemistry of bottom sediments in waterways affected by acid mine drainage.

2.2 Literature Review

2.2.1 Pyrite Oxidation

Pyrite (FeS_2) is one of the most abundant and ubiquitous impurities in coal and associated rocks, and its oxidation has been the subject of a great deal of research. In spite of this research, exact oxidation mechanisms are still in doubt.

Pyrite is stable under reducing conditions and will oxidize abiotically in the presence of oxygen. A number of pathways have been proposed for this inorganic oxidation. These nearly always require water as both product and reactant, and usually involve the action of dissolved oxygen on pyrite to produce ferrous iron and elemental sulfur according to the reaction:

(2.1) $FeS_2 + 1/2O_2 + 2H^+ \longrightarrow Fe^{+2} + 2S^\circ + H_2O$

Then, elemental sulfur is oxidized:

(2.2) $2S^\circ + 3O_2 + 2H_2O \longrightarrow 2SO_4^= + 4H^+$

Next, ferrous iron is oxidized:

(2.3) $4Fe^{+2} + O_2 + 4H^+ \longrightarrow 4Fe^{+3} + 2H_2O$

The fate of the Fe^{+3} produced in reaction 2.3 is considered to be 3-fold: The ferric iron can oxidize more sulfur (2.4); it can oxidize more pyrite (2.5); or it can precipitate as ferric hydroxide (2.6).

(2.4) $S^\circ + 6Fe^{+3} + 4H_2O \longrightarrow 6Fe^{+2} + SO_4^= + 8H^+$

or:

(2.5) $FeS_2 + 2Fe^{+3} \longrightarrow 3Fe^{+2} + 2S^{\circ}$

or:

(2.6) $Fe^{+3} + 3H_2O \longrightarrow Fe(OH)3 + 3H^{+}$

A much more succinct description emphasizing the role of iron in the above reactions is given by Singer and Stumm (1970) in which two phases are proposed:

A. Initiator reaction:

(2.7) $FeS_2 + 1/2O_2 + 2H^{+} \longrightarrow Fe^{+2} + 2S^{\circ} + H_2O$

B. Propagating cycle:

(2.8) $4Fe^{+2} + O_2 + 4H^{+} \longrightarrow 4Fe^{+3} + 2H_2O$

(2.9) $Fe^{+3} + FeS_2 \longrightarrow 2S^{\circ} + 3Fe^{+2}$

The rate of abiotic oxidation of pyrite seems to be closely associated with degree of crystallinity, and FeS_2 may also be more easily attacked in other mineral forms such as marcasite (Harmesen et al., 1954). However, Singer and Stumm (1970) feel that oxidation rates are primarily a function of Fe(III) concentration. Their study indicated that continuous removal of Fe(III) by flowing water decreased the rate of pyrite oxidation by a factor of 10^6. They refer to the oxidation of Fe(II) to Fe(III) as the rate determining step. Further, these researchers showed that inorganic oxidation of Fe(II) is pH dependent, and is rapid above pH 5. At lower pH's inorganic oxidation is slow and bacterial catalysis is required.

Bacterially catalyzed pyrite oxidation has been well documented, and at least two types of microbes appear to be capable of accelerating the oxidation process (Kelley, 1967; Dugan and Randles, 1968). The first are autotrophic microoganisms that rely on the oxidation of minerals for their energy while utilizing carbon dioxide and a few other nutrients in small quantities for life

support. The second are heterotrophic microorganisms which depend upon the oxidation of organic compounds for both their energy and cellular carbon requirements. The autotrophic microorganisms include several species of Thiobacillus and are of primary interest in this discussion. Thiobacilli achieve maximum growth between pH 2 and 3.5, and are classified as acidophilic. Thiobacillus ferrooxidans has been widely implicated as a catalyst in the production of acid mine waters because: it is associated with acid mine drainage waters in significant quantities; it actively increases pyrite oxidation in laboratory experiments; and it can speed up the oxidation of dissolved Fe(II) by 5 to 6 orders of magnitude over inorganic rates (Dugan, 1975). Another Thiobacillus, T. thiooxidans, has been observed in contact with pyrite surfaces (Tuovinen and Kelly, 1972) and is thought to oxidize elemental sulfur by a direct contact mechanism. A "direct contact" mechanism has also been suggested for the oxidation of pyrite by T. ferrooxidans (Arkesteyn, 1979). Thus, iron and sulfur oxidation by autotrophic bacteria can be given as:

(2.10) $Fe^{+2} \xrightarrow{\text{T. ferrooxidans}} Fe^{+3} + e^-$

and

(2.11) $2S^\circ + 3O_2 + 2H_2O \xrightarrow{\text{T. thiooxidans}} 2SO_4^{-2} + 4H^+$

Microbial oxidation may be much more important in oxidation of pyrites than abiotic chemical mechanisms, as microbial activity can be attained under extremely low levels of dissolved oxygen. Brock and Gustafson (1976) report that Fe(III) is used as an energy source by T. ferrooxidans during sulfur oxidation under anaerobic conditions.

Microbially catalyzed pyrite oxidation is only beginning to be understood, and evidence given by Kelly et al. (1979) show that bacteria other than the two Thiobacilli are also active in pyrite oxidation, and that mixed cultures are often

more efficient in oxidizing pyrite than are monocultures. Almost all evidence indicates that microbial catalysis of pyrite oxidation can greatly increase the rate of oxidation above that possible by inorganic mechanisms.

2.2.2 Water Quality Resulting from Acid Mine Drainage

The products of pyrite oxidation, sulfuric acid and dissolved iron, are recognized as the primary pollutants in acid mine drainage (Dugan, 1975). They affect water quality of streams and rivers when surface waters flow across spoil banks or percolate through disturbed land and enter the groundwater. The BUSML (1974) indicates that three quarters of all the acid mine drainage produced in the Appalachian Province originates in underground mines. The underground mines expose the sulfide impurities to atmospheric oxidation and cause alterations in subsurface water patterns which allow for greater water contact with oxidized pyrite. The oxidation products are flushed from the mines after rains or are continually discharged under hydrostatic pressure.

Although spoils in the eastern coal mining province can range in pH from 2.5 to 8 (Berg and Vogel, 1969), depending on differences in local mineralogy, the pH of streams heavily affected by acid mine drainage can be as low as 2.1, as reported for Campbell's Run in southwest Pennsylvania (EPA, 1976). More frequently, however, the pH's of streams affected by acid mine drainage range between 3.7 and 4.2 (EPA, 1977). A number of factors contribute to this variation. The pH is primarily a function of rate of oxidation of the pyrite, rate of flow and discharge from the pyrite source, and amount of dilution after entering a stream system. The acidity levels in acid mine drainage are in sharp contrast to the near neutral pH of other natural groundwaters that are also high in dissolved iron and manganese (Mustoe, 1981; Carlson et al., 1980). Acidity introduced to groundwater, streams, and lakes by coal mine drainage often limits

the use of water for recreation and drinking purposes, and frequently destroys normal biological activity. However, abatement through chemical neutralization might well be possible if acidity were the only pollutant.

Iron concentrations can also be extremely high. Minear and Tschantz (1976), in their water quality study of drainage basins affected by acid mine drainage in eastern Tennessee, report an average of 20 μg/ml total dissolved Fe with highs of up to 80 μg/ml near drainage sources. The EPA (1976) reported total Fe concentrations in a small catchment in Pennsylvania as high as 55 μg/ml. Other reports indicate lower quantities of iron (Cronce et al., 1980) but, regardless of the level reported, the effect of acid mine drainage is usually the same: concentrations of iron are above the 0.3 μg/ml U.S.drinking water standard, and there is considerable visual pollution as a result of iron oxide or oxyhydroxide precipitation.

Sulfate levels are often high as well. Sulfate concentrations ranging up to 2400 μg/ml have been reported for the Campbell Run area of Pennsylvania (EPA, 1976). Studies throughout eastern Tennessee and Pennsylvania indicate that yearly averages in streams receiving acid drainage range between 100-200 μg/ml SO_4 (Minear and Tschantz, 1976; Cronce et al., 1980). Concentrations of SO_4 are dependent on water discharge, and can locally be much higher. Rose (1975), for example, reports an average SO_4 concentration of 700 μg/ml in a small stream tributary to one of those studied by Minear and Tschantz (1976).

In addition to SO_4, Al and Mn can also be significant components of acid mine drainage. Usually, Al is found in higher concentrations than Mn. Various studies of streams in Pennsylvania report average dissolved Al contents of 8-9 μg/ml (EPA, 1977; Cronce et al., 1980) and high concentrations near 80 μg/ml (EPA, 1976). In nearly all cases, manganese is present in much

lower quantities, and levels are usually no more than 3-6 μg/ml in areas affected by acid mine drainage.

Considerable differences in solute levels are reported by researchers working with acid mine drainage within the eastern coal province. These differences are related to type of mining activity, extent of precipitation, runoff, and discharge of receiving streams. Two studies (Curtis, 1972; Minear and Tschantz, 1976) report annual cycles in the quality of water, with increasing concentrations through the summer months, and decreasing concentrations during the winter. Curtis (1972) found that the highest concentrations of dissolved materials were generally associated with late summer rains which he attributed to the role of alternate wetting and drying periods in concentrating salts near spoil surfaces. However, summer increases in temperature may also play a significant role, especially with respect to microbial oxidation.

2.2.3 Sediment Quality in Streams Affected by Acid Mine Drainage

Water quality is usually judged by the types and concentrations of materials found in solution; whereas, sediment quality is related to the physical and chemical characteristics of the solid phase. However, a study of sediment quality in waters influenced by acid mine drainage demands that sediments be examined in light of the quality of the water. During low flow periods, concentrations of iron and sulfate increase in the water. Corollary with this occurrence, great quantities of yellowish, gelatinous precipitates called "yellow boy" are produced. Although most of these precipitates are removed during subsequent storm cycles, it is very likely that these precipitates also influence the character of the more permanent bottom sediments.

Erosion and siltation have long been considered a problem associated with mining activity and affect both suspended and bottom sediments. Dramatic

differences in concentrations of suspended solids between unmined watersheds and those disturbed by surface mining exist. Minear and Tschantz (1976) have reported sediment concentrations of 25 μg/ml in undisturbed watersheds as compared to 100-400 μg/ml in watersheds disturbed by mining activity. Values in the mined watersheds often exceeded 1000 μg/ml following heavy rainfalls. These same researchers also reported increases in bottom sediment loads, especially during the early stages of mining.

Bottom sediment usually occurs when stream energy cannot support the entrainment, suspension and transport of sediment, and the particles subsequently settle out. These particles are deposited along with associated inorganic and organic constituents adsorbed by the sediment. In a study of rock formations containing anakeesta pyrite in the Great Smoky Mountains of Tennessee and North Carolina, Bacon and Maas (1979) reported increases in lead, zinc, sulfate and in some cases, manganese in bottom sediments of streams draining the formation. Although no attempt was made to identify the way these constituents were associated with the bottom sediments in that study, Jenne (1975) has reported that clay-size materials, especially oxides of iron and manganese, carbonates, sulfides, and organic matter, may serve as major sinks for heavy metals in fluvial systems.

The survey reported in Chapter One established an increase in iron and aluminum oxides in sediments from areas influenced by acid mine drainage. Yellowish precipitates were visibly apparent, and these precipitates may greatly influence both the nature and reactivity of stream sediments.

2.3 Materials and Analytical Procedures

2.3.1 Site Selection

During the winter of 1981, field reconnaissance led to the selection of the Black Fork Creek watershed as a detailed study site. This 74 km^2 basin is located in northwest Morgan and adjacent Perry counties, and consists of Black Fork Creek, Ogg Creek, and Bennett Run (Figure 2.1). The watershed has experienced both surface and, especially, deep mine activity. The deep mines are now abandoned and large quantities of acid drainage are released from both mine tunnels and tailings adjacent to the receiving streams. Tailings from the Jones or Misco Mine are a primary source of pollution along Bennett Run. Former entrances to the Tropic Mine and an air vent for the Number 52 Mine affect Black Fork Creek. Groundwater pollution is extensive in the watershed, as nearly 80% of the study area has been undermined; however, unpolluted reference areas exist at the headwaters of all three tributaries.

Coal has been mined in the area since the early 1800's (Norling, 1957), but the greatest activity occurred from the 1930's through the late 1950's. The major source of coal for the mines in the watershed was the Middle Kittanning Number 6 coal seam. The sedimentary sequence associated with the Middle Kittanning Coal is shown in Figure 2.2. This seam is approximately 1.6 meters thick, and is the middle member of the Allegheny Formation which includes acid shales and sandstones of Pennsylvanian Age.

2.3.2 Sample Collection

During March of 1981, water and bottom sediments were collected at periods of low discharge from nine sites indicated in Figure 2.3. Additional water samples were collected at these same sites again in August, 1981, during another period of low flow. Sites 1-3 represent unpolluted reference areas

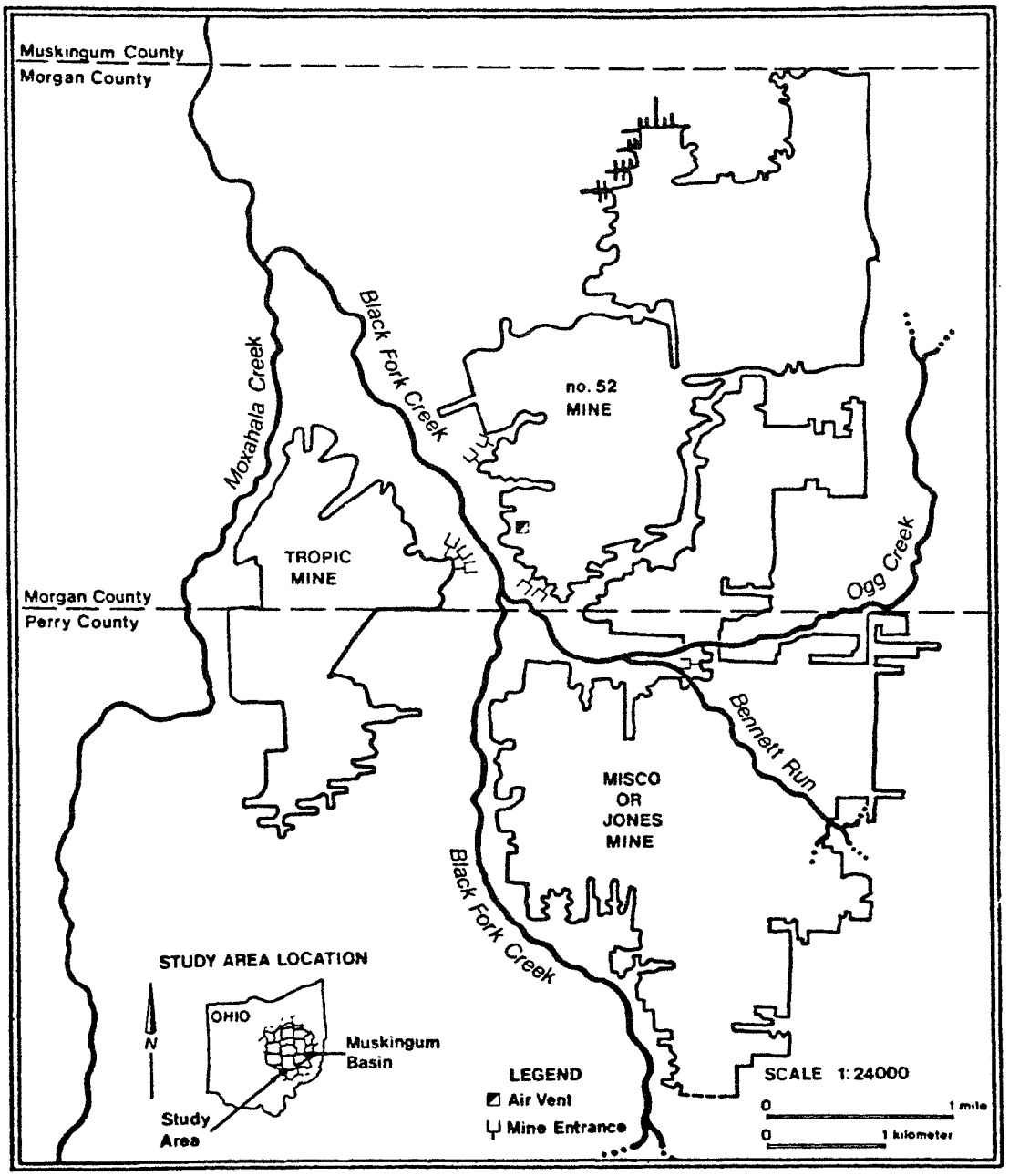

Figure 2.1 Study area location with respect to abandoned underground mines.

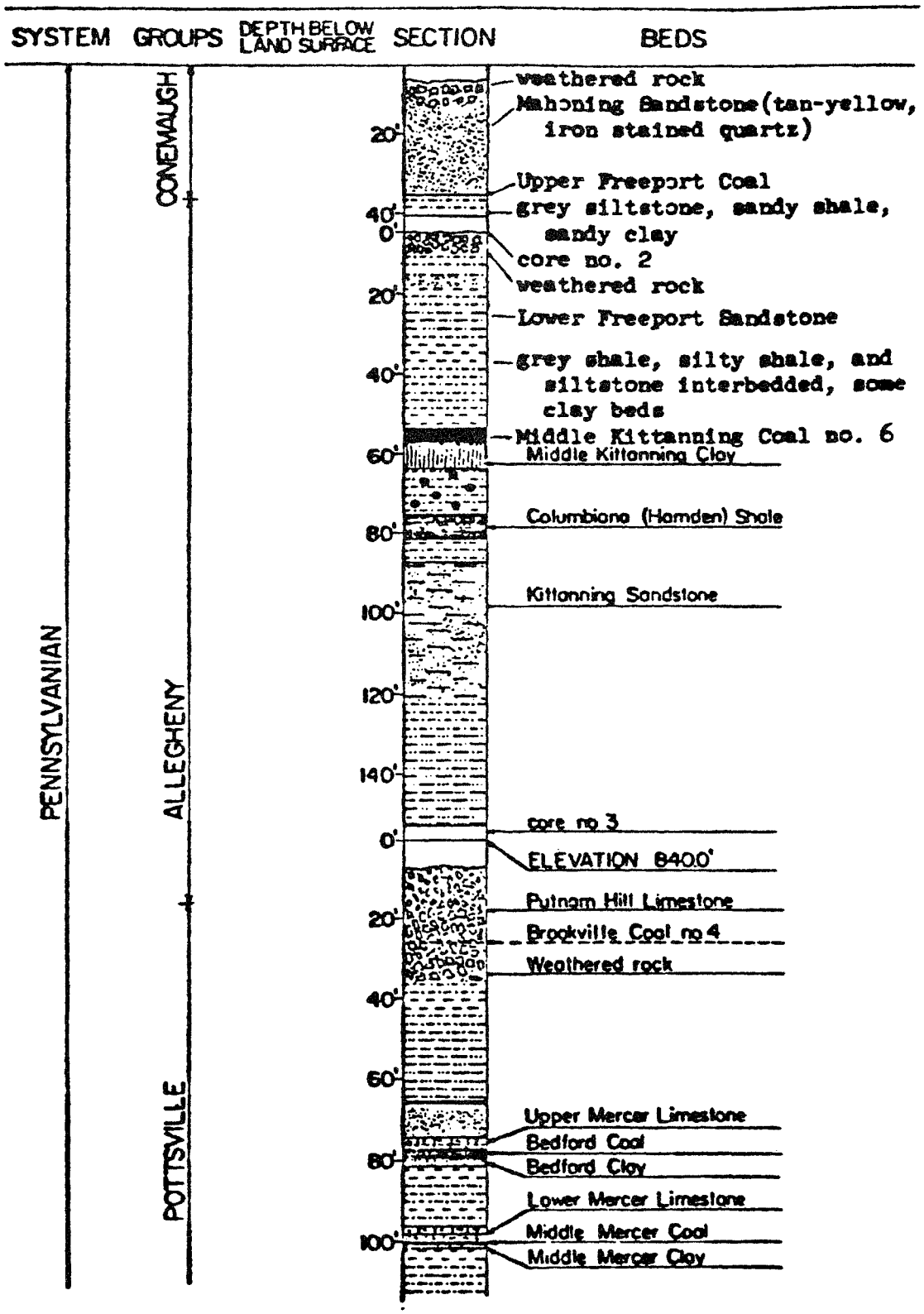

Figure 2.2 Strata associated with Middle Kittanning Coal No. 6. (Bureau of Mines, 1977).

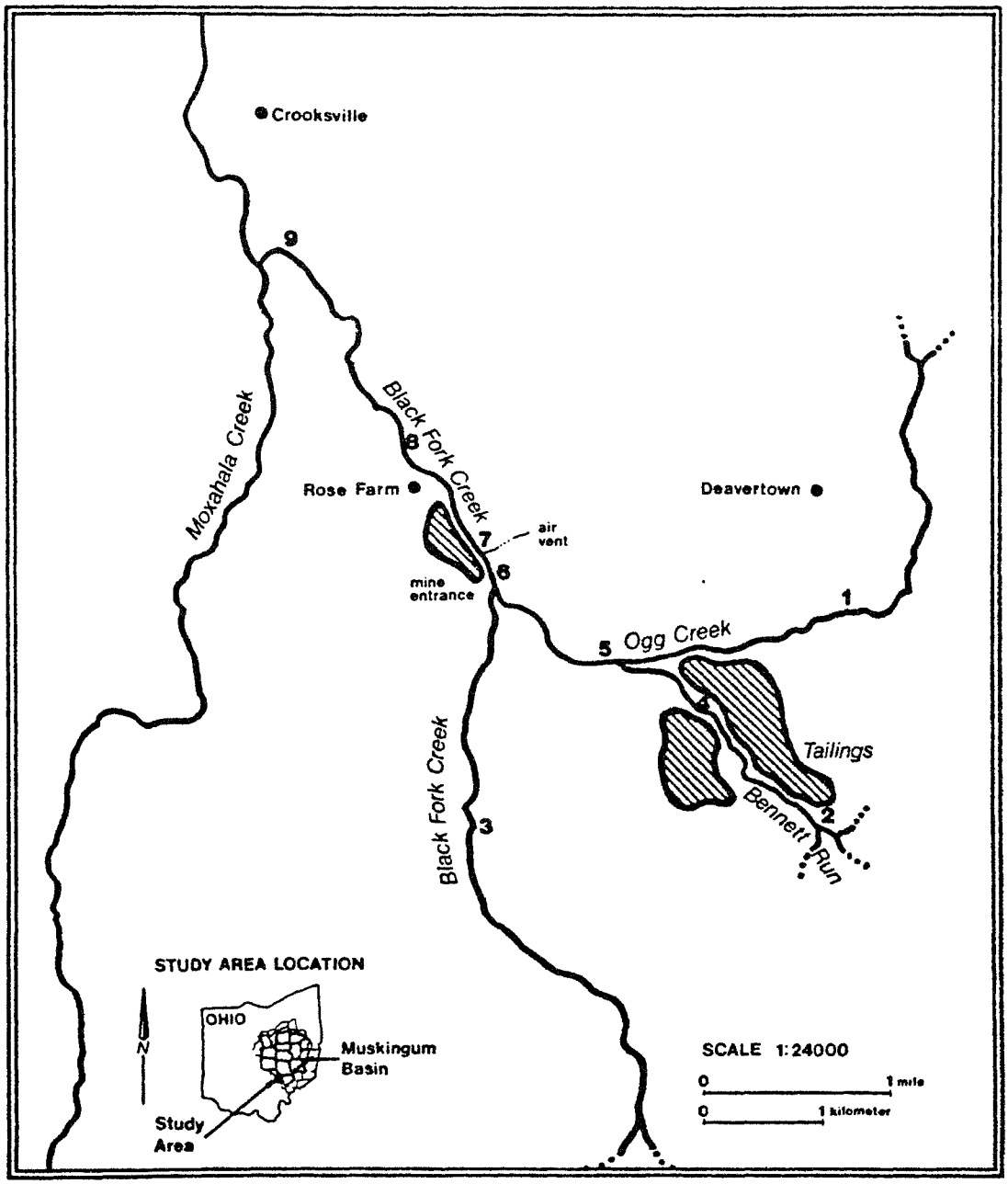

Figure 2.3 Location of collection sites (1-9).

upstream from the zone of pollution along Ogg Creek, Bennett Run, and Black Fork Creek, respectively. Near site 4, approximately 16 ha of mine tailings are exposed. Site 5 is just below the confluence of Ogg Creek and Bennett Run. Site 6 was selected so that the samples would reflect mixing between Ogg Creek and Black Fork Creek and is located just below the confluence of those two streams. Site 7 was chosen to reflect influences in water and sediment quality caused by water flow from the breached air vent. Site 8 was chosen so that changes in water and sediment quality downstream from all known sources of pollution could be monitored. Site 9, located near the mouth of Black Fork Creek, was chosen to provide a final measure of water and sediment quality prior to the merger of Black Fork and Moxahala Creeks.

For each site, three equally spaced samples of water and sediment were collected in transect across the channel of the stream. Water samples were collected in 250-ml polyurethane bottles which had been washed in 5N HCl. The upper 4-5 cm of bottom sediments were collected using a 4-l, flat-bottomed plastic scoop, and were placed in gallon polyurethane containers which had also been washed with 5N HCl. Water samples were transported from the field in an ice chest, and both water and sediment samples were immediately refrigerated at 4° C upon arrival at the laboratory.

2.3.3 Analytical Procedures

The methods of analysis described in this section involve the characterization of both water and sediment. Five of these procedures have been discussed in appropriate sections of Chapter 1 and will not be described again at length. All new or modified procedures will be discussed in detail.

2.3.3.1 pH. The hydrogen ion activity of all water samples was measured in the same manner as that described in Chapter 1, section 1.4.3.1.

2.3.3.2 Sulfate Determination Measurements. Sulfate was measured by a turbidimetric technique (APHA et al., 1980) after filtration of the stream waters through a 0.4 μm filter.

2.3.3.3 Dissolved Metals. Dissolved metal ions were determined by plasma emission spectroscopy (ICAP) after filtration of the stream waters through a 0.4 μm filter. Metals (Ca, Mg, Na, Al, Mn, Sr, Cd, Cu, Pb, Ni, and Zn) were measured with a Jarrell-Ash Model 975 Plasma Automcomp Spectrometer.

2.3.3.4 Fractionation and Particle Size Determinations. During the March, 1981 sampling, triplicate samples of bottom sediment (∿ 5 kg each) were collected across the stream channel at each of the nine sites. Gravel and cobbles (all material >2 mm) were removed from the sediments by sieving, placed in beakers, and then oven dried at 105° C. All materials less than 2 mm were then concentrated by centrifugation at 1500 rpm for 10 min using a Beckman J21B centrifuge and an angle-head rotor. The samples were subsequently frozen in 400-ml polyurethane beakers using trichloroetheylene and dry ice, and freeze-dried in a Virtis lyophilizer. This procedure allowed for estimates of total sediment (<2 mm) available for analysis, and also provided for easy storage of dried samples. In all cases, the freeze-dried whole sediment (except for 0.5 g withheld for organic carbon) was fractionated, and a particle size analysis was performed in the manner described in Chapter 1, section 1.4.3.6.

2.3.3.5 Organic Carbon. Measurements of organic carbon were obtained in the same manner as described in Chapter 1, section 1.4.3.5.

2.3.3.6 Total Sulfur. Duplicate 0.1 g samples of clay (<2 μm) were placed in a crucible containing iron and tin oxide catalysts and then heated to approximately 1650° C in a Leco 521 high frequency induction furnace according

to a procedure recommended by McKibbon (1975). Sulfur evolved as SO_2 was collected in a starch solution and quantified using a semi-automatic titrator with KIO_3 as the titrant. In this manner the percent total sulfur released by each sample was determined. The completeness of combustion and the accuracy of the titration were determined using known samples provided by the Leco Corporation.

2.3.3.7 Selective Dissolution Analyses. Due to extremely limited net quantities of clay materials, Na-pyrophosphate, acid NH_4-oxalate, and CBD extractions were performed in a sequential fashion on duplicate, 0.25 g samples of clay. Analyses were otherwise conducted in the same manner as described in Chapter 1, sections 1.4.3.7-9. In order to express the results in a meaningful way, metal ion concentrations in the Na-pyrophosphate extracts were reported as measured. These values were then summed with those obtained by acid ammonium oxalate extraction to yield a final data set for oxalate-extractable metals. Likewise, results from the Na-pyrophosphate, ammonium oxalate, and citrate-bicarbonate-dithionite extractions were summed to yield a final data set for CBD-extractable metals.

2.3.3.8 Total Chemical Analysis. Clays from the bottom sediments were analyzed for total contents of K, Fe, Mn, and Al. Digestion and analysis procedures were the same as those given in Chapter 1, section 1.4.3.10.

2.3.3.9 X-ray Diffraction Analysis. Portions of clay from the bottom sediments were prepared and analyzed in the same manner as that described in Chapter 1, section 1.4.1.1.

2.3.3.10 Phosphate Adsorption. Standard phosphate adsorption isotherms were determined for clays from sites 3, 5, and 6.

Air dried equivalents of 0.25 g of oven-dried clay were weighed into 50-ml polyethelyne centrifuge tubes which had been acid washed. Appropriate amounts of 0.01M $CaCl_2$ and KH_2PO_4 solutions were added to duplicate clay samples to make suspensions that contained 0.0, 0.2, 0.5, 1.0, 5.0, 10.0, 15.0, and 20.0 μg/ml phosphate while maintaining a solid-solution ratio of 1/100. The tubes were sealed with plastic caps and placed in a rotary shaker for 24 hr.

After shaking, the soil suspensions were centrifuged for 15 min at 5,000 rpm. Appropriate aliquots of the supernatant liquids were analyzed colorimetrically for P by the heteropoly blue method of Watanabe and Olsen (1965). Absorbance values were obtained using a 1 cm quartz cell in a Beckman Model 24 spectrophotometer at a wavelength of 730 nm. Equilibrium P concentrations were calculated from a standard curve prepared from 0, 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 μg/ml P solutions. Sample 6 proved so adsorptive that it was necessary to use initial P concentrations as high as 400 μg/ml to achieve an adequate isotherm. The difference between the P contents of the solutions before and after equilibration with the clay materials was considered to represent the quantity of P adsorbed by the clay.

After sampling for P analysis, the pH of the remaining equilibrium solution was determined using a Corning Research Model 12 pH meter with a combination electrode.

2.3.3.11 Surface Area. Non-expanded (external) surface areas of clay materials from sites 3, 5, and 6 were determined by nitrogen gas (N_2) adsorption after the procedure of Brunauer, et al. (1938).

A sample of clay was dried for 2 weeks over concentrated H_2SO_4, and then for 48 hours over P_2O_5. It was then placed into an adsorption cell and "outgassed" at ambient temperature for 12 hr before analysis. This procedure

was necessary to assure replacement of H_2O by the N_2 gas and also to protect against possible alterations in the iron oxides which can result from treatment at elevated temperatures (above 60° C). Post adsorption sample weights were determined by weighing the filled adsorption cell and then subtracting the weight of the washed and dried glass cell.

Nitrogen adsorption on the clay was achieved by immersing the adsorption cell in liquid nitrogen while passing a mixture of N_2 and He gases through the cell and sample. After the adsorption process was finished, the cell was removed from the liquid nitrogen bath and the sample was allowed to warm. As the sample warmed, desorption of N_2 was followed using a thermal conductivity detector. The desorption signal was calibrated by manually injecting a known quantity of pure N_2 into the sample stream with a syringe.

A triple point adsorption isotherm was calculated for each sample using N_2 -He gas mixtures of 10.14, 20.45, and 30.48 percent N_2. The size of the sample used ranged between 0.03 and 0.15 g, and the attenuator settings were varied between 28 and 256 to optimize the intensity of the desorption signal. The bridge current was held at 130 mA. The instrument used was a Quantachrome Quantasorb Surface Area Analyzer.

2.4 Results and Discussion

2.4.1 Water Quality Analysis

Water quality data from samples collected during March and August, 1981 under low flow conditions (Table 2.1) show a marked change in stream environment as a result of acid mine drainage. Waters from the reference areas have neutral pH's and low background levels of all other measured parameters. Data from the reference areas are, in fact, so similar that they are presented as averaged values. No difference in pH was detected at the reference sites for the

Table 2.1 Water Quality of Black Fork Creek Watershed

Site	Basic* Cations	Metals**	SO_4	Mn	Al	Fe	pH
	μg/ml						
			March, 1981				
1-3	48.8	0.04	41	0.0	0.1	0.1	6.8
4	70.6	0.35	589	1.2	37.4	94.6	3.3
5	62.5	0.26	254	0.8	13.7	18.0	4.6
6	59.1	0.07	163	0.5	2.0	15.2	4.8
7	65.3	0.07	193	0.6	2.9	19.7	4.9
8	67.8	0.08	199	0.6	3.4	19.0	4.8
9	84.4	0.09	207	0.8	3.3	18.0	4.8
Air Vent	381.5	0.44	1750	6.6	9.0	301.0	4.8
			August, 1981				
1-3	74.6	0.02	39	0.1	0.1	0.5	6.8
4	116.9	0.57	1630	4.4	94.3	329.0	2.7
5	105.2	0.20	570	2.4	33.3	52.6	2.8
6	143.4	0.32	777	3.7	40.8	61.1	2.8
7	222.9	0.39	1007	5.0	34.3	132.0	2.9
8	251.5	0.39	1080	5.2	30.3	123.0	2.9
9	308.2	0.42	963	5.0	27.7	69.3	2.9
Air Vent	495.0	0.66	2360	9.9	12.9	466.0	4.4

*Calcium, magnesium and sodium (See Appendix A for individual analyses).
**Cadmium, copper, lead, nickel, and zinc (See Appendix A for individual analyses).

two different sampling dates. All other values indicate that lower concentrations of pollutants were present in waters sampled in March due, most likely, to higher total discharge at that time. Discharge measurements for the watershed were taken only at site 9 and only during the August collection; the calculated discharge at that time was 62 l/sec. The August data represent the most extreme example of poor water quality observed in the Black Fork Creek watershed.

Data from site 4 reflect the immediate impact that runoff waters from exposed tailings have on streams in the watersheds. While the levels of dissolved pollutants at this site are substantial, they are a fraction of those contained in waters exiting the former air vent between sites 6 and 7 (Table 2.1).

Basic cations (calcium, magnesium, and sodium) increase at all points downsteam from the initial source of acid drainage. Heavy metals also increase, with zinc accounting for about 95% of the total metal load at all sites. Manganese shows a more dramatic rise in the zone of pollution, especially in the samples collected in August. However, the most significant increases are in concentrations of sulfate, aluminum, and iron, with an accompanying decrease in pH. Sulfate is clearly the most concentrated and Fe the next most concentrated pollutant. The pH is lowest at site 4 for both sampling dates and increases somewhat downstream from the tailings, but levels off near site 6.

Levels of all pollutants in the receiving streams fluctuate, as expected, with inflow of low or high quality water. Trends in data from the March sampling show that pollutants, except for pH, uniformly decrease with distance from the tailings site, and then show increases at site 7 due to discharge from the abandoned air vent on the east side of Black Fork Creek. By contrast, an increase in pollutants is also noticeable at site 6 in the August samples. Site 6 is

just below the confluence of Black Fork Creek and Ogg Creek, and seepage from shafts of the Tropic Mine (see Figure 2.1) are probably the cause of this increase. At slightly higher flow periods, as exemplified by the March sampling, the influence of acid drainage from the west side of Black Fork Creek is not readily detected at site 6. At the August sampling, no major quantities of acid drainage or fresh water entered Black Fork Creek below site 8. Consequently, the concentrations of heavy metals, aluminum, manganese, and sulfate, as well as the pH at site 8, are very similar to the measurements taken at site 9. However, concentrations of dissolved iron decrease by almost one half from site 8 to site 9. This decrease over a linear distance of 2.5 km is possibly indicative of the rapidity with which iron is removed by precipitation.

2.4.2 Bottom Sediment Analyses

Coarse fragments comprised 47.4 to 88.0% by weight of all bottom sediments collected in the Black Fork Creek watershed; the average over all sites was 58.2%. Most of the fragments consisted of shale and sandstone, but an increase in coal fragments was noted at sites 4 and 5. Gravel and cobbles removed from sites within the polluted zone were generally coated with reddish-yellow, CBD-soluble material considered to be iron oxide. While coarse fragments comprise a significant portion of the total mass of bottom sediment, they are not the mobile, reactive fraction of the sediment load. Consequently, most attention is focused on the <2 mm fractions.

Particle size data for the <2 mm fractions of the sediment are given in Table 2.2. They are variable, but also show a distinct trend toward higher silt and especially clay contents in sections of the stream influenced by mining activities. For the same sites, increases in organic carbon are also noted. These increases are most likely due to coal fragments observed to be concentrated in

Table 2.2 Particle Size Distribution and Organic Carbon Content of Bottom Sediments from Black Fork Creek Watershed

Site	Sand	Silt	Clay	Organic Carbon
	%			
1-3	81.7	13.4	4.9	0.8
4	82.0	12.1	5.9	2.5
5	66.3	16.6	17.1	2.2
6	44.9	48.2	6.9	2.3
7	70.9	17.3	11.8	1.5
8	83.1	5.1	11.8	2.3
9	75.3	17.0	7.7	2.3

the sand fractions. After the sediments were fractionated, the yellowish coloration characteristic of polluted sections of the stream was exhibited primarily by the clay-sized materials. As a result of this observation, the clay fractions were studied in more detail.

The mineralogy of the bottom sediment clays (<2 μm) as estimated from X-ray diffraction analyses are presented in Table 2.3 and representative X-ray patterns from three sites in the watershed (sites 3, 6, and 9) are given in Figures 2.4 and 2.5. Results indicate that several crystalline clay minerals are uniformly present in the bottom clays at all nine locations. All samples contain high amounts of kaolinite, illite, and aluminum interlayered vermiculite with lesser amounts of smectite and quartz. Table 2.4 presents total K values for these clays, and permits estimation of the amount of illite (clay mica) in the samples by employing the relationship 1% K_2O = 10% mica (Jackson, 1975). A slight decrease in total K in the zone of pollution is associated with increases in smectite. In addition, expansion of the smectite peak with ethylene glycol is evident in the CBD-treated clays (Figure 2.4), but is not apparent in the natural clays (Figure 2.5). This behavior suggests that poorly crystallized hydroxides of Fe or Al may fill the interlayers and prevent expansion of the smectites under natural conditions. Samples untreated by CBD, (Figure 2.5) are remarkably similar and reveal low background levels of crystalline goethite and lepidocrocite in both the reference and polluted samples. Hence, no crystalline iron oxides can be directly related to the gelatinous precipitates resulting from acid mine drainage.

Total sulfur contents of the bottom sediment clays are given in Table 2.4. The contents are considerably higher in clays from polluted sections of the stream, but are much lower than levels which would be expected if bottom

Table 2.3 Estimated Clay (<2 μm) Mineralogy[+] of Bottom Sediments from Black Fork Creek Watershed

Site	[ξ]K	M	AV	S	Q	G	L
1-3	XXXX	XXX	XXX	X	X	X	X
4	XXX	XX	XXX	XX	X	X	X
5	XXXX	XXX	XX	XX	X	X	X
6	XXXX	XXX	XX	XX	X	X	X
7	XXXX	XXX	XX	XX	X	X	X
8	XXXX	XXX	XX	XX	X	X	X
9	XXXX	XXX	XX	XX	X	X	X

[+] Relative quantities: XXXX = 35-50%, XXX = 20-35%, XX = 5-20%, X = <5%
[ξ] K = Kaolinite, M = Clay Mica, AV = Al/Fe interlayered vermiculite, S = Expanding component (smectite), Q = Quartz, G = Goethite, L = Lepidocrocite

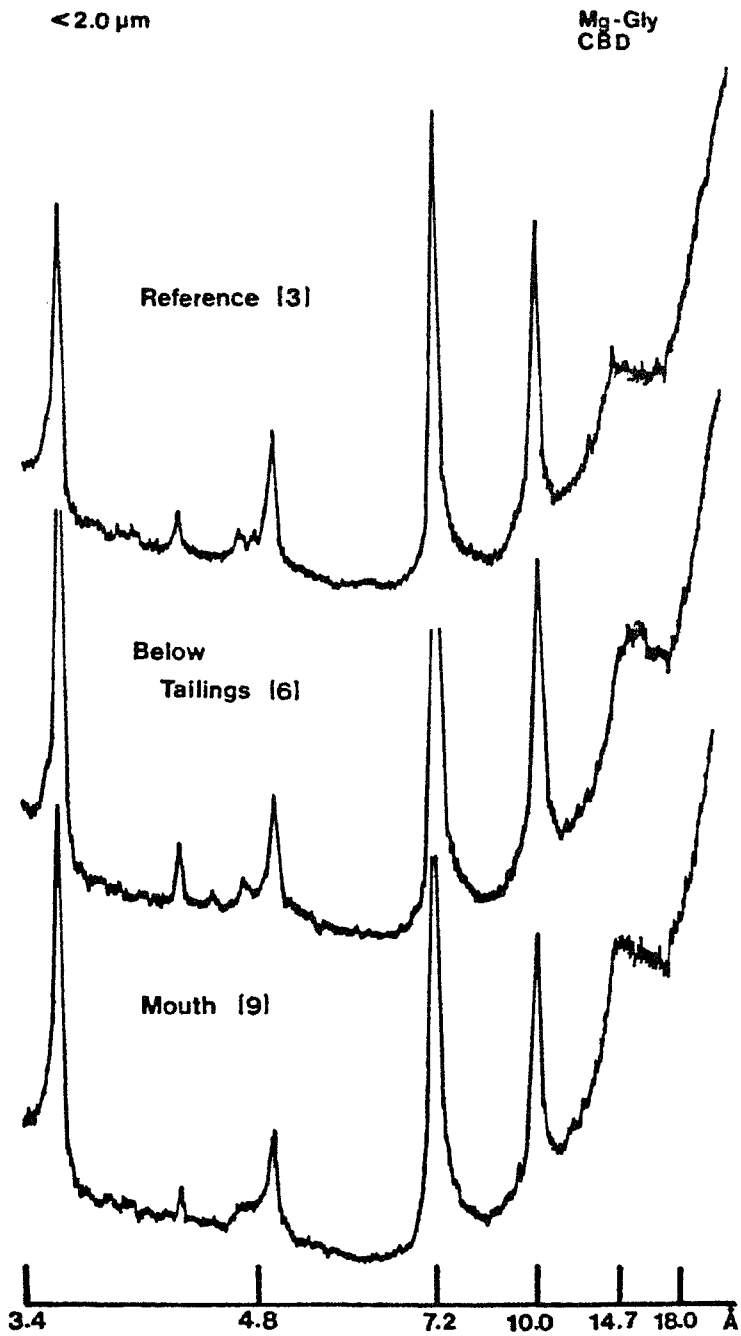

Figure 2.4 XRD spectra for selected sites in the Black Fork Creek watershed; CBD treated clay.

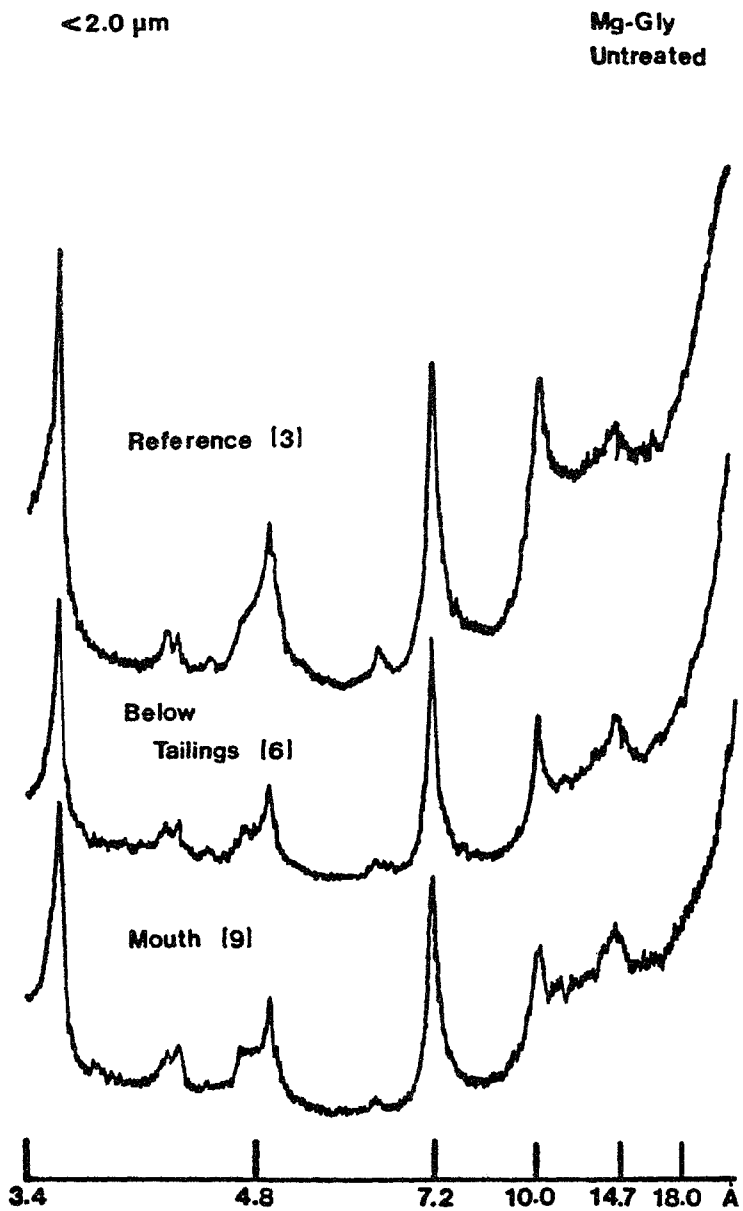

Figure 2.5 XRD spectra for selected sites in the Black Fork Creek watershed; total clay.

Table 2.4 Total Potassium and Total Sulfur Contents of Bottom Sediment Clays (<2 μm) in the Black Fork Creek Watershed

Site	K	K_2O	S
	%		
1-3	2.11	2.54	0.06
4	1.79	2.16	0.38
5	1.85	2.23	0.21
6	1.69	2.04	0.44
7	1.65	1.99	0.29
8	1.55	1.87	0.36
9	1.83	2.20	0.16

sediments in the zone of pollution contained sulfate minerals precipitating as a direct result of acid mine drainage. For example, if all the extractable iron ($Fe_d \sim 10\%$; See Table 2.5) in the contaminated clays were due to the mineral jarosite, then at least 3.8% total sulfur should also be present. The sulfur contents of these clays are less than one tenth the stoichiometric requirement for jarosite and could easily be due to surface adsorbed sulfate. In addition, no sulfate minerals were identified by X-ray diffraction.

Selective dissolution and total chemical analyses for iron, aluminum, and manganese (Tables 2.5, 2.6, and 2.7, respectively) provide evidence that oxides and/or oxyhydroxides of these metals are important components of the bottom sediments. Secondary iron compounds provide the most significant contribution of materials followed by aluminum and manganese.

All forms of extractable iron in the reference areas are relatively low (Table 2.5), but increase markedly at and below sources of pollution. Increases in iron held by organic matter (Fe_p) are notable, and are most likely due to the breakdown and release of organics from coal. Ratios of CBD extractable to total iron (Fe_d/Fe_t) indicate that a majority of the iron in the reference areas is held within the structures of silicate clay minerals, but in the zone of pollution, iron held by the silicate minerals is greatly diminished in importance. Between 70-90% of the iron is CBD extractable in this zone. In addition, ratios of oxalate to dithionite extractable iron (Fe_o/Fe_d) suggest that 75-90% of the secondary iron extracted from the clays is in the form of a very poorly crystallized iron oxide.

Selective dissolution and total chemical data for aluminum (Table 2.6) suggest a pattern similar to that observed for iron. All forms of extractable aluminum in the reference areas are low and increase in the zone of pollution;

Table 2.5 Extractable and Total Iron Contents* of Bottom Sediment Clays (<2 μm) in the Black Fork Creek Watershed

Site	Fe_p	Fe_o	Fe_d	Fe_t	Fe_d/Fe_t	Fe_o/Fe_d
	%					
1-3	0.19	2.24	3.65	8.43	0.43	0.61
4	0.45	10.27	11.64	14.27	0.81	0.88
5	0.77	9.37	10.50	11.80	0.88	0.89
6	0.28	11.40	13.63	16.80	0.81	0.84
7	0.18	10.36	12.35	14.30	0.86	0.84
8	0.51	8.46	10.88	15.03	0.72	0.78
9	0.86	8.40	10.35	13.03	0.79	0.81

* Fe_p, Fe_o and Fe_d are pyrophosphate, ammonium oxalate, and CBD extractable Fe, respectively. Fe_t is total iron.

Table 2.6 Extractable and Total Aluminum Contents* of Bottom Sediment Clays (<2 μm) in the Black Fork Creek Watershed

Site	Al_p	Al_o	Al_d	Al_t	Al_d/Al_t	Al_o/Al_d
	%					
1-3	0.03	0.40	0.58	11.02	0.05	0.68
4	0.19	1.01	1.10	10.50	0.10	0.92
5	0.07	0.47	0.60	9.23	0.06	0.78
6	0.06	0.93	1.21	9.10	0.13	0.77
7	0.04	0.80	1.04	9.40	0.11	0.77
8	0.14	1.45	1.69	9.33	0.18	0.86
9	0.20	0.83	1.19	10.00	0.12	0.70

*Al_p, Al_o and Al_d are pyrophosphate, ammonium oxalate, and CBD extractable Al, respectively. Al_t is total aluminum.

Table 2.7 Extractable Manganese Contents* and Surface Area of Bottom Sediment Clays (<2 μm) in the Black Fork Creek Watershed

Site	Mn_o	Mn_d	Mn_o/Mn_d	Surface Area Natural Clay	Surface Area CBD Clay
	μg/g			m^2/g	
1-3	722	712	0.89	28	22
4	237	267	0.89	--	--
5	207	227	0.91	52	21
6	200	263	0.76	77	32
7	265	365	0.73	--	--
8	303	393	0.77	--	--
9	277	283	0.98	--	--

* Mn_o and Mn_d are oxalate and CBD extractable Mn, respectively.

however, values are always a fraction of those obtained for iron. Total aluminum levels are similar in magnitude to total iron values but are more uniform throughout the watershed. CBD extractable aluminum accounts for only about 10% of the aluminum in the bottom sediments, and 70-90% of this amount is also oxalate-extractable. These results suggest that some aluminum is probably co-precipitated with iron as acid drainage waters are introduced to the receiving streams.

Secondary manganese components are present in the bottom sediments in much smaller amounts (Table 2.7), and the distribution is opposite to that observed for aluminum and iron. Total manganese is not reported, as it is within the range obtained by dithionite extraction. Contents of manganese oxides appear to be higher in the bottom sediments of the reference areas, and to decrease in the zone of pollution. Although oxalate extractable manganese accounts for between 75-98% of the CBD extractable manganese, the distribution is puzzling, especially when water quality data (Table 2.1) are considered. These data show low concentrations of manganese in the reference areas, and high concentrations in the zone of pollution, exactly the opposite trend from that observed for the bottom sediments. The data suggest that the solubility of secondary manganese minerals is increased in the zone of pollution, perhaps due to the effect of reduced pH. This may have implications for the preferential dispersal of Mn from a source of pollution and warrants further study.

In any case, selective dissolution analyses indicate that poorly crystallized iron oxide is a major product of acid mine drainage in the Black Fork Creek watershed. This poorly crystallized iron oxide, besides enlarging the sediment

load of the receiving streams, also increases the surface area and chemical reactivity of the bottom sediments.

A comparison of surface areas for clays from one reference (site 3) and two sampling points in the zone of pollution (sites 5 and 6) reveals almost a three-fold increase in the downstream samples (Table 2.7). Since all three clays have similar surface areas after secondary iron compounds are removed with CBD, the increases must be due to the accumulation of iron precipitate in the receiving stream. Note also that there is little difference in the measured surface area of the reference clay before and after extraction with CBD.

Increases in surface area generally produce greater chemical reactivity. This is especially true when the increase is due to additions of poorly crystallized iron oxide, which is widely recognized as a scavenger of heavy metals and certain anions, such as phosphate, in fluvial environments (Chao and Theobald, 1976). An example of its effect on the sorptive capacity of bottom sediment clays from Black Fork Creek is given in Figure 2.6. Phosphate adsorption isotherms from a reference site (3) and from two polluted sites (5 and 6) show that clays from the polluted sections of Black Fork Creek are at least 2 to 4 times more adsorptive of added phosphate than are clays from the reference sites. The clay from site 6, constituted primarily of colloidal iron precipitate, probably represents an extreme case. The general reactivity of clays from sediment within the polluted portion of the basin is considered to be best represented by data for site 5.

2.5 Summary and Conclusions

Although water quality of streams affected by acid mine drainage varies with the season and with rainfall, the greatest contributors to pollution are increases in sulfate, iron, and aluminum with an associated decrease in pH.

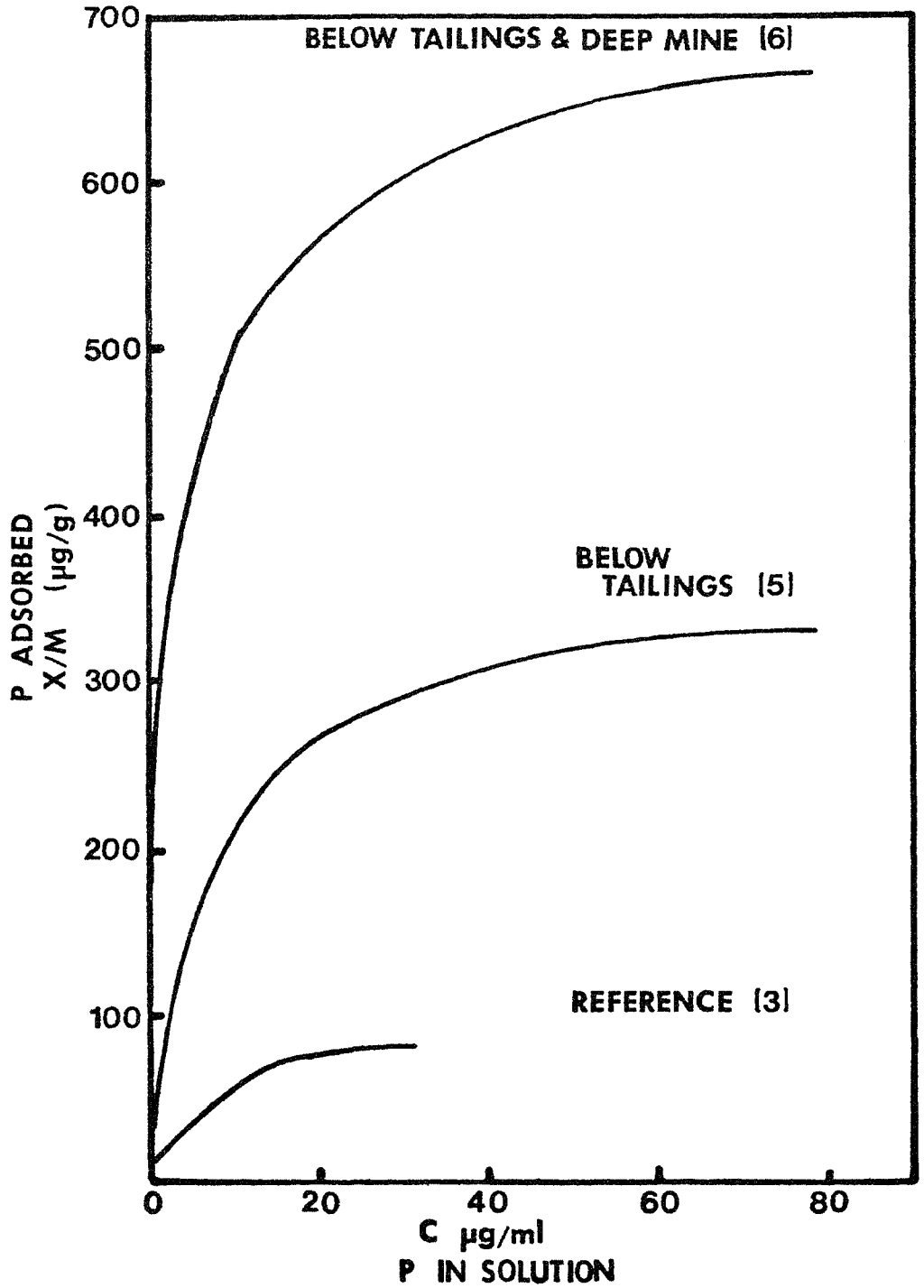

Figure 2.6 Phosphate adsorption isotherms of selected bottom sediments (<2 µm) from the Black Fork Creek watershed.

Crystalline clays contained in the bottom sediments of the Black Fork Creek watershed are remarkably similar throughout all portions of the drainage catchment. However, poorly crystallized minerals, particularly of iron, are significantly represented in the bottom sediments below sources of pollution. These iron oxide or oxy-hydroxide minerals greatly increase the surface area and reactivity of the bottom sediments, and are directly linked to the gelatinous precipitates resulting from acid mine drainage.

CHAPTER 3

INTERLABORATORY COMPARISON OF A STANDARDIZED PHOSPHORUS ADSORPTION PROCEDURE

3.1 Introduction

Laboratory adsorption procedures have been used for many years to measure phosphate (P) retention characteristics of soils and sediments (Logan, 1982; Nelson and Logan, 1983; Rao et al., 1980) and the results have been used to represent P adsorption by standard isotherm models such as those of Langmuir and Freundlich (Barrow, 1978; Olsen and Watanabe, 1957; Holford et al., 1974). The procedures used by researchers over the years have varied widely, and this has made comparison of isotherm coefficients from different research difficult if not impossible (Rao et al., 1980). Phosphate adsorption has been shown to vary with soil:solution ratio (Hope and Syers, 1976; Barrow and Shaw, 1979), ionic strength (Ryden et al., 1977) and cation species of the supporting electrolyte (Barrow et al., 1980; Helyar et al., 1976). Researchers have also used varying equilibration periods (Rao et al., 1980), and although adsorption is rapid, differences can occur in the range of 0.5 to 7 days most commonly used for equilibration. Other variables likely to affect equilibration are range of initial P concentrations, geometry of mixing (volume of soil suspension to headspace volume in equilibration vessel), rate and type (reciprocal vs end-over-end) of shaking (Barrow and Shaw, 1979) and type and extent of solid/solution separation after equilibration.

Adsorption procedures have been suggested for use in predicting partition of P between solution and solid phases in the environment (Logan, 1980, 1982; Nelson and Logan, 1983; Sharpley et al., 1981; McDowell et al., 1980), but these

are not likely to be routinely used until a standard procedure is developed. The objective of this study was to propose a standard P adsorption procedure and to determine the ability of individual laboratories to produce consistent results over a wide range of soils.

3.2 Methods and Materials

As a result of concerns about the difficulty of comparing results from much of the published literature on P adsorption, a group of researchers met in Fort Collins, Colorado in 1979 to propose a standard P adsorption procedure for soils and sediments. This group included: Vaughn Berkheiser and Suresh Rao, University of Florida; Boyd Ellis, Michigan State University; Terry Logan, The Ohio State University; Doyle Peaslee, University of Kentucky; Andrew Sharpley, USDA-ARS, Durant, Oklahoma; Lee Sommers, Purdue University and Ali Tabatabai, Iowa State University. After revision, the following procedure was produced:

1. Weight of soil/sediment - 0.5-1.0 g
2. Soil:solution ratio - 1:25
3. Extraction time - 24 h.
4. Electrolyte - 0.01 mol L^{-1} $CaCl_2$, unbuffered
5. Initial dissolved inorganic P concentrations - 0, 6.45, 16.13, 32.26, 161.3 and 323 μmol $P.L^{-1}$ as KH_2PO_4 or NaH_2PO_4
6. Temperature - 24-26°C
7. Microbial inhibition - 20 g L^{-1} chloroform
8. Equilibration vessel - 50 mL or other size to provide at least 50% head space
9. Shaking - end-over-end shaker if available

10. Separation - filter through 0.45 μm pore diameter filter (0.2 μm for clays)
11. Analysis - Any procedure for determination of orthophosphate, manual or automatic, capable of detecting >750 μmol P
12. Replication - duplicate equilibrations; single analysis of orthophosphate in solution

The proposed batch equilibration procedure was developed on the basis of published research and the shared experiences of the committee. It was recognized that, while there is no one correct procedure, previous research indicates that there is a range of conditions under which the equilibration must be conducted if the results are to have any meaning. The aim of the committee was to standardize the procedure by selecting a fixed set of conditions which could be followed rigorously by any laboratory. In particular, the procedure uses a low and narrow range of initial dissolved inorganic P concentrations (0-323 μmol L^{-1}) because these are more likely to be encountered in natural systems, because the higher levels often used in P adsorption research may result in precipitation of phosphorus solid phases, and because P adsorption at low concentrations give a better fit to linear adsorption models than data over a wider P concentration range (Holford et al., 1974).

Each researcher at the original meeting agreed to provide two soils from his region and to test the procedure on all the soils. Soils were provided by Iowa State University, Michigan State University, Ohio State University, Purdue University (Indiana), University of Florida and USDA-ARS (Oklahoma). The procedure was tested by Iowa State, Ohio State, Purdue and USDA-ARS (Durant, Oklahoma).

Approximately 1 kg of each soil was provided prescreened (<2 mm) to Ohio State University which agreed to distribute them and to collect and analyze the results. Lots of each soil identified only by number were then distributed to each laboratory. Duplicate values for the final solution inorganic P concentration for each of the six initial P concentrations was reported by each laboratory and any deviations from the proposed procedure were noted. All laboratories used the procedure as given above, with the exception of the University of Florida. Their work, performed by T. L. Yuan, used 0.03 mol L^{-1} KCl instead of 0.01 mol L^{-1} $CaCl_2$, and their results were not used in the general comparison, but were used to indicate effect of electrolyte cation. In addition, Iowa State performed the procedure at a soil: solution of 1:10 as well as at 1:25.

The 12 soils used in the study were analyzed at Ohio State University for total P by perchloric acid digestion (Sommers and Nelson, 1972) and for Bray P1 extractable P (Bray and Kurtz, 1945). Sharpley at USDA-ARS (Durant) determined labile P by ^{32}P isotopic exchange (Olsen and Dean, 1965).

The data was subjected to various statistical analyses using the SAS package at the Ohio State University Computer Center. Combined adsorption data for the four laboratories was corrected for previously adsorbed P by subtracting the measured labile P values for each soil and the data was fit by regression analysis to the linear Freundlich, Langmuir and Tempkin equations (Sibbesen, 1981).

3.3 Results and Discussion

3.31 Differences Among Laboratories

The 12 soils used in this study exhibited a wide range of properties (Table 1). Nine had medium textures (loam, silt loam, sandy loam, clay loam

Table 3.1 Total, Bray P1 extractable and isotopically exchangeable phosphorus of the 12 soils studied.

Soil Series	Soil Order	State	Total P	Bray-1 P	Isotopically Exch. P
			mmol kg^{-1}	—— μ mol kg^{-1} ——	
Blount silt loam	Alfisol	Indiana	17.34	939	1600
Canover loam	Alfisol	Michigan	18.15	784	1370
Chalmers silt loam	Alfisol	Indiana	19.76	2050	1880
Clarion loam	Mollisol	Iowa	14.11	1710	1730
Houston Black clay	Vertisol	Texas	15.73	610	1160
Hoytville silty clay loam	Alfisol	Ohio	27.21	594	1530
Locke sandy loam	Alfisol	Michigan	9.474	1130	748
Myakka fine sand	Spodosol	Florida	1.813	681	352
Nicollet clay loam	Mollisol	Iowa	13.10	216	768
Orangeburg loamy sand	Ultisol	Florida	1.813	119	371
Porte silt loam	Mollisol	Oklahoma	11.89	1200	1480
Rossmoyne silt loam	Alfisol	Ohio	21.77	284	865

and silty clay loam), and there were two sands and one clay. Total P ranged from 1.813 mmole kg^{-1} for the two Florida sands to 27.21 mmole kg^{-1} for the Hoytville silty clay loam from Ohio. Bray P1 also ranged widely from a low of 119 μmole kg^{-1} in the Orangeburg loamy sand to a high of 2050 μmole kg^{-1} in the Chalmers silt loam. There was some correspondence of isotopically exchangeable P and Bray P1 phosphate, but not in all cases.

Phosphorus adsorbed was calculated for each initial P concentration level, and the results are presented in Table 2 for the four laboratories and the 12 soils. The data indicate that there was good agreement among the laboratories in all cases. Coefficients of variation (CV) ranged from 0.04 to 7.23% with a mean over all initial P levels and soils of 0.91%. Averaged over initial P levels, CV's were highest for Myakka fine sand (2.95%) and Locke sandy loam (1.87%) and lowest for Nicollet clay loam (0.15%) and Hoytville clay loam (0.29%). The higher clay soils may have more readily buffered solution P concentrations and, therefore, reduced variation. Averaged over the 12 soils, CV's were lowest for the four lowest initial P levels (0.48, 0.41, 0.77 and 0.29%) and highest for 161.3 and 322.6 μmol L^{-1} (1.03 and 1.87%, respectively). This would indicate that the four laboratories had analytical detection limits for orthophosphate that were adequate to measure, with precision, the concentration differences found for the lowest initial P levels (0-32.25 μmole L^{-1}).

The laboratories also exhibited a high degree of replication of individual treatments. Because of this, there were significant differences among laboratories for most of the comparisons (Table 2) even though the coefficients of variation were low. These differences must be viewed, however, in terms of acceptable variation. For example, laboratory No. 3 had significantly more P

Table 3.2 P adsorbed by 12 soils at six initial phosphorus solution concentrations as reported by the four laboratories.

Lab	Initial P Conc (μmol L^{-1})					
	0.0	6.45	16.13	32.25	161.3	322.6
	P adsorbed (mmol kg^{-1})					
			Blount silt loam			
1	1.573c	1.731c	1.931ab	2.340a	4.860a	6.883a
2	1.577b	1.736b	1.888b	2.325b	4.608b	6.434c
3	1.584a	1.741a	1.968a	2.335a	4.803a	6.646b
4	1.573c	1.727d	1.957a	2.315b	4.612b	6.297c
Error CV (%)	0.04	0.05	1.17	0.16	0.69	0.92
			Canover loam			
1	1.335a	1.484a	1.712a	2.061b	4.243b	5.948ab
2	1.336a	1.488a	1.642b	2.069b	3.948c	5.710c
3	1.345a	1.500a	1.713a	2.068b	4.271b	5.850b
4	1.339a	1.489a	1.720a	2.082a	4.409a	6.002a
Error CV (%)	0.30	0.42	0.28	0.18	0.72	0.84
			Chalmers silt loam			
1	1.794a	1.920b	2.132a	2.462b	4.565a	6.189b
2	1.779a	1.922b	2.071b	2.456b	4.345c	5.937c
3	1.797a	1.937a	2.138a	2.455b	4.463b	5.858c
4	1.793a	1.937a	2.119a	2.483a	4.295c	6.303a
Error CV (%)	0.35	0.19	0.54	0.29	0.65	0.61

Table 3.2 Continued.

Lab	Initial P Conc (μ mol L^{-1}) 0.0	6.45	16.13	32.25	161.3	322.6
	P adsorbed (mmol kg^{-1})					
			Clarion loam			
1	1.652a*	1.793a	2.021a	2.287b	4.410a	5.775a
2	1.648a	1.776b	1.919d	2.316a	4.138c	5.405b
3	1.644ab	1.792a	1.998b	2.294a	4.258b	5.529b
4	1.634b	1.791a	1.969c	2.282b	4.040d	5.185c
Error CV (%)	0.24	0.12	0.37	0.18	0.76	1.42
			Houston Black clay			
1	1.129a	1.278a	1.515a	1.892a	4.411a	6.991a
2	1.124b	1.271b	1.423d	1.853b	4.221d	6.344c
3	1.133a	1.280a	1.503b	1.852b	4.276c	6.764b
4	1.123b	1.274ab	1.496c	1.858b	4.332b	6.699b
Error CV (%)	0.14	0.21	0.14	0.13	0.15	1.23
			Hoytville silt clay loam			
1	1.512a	1.665a	1.905a	2.297a	5.219a	8.098a
2	1.507b	1.669a	1.825b	2.290a	5.103b	7.753c
3	1.511a	1.673a	1.907a	2.291a	5.124b	7.930b
4	1.511a	1.665a	1.904a	2.291a	5.108b	7.671c
Error CV (%)	0.04	0.20	0.15	0.11	0.61	0.61

Table 3.2 Continued.

Lab	Initial P Conc (μmol L^{-1}) 0.0	6.45	16.13	32.25	161.3	322.6
	P adsorbed (mmol kg^{-1})					
			Locke sandy loam			
1	0.633a	0.779b	0.917b	1.146c	2.611a	3.799a
2	0.644a	0.781b	0.929b	1.194b	2.358bc	3.089b
3	0.668ab	0.775b	0.941b	1.175b	2.292c	3.019b
4	0.700a	0.833a	1.018a	1.257a	2.434b	3.297b
Error CV (%)	1.91	0.44	1.82	0.65	1.82	4.58
			Myakka fine sand			
1	0.286a	0.390b	0.528bc	0.670c	1.818a	2.546a
2	0.290a	0.394b	0.504c	0.724b	1.427c	1.835b
3	0.304a	0.406a	0.556ab	0.745ab	1.587bc	2.039b
4	0.300a	0.414a	0.563a	0.750a	1.642ab	1.721b
Error CV (%)	2.06	0.83	2.29	1.11	4.15	7.23
			Nicollet clay loam			
1	0.766a	0.927a	1.167a	1.562a	4.641a	7.937a
2	0.762b	0.922b	1.082c	1.562a	4.638ab	7.952a
3	0.766a	0.926a	1.168a	1.561a	4.597bc	7.861b
4	0.760c	0.919c	1.160b	1.558a	4.583c	7.828c
Error CV (%)	0.11	0.06	0.05	0.17	0.33	0.18

Table 3.2 Continued.

Lab	Initial P Conc (μmol L^{-1}) 0.0	6.45	16.13	32.25	161.3	322.6
	P adsorbed (mmol kg^{-1})					
			Orangeburg loamy sand			
1	0.365b	0.523a	0.727a	1.127d	3.328bc	4.296b
2	0.366b	0.524a	0.688b	1.149c	3.224c	4.306b
3	0.370a	0.531a	0.768a	1.155b	3.395b	4.634ab
4	0.365b	0.530a	0.768a	1.164a	3.677a	4.774a
Error CV (%)	0.09	0.59	1.95	0.05	1.33	3.28
			Porte silt loam			
1	1.383c	1.526b	1.732b	2.042b	3.864a	5.032a
2	1.407b	1.534b	1.675c	2.025b	3.510c	4.665b
3	1.421a	1.560a	1.756a	2.066a	3.743b	4.785b
4	1.426a	1.577a	1.766a	2.080a	3.698b	4.642b
Error CV (%)	0.20	0.49	0.23	0.35	0.79	1.23
			Rossmoyne silt loam			
1	0.859a	1.016a	1.264a	1.644b	4.518b	7.178b
2	0.858a	1.018a	1.176c	1.652a	4.493b	6.974c
3	0.861a	0.988a	1.256ab	1.648ab	4.518b	7.186b
4	0.852b	1.013a	1.247b	1.652a	4.599a	8.174a
Error CV (%)	0.23	1.35	0.27	0.12	0.41	0.35

* Mean within a vertical column for each soil not followed by the same letter are significantly different at the 0.05 level.

adsorbed by Orangeburg loamy sand at the 0 μmole L^{-1} initial P level than the other three labs (Table 2), yet the absolute difference among the four labs was only 0.005 mmole kg^{-1}. The environmental implications of this difference would be considered insignificant in most cases.

Although significant differences did exist between the four laboratories, there appeared to be no evidence of bias. This was determined by examining the ranking of each laboratory at each initial P level. The number of times a laboratory ranked first highest P sorption or last lowest P sorption was summed over the 12 soils and presented in Table 3. If there were no bias, each laboratory should rank first and last three times. Cases where two laboratories had the same result for P adsorption were not included. Laboratory No. 1 appeared to be biased towards high P adsorption at the two highest initial P levels and laboratory No. 3 to high P adsorption at the lowest initial P level. Laboratory No. 4 showed little evidence of bias while laboratory No. 2 showed a consistent bias toward low P adsorption, especially at the 16.13 and 161.3 μmol L^{-1} initial P concentration. No laboratory showed a strong consistent bias across all soils and initial P levels, however, and determination of bias is made difficult by the small number of laboratories involved.

3.32 Fit to Equilibrium Adsorption Isotherms

The data for the four laboratories were combined and used for each soil to fit three equilibrium adsorption models (adsorption data was corrected for previously adsorbed P by subtracting isotopically exchangeable P): Langmuir, Freundlich and Tempkin (Sibbesen, 1981). All three models were highly correlated with the adsorption data with R^2 values ranging from 0.89 to 0.99. The mean correlations for the 12 soils were 0.98, 0.97 and 0.95 for the

Table 3.3 Frequency of each laboratory ranking first (highest P sorption) or last (lowest P sorption) with respect to each other in P adsorption at each initial P concentration. Uses data for the 12 soils.

	Initial P Conc (mmol L^{-1})													
	0.0		6.45		16.13		32.25		161.3		322.6		Mean	
Lab	1†	4†	1	4	1	4	1	4	1	4	1	4	1	4
1	3	4	2	5	3	1	3	5	9	1	7	1	4.5	2.8
2	0	2	1	2	0	11	1	2	0	7	1	3	0.5	3.7
3	7	0	5	2	4	0	0	2	0	1	0	2	2.7	1.2
4	2	4	3	2	4	0	6	2	2	3	4	6	3.5	2.8
M‡	12	10	11	11	11	12	10	11	11	12	12	12	--	--

† 1 and 4 represent laboratory ranking as first or last, respectively.
‡ M = No of comparisons. M will be <12 if two or more labs had identical results.

Langmuir, Freundlich and Tempkin models, respectively. Figures 1-3 give the best fit plots for the three equations and the data points for three of the soils. The form of the curves were representative of that found for the other soils. All three plots show a deviation of the Freundlich isotherm to higher predicted P adsorption compared to the other two equations, but the Freundlich equation best represented the data, especially at higher P concentrations. The good fit of the data for the 12 soils to the three models can be attributed to the low initial P concentrations used in the procedure, which probably precluded any precipitation of dissolved inorganic P. Yet these levels are in the range found most often in natural environments, even those perturbed by livestock and human wastes and fertilizers (Armstrong et al., 1974).

3.33 Effect of Soil:Solution Ratio and Supporting Electrolyte on P Adsorption

The standard procedure used a soil:solution ratio of 1:25 and 0.01 mol L^{-1} $CaCl_2$ supporting electrolyte. In addition, one laboratory used a 1:10 soil: solution ratio and another used 0.03 mol L^{-1} KCl supporting electrolyte. The effects of varying these two factors was examined by looking at the EPC_0 (the equilibrium P concentration at P adsorption = 0). The results (Table 4) show that P adsorption was generally greater with K^+ as the supporting electrolyte cation compared to Ca^{2+}. This is similar to findings of Barrow et al. (1980) and Helyar et al. (1976). The effect was most pronounced at higher equilibrium P concentrations. The effect of soil:solution ratio was inconsistent and generally smaller than the effect of supporting electrolyte, yet large enough to warrant standardizing both factors in the procedure.

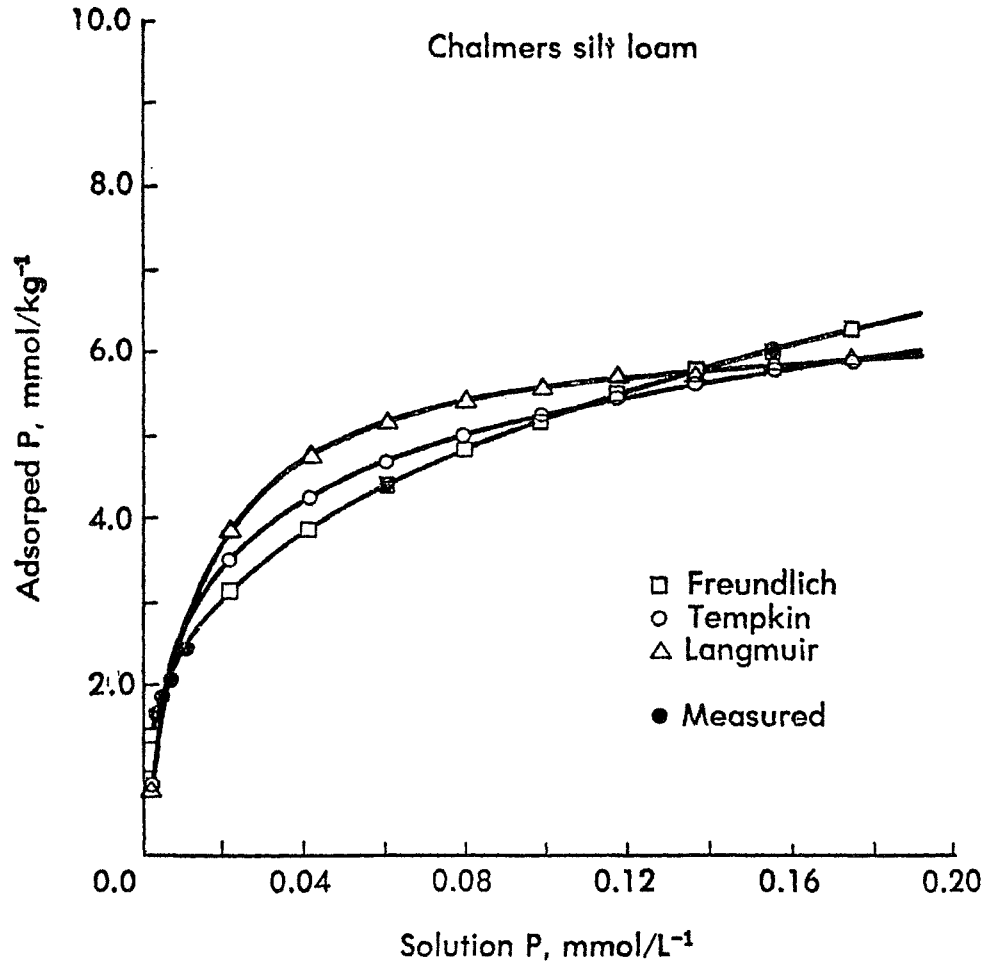

Figure 3.1 Best fit lines for the Freundlich, Tempkin and Langmuir adsorption isotherms for dissolved inorganic P adsorbed by Chalmers soil. The data points are the closed circles. Mean of data for the four laboratories.

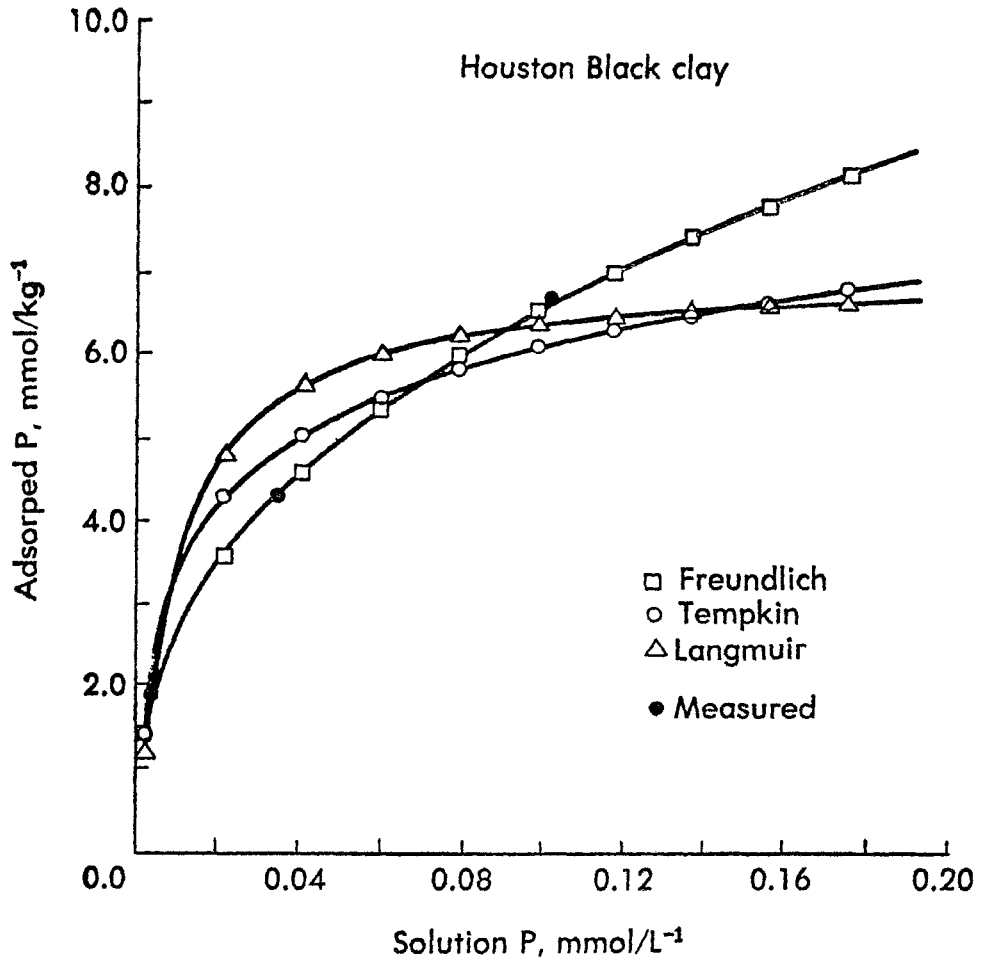

Figure 3.2 Best fit lines for the Freundlich, Tempkin and Langmuir adsorption isotherms for dissolved inorganic P adsorbed by Houston Black soil. The data points are the closed circles. Mean of data for the four laboratories.

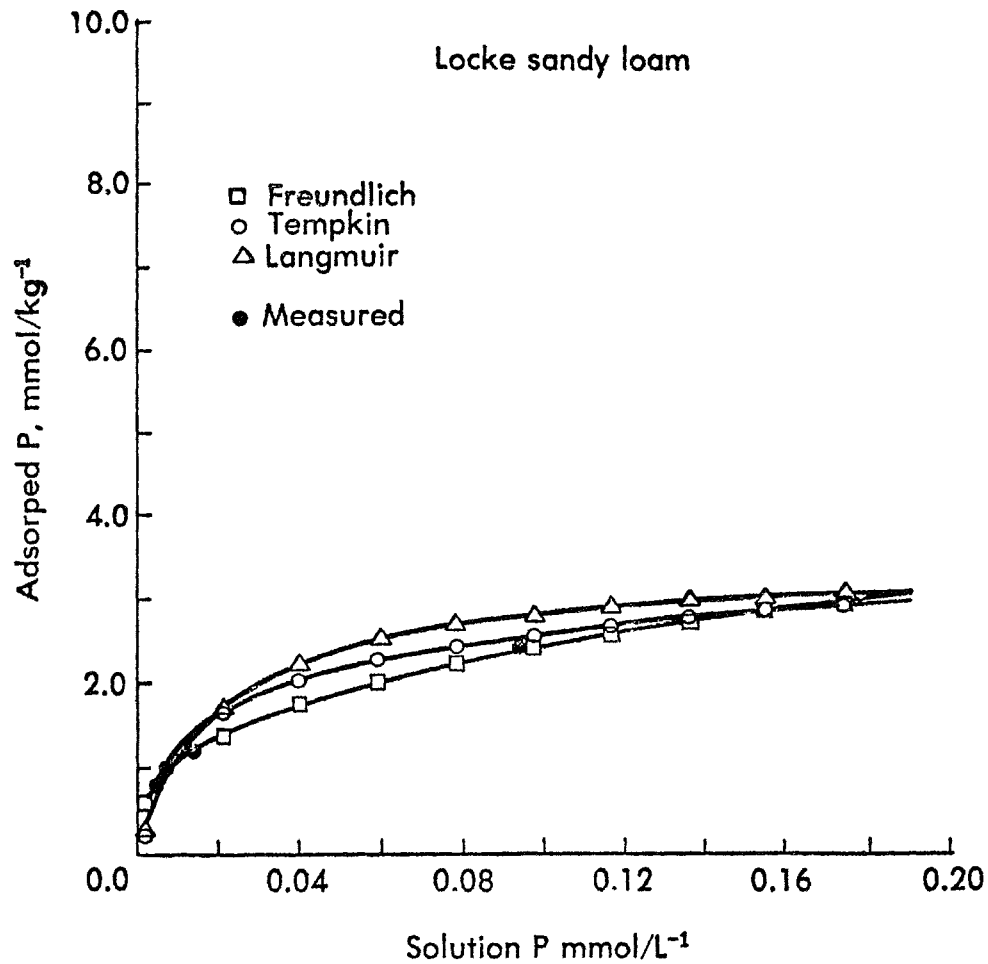

Figure 3.3 Best fit lines for the Freundlich, Tempkin and Langmuir adsorption isotherms for dissolved inorganic P adsorbed by Locke soil. The data points are the closed circles. Mean of data for the four laboratories.

Table 3.4 Effect of soil:solution ratio and background electrolyte on equilibrium phosphorus concentration (EPC_0) of the 12 soils studied.

Soil	EPC_0		
	Soil:Soln. 1:25 0.01 mol L^{-1} $CaCl_2$†	Soil:Soln. 1:10 0.01 mol L^{-1} $CaCl_2$	Soil:Soln. 1:25 0.03 mol L^{-1} KCl
	μmol L^{-1}		
Blount silt loam	1.16	1.42	2.58
Canover loam	1.32	1.26	1.90
Chalmers silt loam	4.71	4.52	6.10
Clarion loam	4.00	4.42	7.84
Houston Black clay	1.45	1.71	1.68
Hoytville silty clay loam	0.710	0.710	1.19
Locke sandy loam	5.52	2.87	6.77
Myakka fine sand	4.13	3.23	12.5
Nicollet clay loam	0.129	0.323	0.323
Orangeburg loamy sand	0.129	0.129	0.581
Porte silt loam	4.03	2.87	4.03
Rossmoyne silt loam	0.258	0.516	0.452

† Mean of data from three laboratories.

3.4 Conclusions

This study showed that individual laboratories can obtain reproducible results when using a standarized procedure for P adsorption by soil, and that the data can be fit to one or more adsorption isotherms. The procedure given here incorporates features from many of those published previously, and while no one method is the best, this method has the potential to produce consistent results which can be used to predict partitioning of dissolved inorganic phosphorus between solid and solution phases in the environment.

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