Effects of Brining and Salt By-Products Operations on the Surface and Ground Water Resources of the Muskingum Basin, Ohio

Jon L. Rau
Department of Geological Sciences
The University of British Columbia
Vancouver, B. C.

ABSTRACT

The soda ash operation of Pittsburgh Plate Glass (PPG) Industries at Barberton, Ohio, has been a major contributor of dissolved solids, especially chloride, in the Tuscarawas and Muskingum Rivers. Chloride rich effluent discharged to the Tuscarawas River at Clinton effects the quality of both surface and ground waters for considerable distances downstream. Chloride levels fluctuate widely depending on the rate of effluent discharge at Clinton, the flow of the river, and the degree of seepage from brine disposal ponds at Barberton. Low flow periods are especially critical to ground water reservoirs which are pumped to induce river water through sand and gravel sequences of a buried valley system along the main stem of the Muskingum drainage. The Barberton municipal well field was abandoned in 1926. The Massillon well field was seriously affected in 1952–1953 and was relocated in 1955. Brine contamination forced abandonment of a well field at Coshocton in 1953 and the development of a new field cost 500,000 dollars. Zanesville and Marietta suffered from serious quality problems during low flow periods between 1945 and 1972 whenever the Muskingum River chloride levels exceeded 250 mg/l.

Such problems have caused considerable concern and expense to these five municipalities which have contended with the high choloride levels for many years. Chloride levels in the river have ranged as high as 10,050 (1953) but low flow periods from 1900 to 1971 have always had some days when chloride exceeded the maximum level recommended for domestic drinking water. The soda ash operation was terminated in 1973 and new proposed regulations by the U.S. Environmental Protection Agency will limit chloride to a maximum of 60 mg/l at any time.

INTRODUCTION

Most corporations in the salt industry are aware of the effect of their corporate image on the eventual acceptance of their products. As a result, profitability is tied to a "good neighbor" policy in the company town as well as to other factors which enhance the company's national image. A part of protecting this image forces company management to maintain a plant that has become obsolete either through increased cost of production or due to lack of proper waste disposal facilities which are costly to install and maintain. Consequently, company management may find it worthwhile to perpetuate the operation of a plant long after it has become an environmental hazard rather than endure the publicity attendant upon plant shut-down in the company town. But what may be a good neighbor policy in the company town may be viewed as arrogant by downstream users on the same watercourse where the quality of both domestic and industrial water is impaired. There is never an easy solution to this problem that is satisfactory to the company, the employees of the company as well as to the downstream users affected by the company's disposal practices. The question remains as to how far the good neighbor sphere should extend in any single watershed.

The author takes the point of view that each user is responsible for returning the water to the system in a condition that is reasonably close to maintaining the pre-industrial ecology of the watershed. Such a philosophy requires, in some cases, treatment beyond that demanded by state and federal water quality standards, which to a large extent are determined after considerable political maneuvering and negotiation on the part of government and industry.

Problems with chloride rich waters

Large quantities of chloride in water cause serious problems for both domestic and industrial users. Chloride in excess of 300 to 500 mg/1 can alter the taste of domestic water. Further, water that contains more than 500 mg/1 of chloride in the form of calcium or magnesium chloride is highly corrosive. Industries cannot tolerate such waters in processing, cooling and distribution systems. For example, the pharmaceutical, food processing and soft drink industries are only a few of many industries requiring water low in chloride. Even water with less than 10 mg/1 must be treated by some industries before processing. Obviously, the costs of plant operation are closely related to the degree of treatment required.

Waters which are excessive in chloride are defined as those which contain more than 250 mg/1. Such quantities in shallow ground water are generally the result of a surface source of contamination either by direct leakage from brine wells, oil wells, brine disposal ponds, or by infiltration of brine rich surface waters during pumping of ground water reservoirs.

Chloride behavior in water. The chloride ion, Cl^-, does not significantly react to form solute complexes with other ions, nor does it become adsorbed on mineral surfaces. It tends to move through most soils with less loss than most other ions. Concentrations of chloride are lower than either sulfate or bicarbonate in most surface waters (Hem, 1970, p. 172). On the other hand substantial contributions of chloride from hot springs and volcanic gases may contribute to the chloride load in some streams but neither of these sources is present in northeastern Ohio. Unfortunately, the chloride ion tends to be retained in solution while most processes remove other ions. The only important barriers to chloride movement in soils and rocks are clay and shale because the chloride ion is so large that its migration through the microscopic pores in such fine-grained material is negligible.

Present standards and physiological effects on health of Muskingum basin water

Present standards as set by the Water Pollution Control Board, Ohio Department of Health on March 14, 1972 require that the waters of the Muskingum River Basin be "free from substances attributable to municipal, industrial or other discharges, or agricultural practices in concentrations or combinations which are toxic or harmful to terrestrial and aquatic life." Dissolved solids are not to exceed 500 mg/1 as a monthly average value, nor exceed 750 mg/1 at any time. Further, the present standards also indicate that public water supplies must meet Federal drinking water standards for finished water. This means such waters must not contain over 250 mg/1 of chloride.

The Ohio River Valley Water Sanitation Commission discussed the physiological effect on health of sodium rich waters (1951, p. 15–16).

> The medical profession in recent years has compiled evidence to indicate that sodium intake is an important factor in the treatment of cardiac and hypertension patients. One authority recommends 200–400 milligrams of sodium per day as the permissible limit of intake in such cases (Principles of Internal Medicine, T. R. Harrison, editor, Blakiston Company, Philadelphia, 1950, page 1323).

A patient consuming more than two quarts daily of surface or ground water with an average sodium concentration of 253 mg/1 would exceed the upper limit recommended by some medical practitioners.

Current data on sodium is not available for the Tuscarawas or Muskingum Rivers except for one or two well fields in the lower part of the basin (Fig. 1). An estimate of sodium content may be made by taking half of the chloride ion concentration. The only area in the basin where sodium concentrations are likely to exceed 250 mg/1 in the Tuscarawas River is between Clinton and New Philadelphia. In 1971 (U. S. Geological Survey Water Year for the period October, 1969–September, 1970) the mean chloride concentrations at Navarre, Ohio, 3.5 miles downstream from Massillon, was 1534 mg/1 (U.S. Geological Survey, 1972, p. 33). Sodium concentrations in river water probably range from 500 to 700 mg/1 at Navarre and, no doubt, are higher upstream near Clinton where brine from the soda ash plant of PPG Industries is discharged.

In 1951 the average sodium concentration of the Tuscarawas River between Clinton and Coshocton was 253 mg/1 whereas chloride levels averaged 817 mg/1 during the same period. (Ohio River Valley Water Sanitation Commission, 1951, p. 13).

BRINE WASTE DISPOSAL IN THE UPPER TUSCARAWAS RIVER

PPG Industries is one of two leading producers of plate and float glass in the U.S. Such glass is used by the auto industry in the manufacture of safety glass. Other uses include glass for store fronts, mirrors, etc. PPG Industries

Figure 1. Index map showing location of Muskingum Basin in Ohio.

ranks as one of the leading producers of sheet or window glass as well as soda ash for the manufacture of glass, soap, oil, textiles, drugs, pulp and paper and for water softening purification processes.

The company was formed in 1883 and in 1899 it created a major subsidiary known as the Columbia Southern Chemical Corporation which located its plant in Barberton, Ohio. This subsidiary was merged with the parent company on December 31, 1960. Net sales of PPG Industries were $1,238,472,000 in 1971 (Moody's Industrial Manual, 1972, p. 2678). The Chemical Division of PPG Industries has enjoyed a remarkable growth rate, the envy of the industry, and boasted that in 1965 its sales were more than 7 times those of 1945, and substantially better than the average growth rate of the industry.

The by-products of the Chemical Division's plant at Barberton on the Upper Tuscarawas River contribute to major water quality problems in both surface and ground waters of the Muskingum Basin (Fig. 2). The problem has had a remarkably long and consequently, a costly history in the Upper Tuscarawas River. Not only are the water resources of this river affected but also those of the Mus-

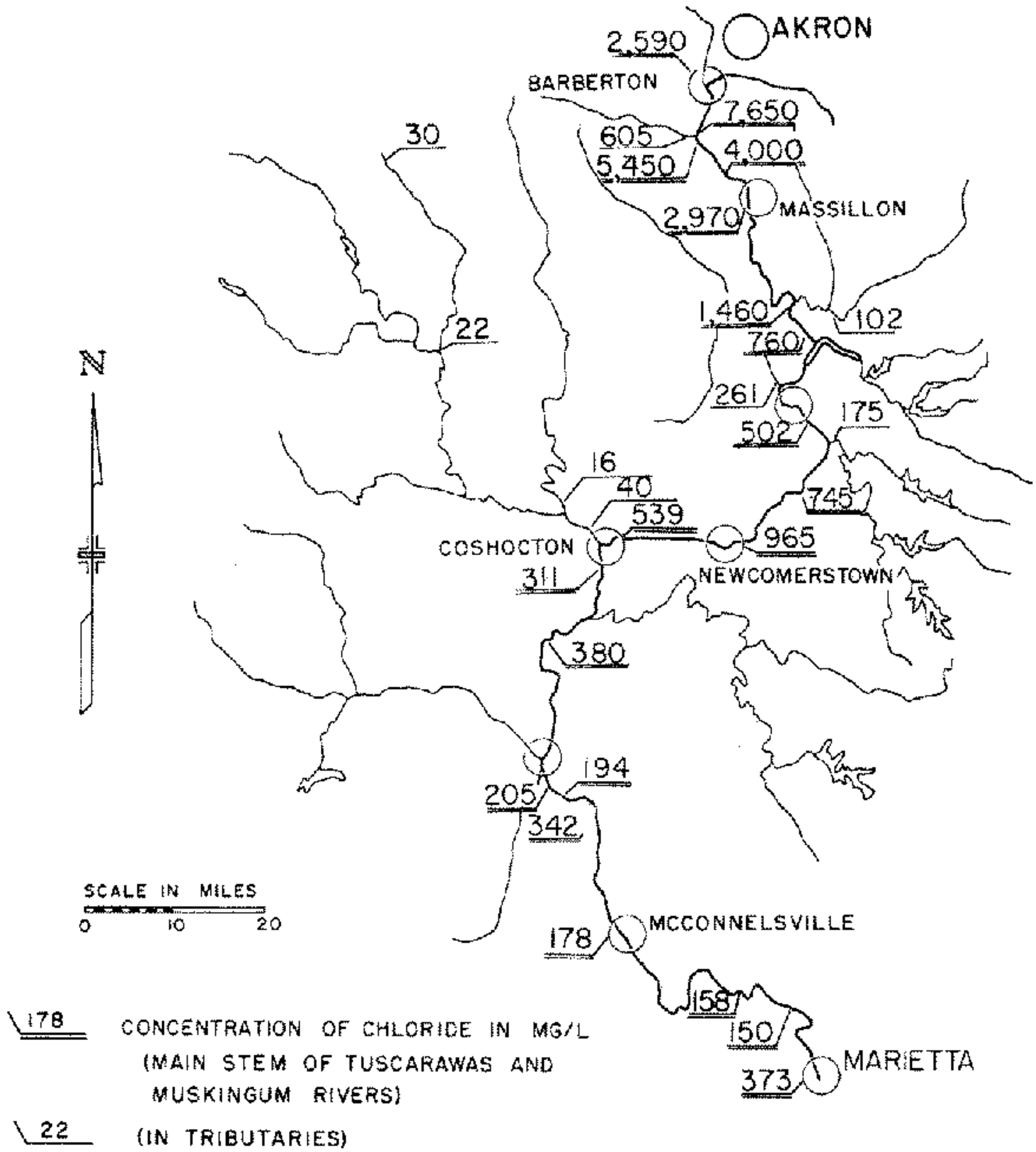

Figure 2. Chart showing chloride concentration range in selected streams of the Muskingum Basin as well as water-quality criteria for selected industries. (Data from Ohio Department of Health, 1968).

kingum River, rising more than 100 miles downstream where the Tuscarawas and Waldonding Rivers merge. Data were collected on the chloride concentration, hardness and total dissolved solids of both surface and ground waters of these areas to show the widespread effects of brine waste disposal in the Muskingum Basin.

Robinson (1955, p. 153) reported that the Columbia Southern Chemical Company had a $60,000,000 investment at Barberton and that the firm employed more than 2,000 people. Up until 1955 the Company had invested more than $1,000,000 to reduce waste discharge and may have spent another million in the period 1955–61. In 1956 new trichlorethylene and calcium chloride plants were put into operation at Barberton. This represents a major effort to reduce the calcium chloride discharge by producing a marketable by-product from the soda ash operation.

Soda ash problem at Barberton

Pittsburg Plate Glass Industries uses the Solvay ammonia soda process for the manufacture of sodium carbonate which is necessary in the manufacture of soda glass. Glass of this type constitutes 90 percent of the total U.S. glass production. The Solvay process is the most economical process for making soda ash which generally is not present in sufficient amounts in rocks and sediments to be economically extractable. The very large volume of very highly concentrated sodium chloride-calcium chloride waste generated by the production of soda ash constitutes one of the most difficult pollution control problems facing the salt industry (Cecil, 1971). One may argue that technology is available to handle this pollution problem by when cost-benefit ratios are computed, and placed next to the competitive nature of the chemical manufacturing industry, by-product recovery operations remain too expensive to adopt for most companies.

The only practical method of disposal for plants discharging to fresh water in mid-continent locations is by controlled dilution (mainly during high flow periods) to streams. A second method, commonly used conjunctively with controlled emission to a river is to remove the solids by settling in large lagoons or waste lakes, several hundred acres in extent. Impounding on this scale is expensive and troublesome, even though land availability is not a serious problem in the Barberton area, all other factors neglected. During its life, a soda ash plant may require several waste lakes, with new areas opened as old ones are filled, as it has at Barberton. When the solids are settled, the dissolved chloride problem remains. The ammonia-soda ash process is only about 75 percent efficient in terms of sodium and uses none of the chloride occurring in the original brine. Production of 1 ton of soda ash results in about 1-1/2 tons of soluble chlorides as waste.

A portion of the calcium chloride generated at Barberton is now recovered by evaporation of the brine waste. In 1966 such waste was estimated to total 5.7 mgd with an average chloride ion concentration of about 64,000 mg/1. The daily discharge of chloride averaged about 1,500 tons or more than 500,000 tons in 1966. The average chloride concentration in 1965 at Clinton where the plant discharges its waste by controlled dilution to the Tuscarawas River was 3,900 mg/1. Only partial records of chloride concentration are available for the 1971 water year at Clinton. If one assumes that the maximum chloride concentration can be correlated with the maximum specific conductance and that the mean chloride concentration can be computed by averaging the minimum and maximum chloride levels reported, the mean chloride concentration at Clinton in 1971 was 4680 mg/1 (U.S. Geological Survey, 1972, p. 350). Maximum chloride concentration reached 6000 mg/1 on September 20, 1971 at the U.S. Geological Survey gaging station on the Tuscarawas River near Clinton during the 1971 water year.

Effect of brine discharge at Barberton

The PPG plant at Barberton utilizes both methods of waste disposal previously discussed. In 1971, the two southernmost disposal ponds were being utilized and two others further north and closer to Barberton had been filled during the operation of this plant over 70 years of soda ash production. The total area covered by the four ponds exceeds 520 acres and they rise at least 20 feet above the flood plain surface of the Tuscarawas River. No estimate has been made of the volume of precipitated salt held in these disposal areas. It is not known whether these ponds spill or leak brine but the following data suggest that there is a seepage loss from the waste lakes.

A field study of the disposal pond area and adjacent area by the author in 1968–69 revealed that substantial amounts of brine reached the Tuscarawas River which contained chloride ranging from 2,090 to 2,610 mg/1 near the southernmost lakes (Fig. 3). Narrow shallow trenches bordering the ponds contained water ranging from 1,030 to 1,140 mg/1. Small tributaries draining upland areas east of the Tuscarawas River and above the ponds contained concentrations of chloride ranging from 15 to 53 mg/1. A spring, emerging from the glacial drift south of the lakes, contained 15 mg/1. Surface waters north of the industrial area but within the Barberton city limits contained chloride ranging from 150 to 500 mg/1. Water wells north of Barberton and on the west side of Wolf Creek ranged from 25 to 88 mg/1 of chloride. Wolf Creek, 1/2 mile north of the Barberton city limit, contained 100 mg/1 of chloride. In general, the wells which were sampled were shallow domestic wells utilizing less than 2 gpm during part of each day and were not pumped continuously for more than 1 hour. Such wells cannot induce

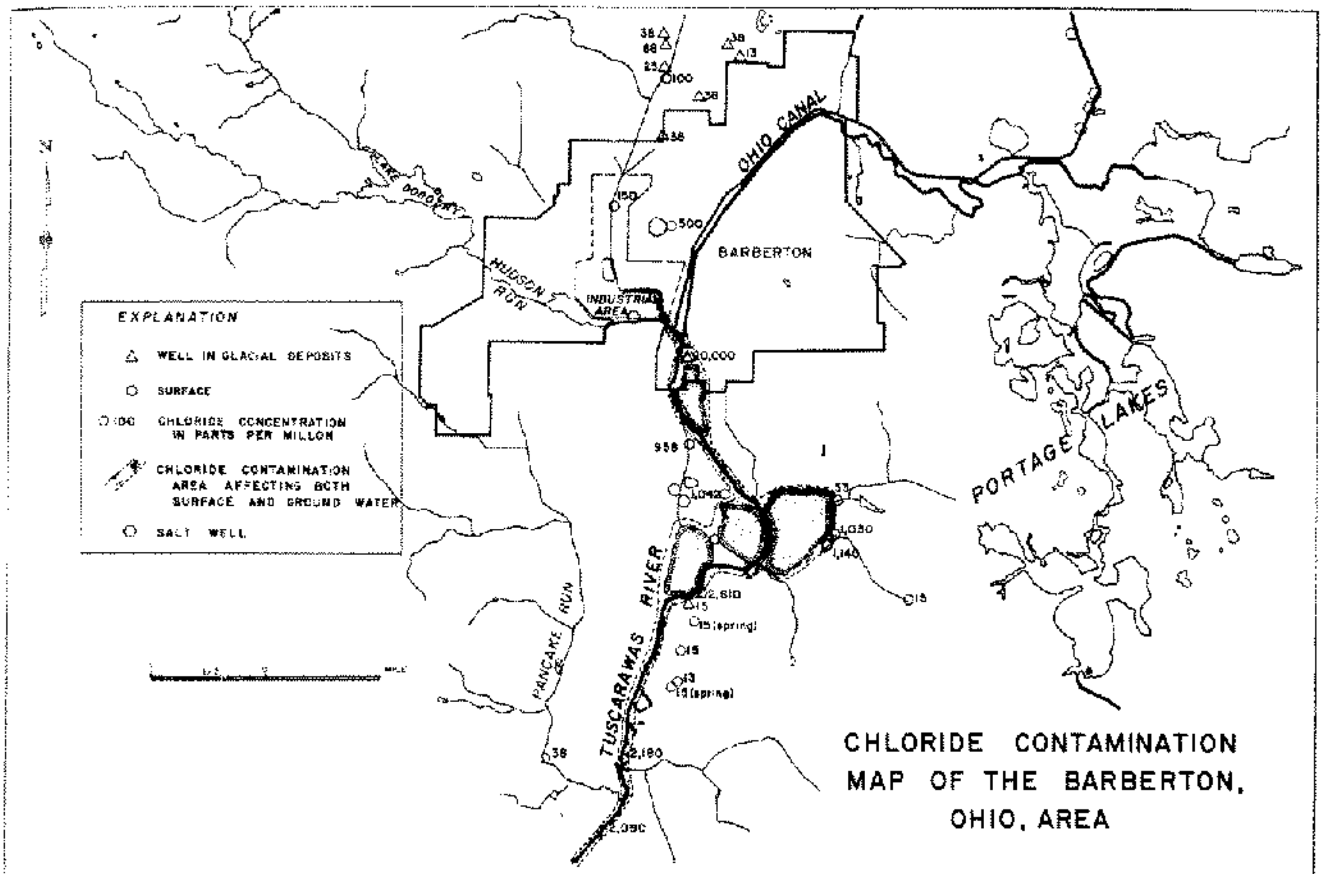

Figure 3. Map showing chloride contamination and levels in selected wells, springs and streams in the Barberton area.

water from the Tuscarawas River because the hydrostatic head between them and the River is still above river level. Therefore these wells must be recharged from upland sources and not river water. Streams heading in upland areas both east and west of the River are only slightly richer in chloride than the ground water and may reflect airborne contamination from the disposal operations in the lakes where the water vapor from the warm slurry contains more than the average concentration of chloride. Adjacent soils, no doubt, also contain somewhat abnormal chloride concentrations.

Effect of chloride on ground water resources at Barberton

Along the west edge of Akron and following the route of the old Ohio Canal a wide and moderately deep buried valley is present. It continues beneath the city of Barberton and follows the main stem of the Tuscarawas south through Canal Fulton to join a complex of meltwater channels south of Canton (Fig. 4). In most places this valley is filled with more than 200 feet of glacial material consisting locally of thick sequences of alluvial sand and gravel laid down by the ancestral Cuyahoga and Tuscarawas River systems. The surface of most of this valley is also underlain by coarse outwash which allows rapid infiltration of surface water. North of Barberton and along Wolf Creek about 2 billion gallons of ground water are pumped from buried valley aquifers each year (Smith and White, 1953, p. 50).

Barberton well field. The old Barberton well field was located near the present north limit of the city and in the valley of Wolf Creek. These wells yielded from 1,000 to 1,500 gallons a minute (Smith and White, 1953, p. 50). Barberton's well field had to be abandoned in 1926 because of high salt content and the city now relies upon reservoirs on Pigeon and Wolf Creeks. This may be the first recorded adverse effect to a municipal supply by the soda ash operation at Barberton. There is also a possibility that leaky casings in nearby brine wells may have been responsible for the contamination.

Prior to 1947 the Columbia Southern Chemical Corporation drilled a well on the east side of the Tuscarawas River adjacent to one of their disposal operations on the other side of the river. The geologic conditions were excellent for the development of a well which could have yielded upwards of 1,000 gpm but the water contained

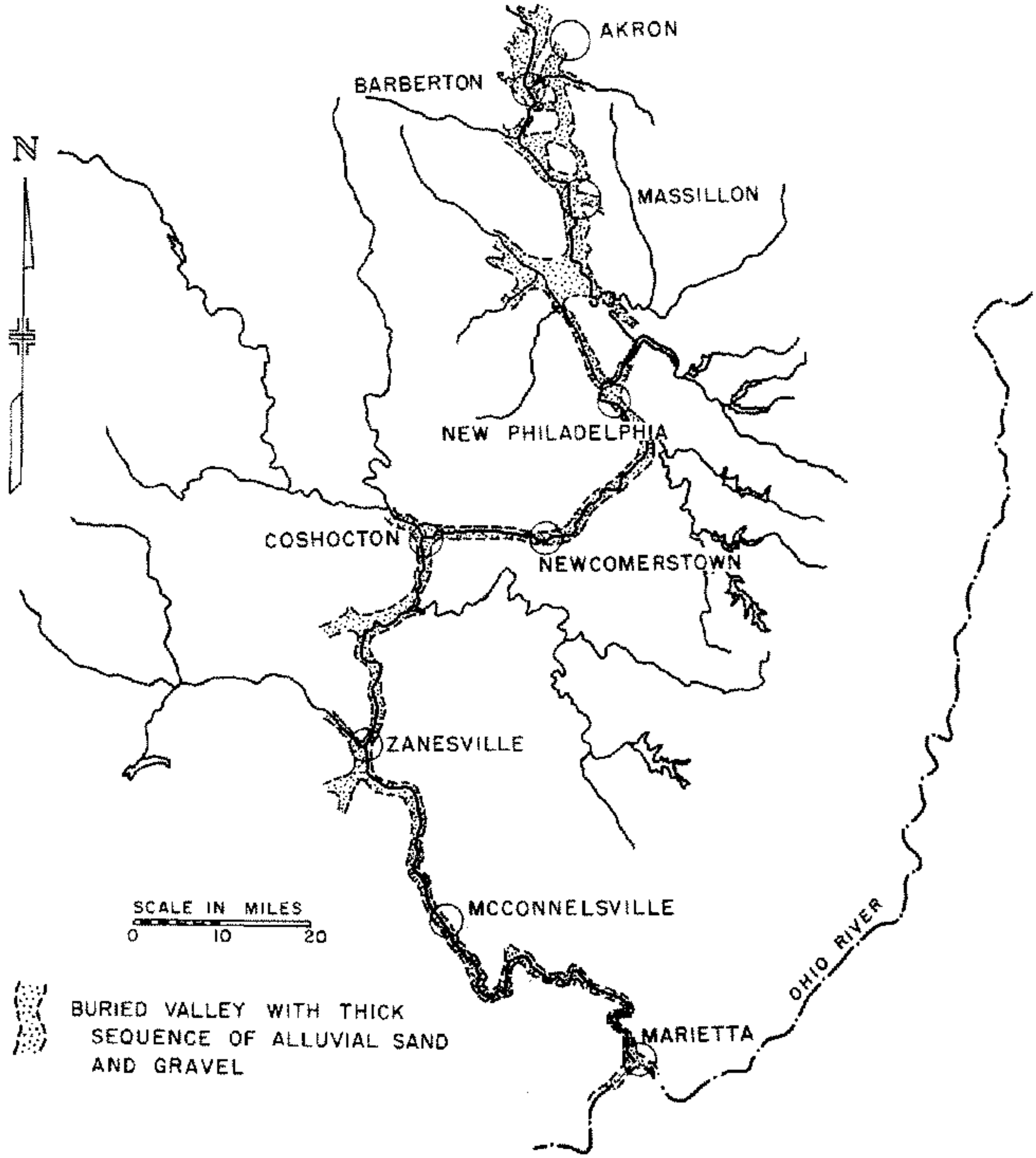

Figure 4. Map showing buried valleys along the main stem of the Tuscarawas and Muskingum Rivers (after Cummins, 1959).

more than 20,000 mg/l of chloride. Today, PPG Industries is one of the major users of ground water and pumped more than 4 million gallons a day in 1950 from large diameter wells adjacent to Wolf Creek but above the company's disposal ponds.

The average use per day of all Barberton industries in 1955 was 44 million gallons of which 10 percent comes from ground water (Tricounty Regional Planning Commission, 1963, p. 5–15). The Barberton area is expected to grow from 35,000 (1960) to 98,000 in the year 2000. It is unfortunate that more than a mile and one-half of the buried valley beneath Barberton is contaminated by salt water which may still be there in the year 2000. Water is already at a premium in the Akron-Barberton area and the municipal water supply of the Akron Metropolitan area comes mainly from the main stem of the Cuyahoga River more than 15 miles northeast of the city. Obviously, continued growth and industrial development in this region is now limited by the single factor of water availability. It is ironic that the salt industry has contributed to a problem which affects not only itself but the water needs of one of the largest cities in northeast Ohio. The effect of brine leakage in the plant area of PPG is not limited to the immediate area but is felt by a number of communities downstream which rely upon ground water for their source of domestic supply.

Chloride problems below Barberton

Chloride contamination is a serious threat to further development of the ground water resource along the main stem of the Tuscarawas and Muskingum Rivers more than 50 years after its first effect on a municipal supply at Barberton (Fig. 5). Perhaps the problem would not be so acute if water was plentiful in this part of eastern Ohio. This is not the case. Most streams have very low flows, have already been regulated for flood control purposes and cannot provide large sources of water to heavy industry (Fig. 6). On the other hand, the buried valley beneath the Tuscarawas River throughout its length is virtually the only source for large amounts of cool ground water necessary for most heavy industrial development and for domestic supplies. There is a sharp contrast in the water quality of the Tuscarawas River above the PPG plant at Barberton and below it. Above Barberton the ground water and surface water quality is good and waters rarely contain over 15 to 20 mg/l of chloride. Some areas are

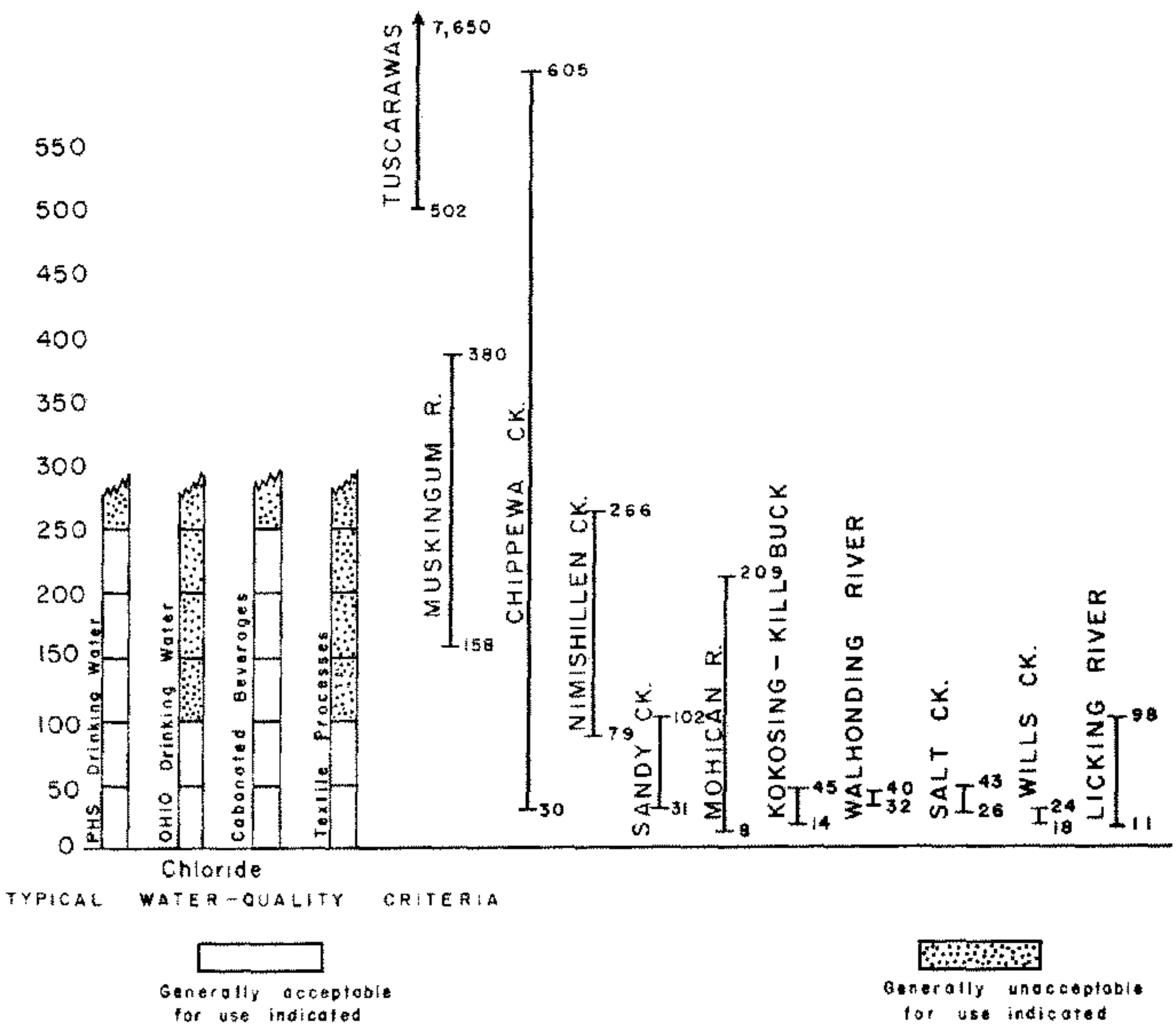

Figure 5. Map showing concentration of chloride in the main stem and tributaries of the Muskingum Basin. (Data from Ohio Department of Health, 1968).

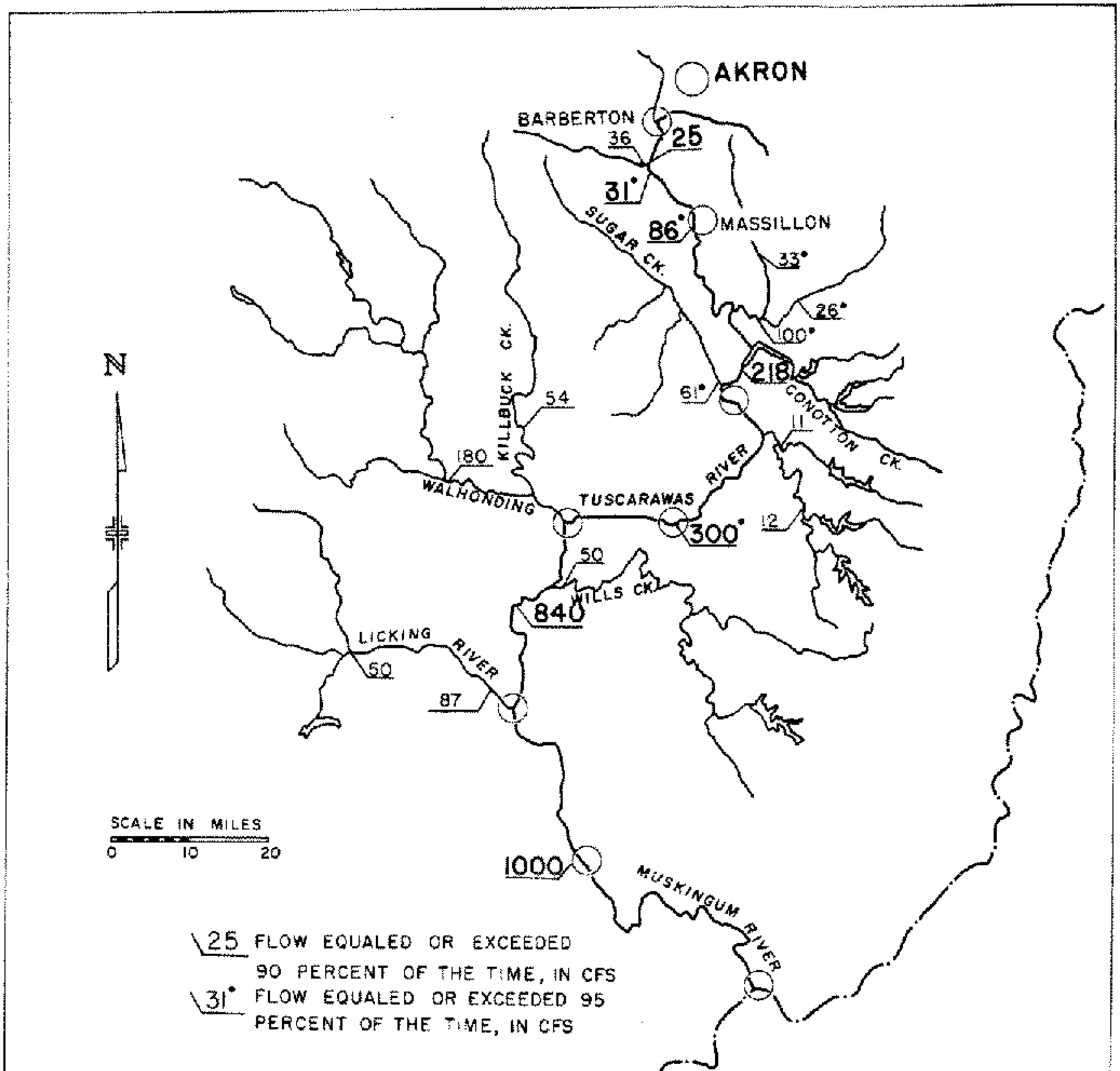

Figure 6. Map showing low flow in the main stem of the Muskingum Basin between Barberton and Marietta. (Data from Ohio Department of Health, 1957).

troubled by hard water and iron concentrations above the recommended limit of the U.S. Public Health Service. But more serious problems exist below Barberton at Massillon.

Massillon well field

Ulrich reported that the ground water pumped by the Ohio Water Service Company and sold to the city of Massillon was of "very high quality, although fairly hard" between 1922 and 1952 (Ulrich, 1955, p. 141). The softer waters of Newman Creek were used during periods of pump failure or repairs to the single 36-inch diameter well which produced 2 million gallons a day. A new well located only 200 feet from the original well was drilled in 1951 and produced 3 mgd. Both wells were only 600 feet west of the Tuscarawas River and penetrated very permeable gravel of Newman Creek (Fig. 7). During the period 1922–1952 Ulrich (1955, p. 152) reported that the hardness averaged 380 ppm of which 140 ppm was noncarbonate. Chloride content remained low at 8 ppm during this

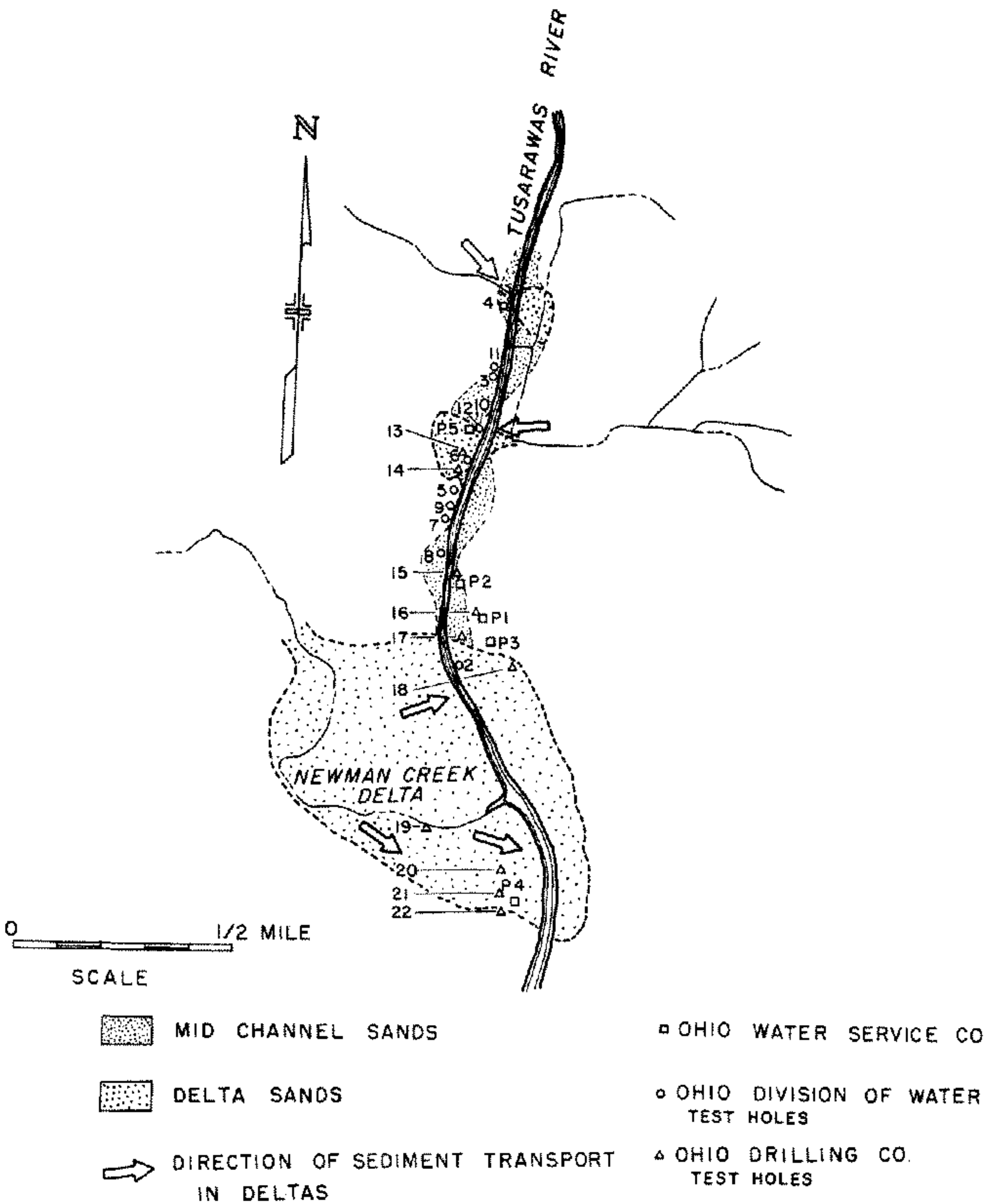

Figure 7. Map showing location of test wells and production wells in the Massillon area and the location of major tributary deltas.

30 year period. This was in spite of the fact that chloride contamination of Barberton's well field occurred in the period 1920–26.

Beginning in August of 1952, a low flow period, the original production well began to pump saltier water until by November of 1953, almost one year later, the chloride level had reached 1,700 ppm and hardness had increased to 1,686 of which 1,469 was non-carbonate. During the same period well number 2 experienced substantial deterioration in water quality and chloride levels rose to 670 ppm. By 1953, the cost of treating the water had risen from $18 to $55 per million gallons or approximately 300 percent. In 1953 maximum values of chloride in the Tuscarawas River adjacent to the Massillon well field reached 10,050 ppm. Both wells had to be abandoned as the quality further deteriorated. The company first switched to Newman Creek for its primary supply and then developed a new well field one-half mile north of Newman Creek on the east side of the River (Fig. 8).

The new well field was constructed in the late 1950's after the Newman Creek wells were severely affected by salt and almost immediately began to show slow but steady increases in chloride content. Chloride levels of bulk water from several wells after mixing had reached 250 mg/l by 1969. (Fig. 9)

Causes of chloride contamination at Massillon

The analysis of the cause of chloride contamination at Massillon has been the subject of several investigations. This study focuses on the geology and its relation to the paths that river water would follow during infiltration to the well field.

Bedrock

The bedrock in the Massillon area consists of a sequence of shale, sandstone and conglomerate which changes laterally within short distances. It is difficult to generalize the stratigraphic section because sandstone at one locality may grade to shale only one-half mile distant. Nevertheless, the stratigraphy has been revealed by study of the logs of water wells in Massillon Township.

The Pottsville Formation of Pennsylvanian age crops out beneath the glacial drift in the Massillon area. The uppermost bedrock unit consists of an interbedded sandstone and shale sequence in the basal part of the Massillon Member. The sandstones are lenticular and commonly appear at elevations of 1070 to 1085 in the uplands on the west side of the River. The sandstones of the Massillon Member rarely exceed 20 feet in thickness and most of the unit is shale. The Massillon is underlain by the Sharon Member represented here by a sandstone and conglomerate ranging from 100 to 150 feet thick. Its upper surface occurs at an elevation of about 940 feet near the north edge of Massillon Township. Regional dip is southeast at a slope of about 20 feet per mile. The depth to bedrock beneath the Tuscarawas River is not known precisely but exceeds 192 feet in the old field of the Ohio Water Service Company on Newman Creek. Wells which do penetrate bedrock on the flank of the valley encounter the upper part of the Sharon Member. The Sharon consists of sandstone and conglomerate which contains potable water low in chlorides throughout Tuscarawas and Lawrence Townships of Stark County. The Massillon Member also yields hard but otherwise potable water.

Unconsolidated deposits

The area adjacent to the Tuscarawas River in Massillon is covered with glacial deposits ranging in thickness from 15 feet in the upland areas to more than 200 feet near the center of the present valley. The valley walls of the Tuscarawas River are mantled by a kame complex consisting of sand and gravel deposited by the melting back of the Killbuck Ice Lobe of Wisconsin age (White, 1963). Most of the valley fill along the main stem is probably younger and includes post-glacial sediment at the surface. This sequence consists of a mixture of sand and gravel, clay, silty clay, sandy clay, and gravelly till. The lenticular nature of the clays and silts near the surface and their hydrologic properties play an important role in controlling the rate of infiltration in the Massillon well field. A geologic cross section reveals that for the most part, the upper surface of the flood plain is covered with a layer of clay or till of variable thickness but averaging between 10 and 25 feet. It is impossible to predict the character of the glacial drift before test holes have been dug.

In several places small tributaries to the Tuscarawas such as Newman Creek washed considerable amounts of sand and gravel from the kames in the uplands onto the main valley floor. Such deposits are lobe shaped and fan out against the opposite valley wall. Newman Creek has developed the largest of these deltas but two smaller gravel fans are present near the site of the newer of the two well fields (Fig. 7). The sand and gravel deposits making up the fans consists of clean coarse and highly permeable material. Hence they are ideally suited for the development of shallow wells or for recharging deeper wells adjacent to the River.

Contamination at Newman Creek Massillon well field

It is no coincidence that the original well field of the Ohio Water Service Company was located in the Newman Creek delta. Beneath the delta sands and gravels a thick sequence of gravel interbedded with thinner clay zones is present. The interval at depth between 80 and 190 feet apparently consists entirely of sand and gravel in most of the southern part of the delta (Fig. 10). This deep aquifer is hydraulically connected to shallower sands and gravels in the delta. North of Newman Creek the surficial deposits contain more clay and fewer connections exist between the screened part of the buried valley gravels and the River.

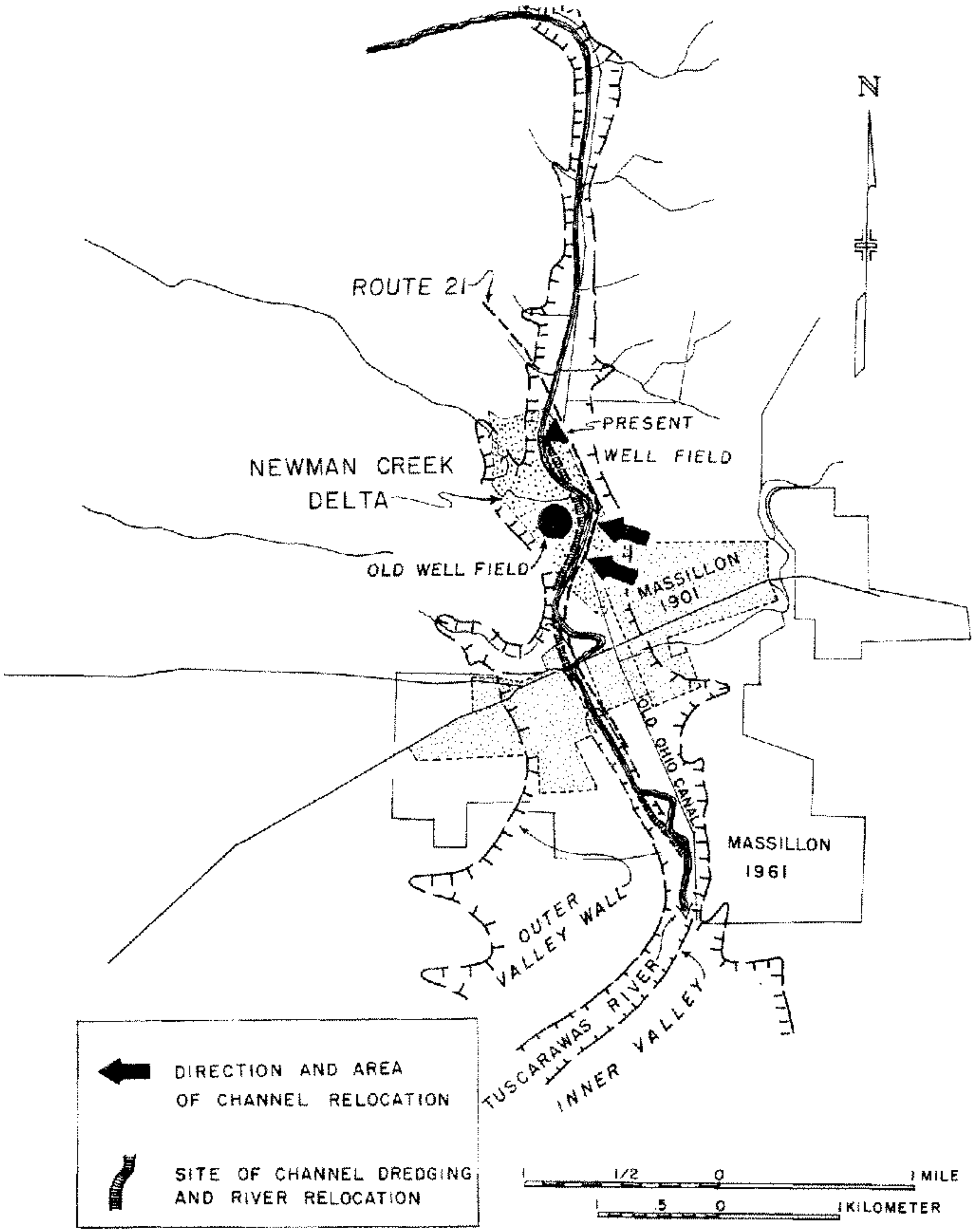

Figure 8. Map showing growth of Massillon (1901-1961) and area of channel dredging and relocation by the U.S. Corps of Engineers on the Tuscarawas River.

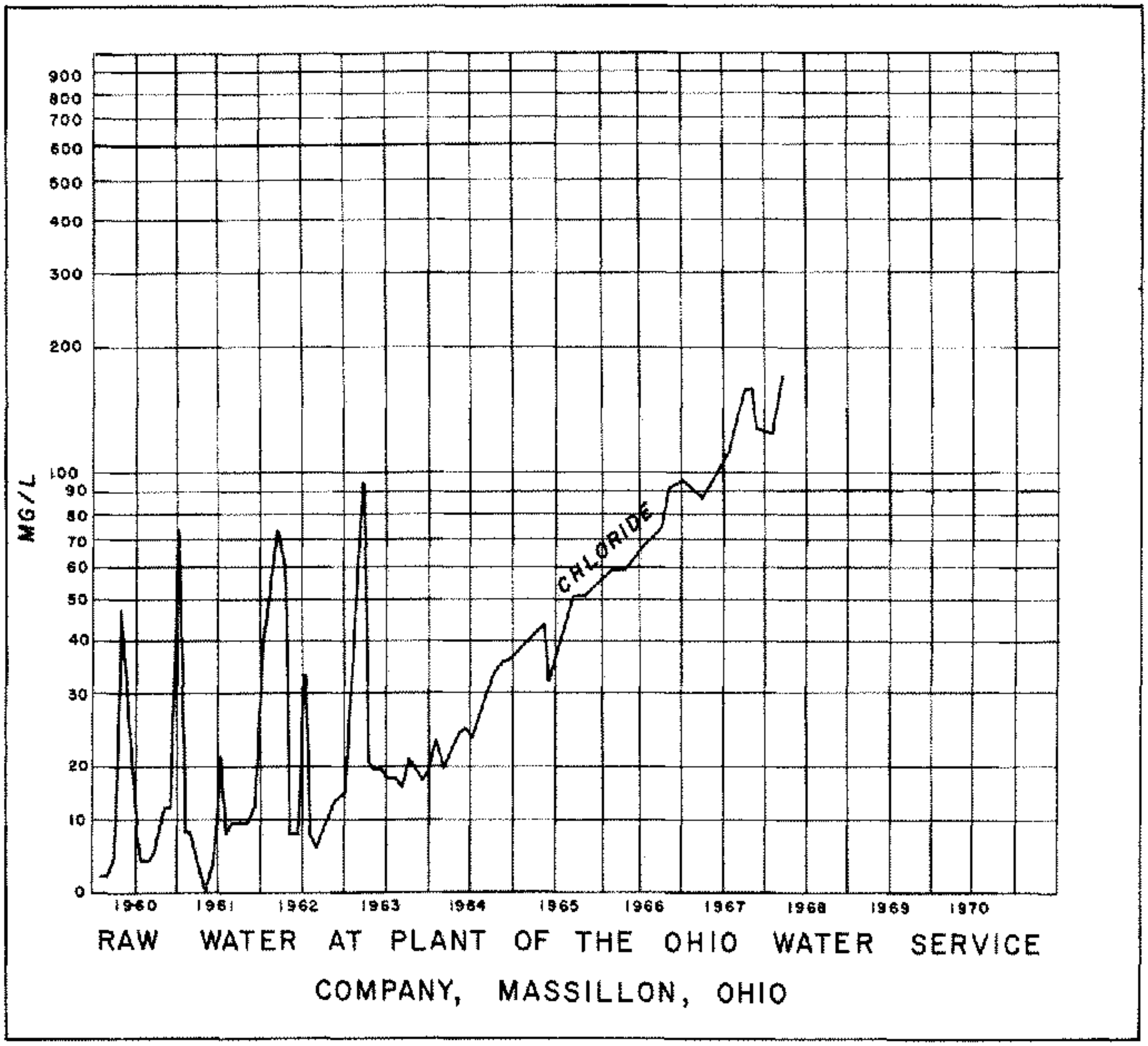

Figure 9. Chart showing chloride concentration in the raw water produced by the well field of the Ohio Water Service Company from 1959 to 1968.

The ground surface elevation of the old well field is between 940 and 950 feet above sea level. The Tuscarawas River adjacent to the field flows at an elevation of about 925 feet. The static level in the well field fluctuated around the mean elevation of the river. About .1 mile north of the Newman Creek well field dikes separate the floodplain from the River. The dikes continue from that point downstream through the City.

The abrupt increase in chloride levels in the period August, 1952 to November, 1953 suggests a rapid change in the rate of infiltration through the sediments on the floor of the river. Such a change could have been accomplished in either of two ways. Each would have the effect of removing the relatively impermeable cap of clay, revealed in well logs of the Ohio Division of Water and the Ohio Water Service Company, which lies at the surface of the valley fill. The River could have scoured its clay bed during an exceptional high flow period during the 1952 spring run-off. A study of flow frequency data and discharge records for this period indicates that the Tuscarawas River did not attain high enough velocities to cause the kind of scour necessary to remove a 10 to 25 foot thick silt and clay cap on the floor of the River.

The other possibility is that man could have removed the clay cap by dredging the River channel. Such an event would have the effect of opening up the deeper gravels to direct infiltration during critical periods of low flow and high pumpage. It has already been noted that pumpage was more than doubled during the period of rapid chloride contamination. Consequently, the cone of depression enlarged to capture more surface water than previously infiltrated to the production wells. The Ohio Department of Transportation indicated that the relocation of State Route 21, Sections 10.23 and 11.39 near the affected well field occurred in the late 1950's *after* the abandonment of the wells in the southern field (K. S. Albrink, written communication, February 28, 1973). Further, he indicated that during the relocation of Route 21 and its upgrading to four lanes only minor work was performed on the existing dikes and that the river was not dredged. However, the Tuscarawas River was relocated, straightened, and dredged by the U.S. Corps of Engineers in 1951–52 and dikes were constructed at that time (Fig. 8). The removal of the surficial clay plug by the Corps contributed to more rapid infiltration of River water in succeeding months. Dredging the river to a depth of 15 feet would have been sufficient to remove the clay in some areas. Although some clays occur at deeper levels they tend to consist of sand-clay and sand-gravel mixtures rather than clean silt and clay. Such horizons would have much higher permeabilities than clean silt or clay. The dredging would explain why the chloride levels increased so abruptly even though the River contained high chloride levels during the preceeding 50 years.

The River adjacent to the new well field was not dredged but production well P5 is one of the few wells in the north field which penetrated sand and gravel from the surface of the floodplain downward to a depth of 182 feet. Only one thin clay was encountered at a depth of 142 feet. Generally, fewer connections exist between the screened part of the buried valley gravels and the River in the newer well field (Fig. 10). Moreover, the well field contains thicker deposits of sand and gravel which range downward from a depth of 25 to about 170 feet where a basal till is present. Fewer 'holes' are present in the clay plug and consequently, the rate of river infiltration is lower causing the slow but steady chloride increases already noted there.

The problem of salt contamination of Ohio Water Service Company wells at Massillon stimulated two separate studies of the geology, hydrology, and water quality in the 1960's. Ohio Drilling dug 12 test holes and the Ohio Division of Water drilled 11 more in 1968 (Fig. 7). These wells have provided us with an adequate picture of the subsurface geology. The Ohio Division of Water attempted to establish the hydrologic properties of the upper part of the

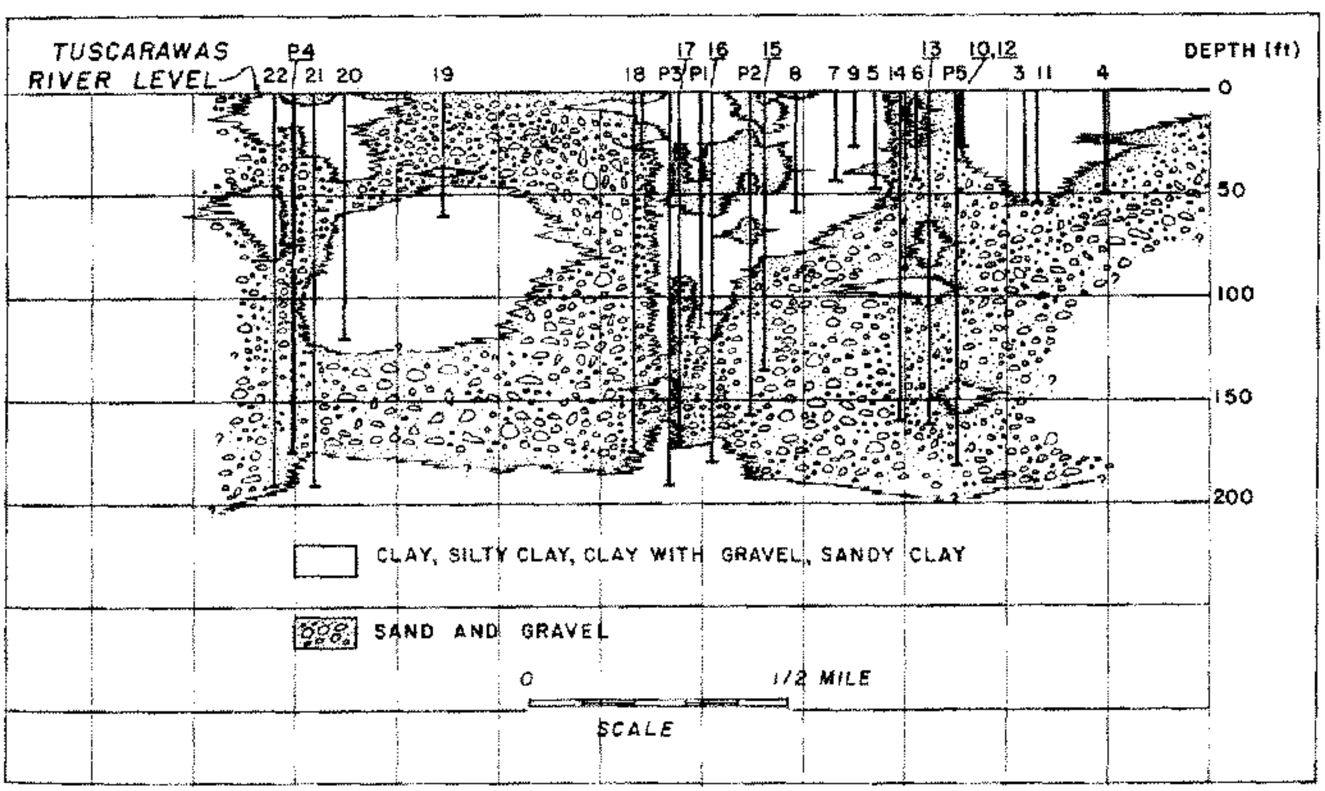

Figure 10. Geologic cross section of the buried valley deposits along the axis of the Tuscarawas River in the Massillon area.

section. Their test holes ranged in depth from 27 to 58 feet and were tested several times to determine the permeability and storage coefficient of the material beneath the River. A number of important conclusions were reached (Eagon, written communication, Oct. 10, 1972).

1. "It is most likely that significant recharge is derived from vertical leakage.

   This is supported by:

   a. Estimates of leakage during the tests.
   b. Estimates of vertical permeability.
   c. Consideration of the geology and hydrology of the area.
   d. Chloride concentrations in the upper material. Chloride concentrations in observation wells clearly point to the river as the source for the upper zones.
2. It is felt that sufficient evidence is presented to indicate the River as the source of contamination. It is also felt that the quantitative analysis supports this conclusion.
3. However, an estimate of total leakage is not attempted because numerical values are not absolute. Figures point to the right range so as to make the amount of leakage required seem reasonable, but since this is a complex system additional data would be needed to extrapolate and predict the total amount of water derived from leakage."

Eagon also indicated that the most reasonable value for T (transmissibility) was 140,000 gpd and that for S (storage coefficient) was $.3 \times 10^{-4}$. The leakage rate was estimated to be 96,000 gpd or 67 gpm. However, the author's studies of the subsurface geology indicate that there are holes in the till immediately beneath the river which would allow much higher rates of infiltration in some local areas such as in the vicinity of Ohio Water Service Company production well 5.

Theis (1947, p. 734–738) presented a method of estimating the proportion of the water pumped by a well represented by a decrease in stream-flow. It would be useful to know what percentage of the water pumped by the well field is induced from the Tuscarawas River. Some of the assumptions which must be made in this method may not be valid for the Massillon area. The following assumptions are made: The aquifer is considered to be homogeneous and isotropic. The transmissibility of the aquifer is constant. The course of the river is idealized as a straight line. It is also assumed that the ground-water is hydraulically connected to the river and that the stream-bed is not so heavily silted that there is severe restriction of flow from the river into the aquifer. The head at the stream is assumed to not change significantly because of pumping. By using the chart devised by Conover and Theis in an open-file report prepared in September of 1947 it is possible to determine for a pumped well at any distance from the stream the percentage of pumped water being diverted from that stream at any given time provided transmissibility and storage coefficient are known. If we use the data provided by Eagon with regard to T and S we obtain the following interpretation of the percentage of river water induced from the Tuscarawas at Massillon. This data would be applicable only where the River is in direct communication with the ground water in the aquifer.

Time from Beginning of Pumping (days)	Percentage of Pumped Water Being Diverted from the Tuscarawas
4	40
17	70
22	75
35	80
66	85
125	90

This data suggests that during low flow periods when water quality is most severely affected by chloride contamination significant amounts of river water would be induced in less than two weeks and that substantial amounts of poor quality water are induced if critical flows persist for 1 month or more (Fig. 11). In areas where channel dredging has removed the clay floor of the stream to a depth of 10 feet the possibility of completely sealing the leakage from the stream is remote. Siltation would occur during low flow but normal scour would remove the silts during high spring run-off and unless infiltration could be kept to a minimum during these periods ground water quality would be severely impaired.

Coshocton

The first indication of the extent of the chloride contamination of the Tuscarawas River below Massillon was provided by the Ohio River Valley Water Sanitation Commission (1951, p. 13–15). Norris reviewed the general geology and source of contamination at Barberton as well as the problem at Coshocton (Parker, 1955, p. 627–628). Brine contamination at Coshocton forced the construction of a new city well field prior to 1954 at a cost of more than 500 thousand dollars (Ulrich, 1955, p. 151). The problem at Coshocton was similar to the one at Massillon. A shallow sand and gravel aquifer was pumped so as to induce water from the Tuscarawas River which flows over a very permeable sequence of sediments along the same buried valley which extends northward to Cleveland. More than 25 years later in 1970 the Tuscarawas River at Coshocton still exceeded the 250 mg/l chloride level during part of the year. The U.S. Geological Survey (1971, p. 366; 1972, p. 356) provides water quality data from a partial-record station sampled no less than 6 times each year. Maximum

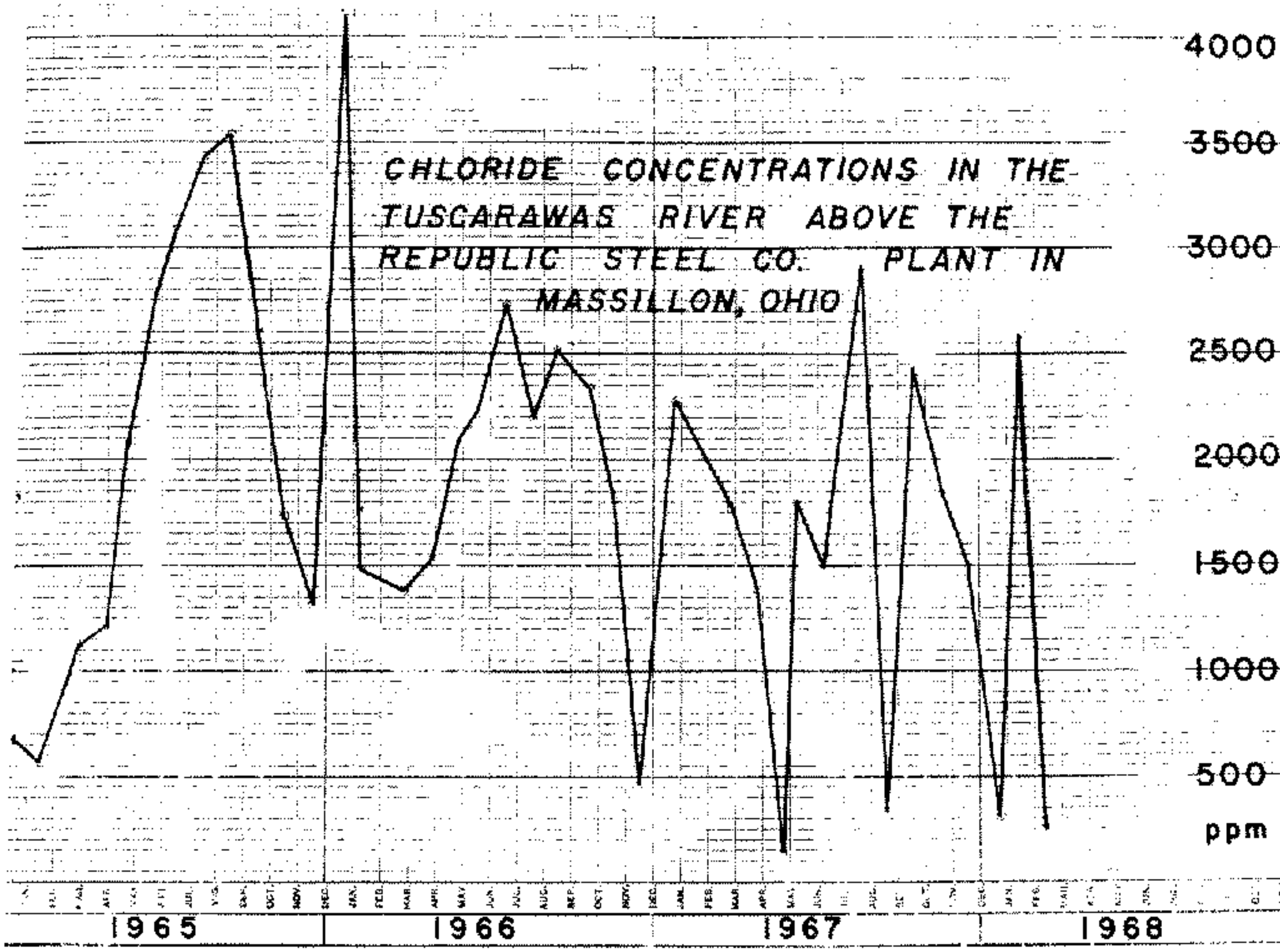

Figure 11. Chart showing chloride concentrations in the Tuscarawas River above the Republic Steel Company in Massillon from 1965 to 1968.

concentrations of chloride reported were 256 mg/l in 1970 and 300 mg/l in 1971. During this period hardness reached a level of 440 mg/l on July 1, 1971, exceeding the hard water level of 200 mg/l by more than 140 percent. Total dissolved solids were reported to be 816 mg/l in October of 1969 and 796 in September of 1970 (U.S. Geological Survey, 1971, p. 366). Both of these concentrations of total dissolved solids exceed the current water quality standards for the River set by the Ohio Water Pollution Control Board.

Zanesville

The city of Zanesville, more than 135 river miles downstream from Barberton suffers from the effects of chloride induced by wells from the Muskingum River. During low flow this problem is "acute" (Parker, 1955, p. 628). U.S. Geological Survey data from the period 1949–50 showed that the raw water of the city's 24 wells ranged between 80 and 222 ppm. More than 6 of these wells pumped between 1,030 and 1,800 gpm from a buried valley aquifer in 1963. Hardness (as $CaCO_3$) ranged from 379 to 606 mg/l in 1963. What is the current situation at Zanesville more than 10 years later? Maximum chloride levels at Philo, 9 miles below Zanesville, ranged between 110 and 580 mg/l in the 1971 water year (U.S. Geological Survey, 1972, p. 58) even after dilution by the Licking River. The 250 mg/l chloride level was exceeded during four months of the year and total dissolved solids exceeded 750 mg/l during parts of five months. The most critical period for these quality parameters was from July to October and during the winter low flow period in March.

In 1963 Zanesville considered the abandonment of its well field in favor of the Licking River below Dillon Dam. A partial record monitoring station on the Licking River below Dillon Dam near Dillon Falls was sampled and chloride ranged from 14 to 47 mg/l in 1971 (U.S. Geological Survey, 1972, p. 357). The mean chloride level in the Muskingum River in 1971 was 155 mg/l (U.S. Geological Survey, 1972, p. 58). The Muskingum contains more than 3 times the amount of chloride that the Licking River

TABLE I

Chloride and Total Dissolved Solids Concentration in the Tuscarawas River in 1970 and 1971 (water years) [U.S. Geological Survey, 1971: 1972].

Location and Date	Chloride (mg/l) 1969-70	Chloride (mg/l) 1970-71	Total Dissolved Solids (mg/l) 1969-70	Total Dissolved Solids (mg/l) 1970-71
Tuscarawas River at Clinton				
Oct.	—	—	—	—
Nov. 1969	5600	—	—	—
Dec.	3200	—	—	—
Jan. 1970	—	3600	—	—
Feb.	5750	—	—	—
Mar.	—	—	—	—
Apr.	2800	4300	—	—
May	—	4300	—	—
June	3880	—	—	—
July	—	5200	—	—
Aug.	3920	—	6890	—
Sep.	5200	6000	—	10500
Tuscarawas River at Massillon				
Oct.	—	—	—	—
Nov.	1750	—	3510	—
Dec.	1420	—	—	—
Jan.	—	2200	—	—
Feb.	1720	—	—	—
Mar.	2140	—	—	—
Apr.	1080	—	—	—
May	—	1800	—	—
June	416	—	—	—
July	—	2100	—	—
Aug.	1760	—	3450	—
Sep.	—	1100	—	2020
Tuscarawas River below Dover Dam near Dover, Ohio				
Oct.	780	480	—	1300
Nov.	225	—	—	—
Dec.	—	—	—	—
Jan.	—	—	—	—
Feb.	—	140	—	—
Mar.	—	—	—	—
Apr.	304	590	—	—
May	—	—	—	—
June	117	—	—	—
July	—	—	—	—
Aug.	650	970	—	—
Sep.	—	910	—	1960
Tuscarawas River at Newcomerstown, Ohio				
Oct.	424	290	1280	928
Nov.	—	—	—	—
Dec.	—	—	—	—
Jan.	300	—	—	—
Feb.	224	330	—	—
Mar.	—	—	—	—
Apr.	224	—	—	—
May	—	—	—	—
June	320	280	—	—
July	—	—	—	—
Aug.	140	720	—	—
Sep.	—	810	—	1770

Location and Date	Chloride (mg/l) 1969-70	Chloride (mg/l) 1970-71	Total Dissolved Solids (mg/l) 1969-70	Total Dissolved Solids (mg/l) 1970-71
Muskingum River at Coshocton, Ohio				
Oct.	218	—	816	—
Nov.	—	—	—	—
Dec.	110	—	—	—
Jan.	118	110	—	—
Feb.	—	—	—	—
Mar.	240	—	—	—
Apr.	—	—	—	—
May	69	220	—	—
June	—	—	—	—
July	130	300	—	—
Aug.	—	—	—	—
Sept.	256	190	796	320
Muskingum River at Dresden, Ohio				
Oct.	235	330	872	932
Nov.	—	—	—	—
Dec.	—	—	—	—
Jan.	—	—	—	—
Feb.	34	180	—	—
Mar.	—	—	—	—
Apr.	92	220	—	—
May	—	—	—	—
June	124	—	—	—
July	—	—	—	—
Aug.	92	250	—	866
Sep.	—	—	—	—
Muskingum River at McConnelsville				
Oct.	198	—	720	—
Nov.	—	100	—	426
Dec.	—	—	—	—
Jan.	—	—	—	—
Feb.	—	35	—	—
Mar.	—	—	—	—
Apr.	—	130	—	—
May	—	—	—	—
June	—	—	—	—
July	—	—	—	—
Aug.	—	210	—	784
Sep.	—	—	—	—

Muskingum River at Philo (maximum specific conductance days)	Chloride 1969-70	Chloride 1970-71	Day	TDS 1969-70	TDS 1970-71
Oct. 28	280	510	(19)	982	1350
Nov. 03	170	180	(02)	792	696
Dec. 31	140	140	(04)	634	608
Jan. 22	178	110	(25)	682	590
Feb. 28	135	120	(10)	606	562
Mar. 02	126	140	(29)	618	594
Apr. 18	87	220	(30)	456	776
May 26	65	190	(04)	412	618
June 12	219	200	(30)	742	652
July 24	166	400	(16)	616	966
Aug. 29	215	340	(25)	768	976
Sep. 08	243	580	(18)	768	1310

showed on its maximum specific conductance day.

Obviously, the water quality problem in 1971 at Philo is not substantially improved over the 1949–50 levels. Treatment costs at Zanesville are unnecessarily high and even after treatment the inducement of chloride rich low flow river water will leave the tap water close to the recommended limit of the U.S. Department of Health, Education and Welfare. River waters are much improved during periods of high discharge but a well field without the capacity to store these waters and recharge them during low flow periods is forced to face a quality 'battle' at least part of each year.

Marietta

Marietta is located at the mouth of the Muskingum River at its confluence with the Ohio (Fig. 4). Almost 20 years ago the city officials of Marietta reported that they were concerned over the marked increase in chloride in its well water during the preceding 10 years. (Parker, 1955, p. 628). These wells, like those at Coshocton, Massillon and Zanesville, tap shallow sand and gravel deposits beneath the Muskingum River. The city is located over 200 river miles below Barberton. The problems here are significant considering the distance from the source at which chloride continues to be troublesome after dilution by several major tributaries, several dozen minor tributaries and 15 flood control reservoirs, two of which are on the main stem. Does the chloride problem continue to exist at Marietta?

The U.S. Geological Survey maintains a gaging and water quality station at Beverly which is only 20 miles upstream from Marietta. Daily samples are collected at this station but only three are analyzed for water quality each month. The three samples chosen are based upon: (1) maximum daily specific conductance for each month, (2) minimum daily specific conductance for each month, and (3) median daily specific conductance for each month. It is interesting to note that in the 1970 water year the U.S. Geological Survey reported that maximum level of chloride recommended for domestic drinking water was exceeded in October (278 mg/l), November (264 mg/l) and May (320 mg/l). The median level for chloride can be assumed to be correlatable with the median daily specific conductance. The median level for chloride during October, 1969, was 238 mg/l. Further, chloride levels were very close to the maximum permissible in domestic drinking water when the River was sampled in January (210 mg/l), August (220 mg/l), and September (236 mg/l) of the 1970 water year. Such levels suggest that the Muskingum chloride concentrations are still much too high considering the distance from the source. In comparison the U.S. Geological Survey reports that in 1970 the Hocking River at Athens had a high of 115 mg/l; the Scioto River at Columbus contained 102 mg/l; the Great Miami River at Franklin measured 70 mg/l; the Maumee River at Toledo only 72 mg/l (U.S. Geological Survey, 1971, p. 264); and the Ohio River at Markland Dam near Warsaw, Kentucky, had a maximum chloride concentration of 68 mg/l during the 1970 water year (U.S. Geological Survey, 1971, p. 202). Even the Mahoning River after passing through one of the great steel complexes in North America had a maximum of only 216 mg/l reported during the 1970 water year (U.S. Geological Survey, 1971, p. 40). We conclude that in order to make Marietta water potable it will have to be treated to substantially reduce chlorides during at least six months of each year. The major problem will be the removal of non-carbonate hardness as the chloride ion is unlikely to be recoverable during the treatment process.

CONCLUSIONS

In spite of the fact that more than 40 mgd of ground water is used in the Muskingum Basin the relation of surface water quality to ground water quality has been misunderstood.

Ground water quality is related to the geology of the basin, especially the character of the buried valley deposits. The degree of interconnection between surface water and ground water is closely related to the geology of the surficial parts of the buried valley sequence. Low flows and quality problems have long been a source of concern along watercourses where ground water supplies are induced from shallow aquifers hydraulically connected to rivers and streams. Quality standards set for domestic water supplies must also be applicable to surface waters where these waters are induced by municipal well systems. Chloride levels in main stem streams must not exceed 250 mg/l at any time for such systems to function properly.

The contamination of the Tuscarawas River at Clinton has resulted in the pollution of the main stem all the way to Marietta. In past years other problems of this Basin have been controlled by the expenditure of considerable funds. Flood flows on the main stem have been eliminated by the construction of reservoirs which provide more than 1.5 million acre-feet of useable storage and a conservation pool of 212,800 acre-feet (Ohio Dept. Health, 1968, p. 10). Such controls were possible only because of the investment of millions of federal dollars in 1930–38. The investment in the waters of the Muskingum Basin by past, present and future users has been and will be enormous. The entire nation has contributed to the development of flood control reservoirs, recreational projects, water supplies, sewage treatment plants, transportation networks, and channel improvement in the Muskingum Basin. The water resources of the Basin cannot continue to be seriously affected by waste disposal practices within the salt industry. Too much is at stake.

In recent months the soda-ash processing operation at Barberton has shut down (R. B. Stein, written communication, March 26, 1973). No data is available at this time as to the future intentions of PPG Industries regarding their soda-ash plant. The State of Ohio Environmental Protection Agency has proposed new regulations regarding maximum chloride levels permissible in the Muskingum Basin. Such regulations are in response to Public Law 92–500, 92nd Congress, S2770, October 18, 1972, which requires that waters of states shall be raised to a level of quality consistent with preservation of aquatic life and use as public, industrial and agricultural water supplies, and for primary contact recreation. Ohio EPA (1973, p. 3) is proposing a maximum chloride concentration of 60 mg/l. Such a proposal is close to the maximum chloride concentrations obtainable in Ohio's streams and rivers under natural conditions. This level is going to be difficult to obtain for salt operators and some chemical manufacturers in Ohio. If there is a variance to this proposed regulation it should not allow concentrations greater than 250 mg/l of chloride at any time.

ACKNOWLEDGMENTS

I am especially grateful to H. B. Eagon, Ohio Division of Water, who furnished valuable data regarding his studies of chloride contamination at Massillon. Thanks are also due to S. E. Norris, U.S. Geological Survey, K. S. Albrink, Ohio Division of Highways, R. B. Stein, State of Ohio Environmental Protection Agency and Mr. Bickel, Ohio Water Service Company, for their kind assistance in providing current information on several important aspects of this problem. Dr. Alan Coogan, Kent State University, kindly assisted the author in the collection of water samples and in boat navigation on the upper Tuscarawas River in 1969. PPG Industries, Inc. is to be commended for the forthright way in which it has cooperated in providing data to a number of State and Federal agencies. The author assumes sole responsibility for the accuracy of the data herein presented and for its interpretation.

REFERENCES

Cecil, L. K., 1971, Difficult pollution control problems, *in Industrial process design for water pollution control: Am. Inst. Chem. Engineers,* AICHE Workshop, 3:99-103.

Cummins, J. W., 1959. Preliminary map showing water possibilities in buried valleys in Ohio: *Ohio Water Plan Inventory,* Rept. 10.

Hem, J. D., 1970, Study and interpretation of the chemical characteristics of natural water: *U.S. Geol. Survey Water-Supply Paper* 1473.

Moody's Investor's Service, Inc., 1972, *Moody's Industrial Manual,* V. II, PPG Industries, Inc., p. 2678.

Ohio Department of Health, Division of Engineering, 1968, *Report and recommendations on water quality for Muskingum River Basin,* 85 p.

Ohio Department of Health, Division of Sanitary Engineering, 1958. *Report of water pollution study of Muskingum River Basin* – 1951, 1953, and 1954: 116 p.

Ohio Department of Health, Water Pollution Control Board, 1972. *Resolution establishing amended criteria of stream-water quality for various uses adopted by the Board on March, 14,* 1972, 6 p.

Ohio River Valley Water Sanitation Commission, 1951. *Brine contamination in the Muskingum River,* 20 p.

Parker, G. G., 1955. The encroachment of salt water into fresh, *in Water, Yearbook of Agriculture:* Dept. Agriculture, p. 615–635.

Rau, J. L., 1969. The evolution of the Cuyahoga River; its geomorphology and evironmental geology, *in The Cuyahoga River Watershed* [Symposium]: Kent State University, Institute of Limnology, p. 9–41.

Rau, J. L., 1972. Chloride contamination of ground water at Massillon, Ohio (abs): *Geol. Soc. America, Abstracts with program,* 4, no. 7: 633.

Robinson, Art, 1954. Discussion, Chloride contamination of ground water in Ohio: *Am. Water Works Assoc. Jour.,* 47, no. 2:153–154.

Smith, R. C., and White, G. W., 1953. Water resources of Summit County, Ohio: *Ohio Dept. Nat. Resources, Div. Water Bull.* 27.

State of Ohio, Environmental Protection Agency, 1973. *A proposal to adopt new regulations EP-1-01 through EP-1-05 setting forth water quality standards for all waters of the State of Ohio:* 11 p.

Theis, C. V., 1935. The relation between the lowering of the piezometric surface and the rate and duration of a well using ground-water storage: *Am. Geophys. Union Trans.,* p. 520–524.

Theis, C. V., and Conover, C. S., 1947. Preliminary memorandum on ground-water supplies for Elephant Butte Irrigation District, New Mexico: *U.S. Geol. Survey Open File Report.*

Tri-County Regional Planning Commission, 1963. *Water resource development plan:* Akron, Ohio, 205 p.

U.S. Geological Survey, 1971, Water resources data for Ohio: pt. 2, *Water Quality Records,* 400 p.

U.S. Geological Survey, 1972, Water resources data for Ohio: pt. 2, *Water Quality Records,* 409 p.

Ulrich, A. A., 1954, Chloride contamination of ground water in Ohio: *Am. Water Works Assoc. Jour.,* 47, no. 2:151–152.

White, G. W., 1963, Glacial map of Stark County, Ohio: *Ohio Dept. Nat. Resources, Div. Geol. Survey, Bull.* 61.