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ENVIRONMENTAL IMPACT OF COAL ASH ON TRIBUTARY STREAMS AND NEARSHORE WATER OF LAKE ERIE

Final Report

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ABSTRACT

The environmental impact of coal ash disposal at a landfill site in north-central Chautauqua County, New York was studied from June 1975 through July 1977.

Water samples taken from wells, ponds, and streams at 67 sites were analyzed for specific conductance, pH, alkalinity, arsenic, calcium, cadmium, chloride, chromium, copper, iron, magnesium, manganese, potassium, selenium, sodium, sulfate and zinc. Standard deviations among groups of samples were generally so high that statistically sound conclusions cannot be drawn. Evidence suggests that ponds at the landfill were high in Ca, Fe, Mg, Mn, and SO_4 compared to control ponds. A stream adjacent to the site contained greater Mn (207 ug/l) and SO_4 (229 ppm) than control streams. Shallow alkaline test wells in the landfill had elevated As, Ca, and Se. Acid-neutral test wells had elevated As, Ca, Cr, Mg and Mn. Highest average concentrations of important metals in the groundwater included 83 ug/l of arsenic and 10 ug/l of selenium in the alkaline wells; 10 ppm of manganese and 6 ug/l of chromium in the neutral-acid wells. Sulphate averaged 1798 ppm in the alkaline test wells.

The movement of coal ash leachate is thought to be restricted by adsorption and/or exchange of chemical constituents by clay minerals in the vicinity of the landfill.

Household wells in the vicinity of the landfill showed no evident contamination from the landfill.

Average iron concentrations in the biota were tripled, and manganese concentrations doubled in biota affected by the coal ash dump. However, any effects of the disposal area on the distribution of the biota could not be separated from effects of varying environment factors such as water movements, substrate composition and food availability. No harmful effects could be demonstrated on the biota in the creek which flowed past the disposal area.

INTRODUCTION

Coal ash comprises two distinct fractions of solid residue. Fly ash, which may constitute 75-80 weight percent of the total ash (suspended burning of pulverized coal), is the finer-grained, less dense type of ash collected from exhaust stacks of the coal furnaces; it consists of tiny hollow or pitted glassy spheroids. Bottom ash, so called because it settles to the bottom of the furnace, is coarser, denser, more angular and irregular than fly ash.

The chemical composition of the two types of ash can vary greatly as a result of the large variation in the composition of the coal from which the ash is produced. Relatively recent bibliographies covering the chemistry of coal, coal ash, and leachate are those of Sun et al. (1971) and Averitt et al. (1972). Ruch et al. (1974) cites at least 18 references dealing with the chemical nature of coal ash, mostly with special emphasis on trace elements, and itself presents chemical analyses on over 100 coal samples.

The disposal of coal ash can create serious environmental problems, especially if uncontrolled or uncontained. Many elements, including toxic ones that may be present in microgram-per-gram levels, are readily leachated from ash and can result in the contamination of surface and groundwaters (Theis, 1976; Guthrie, 1974). In addition to possible chemical hazards, disposal of coal ash can present physical and aesthetic problems: if not properly covered and contained, ash is subject to severe erosion by wind and water.

The primary purpose of this study, initiated in June 1975, was to investigate the impact of a coal ash landfill on water quality, and on aquatic biota. The landfill and the immediate surrounding area is a proposed site for a 1700 megawatt generating plant, with on-site ash disposal, to be constructed beginning in 1980. Thus, in addition to accumulating information on the concentrations of elements mobilized from coal ash and transported as leachate, this study supplements an extensive environmental study recently undertaken by several consulting firms retained by Niagara Mohawk Power Corporation (Niagara Mohawk Power Corp., 1976). Also, aquatic invertebrates could conceivably accumulate metals to harmful or toxic degrees. To test this hypothesis aquatic invertebrates, mostly aquatic insects, were collected from control and experimental sites and their bodies analyzed for quantitative amounts of various metals by atomic absorption spectrophotometry.

This study was performed at State University College, Fredonia, New York. Groundwater, surface water and chemical methods were directed by Dr. Walther M. Barnard. Dr. Robert K. Fahnestock directed the hydrology studies. Studies of fly ash chemistry were directed by Dr. David Dingledy early in the study, and then by Dr. John F. Gaasch. Aquatic biota studies were directed by the project director, Dr. Kenneth G. Wood.

Publications emanating from this study are listed in the references section of the paper as follows: Corbin and Barnard 1976; Ash and Fernald 1977; Gaasch and Law 1977. One thesis (Harriger 1977) was also presented, directed by Dr. W. Barnard.

Important contributions were made by students from the National Science Foundation Undergraduate Research Participation Program directed for several years by Dr. Walther Barnard. A videotape on structure and identification of larval Chironomidae was produced by Dr. Kenneth Wood and Thomas Fink. It is currently being revised.

PHYSICAL DESCRIPTION OF THE LANDFILL

The Pomfret coal ash disposal site is located on the Lake Erie coastal plain in northcentral Chautauqua County, New York (Figure 1) and has been in operation since 1971. It is supplied with approximately 153,000 metric tons of fly ash, 31,000 metric tons of bottom ash, and 3,800 metric tons of pyrite annually from the Niagara Mohawk Power Corporation's 600 megawatt coal-fired electricity generating plant in Dunkirk (Donald Frame, trucking contractor and landfill operator, personal communication). The present plant is fueled by eastern coal.

Bedrock

Bedrock in the study area consists of approximately 600 meters of relatively flat-lying Upper Devonian (Chautauquan Series) marine shales and siltstones. The bedrock directly beneath but not outcropping at the landfill site is the South Wales Shale Member of the Canadaway Formation. This member varies in thickness from 18 to 24 meters and consists of medium light gray to medium dark gray shale, with some interbedded dark gray shale and light gray siltstone (Tesmer 1963, p. 15).

Bedrock exposures along the Lake Erie shore near the study area exhibit two sets of well-defined joints, striking N73°E and N56°W with 80° to 90° dips and 0.3-1 meter spacings (Niagara Mohawk Power Corp. 1976, p. 76.2-1).

No sizable groundwater aquifers exist in the immediate area; the groundwater in the bedrock is confined to joints and fractures.

Soils

The surficial materials of the site are primarily lacustrine silts and clays deposited in the former Lakes Whittlesey and Warren during Late Wisconsin glaciation (Muller 1963, p. 51). They are classified as silt loam or silty clay loam with thicknesses varying from 1 to 6 meters. These are underlain by a gray till containing fragments of the shale bedrock on which it lays. Ranging in thickness from 1.5 to 7.3 meters, the till is predominantly a silty gravel or gravelly silt with varying amounts of sand and clay (Niagara Mohawk Power Corp. 1976, p. P76.2-8). These soils are assigned a rating of poor to severe for most uses due to seasonal wetness, slow percolation, and ease of erosion (U.S. Dept. of Agriculture Soil Conservation Service 1972).

The value of these deposits as a disposal site is suggested by Hughes (1972) who states that "Earth materials with low permeability . . . such as the silty clay tills in northeastern Illinois will retard the movement of leachate and will also significantly reduce the dissolved solids content of leachate within a relatively short distance." Griffin et al. (1977) and Frost and Griffin (1977) report attenuation of various chemical constituents in landfill leachate by clay minerals and discuss the variation of absorption by clays with changing pH. The cation exchange properties of coal fly ash are shown by Gaasch and Law (1977).

Topography and Development of Landfill

Physical features in the landfill area are shown in Figure 2. The principal stream, Van Buren Bay Creek, flows northward along the eastern side of the landfill. It has an average flow of perhaps 30 cfs. A major tributary enters from the east, passing under the north-south runway of the Fredonia Airpark. An intermittant remnant tributary joins the main stream just south of the east-west airport runway; it receives groundwater seepage from the east border of the recent landfill. For convenience the stream is divided into four segments for data analysis: remnant tributary; east branch; west branch (headwaters of main stream); and main stream downstream from the junction with east tributary.

The present topography of the coal ash landfill is almost completely man-made. Alteration began in 1965 with the extension of two airport runways, using coal ash as a fill material, across Van Buren Bay Creek and its major tributary.

During runoff produced by Hurricane Agnes in 1972 a culvert under the east-west runway became blocked and the runway served as a dam. When the ponded waters overtopped the runway, headcuts produced by the very high slope on the downstream side of the runway eroded large chunks from the cover and the coal ash fill. These materials were carried several miles down the small stream channel to Lake Erie. They formed berms along the stream channel and nearly filled a small pond which had been excavated in the channel.

The main stream and/or its tributary have been rechanneled three times in order to move them away from an active face of the landfill and to prevent erosion of coal ash already emplaced; the present (1977) stream courses are shown. Part of the need for such rechanneling was caused by the mode of disposal prior to 1971; the ash was literally dumped and left unattended. Because the ash was neither compacted nor covered with soil, as is done in the present trench and fill operation, wind and surface runoff carried the ash into the streams in large quantities. At one location downstream from the landfill, layers of coal ash, interbedded with silt and sand, accumulated to a thickness of 10 cm. in the stream bed. Despite a systematic operation of compacting the ash with bulldozers and covering it with soil, erosion continues to present a problem.

In subsequent expansion of the landfill since 1973, ash is laid down in lifts 3 meters thick. Soil dikes are built around the perimeter of the fill during expansion to prevent uncontrolled erosion of the ash and contamination of surrounding areas. Occasional breaching of the dikes or erosion of cover material (often only 5 cm. thick), allowing piping and undermining of the ash, still occurs in spite of these precautions.

On the east side of the landfill, groundwater emerges at several points as seeps or springs (e.g., remnant tributary) where the water table intersects the ground surface. On the west, however, the cover materials and some coal ash have flowed or slumped, almost certainly as a result of seepage forces from a higher water table in the landfill. This failure of the impermeable cover has permitted the water table to drain to the level of the base of the failed slope and now limits to a major degree the height of the water table in the landfill. A cross section of the landfill is shown in Figure 4 with the location of five of the test wells. Contours at the site are shown in Figure 5.

Infiltration into the landfill emerges readily from the highly permeable ash deposits, all along the open western face, to stand in shallow ephemeral ponds along the margin. None of this surface water is thought to leave the site as there is a low berm west of the ponds capable of containing any runoff.

Eight ponds have been constructed at the edge of the landfill to serve as runoff catchment basins. These vary from 28 to 6950 square meters in area, from 0.1 to 3.2 meters in depth, and from 10 to 14000 cubic meters in volume.

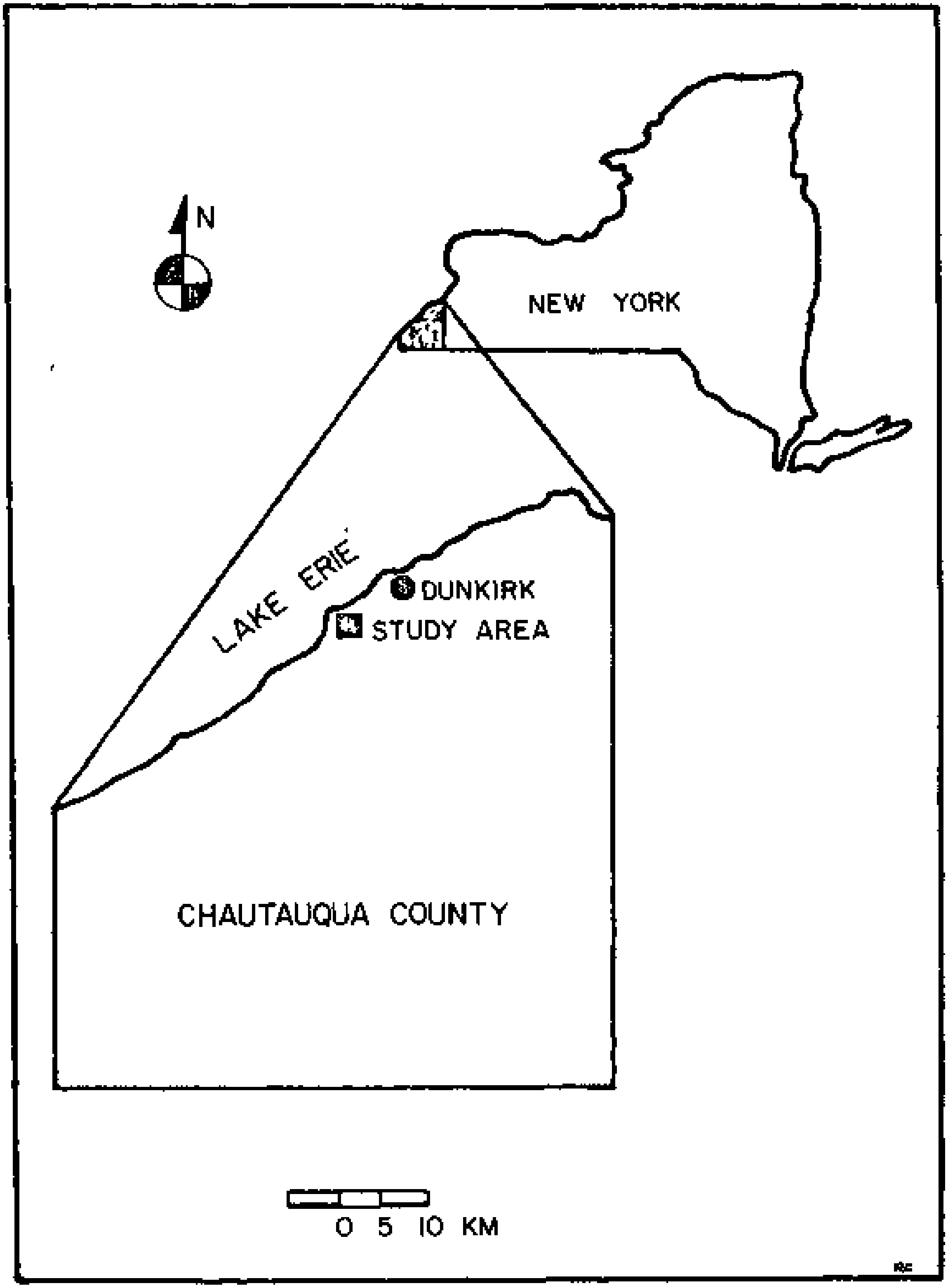
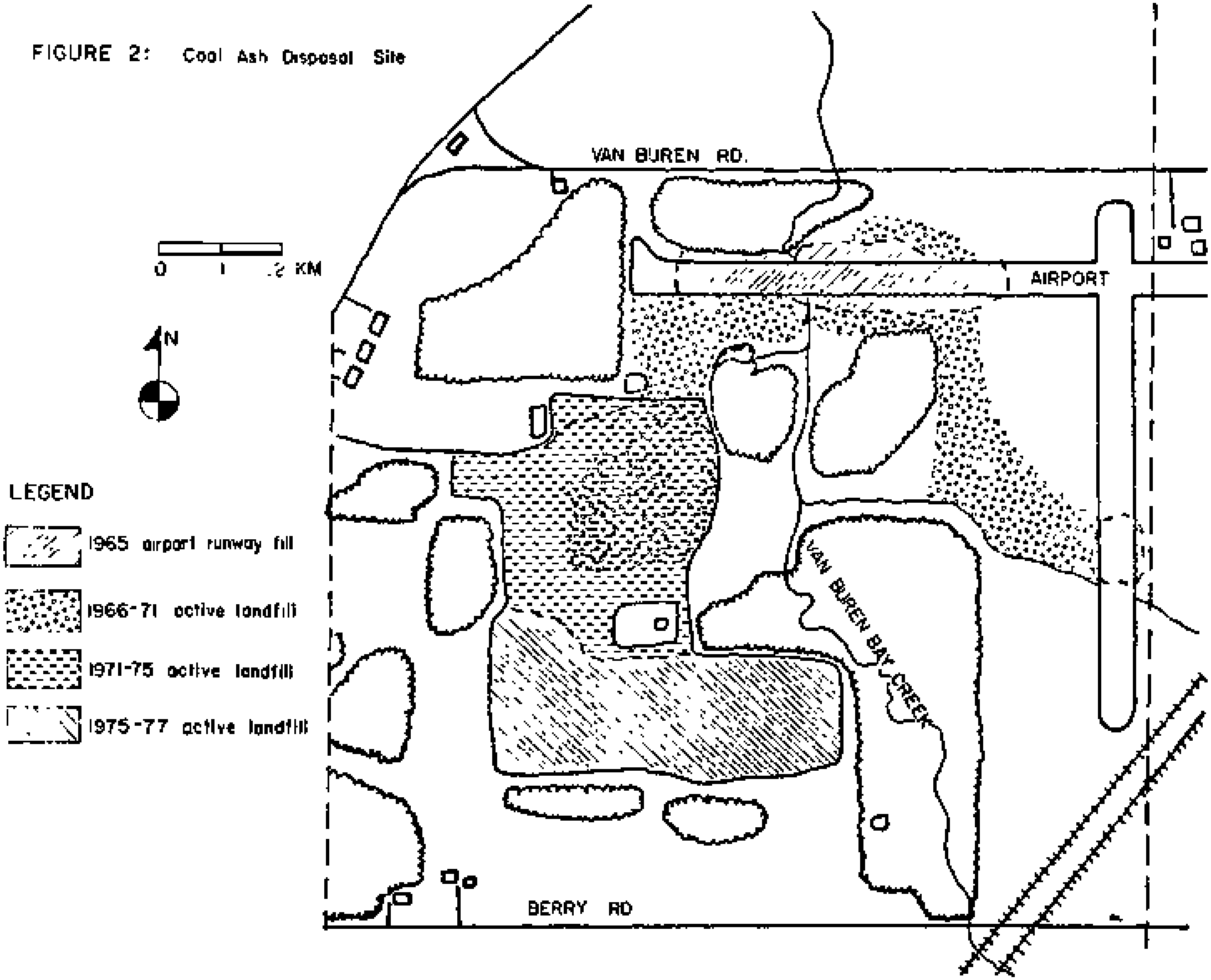


FIGURE 1: Location of study area in Chautauqua County, New York.

FIGURE 2: Coal Ash Disposal Site



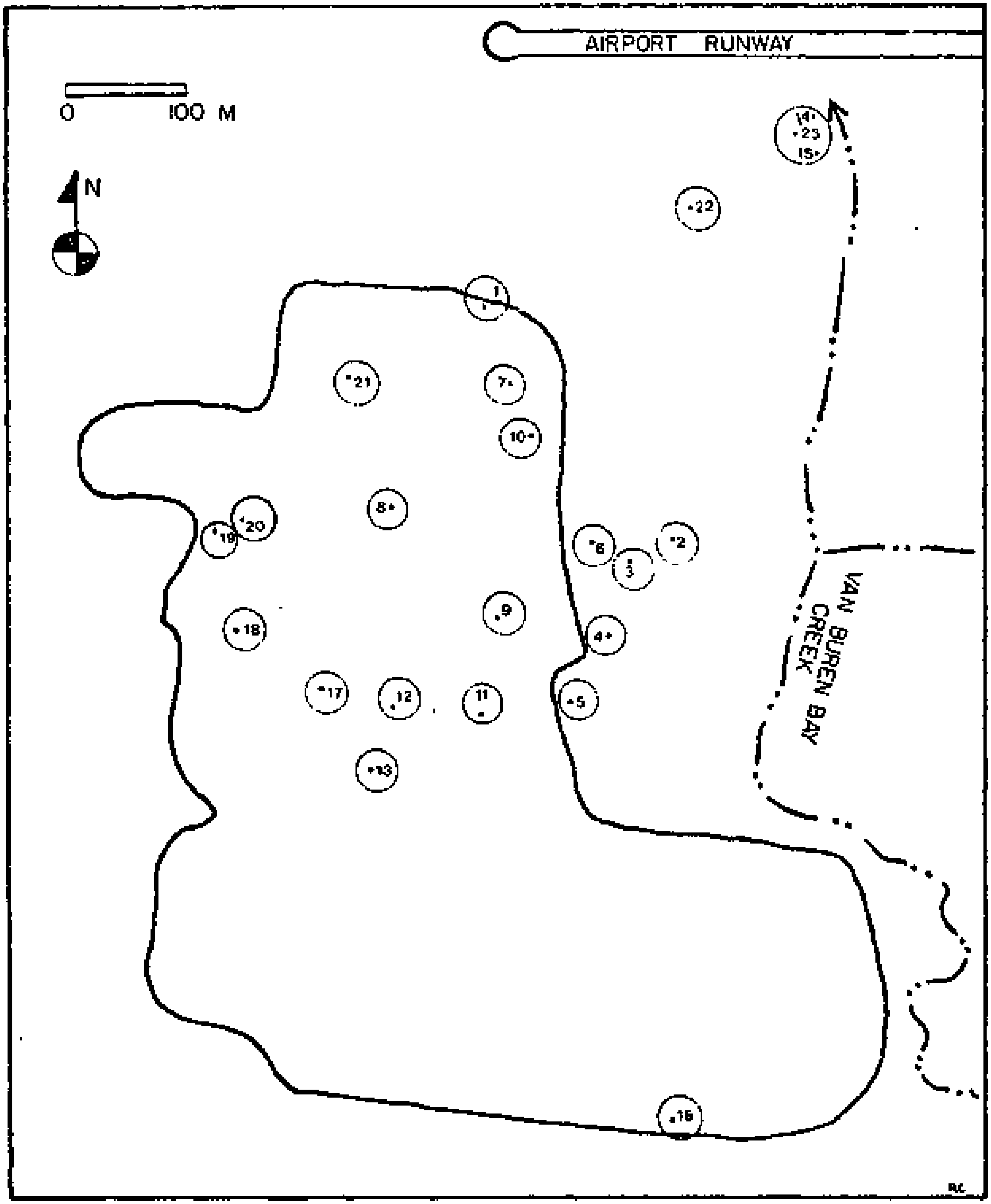


FIGURE 3: On-site groundwater sampling stations (with outline of 1971-77 ash landfill)

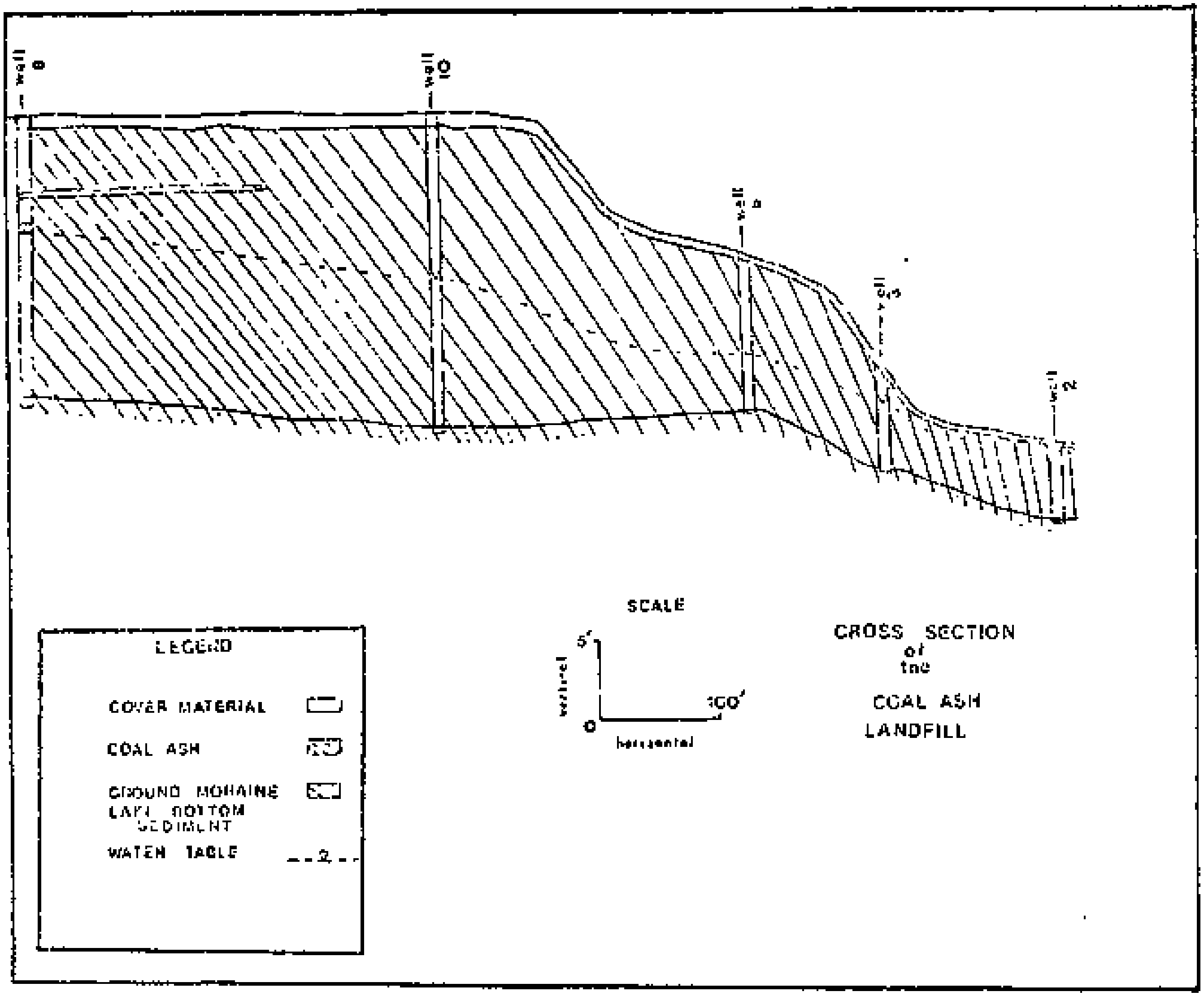

well 10
LEGEND
COVER MATERIAL
COAL ASH
GROUND MORAINE
LAKE BOTTOM
SEDIMENT
WATER TABLE
SCALE
5'
0
100'
horizontal
CROSS SECTION
of
the
COAL ASH
LANDFILL

Figure 4

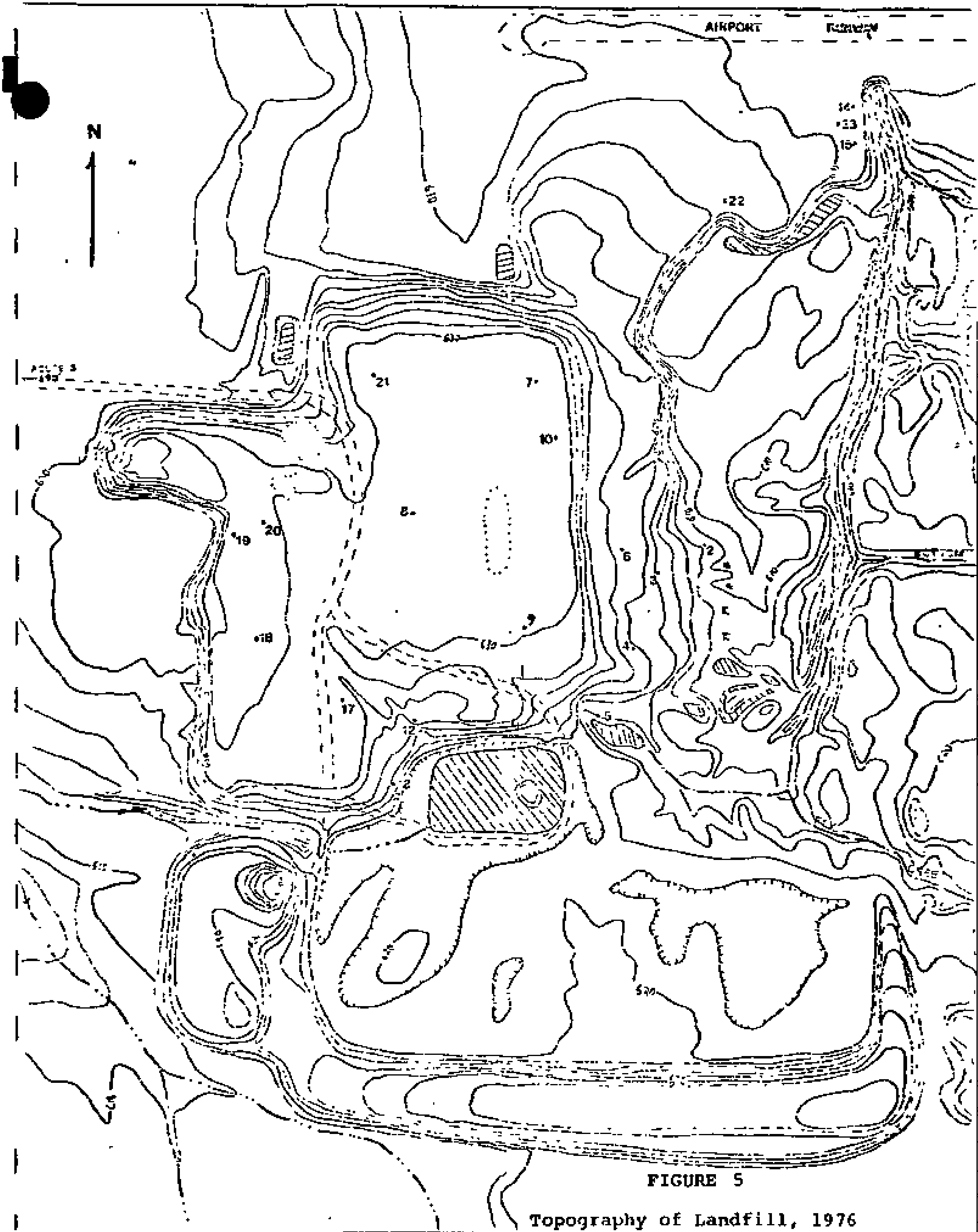


FIGURE 5

Topography of Landfill, 1976

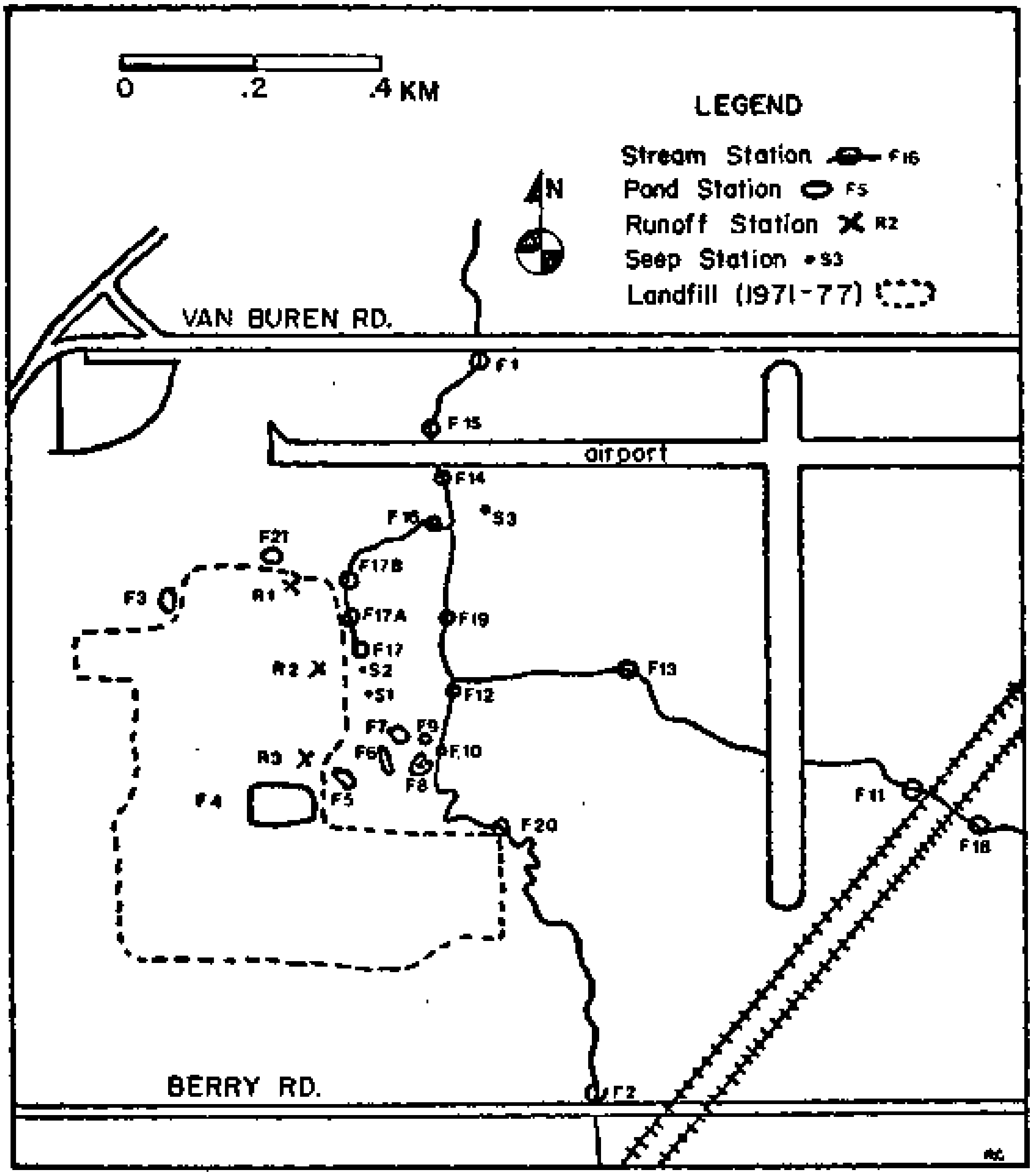


FIGURE 6 ; On-site surface water sampling stations

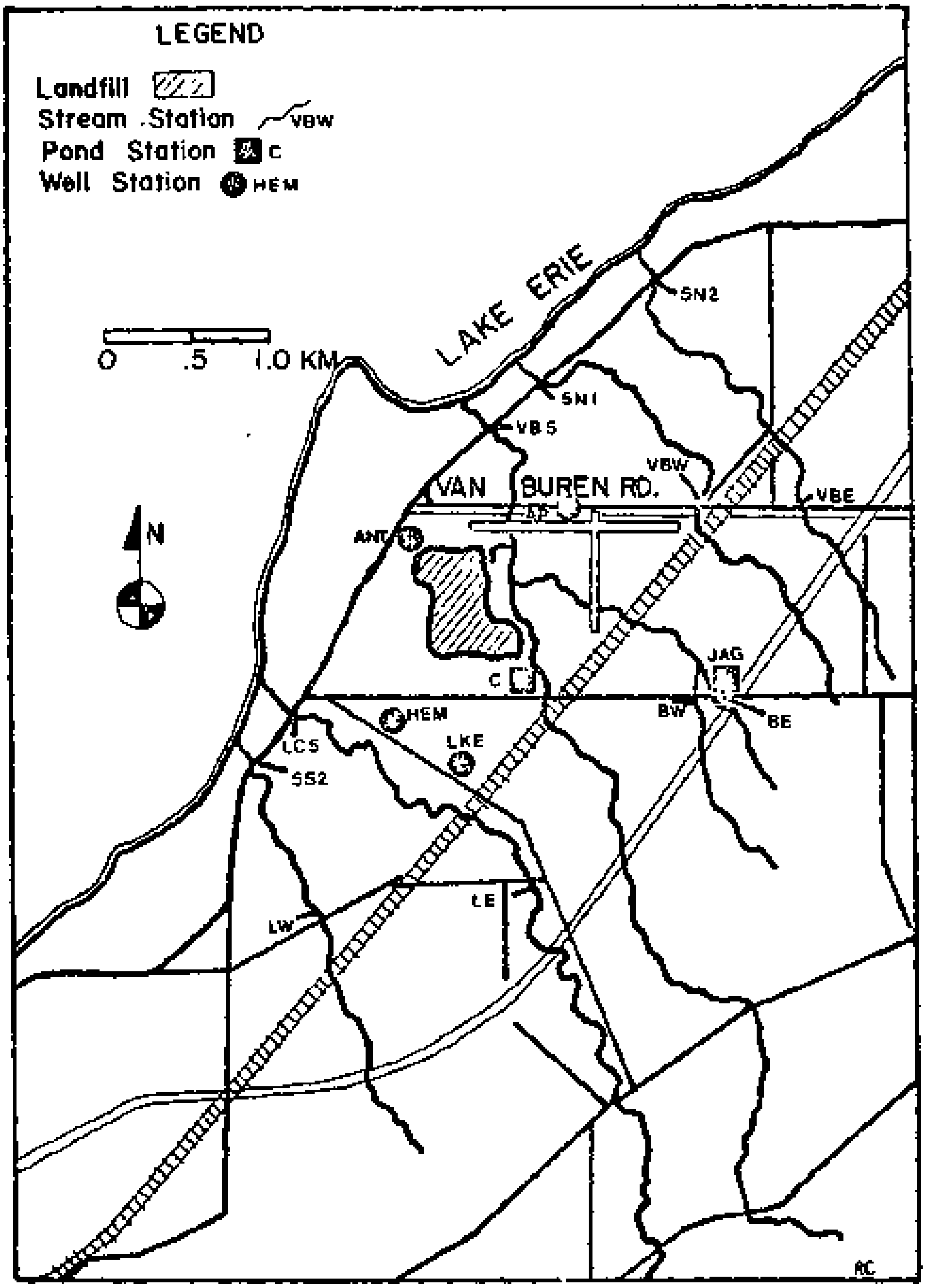


FIGURE 7: Off-site sampling stations

METHODS FOR CHEMICAL STUDIES

Sampling Sites

Groundwater and leachate in the landfill was sampled from 17 wells (Figure 3). These wells were hydraulically drilled into the landfill to depths which vary from 1.5 to 6 meters. Casings consisted of CPVC tubing of 1.9 cm. internal diameter with the lower 1.5 to 3 meter section perforated with 1.6 mm. diameter holes.

The wells could be divided into 2 groups on the basis of pH. Alkaline wells (pH $<$ 9) included 11, 12, 14, 20 and 22. The remaining wells were acid to neutral in pH (wells 1, 2, 3, 6, 8, 9, 10, 13 and 15). As seen in Figure 3 neither group could be fitted into a consistent geographical pattern.

Nearby domestic wells (used to determine if contamination from the landfill extended into deeper groundwater) included those labelled HEM, LKE, ANT and AP (Figure 7) plus 3 wells adjacent to ANT on state route 5. These are all drilled private wells formerly used as domestic water supplies. No subsurface control wells were established.

The sampling program included regular surveys of six catchment ponds (F3-F7, F21) as experimental ponds at the landfill (Figure 4). Control ponds included F8 and F9 (Figure 6) and ponds C and JAG (Figure 7). Ponds 8 and 9 were onsite but remote from possible contamination by leachate. Stream samples included remnant tributary (F16, F17); west branch (F12, F10, F20 and F2); east branch (F13, F18, BE, BW); main stream (F19, F15, F14, F1 and VB5) (Figures 6 and 7).

Sampling stations along the four streams neighboring the study area (Figure 7) are used for comparing the water quality of the surrounding area. Three of the streams are very similar to Van Buren Creek: they originate on the Lake Plain, don't encounter bedrock, and intersect approximately the same number of highways and railroads. The fourth stream (Little Canadaway, LC5-LE in Figure 7) originates on the escarpment, has a greater discharge, and flows on bedrock most of its length.

The wells in the landfill were drilled during the summer of 1976 and were initially sampled as they were completed. The first wells drilled were sampled weekly in order to establish a baseline for their water quality; later they were sampled monthly. Control wells LKE and HEM were sampled infrequently.

Sampling of ponds and streams in the landfill began in the summer of 1975 and continued through October 1976 on an approximately monthly basis and intermittently thereafter. Control ponds C and JAG were sampled once during the summer of 1976. Control streams were sampled several times during the fall of 1976.

Sediments for chemical analysis were taken from six experimental ponds from the remnant tributary, and from three control ponds during 1976 on several occasions.

Field Methods

Samples were taken in polyethylene bottles previously washed with dilute nitric acid and rinsed with distilled, deionized water. In the belief that the dissolved components of the leachate give the best evidence of environmental impact, all principal samples were filtered in the field. No measures of particulate matter were attempted in the streams although pond sediments were analyzed as described below.

Field-filtration of water samples by vacuum employed 47 mm. diameter, 0.45 um. pore size filters in a coarse-frit-glass filtering apparatus. Turbid waters required an initial filtration with large pore paper and a Buchner funnel fitted to a filtering flask. All filter papers were rinsed or soaked in distilled, deionized water and dried prior to use to lessen possible contamination. Water samples for metal analysis were acidified with two ml. concentrated nitric acid per liter of sample.

Groundwater was sampled by inserting a six meter length of polyvinyl tubing, fitted to a 500 ml. vacuum flask, down the well casing and creating a vacuum with a hand pump. Stream water samples were collected by submersing the collecting bottle to about one half the stream depth mid-way across the stream. Pond samples were usually collected from just under the water surface at the same spot near the edge of the pond.

Samples used for determinations of pH, specific conductance, temperature, alkalinity and chloride were collected in the same manners but were not filtered or acidified.

Sediment samples were dried under infrared lamps and placed in desicators. For each analysis a 0.5 g portion was placed in a 125 ml. Erlenmyer flask and digested in a solution of 7 ml. conc. HNO_3 and 14 ml. of 9M H_2SO_4. Samples were gently heated until SO_3 fumes evolved. After cooling, 25 ml. of distilled, deionized water was added and samples were heated again to evolution of SO_3 fumes, maintaining an excess of HNO_3. Solutions were then filtered through .45 um. papers and the filtrate diluted to 200 ml. for analysis (U.S.G.S., unpublished).

Analytical Equipment and Procedures

All elemental determinations except chloride were performed on an atomic absorption spectrophotometer equipped with nitrous oxide and three-slot burners and a graphite furnace. Determinations of Ca, Fe, K, Mg, Mn, and Na were made by direct flame aspiration procedures (Brown et al. 1970; Perkin-Elmer Corp. 1968); Cd, Cr, Cu, Fe, Mn, and Zn were determined by furnace analysis (Perkin-Elmer Corp. 1970). Arsenic and selenium were determined following the hydride generation technique described by Corbin and Barnard (1976). The procedure used for sulfate determination is an indirect method which determines the concentration of barium in solution following the precipitation of sulfate as $BaSO_4$ after the addition of $BaCl_2$ (Galle and Hathaway, 1975). Alkalinity and chloride determinations followed standard HCl and mercuric nitrate titration procedures, respectively (American Public Health Association et al. 1971).

RESULTS OF CHEMICAL STUDIES

Groundwater

Groundwater was analyzed for 17 constituents as shown in Table 1. Stations were divided into three groups, five alkaline wells (average pH 9.15), 12 acid-neutral wells (average pH 6.77), and seven off-site domestic wells. Locations of the wells are shown in Figures 3 and 7, and a cross section of the landfill in Figure 4. Individual analyses for each well are tabulated by Harriger (1977). For each constituent in Table 1 the average, standard deviation and number of analyses are given for each type of well. For these calculations each group of analyses was treated as a single population and the "F test" was used to evaluate the validity of the grouping.

Alkaline wells. The "F test" for validity of grouping gave a significance of 0.9 for pH and Fe, 0.7 for Cr, and 0.4 for alkalinity and Cl. Thus for most other constituents, factors other than high pH would most likely account for variations. An important characteristic of these data is that the standard deviations often equal or exceed the mean even in a population of 70 to 80 analyses.

At high pH the solubility of many metals is reduced and they may precipitate as carbonates or as hydroxides. This may explain the lower average concentrations in the alkaline wells of Cr, 1.6; Cu, 2.9; Fe, 60; Mn, 112; and Zn, 1.6 ug/l. However,

Table 1

The mean, standard deviation, and number of analyses for the various chemical tests of filtered water from alkaline wells and acid-neutral wells at the landfill, and from nearby domestic wells

parameter	units		alkaline wells (5)	acid-neutral wells (12)	domestic wells (7)
Ls	umhos/cm	X	2716	2806	1229
		S.D.	918	1195	878
		N	28	78	10
pH		X	9.15	6.77	-
		S.D.	0.18	0.45	-
		N	7	29	-
As	ug/l	X	83	54	0.7
		S.D.	69	51	1.2
		N	28	78	10
Ca	mg/l	X	421	354	80
		S.D.	107	140	44
		N	28	78	10
Cd	ug/l	X	3.2	3.7	1.8
		S.D.	4.6	6.5	2.0
		N	28	78	10
Cr	ug/l	X	1.6	6.5	1.0
		S.D.	1.0	6.9	0
		N	18	65	4
Cu	ug/l	X	2.9	5.1	5.9
		S.D.	2.6	4.4	6.5
		N	28	78	10
Fe	ug/l	X	60	45072	697
		S.D.	46	48019	462
		N	28	78	10
K	mg/l	X	99	66	4.6
		S.D.	102	83	2.2
		N	28	78	10
Mg	mg/l	X	14.0	76	30
		S.D.	10	41	22
		N	28	78	10
Mn	ug/l	X	112	10118	157
		S.D.	160	11387	163
		N	28	78	10

Na	mg/l	X	192	128	135
		S.D.	205	151	203
		N	28	78	10
Se	ug/l	X	10.2	4.2	1.6
		S.D.	7.4	8.4	1.1
		N	28	78	10
Zn	ug/l	X	1.6	49	35
		S.D.	1.4	55	64
		N	28	77	10
Cl	mg/l	X	22.4	10.1	-
		S.D.	15.4	11.3	-
		N	4	11	-
SO_4	mg/l	X	1798	1651	-
		S.D.	1111	1426	-
		N	6	21	-
Alk	uequiv/l	X	1803	9358	-
		S.D.	635	5525	-
		N	4	11	-

arsenic was highest in average concentration at 83 ug/l. This statistic was derived from the averages of individual wells as follows: W14, 33; W22, 21; W20, 128; W12, 117; W11, 191 ug/l. Wells with the highest averages were within the 1971-77 landfill. Selenium was also high in the alkaline wells with an average of 10 ug/l.

Acid-neutral wells. The "F test" for validity of grouping indicated a high significance only for Cd. Thus for most other constituents, unknown sources of variation predominated as shown by the high standard deviations in Table 1. However, the solubilizing effects of acid conditions was evidenced by elevated concentrations of many metals. Average concentrations for the 12 wells were: As, 54 ug/l; Cr, 6.5 ug/l; Fe, 45 ppm; Mn, 10 ppm, and Zn, 49 ug/l. The arsenic average included a range of 8-141 ug/l. The wells of highest concentration were W8 at 122 ug/l, W10 at 141 ug/l, and W23 at 94 ug/l. These wells of elevated arsenic were both within and without the 1971-77 landfill (Figure 3). With arsenic, as with other parameters, dispersal patterns could not be recognized.

Domestic wells. Average concentrations for seven domestic wells are shown in Table 1. These wells were located adjacent to the dump site and showed low levels of all trace metals except zinc. Wells BER and DAY showed 100 ug/l of zinc probably due to the plumbing. Iron was high in these wells at an average of 697 ug/l.

Surface Water

Ponds. A pond-like remnant tributary, six experimental ponds, and four control ponds were studied. The average, standard deviation and number of analyses for each of the 17 parameters for each group are given in Table 2.

The remnant tributary is located north and east of the 1971-77 landfill as shown by stations F16-F17 (Figure 6). This water body is part of the former stream and is connected to the existing rechanneled stream by a ditch which serves as an overflow channel at its eastern end. To the west it drains a swamp that lies well below the elevation of the landfill so that a steep slope exists to the edge of the water in most places. As shown by the cross section of the landfill (Figure 4) groundwater seeps into the remnant tributary resulting in perhaps the most polluted surface water at the site.

The waters of the remnant tributary were high in alkalinity (average 7616 uequiv/l) and in sulfate (1807 ppm) similar to groundwater from the acid-neutral wells. These waters also averaged 18 ppm of iron and 4.3 ppm of manganese. Arsenic averaged 10.6 ug/l with a standard deviation of 12. Groundwater emergence is evidenced by bright red stains of iron in the swamp.

The six experimental ponds were located adjacent to, or on the landfill. The averages from Table 2 indicate that the most detrimental measures of water quality included Mn, 2.5 ppm; SO_4, 638 ppm; and Fe, 920 ug/l. The high standard deviations indicate that many factors must influence these ponds. The "F

Table 2

The mean, standard deviation, and number of analyses for the various chemical tests of filtered water from the remnant tributary and from experimental and control ponds

parameter	units		remnant tributary (2)	experimental ponds (6)	control ponds (4)
Ls	umhos/cm	X	2066	918	215
		S.D.	996	451	133
		N	23	78	27
pH		X	7.0	5.7	7.0
		S.D.	0.4	1.4	0.4
		N	7	29	10
As	ug/l	X	10.6	3.6	1.1
		S.D.	12.3	12.7	1.4
		N	16	53	19
Ca	mg/l	X	352	137	22
		S.D.	170	74	16
		N	21	73	25
Cd	ug/l	X	2.8	2.6	3.9
		S.D.	3.2	5.0	10.1
		N	16	63	21
Cr	ug/l	X	4.2	1.7	2.0
		S.D.	3.5	1.1	1.1
		N	19	57	21
Cu	ug/l	X	7.2	10	16
		S.D.	7.3	15	20
		N	21	73	25
Fe	ug/l	X	18052	920	503
		S.D.	24270	1675	382
		N	21	72	25
K	mg/l	X	34	4.2	3.6
		S.D.	18	2.0	2.2
		N	21	73	25
Mg	mg/l	X	94	29	5.3
		S.D.	53	16	2
		N	21	72	25
Mn	ug/l	X	4270	2500	406
		S.D.	3012	3385	547
		N	21	73	25

Na	mg/l	X	71	14	4.5
		S.D.	33	16	3.8
		N	21	73	25
Se	ug/l	X	1.0	0.6	0.9
		S.D.	1.5	1.0	0.9
		N	15	49	19
Zn	ug/l	X	4.6	51	18
		S.D.	4.6	61	27
		N	21	73	24
Cl	mg/l	X	7.8	6.7	5.2
		S.D.	6.9	7.5	2.1
		N	8	33	10
SO_4	mg/l	X	1807	638	60
		S.D.	1539	463	80
		N	13	30	11
Alk	uequiv/l	X	7616	300	499
		S.D.	1539	395	425
		N	4	16	8

test" showed significance of grouping of 0.3-0.4 for Cu, Cr, Cd, Se, and alkalinity.

Some ponds were located right in fly ash. Pond 3 is situated on the western side of the fly ash dump and has a large fly ash delta where runoff enters it. The access road to the landfill is constructed in part with pyrite refuse and this provides an acid leachate to the pond. The volume of 140 m^3 readily relects variations in the inflow. The low average pH of 5.7 and the high iron, 2 ppm, high sulfate, 1272 ppm, and high manganese, 2.5 ppm, are all indicative of fly ash leachate from pyrite.

Pond 4 is the largest (14000 m^3) and deepest pond at the site. It was constructed on the 1971-75 landfill as a demonstration project for recreational use of landfills. The high elevation of this pond, and the method of construction has virtually isolated the pond from the landfill. Therefore, most of the chemical measurements are within the normal range. For example, iron is 90 ug/l; Mn, 120 ug/l; and SO_4, 810 ppm on the average (Harriger 1977). The average pH was 7.2.

Pond 5 (volume 400 m^3) is located in the drainage from the access road from which it receives a highly acid leachate. Roadside black ash plus distilled water had a pH of 2.7, and the pond had an average pH of 3.8. Pond 5 also averaged 1.6 ppm in Fe and 4.1 ppm in Mn. Sulfate was 699 ppm.

Pond 6 (volume 10 m^3) is a marshy area on the eastern side of the dump near pond 5, and it too receives acid runoff from the roadway. It had an average pH of 4.7 with 441 ug/l of Fe, 5.6 ppm of Mn, and 490 ppm of SO_4 (Harriger 1977).

Pond 7 (volume 150 m^3) is at a slightly higher elevation than ponds 5 and 6 and did not receive runoff from the access road. Soil from drainage to the pond had a pH of 5.2 to 6.3. The pond had an average pH of 6.1; average Fe, 1.3 ppm; Mn, 3.1 ppm; and SO_4, 271 ppm.

The four control ponds included ponds 8 and 9 on the site. Pond 8 (volume 119 m^3) is a horseshoe shaped pond that is a former stream segment. It is remote from the principal landfill but has slightly elevated iron (average 656 ug/l) and manganese (average 689 ug/l) (Harriger 1977). Averages which include the two off-site control ponds as well (Table 2) show average Fe of 503 ug/l; Mn, 406 ug/l; and SO_4, 60 ug/l.

Despite the presence of the landfill most of these ponds support a variety of aquatic plants. These included <u>Typha latifolia</u>, <u>T. angustifolia</u>, <u>Alisma triviale</u>, <u>Eleocharis obtusa</u>, <u>Juncus effusus</u> and <u>J. tenuis</u>. Ponds 3 and 4 also contained <u>Potamogeton crispus</u> and <u>Sagitaria sp</u>. <u>Elodea</u> was found in ponds 4 and 7. The remnant tributary lacked submergent vegetation.

<u>Streams</u>. Van Buren Bay Creek is the principal stream neighboring the landfill (stations F1-F2 in Figure 6). A major tributary arises in flat farmland east of the site (BW-BE in Figure 7) and joins Van Buren Bay Creek opposite the center of the landfill (near F12 in Figure 6). For convenience during our study, the data were averaged in 3 groups: the portion of

Van Buren Bay Creek south of the confluence (west branch); eastern tributary; and main stream north of the confluence (Table 3).

The Texas Instruments, Inc. (Niagara Mohawk Power Corp. 1976) surveyed Van Buren Bay Creek from November 1974 until September 1975 at one upstream and one downstream location. Dissolved oxygen levels (generally at saturation throughout the survey), temperature, specific conductance, pH (average difference between the two stations was only 0.3 pH units), total dissolved solids, suspended solids (the downstream station averaging only approximately 1.1 mg/l higher loads than the upstream station), chloride and biological oxygen demand values were very similar for both stations. However, sulfate and nutrient (nitrate, nitrogen, orthophosphate and total phosphate) levels did show observable differences between the two stations, with the downstream station having higher values.

The present study (Table 3) shows that Van Buren Bay Creek downstream from the confluence with the east branch had elevated specific conductance (295 upstream west versus 453 downstream). This can be correlated with elevated sodium, chloride, sulfate and alkalinity. Manganese averaged 97 ug/l upstream and 207 ug/l downstream; iron was 206 ug/l upstream and 293 ug/l downstream; SO_4, 90 ppm upstream and 229 ppm downstream. These increases are partly due to the contributions from the east branch which drains the relatively polluted lake plain. The west branch (as listed in Table 3; this is really the main stream) receives

Table 3

The mean, standard deviation, and number of analyses for the various chemical tests of filtered water from control streams and from three sections of Van Buren Bay Creek

		Van Buren Bay Creek			
parameter	units	west branch(4)	east branch(4)	main stream(5)	control streams(8)
Ls	umhos/cm	295 89 41	460 89 23	453 160 42	532 214 20
pH		7.7 0.2 13	8.0 0.4 8	7.9 0.4 13	7.7 - 8
As	ug/l	0.4 0.8 13	0.3 0.4 10	0.6 0.9 16	0.6 0.8 20
Ca	mg/l	37 12 34	51 14 20	52 20 37	57 24 20
Cd	ug/l	0.9 0.2 18	0.7 0.5 11	1.6 2.0 23	1.6 1.4 20
Cr	ug/l	1.6 0.8 24	1.5 0.8 15	1.4 0.6 28	1.1 0.3 20
Cu	ug/l	8 11 34	15 28 20	9 11 37	4.9 4.2 20
Fe	ug/l	206 167 34	367 646 20	293 589 37	125 123 20
K	mg/l	2.9 0.9 34	4.2 1.6 20	4.4 2.2 37	7.3 3.8 20
Mg	mg/l	7.6 2.7 34	8.4 1.7 19	9.2 2.7 37	9.6 3.4 20

Mn	ug/l	97	92	207	82
		82	70	175	75
		34	20	37	20
Na	mg/l	12	25	20	39
		4	28	12	32
		34	20	37	20
Se	ug/l	0.7	1.2	1.4	0.7
		0.9	1.7	2.6	0.7
		16	11	19	20
Zn	ug/l	7	9	7	5
		9	15	8	5
		34	20	37	20
Cl	mg/l	18.9	48	33.2	36.5
		2.7	7	8.9	14.6
		18	11	16	10
SO_4	mg/l	90	69	229	62
		78	29	250	27
		16	11	17	10
Alk	uequiv/l	912	1123	1034	-
		256	54	193	-
		14	7	11	-

relatively clean water from the escarpment. The result is that Van Buren Bay Creek north of the confluence generally contains concentrations intermediate to those of the two headwaters. This makes it difficult to evaluate contributions from the disposal area to the stream. However manganese, iron, and sulfate were generally higher north of the confluence than in either branch of the stream.

The previous study (Niagara Mohawk Power Corp. 1976) involved two stations on Van Buren Bay Creek and 12 analyses for each parameter. Results were similar to the present study for K, Ca, Mg and Fe. However, our survey showed twice as much Na and Cl, three times as much SO_4, and eight times as much Mn as in the summer of 1975.

Sediments. Sediment analyses from the remnant tributary, six experimental ponds and three control ponds are averaged and presented in Table 4. Sediments from the remnant tributary showed high average concentrations of As, 65 ug/g; Fe, 90 mg/g; and Mn, 2 mg/g. This indicates some amount of groundwater precipitation. Experimental pond sediments averaged 29 ug/g of arsenic (standard deviation 26) while the control ponds averaged 8 ug/g. Apart from slightly higher As, Fe, and Mn, averages of the various constituents were similar between the control and experimental ponds.

Table 4

The mean, standard deviation, and number of analyses for the various chemical tests of sediment from the remnant tributary, experimental, and control ponds

parameter	units		remnant tributary(3)	experimental pond(6)	control ponds(3)
As	ug/g	X	65	29	8.2
		S.D.	73	26	5.4
		N	12	34	15
Ca	mg/g	X	3.8	1.1	0.4
		S.D.	4.5	1.6	0.6
		N	12	34	15
Fe	mg/g	X	90	36	23
		S.D.	72	15	11
		N	12	33	14
K	mg/g	X	8.5	11.6	8.4
		S.D.	3.1	5.1	4.2
		N	12	34	15
Mg	mg/g	X	4.7	6.2	4.1
		S.D.	1.5	2.2	1.7
		N	12	34	15
Mn	ug/g	X	2070	484	367
		S.D.	3243	271	243
		N	12	34	15
Na	ug/g	X	721	589	403
		S.D.	180	167	154
		N	12	34	15
Se	ug/g	X	0.68	1.58	0.65
		S.D.	0.85	4.58	0.46
		N	12	33	15
Cr	ug/g	X	-	40.6	42.2
		S.D.	-	14.5	10.6
		N	-	8	5

METHODS FOR BIOLOGICAL STUDIES

Sampling Sites

Four stations were chosen for stream samples of aquatic invertebrates. These correspond to those shown in Figure 6 as follows: station 1 is at the vicinity of F1; station 2 at F15; station 4 at F19; station 5 at F10. From the initiation of the study until the summer of 1976, station 5 was upstream of the landfill and was considered as a control station, while stations 1, 2 and 4 were experimental stations.

Station 1 had the most varied substrate composition with a small fraction <4 mm. and the bulk at 1/4 - 2 mm. It had a moderate degree of penetration. A number of coarse cement blocks were present. Station 2 had easy penetration to a depth of 15-20 cm. with a trowel. It had a large fraction of 4 mm. Station 4 had a large fraction at 4 mm. with many rocks in the cobble to small boulder range. Station 5 had the least penetration of any station with often 1-2 cm. of sand-silt-gravel overlying a very hard layer of clay. Sediment samples showed the highest proportion of clay to fine sand.

Van Buren Bay Creek is a small slow flowing creek, except during spates. Widths were around two meters at all stations and depths generally less than 20 cm. Stations 4 and 2 were generally exposed to the sun while stations 5 and 1 were well shaded by a thick canopy of vegetation. This canopy lowered the temperatures of the water at stations 5 and 1 by a few degrees when the sun was shining.

The surface current velocity was measured at each station during April to July 1976. The velocity at station 5 was less than half that of the other stations. Station 4 showed the less variation in flow suggesting greater stability of the substrate.

In the summer of 1976 the coal ash landfill was extended above and adjacent to the stream at station 5. As a consequence of this, much of the data described here is for the period June 1975 to April 1976. Other control stations included streams and ponds in Chautauqua County and in the coal ash landfill site itself and also in the nearshore waters off South Bass Island in western Lake Erie. These control stations were chosen due to their location in areas remote from sources of industrial trace metal pollution and the fortuitous abundance of aquatic invertebrate fauna comparable to that found in Van Buren Bay Creek.

Methods

Substrate samples were collected with a hand trowel, being careful to shield the sample as much as possible from the current to avoid washing away the lighter particles as the sample was brought out of the water. The larger rocks were estimated qualitatively.

The substrate is an important determinant of invertebrate distribution. It provides the basic microhabitat of the organisms; few organisms live in the water column unattached to the substrate. The substrate provides retreats and protection and provides a surface for epipelic algae and other microorganisms and for accumulation of detritus. The epipelic microorganisms and detritus form an important food source for many aquatic invertebrates. Important parameters of the substrate are particle size, composition, packing and amount of organic material. None of these parameters are mutually exclusive and in fact they are all affected to a great extent by current velocity. High current velocities at a station wash away smaller particle sizes and light organic material.

The degree of penetration or packing of the substrate is also an important parameter influencing invertebrate distribution and abundance. It has been shown by a number of studies (Coleman and Hynes 1970; Mundie 1971; Bishop 1973; Hynes 1974; Williams and Hynes 1974) that many aquatic invertebrates may live in the substrate at depths of up to 40 cm. or so. Even Simulidae larvae and some caddis larvae, normally or previously just thought to be associated with only a free flowing high oxygen surface sediment condition, have been found at depth in the substrate. A substrate that favors penetration at depth might provide a haven for the organisms during a spate and thus provide for rapid recolonization of the new surface layers. This is important since spates are known to be able to drastically reduce the abundance and/or change the composition of the macrobenthos (Hynes 1970).

Quantitative collections of biota were made by the Surber sampler and by artificial substrates of conservation webbing. Invertebrates collected in the field were placed on ice: once back in the laboratory invertebrates were cleaned in several changes of distilled and deionized water and then placed into digestion flasks; invertebrates were digested with a mixture of nitric and perchloric acids; samples were then prepared for spectrophotometric analysis. Problems with this method are many. It was often very difficult to collect adequately large samples for analysis. An adequate sample is between 0.1 to 0.2 grams dry weight; for many groups of aquatic insects such a large sample was impossible to obtain. Even for the more abundant groups, it often took six man hours to collect an adequate sample. A disturbing consequence of this problem was the difficulty in obtaining comparative control and experimental samples; for example, a certain aquatic insect species may have been abundant enough for a sample in an experimental area, but not in a control area.

Contamination of the larval insects was a problem. In some the exterior surface was coated with detritus which may have contained metals. Also the gut contents may be contaminated with metals. To test this source of error, night-flying adult insects were captured at light traps. These would have no food in the gut and a clean body surface.

The chemical matrix resulting from digestion of the insects was highly variable and this created problems in the atomic absorption method. It was difficult to obtain a homogeneous digestate and fats often floated to the surface.

RESULTS OF BIOLOGICAL STUDIES

Distribution of Biota

The lists of taxons for each station are given in Tables 5 and 6. The Chironomidae group have been recognized as important indicators of water quality at the genus and species level of identification. Therefore, the ten most numerous Chironomidae are listed in Table 5, while the ten most numerous non-Chironomidae are listed in Table 6 for each station. More detailed species lists for each station will be presented in a report under preparation by Thomas J. Fink at Florida State University, together with life history studies of the mayfly fauna, especially that of *Ephemera varia*, the dominant burrowing mayfly found throughout the stream.

Non-Chironomidae. Station 1 had 84 non-Chironomidae/m^2. These included greatest numbers of *Chrysops* and *Stenelmis* larvae. Station 2 had 242 non-Chironomidae/m^2 with the greatest numbers of *Cheumatopsyche* (135/m^2), the most Turbellaria, and the second largest numbers of *Simulium*, *Chrysops*, *Caenis*, *Stenelmis* and *Lymnea*. However, *Helisoma* and *Physa* snails were absent or in smallest quantity of any station. Station 4 had 375 non-Chironomidae/m^2 including 115 *Cheumatopsyche*/m^2 and the largest numbers of *Simulium*, *Caenis*, *Physa* and *Helisoma*. *Ephemera* and Turbellaria were also abundant. Station 5 had 58 non-Chironomidae/m^2, of which 67% were *Ephemera varia*. *Cheumatopsyche* were low

Table 5

Number per square meter of the 10 most numerous Chironomidae at each station
July 1975 - April 1976

Taxon	Station 1	2	4	5
Conchapelopia	67.1	112.2	264.4	32.0
Micropsectra	6.5	12.6	106.2	4.4
Stictochironomus	1.2	2.2	4.7	153.4
Cricotopus	33.8	14.7	35.0	6.0
Diplocladius	31.8	12.1	16.3	29.4
Orthocladius	7.9	18.0	11.2	14.2
Pentaneura	4.9	0	0.8	30.0
Parametriocnemus	8.4	7.6	9.9	3.0
Pseudochironomus	2.1	4.0	15.1	0
Microtendipes	1.0	0	1.3	19.4
Unidentified	3.9	5.8	6.3	5.0
Total	168.7	189.3	471.3	297.0

Table 6

Number per square meter of the 10 most numerous non-Chironomidae at each station July 1975 - April 1976

Taxon	Station 1	2	4	5
Simulium vittatum	5.8	29.0	74.2	0
Chrysops	5.3	3.7	0	3.6
Cheumatopsyche	29.4	135.4	115.1	0.6
Caenis simulans	7.4	14.1	24.1	1.1
Ephemera varia	14.2	14.9	22.2	39.2
Stenelmis larva	14.8	5.4	1.3	4.4
Heliosoma anceps	0.7	0.4	22.3	0.5
Physa	6.1	0	64.9	7.8
Lymnea	0.5	2.7	18.7	0.8
Turbellaria	0.2	36.6	31.8	0
Total	84.4	242.3	374.6	58.0

in abundance ($0.6/m^2$) and *Simulium* was absent. Few *Caenis* were taken.

Chironomidae. Station 1 had 168 Chironomidae/m^2, the bulk of which were in the genera *Conchapelopia*, *Cricotopus* and *Diplocladius* (Table 5). Station 2, at 189 Chironomidae/m^2 had $112/m^2$ of *Conchapelopia*, with other genera in reduced numbers. Station 4 contained 471 Chironomidae/m^2 headed by *Conchapelopia* at $264/m^2$ and *Micropsectra* at $106/m^2$. Station 5, at 297 Chironomidae/m^2 contained few *Conchapelopia* but had $153/m^2$ of *Stictochironomus*. *Pentaneura* and *Microtendipes* were far more abundant at station 5 than at the downstream stations.

Discussion on Distribution. It was noted that station 5 had about half the current velocity of the other stations. This is not favorable to organisms which strain their food from the water; these include *Simulium*, the blackfly, and *Cheumatopsyche*, the net-spinning caddis.

Simulidae larvae generally attach to the surface of rocks and debris in the full force of the current where they filter the water with their head fans (Pennak 1953; Macan 1963; Hynes 1970). Simulidae thus usually occur in riffles where good attachment surfaces (rocks, aquatic plants, etc.) and current are present. Station 4 in the present study provided the optimum conditions for *Simulium vittatum*, both in substrate and in water movement. It was absent from station 5.

Cheumatopsyche is a net spinning caddisfly in the larval stage. Requirements generally include a current sufficient for efficient food filtering with its silken net and appropriate attachment surfaces such as the underside of rocks, logs and other debris (Edington 1968; Wallace 1975; Hilsenhoff 1975). In the present study Cheumatopsyche larvae were seen on the undersurface of small (approximately 8 cm. or less in diameter) to large rocks at station 4, and on small rocks (the only ones present) at station 2. It is believed the current velocity at station 5 was far too low for efficient net food gathering and that at station 1 there were too few particles greater than or equal to 4 mm. in diameter for attachment surfaces.

Members of the Caenis genus of mayflies usually inhabit quiet to stagnant water in ponds, and the margin of lakes and streams. Often they are associated with various aquatic plants or with the roots and branches of terrestrial plants trailing in the water. Nymphs of Caenis latipennis were experimentally found to select substrates of <1 mm. in preference to finer sediments (Cummins and Lauff 1969). This may explain the high average abundance of Caenis at station 4 in our study where cobble to small boulders occurred. Caenis was also noticed on the coarse cement blocks at station 1.

Ephemera species are mayflies specifically adapted for burrowing into sandy substrates with a broad frontal head projection, elongated forward directing mandibular tusks, scooplike foretarsi, very broad hind femora and finely dissected gills (providing a large surface area for oxygen absorption in their oxygen-low burrows in the sediment). Cummins and Lauff

(1969) experimentally tested the preference of E. simulans for different sized substrate particles and also found a tendency for the nymphs to favor coarse sand and gravel substrates. However (as shown in Table 6), Ephemera varia was most abundant in the less favorable substrate of station 5. Evidently the exact limits of its microdistribution are set by other factors such as the nature and abundance of detrital foods.

Stenelmis larvae are inhabitants of gravel substrate and waterlogged wood (Hilsenhoff 1975) and may burrow to depths in the substrate (Williams and Hynes 1974). Stenelmis crenata adults, the "riffle beetle," is characteristic of rapid areas of streams on coarse substrates where it supposedly feeds on epilithic algae and detritus (Pennak 1953; Coffman 1967; Cummins and Lauff 1969). Stenelmis larvae were most abundant at station 1 in our study. Adults of Stenelmis crenata were also seen on the few large coarse cement blocks in a riffle area at station 1. This is another example in which substrate and water movement are the prime determinate in the relative abundance of the organisms.

Cummins and Lauff (1969) found Heliosoma anceps to occur on a wide range of substrates, but was most abundant on gravel (2 to 16 mm.) where it feeds on epilithic algae and detritus. They believe the microdistribution of H. anceps is only secondarily related to substrate particle size, in view of its wide selection. Food availability is certainly important. In Van Buren Bay Creek H. anceps also inhabited a very wide range of current velocity areas, from shallow to deep pools to the riffle zone at station 4. In some pools and shallow water (very slow current) H. anceps was found in very large numbers literally coating the bottom. As shown in the periphyton study in this report, the diatoms Cymbella and Diatoma were quite abundant in this reach of the stream, with total abundance of 4392 at station 4 and 806 at station 5. Cladophora, an epiphytic green alga was abundant at station 4, but few at station 5. Thus, the abundance of snails at station 4 can be related to food abundance.

Turbellarians (flatworms) occurred on the underside of small to large rocks at the downstream stations. They were absent from station 5 where no small rocks were found.

Trace Metal Content of Biota

The manganese content of various invertebrates collected from control and experimental sites can be compared to the environmental level in Table 7. The concentration in the biota varied from 19 ug/g for adult caddis flies taken at Dunkirk, New York to 1589 ug/g for Tipula larvae taken from Van Buren Bay Creek. There was no evident correlation between exposure of the biota to the metal and uptake of the metal. However, the winged insects (which would have clean exterior and no gut contents) all contained less than 50 ug/g of manganese.

The selenium content in aquatic invertebrates is shown in Table 8. Concentrations ranged from 0 to 3.8 ug/g dry weight. Results are somewhat inconclusive but it seems that selenium

Table 7

The manganese content of various invertebrates in ug/g dry weight with the manganese content of the water in ug/liter and the standard deviation of the water analysis

site	taxon	conc.in biota	conc.in water	standard deviation
Dunkirk, N.Y.	Leptoceridae adults	19	-	
Canadaway Cr	Chironomus	24	22	18
Little Canadaway Cr	Leptoceridae adults	33	12	5
sta F16	Gomphus	42	1608	1393
Put-in-Bay, O.	Leptoceridae adults	44	-	
study site	Leptoceridae adults	44	-	
Canadaway Cr	Chironomus	44	22	18
Dunkirk, N.Y.	Chironomidae adults	46	-	
Dunkirk, N.Y.	Leptoceridae adults	46	-	
Canadaway Cr	Neoperla clymene	50	22	18
Little Canadaway Cr	Stenomena	62	12	5
Canadaway Cr	Chironomus	83	22	18
pond 7	Chironomus	90	2637	3753
pond 7	Chironomus	107	2637	3753
pond 7	Chironomus	113	2637	3753
pond 9	Physa	113	152	349
sta 1	Chironomus	148	246	153
east trib F13	Physa	163	113	99
College pond	Aeschna	165	?	
sta 5	Physa	180	161	148
Hyde Cr	Orconectes	240	?	

sta 5	Orconectes	267	161	148
sta 5	Ephemera	305	161	148
sta 1	Orconectes	315	246	153
Canadaway Cr	Cheumatopsyche	338	22	18
sta 5	Helisoma	341	161	148
sta 2	Helisoma	503	319	235
sta 1	Ephemera varia	569	246	153
Chautauqua L.	Chironomus	575	?	
sta 1	Stictochironomus	646	246	153
sta 2	Helisoma	683	319	235
sta 5	Ephemera varia	760	161	148
sta 4	Cheumatopsyche	778	106	46
F2	Tipula	889	100	52
sta 1	Helisoma	931	246	153
sta F16	Aeschna	1111	1608	1393
sta 2	Orconectes	1140	319	235
F13	Cheumatopsyche	1340	113	99
F2	Orconectes	1398	100	52
sta 4	Tipula	1589	106	46

Table 8

The average selenium concentrations in aquatic invertebrates (ug/g)

Caddis Fly Adults		
Lake Erie Control (2)	1.92	
Experimental (3)	0.66	
Local Control (1)	1.64	
Caddis Fly Larvae		
Experimental (1)	<1	(≈ 0)
Control (1)	0.98	
Cray Fish		
Experimental (1)	1.28	
Control (2)	1.74	
Chironomid Larvae		
Experimental (3)	3.60	
Control (2)	1.22	
Mayfly Nymphs		
Experimental (1)	3.79	
Dragonfly Nymphs		
Experimental (1)	1.61	
Heliosoma Snails		
Experimental (2)	0.11	
Physa Snails		
Experimental (2)	≈ 0	
Crane Fly Larvae		
Experimental (1)	1.26	
Control (1)	2.58	

was not a problem at the disposal site.

Results are presented in Table 9 according to the type of biota collected for the metals Cd, Cr, Cu, Fe, Mn, and Zn. As previously shown, inconsistencies in the data make discussion unwarranted. Some obvious points can be made however. The high copper in Crustacea, 75-276 ug/g is related to their physiology. The high iron in Chironomidae (883-2001) from control sites may likewise be partly related to blood pigments. External iron was often noticed on larvae of Cheumatopsyche as a precipitate. The reduction in iron content between the larvae (4392-9488 ug/g) and emerged adults of other Trichopetra (258-939 ug/g) is certainly due in part to the departure of the winged adult from its larval skin.

The remnant tributary contained probably the most polluted surface water on the site. However, note that Aeschna dragonflies from that location had only elevated concentrations of Fe and Mn. Other metals were within the general range encountered in other parts of the study.

Periphyton Distribution

The periphyton distribution was studied during June-July 1977 by Kevin W. Johnston under a grant from the National Science Foundation--Undergraduate Research Participation program.

Methods. Studies were made at five stations in Van Buren Bay Creek. Station 1, the most downstream station, was located north of route 5. The remaining stations correspond to those

Table 9

The trace metal concentrations in various invertebrates from experimental (E) and control (C) sites

				metal concentration in ug/g dry weight					
specimen	date	type	location	Cd	Cr	Cu	Fe	Mn	Zn
Cheumatopsyche (caddisfly larva)	6-7/75	E	sta 4	0.43	7.8	7.5	4392	778	246
Cheumatopsyche (caddisfly larva)	7/75	E	V.B.Bay Cr (east)	0.56	17.3	14.5	9488	1340	223
Cheumatopsyche (caddisfly larva)	7/75	C	Canadaway Creek	0.27	4.1	17.4	2219	338	74
Leptoceridae (caddisfly adult)	7/75	C	Lake Erie, Put-in-Bay, O.	0.66	2.4	22.2	415	44	122
Leptoceridae (caddisfly adult)	6/75	C	Little Canadaway Cr	0.14	1.3	39.3	258	33	196
Leptoceridae (caddisfly adult)	6-7/75	C	study site (various)	0.42	2.3	50.1	434	44	139
Leptoceridae (caddisfly adult)	7/75	C	Dunkirk,N.Y.,Rte 5	0.32	4.5	28.8	939	46	102
Leptoceridae (caddisfly adult)	7/75	C	Dunkirk,N.Y.,Urban Rd.	0.60	2.3	44.2	533	19	159
Ephemera varia	6/75	E	sta 1	3.07	9.5	16.6	6295	569	123
Ephemera varia	7/75	C	sta 5	1.46	11.4	14.6	7681	760	139
Ephemera varia	6/75	C	sta 5	-	-	28.7	-	305	-
Aeschna (dragonfly nymph)	6/75	E	remnant trib.	0.38	1.5	22.0	12253	1111	160
Aeschna (dragonfly nymph)	6/75	C	Brocton,N.Y.,college pond	0.43	5.8	20.7	763	165	129

specimen	date	type	location	Cd	Cr	Cu	Fe	Mn	Zn
Gomphus (dragonfly nymph)	6/75	E	remnant trib.	0.10	3.9	3.4	1890	42	33
Stictochironomus (chironomid larva)	7/75	E	sta 1-2 and nearby pool	3.20	13.6	52.6	10519	646	72
Stictochironomus (chironomid larva)	7/75	E	pond 7	0.15	15.9	74.1	27138	107	73
Stictochironomus (chironomid larva)	7/75	E	pond 7	0.20	16.0	65.5	-	113	66
Stictochironomus (chironomid larva)	8/75	E	pond 7	0.0	15.7	100	-	90	93
Stictochironomus (chironomid larva)	6/75	E	sta 1	-	-	28.7	-	148	-
Chironomus	8/75	C	Canadaway Cr	0.54	5.3	48.4	1921	44	105
Chironomus	7/75	C	Canadaway Cr	1.26	11.1	62.4	3998	83	137
Chironomus	8/75	C	Canadaway Cr	0.19	2.3	46.8	883	24	89
Chironomus	7/75	C	Chautauqua Lake	4.18	2.5	84.3	2001	575	149
Chironomidae (adults)	6/75	C	Dunkirk,N.Y.,Urban Rd.	3.85	10.4	67.8	1862	46	239
Tipula larva	7/75	E	sta 3	0.30	4.8	12.8	7232	1589	50
Tipula larva	7/75	C	V.B.Bay Cr at Berry Rd.	0.24	5.2	8.8	4740	889	146
Orconectes (crayfish)	6/75	E	sta 1	0.17	3.4	106.7	808	315	17
Orconectes (crayfish)	6/75	E	sta 2	0.11	2.7	105.6	1281	1140	46
Orconectes (crayfish)	7/75	C	sta 5	0.10	2.8	143.3	402	267	8
Orconectes (crayfish)	6/75	C	Dunkirk,N.Y.,Hyde Cr	0.10	1.6	276.3	412	240	49
Orconectes (crayfish)	6/75	C	V.B.Bay Cr at Berry Rd.	0.53	1.6	75.6	1094	1398	45
Physa (snail)	6/75	C	sta 5	2.82	7.7	42.0	309	180	17
Physa (snail)	6/75	E	pond 9	2.69	8.3	67.3	2075	113	26

specimen	date	type	location	Cd	Cr	Cu	Fe	Mn	Zn
Physa (snail)	7/75	E	V.B.Bay Cr (east)	2.66	10.8	65.4	3907	163	22
Helisoma (snail)	6/75	E	sta 1	2.90	9.4	41.0	1819	931	4
Helisoma (snail)	6/75	E	sta 2	1.09	3.5	7.0	2271	683	3
Helisoma (snail)	6/75	C	sta 5	2.80	8.8	44.4	891	341	13
Helisoma (snail)	7/75	E	sta 2	1.00	4.4	7.5	1865	503	3
Neoperla clymene (stonefly)	6/75	C	Canadaway Cr/Shumla Rd	-	-	47.2	1508	50	-
Stenomena	6/75	C	Little Canadaway Cr	-	-	12.9	-	62	-

shown in Figure 4 as follows. Station 2 was at F15; station 3 at F14; station 4 at F19; station 5 at F20. Numerous samples were taken at each station from scrapings of rocks and debris. Samples were preserved in 10% formalin and examined in the laboratory. In addition, strips of plexiglas were anchored at each station and allowed to colonize for one- and two-week intervals.

Quantitative estimates of colonization were obtained by setting out plexiglas frames containing sets of eight microscope slides (Sladeckova 1962). These were left in place for two weeks and direct counts were obtained by the microtransect method (Lackey 1938). Other slides were extracted with acetone for chlorophyll determinations (Lorenzen 1967). Dry weight was also determined.

<u>Results</u>. Quantitative and qualitative observations are shown in Table 10. One blue green alga, two green algae, three centric diatoms and eight pennate diatoms were recognized in the periphyton.

The green alga <u>Cladophora</u> was most abundant in riffle areas at station 4 where it occurred in a clean, healthy condition. In areas of quiet water both at station 4 and 5, the <u>Cladophora</u> was overgrown with the epiphytic diatom <u>Cocconeis</u>. <u>Cladophora</u> was less abundant at station 5 perhaps as a result of shading in the densely wooded reaches of the creek.

An important observation from Table 10 is that green algae and centric diatoms were mostly replaced by pennate diatoms downstream from station 4. Station 3 was just downstream from

Table 10

The average number per mm^2 of diatoms from glass-slide colonization experiments at each station. The diversity, chlorophyll content and dry weight is also given for the diatoms. The code letters refer to qualitative observations in the stream: (r) rare; (f) few; (c) common; (a) abundant

Taxon	Station 1	2	3	4	5
bluegreen algae					
Oscillatoria	(f)				
green algae					
Spirogyra				(r)	
Cladophora				(a)	(f)
centric diatoms					
Cocconeis	16(f)		66(r)	508(c)	331(c)
Cyclotella			39(r)	4	
Actinella				16	
pennate diatoms					
Tabellaria				40	(r)
Gomphonema	10		57(f)	30(f)	18(r)
Synedra	36(r)		509(f)	214(f)	18
Navicula	272(c)	(f)	487(c)	895	272(f)
Melosira	8	(f)			5
Gyrosigma	10			8(f)	
Cymbella	342	(c)	9841(c)	1938(a)	105(f)
Diatoma	153	(f)	2045(c)	736(c)	53(f)
Unidentified	10		7	1	4
total diatoms	857		13051	4392	806
diversity	2.19		0.83	2.24	1.79
Chl a ug/10 cm^2	2.25		33.5	20.7	5.4
dry wt mg/10 cm^2	2		50	18	10

the remnant tributary (station F16 in Figure 4). Here Cladophora was absent and Cymbella at 9841/mm^2 and Diatoma at 2045/mm^2 made up the bulk of the periphyton collections. The preponderance of these two genera accounts for the low diversity index of 0.83 for the diatom population at station 3. The diversity index at station 4 was 2.24 where Cymbella and Diatoma coexisted with larger proportions of the other diatoms.

It is interesting that qualitative observations in the field mostly agreed with the colonization experiments. Where Cymbella was common at station 3 the total diatoms were 13051/mm^2, the maximum diatom population.

The area of Van Buren Bay Creek that adjoins the mouth of the remnant tributary was observed to have an abundant diatom population, primarily Cymbella, at several times during the study period. During the periods of profuse growth, gelatinous masses completely covered the shallow rocky bottom of Van Buren Bay Creek for approximately 50 meters up and downstream of the remnant tributary-Van Buren Bay Creek junction. These periods of high productivity were substantially reduced during intervals of high runoff.

Waters of the remnant tributary failed to colonize plexiglas strips during two weeks, except that Oscillatoria was occasionally observed on the strips in loosely packed, free-floating masses. Thus it was believed that the remnant tributary contributed chemical wastes to Van Buren Creek that inhibited the growth of certain algae. Patrick et al. (1969) showed that high concentrations of manganese (<1 ppm) are very inhibitory to natural populations of bluegreen and green algae. The mean manganese concentration at F14 (corresponds to station 3 for periphyton) was 106 ug/l (S.D. 46) (Harriger 1977). However, the mean manganese concentration at the mouth of the remnant tributary was 1608 ug/l (S.D. 1393). Harriger reported intermittant flow into Van Buren Creek at this point which could provide sufficient manganese to be inhibitory to Cladophora.

Further study of the Cymbella population above and below the mouth of the remnant tributary in Van Buren Bay Creek was conducted during July 1977. Direct sampling was done by use of a sampler devised by Ertl (1971). Samples obtained by this method were dried in glass vials and "cleaned" at 570 C for one hour. Various dilutions were made with direct counts by the micro-transect method.

Results of the direct sampling corresponded to those obtained by the colonization technique. There was a general trend of increasing diversity and decreasing numbers of Cymbella with increasing distance upstream.

Unlike Cladophora which seemed to be inhibited downstream from the remnant tributary, Cymbella was enhanced. As the two stations (3 and 4) where this difference occurred were quite similar in physical characteristics, it is suggested that Cymbella is not sensitive to the high manganese levels that may inhibit Cladophora, and that Cymbella is actually favored by some leachates from the groundwater of the fly ash disposal area.

DISCUSSION AND CONCLUSIONS

Wide variations in the chemical quality of ground and surface waters at coal ash disposal sites may occur as a result of variations in pH, oxidation conditions, chemical quality of the coal ash, quantitative distribution of the ash, length of time during which ash has been leached, adsorption and ion exchange effects of clays.

Occasionally materials other than coal ash have been transported to the landfill including slag from steel mills and pyrite from the Dunkirk generating station (both used in the construction of roads throughout the landfill), and once an application of sewage sludge spread on site to promote the growth of vegetation.

The amount of ash varies from place to place at the disposal site. Differences in thickness, degree of compaction, and amount of ash relative to cover and admixed materials may influence the degree of leaching that takes place.

The solubility of many elements and compounds is pH dependent. Coal ash and pyrite influence the pH of waters in which they are in contact: depending upon the composition of the coal ash, it may increase or decrease the pH; pyrite, as it is oxidized, produces sulfuric acid and tends to lower the pH. It was not practicable to attempt correlation of most of these variables with the conditions that were measured. However, pH was used to separate the well waters into two groups.

Leachate from fresh ash recently deposited can be expected to have high concentrations of the most readily soluble elements because there is immediate solution of the chemical constituents on the surface of the ash. With time, however, various chemical species in leachate can undergo ion exchange and/or readsorption on the ash itself if still in contact with the ash (Gaasch and Law, 1977) or, where the leachate is effectively removed from the ash, the soluble constituents can be expected to continually decrease in concentration.

Arsenic, at 83 ug/l in the high pH wells was in high enough concentration to impair the water quality. Likewise selenium at 15.7 ug/l was above the USPH recommended level for drinking water of 10 ug/l. Arsenic and Se were two to three times greater in concentration at high than at low pH. This is possibly due to variation in the dump site, or to the fact that clays are not effective in absorption of these constituents at pH $<$ 9.

The general effect of the ash disposal on groundwater has been to more than double the specific conductance. Large increases in the alkalinity components included elevations of Ca, K and Mg. Important amounts of Fe and Mn were released to the groundwater. Elevations in As, Cr, Cu, Cd, Se, and Zn were recorded in on-site shallow wells but not in deeper private wells at nearby off-site locations.

Despite the high variability of these data, both within and between wells, it is possible to draw important conclusions with respect to environmental impact.

The most profound impact on water quality in this coal ash landfill is on the groundwater. The concentrations of all constituents are highly variable and unpredictable, changing spatially and temporally. Toxic elements, including arsenic, selenium, chromium, and cadmium occur in concentrations exceeding the recommended and/or tolerance limits for drinking water established by the U.S. Public Health Service. However, the clayey soils have never been an important aquifer and water movement through the clays is slow. It is also expected that the clays will attenuate the concentrations of undesirable constituents as leachate moves away from the landfill site, although this was not tested.

Metal accumulation studies of freshwater insects and other freshwater invertebrates do not abound. Those that do exist show a large accumulation of certain metals in the invertebrates over that of the water and also often compare the concentrations in the invertebrates to those found in other components of the system of study, such as sediments and fish.

Enk and Mathis in 1977 analyzed the levels of Cd and Pb in several aquatic insects (mayfly, <u>Isonychia</u> sp.; damselfly, <u>Agrion</u> sp.; caddisflies, <u>Cheumatopsyche</u> sp. and <u>Hydropsyche</u> spp.), snails (<u>Physa</u>), several fish species, sediments and water. Their results indicated an increasing progression in the levels of the two metals from water to fish to sediments to aquatic invertebrates.

Brown (1977) analyzed the water, sediments and dominant invertebrate fauna for Cu, Zn, and Fe in the River Hayle situated in the former Cu and tin Mount's Bay Mining District of Cornwall, England. Levels of the metals in Trichoptera, Plecoptera, Odonata, Neuroptera and Coleoptera are quite high, reflecting the relatively high levels in the water and sediments. The levels of Cu and Zn in the Trichoptera and Odonata are much higher in Brown's study but lower for Fe than in the present study, despite fairly similar concentrations of dissolved Fe in the water in both studies. Evidently, it is possible for aquatic invertebrates to concentrate most or all of the metals to a very high degree as compared to the concentrations in the water. Concentration factors for many of the metals range up to 1000 times or more. Good comparisons of metal content between different species or for the same or different species in different localities is not yet possible due to the relative dearth of information on this subject and the probable non-uniformity of the sampling, cleaning and analyzing methodology involved in different studies.

Results from the present study had sufficient unexpected results and high variability to allow discussion only in general terms. It was demonstrated that some animals had elevated uptake of iron and manganese as expected from the water analyses. For all control samples (Table 9) the average Mn was 283, and for experimental, 577 ug/g; the average iron in control was 1750, and in experimental biota, 5552 ug/g. Selenium (Table 9) showed no detrimental levels.

Although the Environmental Protection Agency is interested in the recognition of indicator species of Chironomidae in order to characterize aquatic conditions, it is too early to make many definitive statements. It appears that *Stictochironomus* does well in sandy conditions with slow flow, judging by the extreme abundance at station 5. *Pentaneura* and *Microtendipes* could also be associated with low current velocity while *Conchapelopia*, *Micropsectra* and *Pseudochironomus* were in faster water.

Evidently the distribution and relative abundance of the various aquatic invertebrates within the study area is controlled by a number of environmental factors including the water velocity and variations in flow, the type of substrate, food availability, competition, etc. The differences in chemical environment within Van Buren Bay Creek seemed to affect the distribution of periphyton, and hence indirectly affected the populations of aquatic insects.

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