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Data Collection Methodology Used in the Study of Pollution from Land Use Activities in the Grand and Saugeen Watersheds

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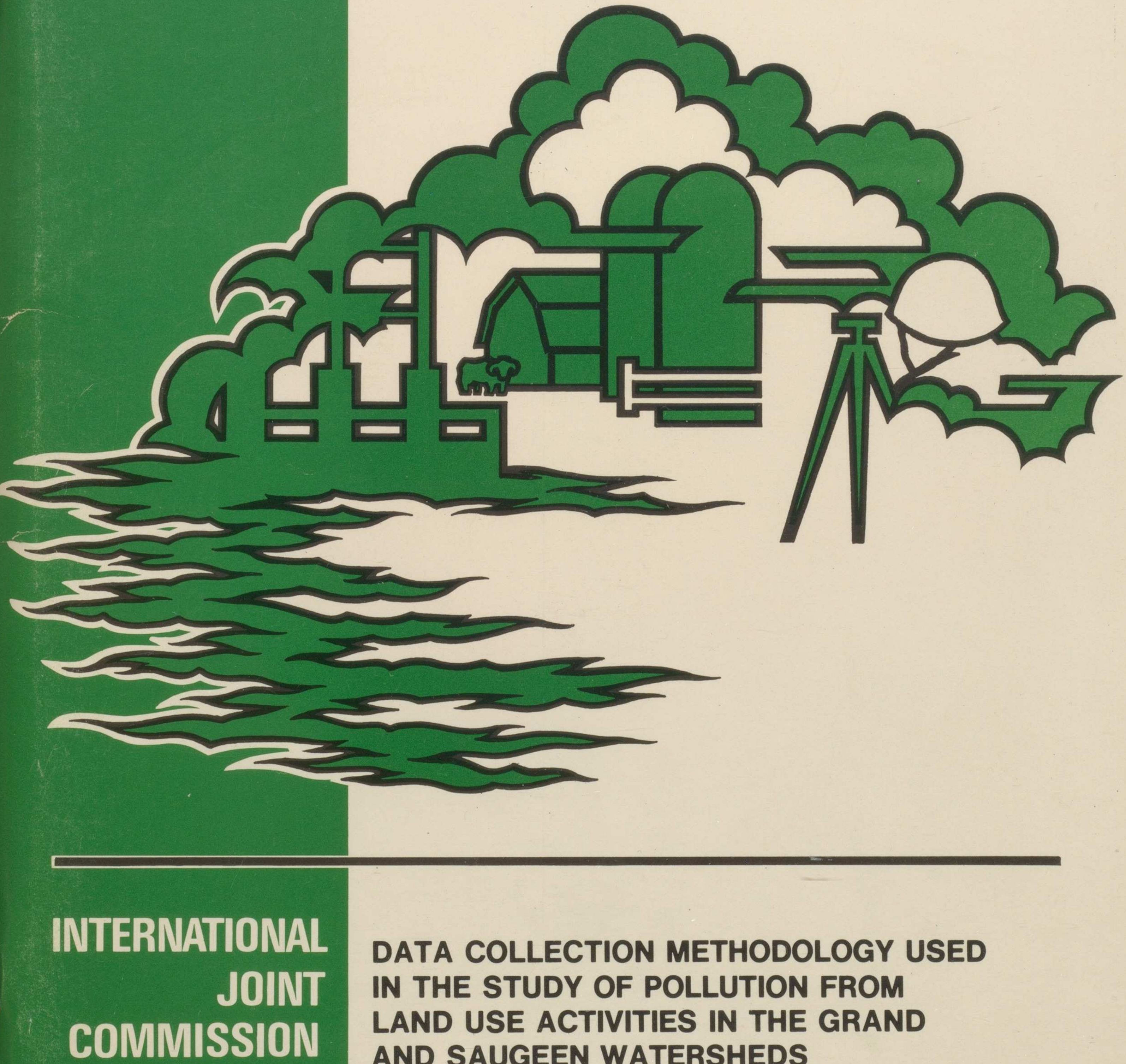
INTERNATIONAL REFERENCE GROUP ON GREAT LAKES POLLUTION FROM LAND USE ACTIVITIES



INTERNATIONAL
JOINT
COMMISSION

DATA COLLECTION METHODOLOGY USED IN THE STUDY OF POLLUTION FROM LAND USE ACTIVITIES IN THE GRAND AND SAUGEEN WATERSHEDS

TASK GROUP C (Canadian Section)
ACTIVITIES 3 AND 4
INTERNATIONAL REFERENCE GROUP
ON
GREAT LAKES
POLLUTION FROM LAND USE ACTIVITIES

DATA COLLECTION METHODOLOGY USED IN THE STUDY OF POLLUTION FROM LAND USE ACTIVITIES IN THE GRAND AND SAUGEEN WATERSHEDS

DENNIS ONN
ONTARIO MINISTRY OF THE ENVIRONMENT
TORONTO, ONTARIO
MARCH, 1980

3.0 DISCLAIMER

The study discussed in this document was carried out as part of the efforts of the Pollution from Land Use Activities Reference Group (PLUARG), an organization of the International Joint Commission, established under the Canada/U.S. Great Lakes Water Quality Agreement of 1972. Funding was provided through the Ontario Ministry of the Environment. Findings and conclusions are those of the author and do not necessarily reflect the views of the Reference Group or its recommendations to the Commission.

Reference to equipment brand names or supplies in this publication is not to be interpreted as an endorsement of that product or supplier by the author or the Ontario Ministry of the Environment.

4.0 ACKNOWLEDGEMENTS

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8.0 SUMMARY

The purpose of this technical report is to document the data collection methodology adopted by the Ontario Ministry of the Environment (MOE) under the Task C (Canadian Section) field studies of the Pollution from Land Use Activities Reference Group (PLUARG) program. The Grand River and Saugeen River pilot watersheds were chosen as part of the PLUARG program for intensive study in Canada, to cover a wide variety of potential sources of pollution to the Great Lakes. Land uses not adequately represented in the pilot watersheds were incorporated into the study by including additional subwatersheds in different parts of the Great Lakes basin. Estimates of pollutant loading (i.e. mass transport) from each investigated land use were derived from the combined field and laboratory measurements of water quantity, water quality and sediment quality to delineate sources, extent and relative significance of pollutant contributions to the Great Lakes. In most cases, a land use under study comprised only a small portion of a watershed and required upstream and downstream monitoring to determine (by difference) the pollutant contribution to the receiving stream from the investigated land use.

Monitoring sites were chosen to collect representative samples. For surface water, physical characteristics of the stream reach, as well as accessibility and availability of electricity, were considered in choosing the site. For ground water, observation wells, lysimeters, etc. were established up and down gradient of the study areas. Rainfall intensity and daily total rainfall were obtained by means of a network of rain gauges which supplemented the data available from other agencies.

The construction, calibration, equipment and procedures used to establish all monitoring sites are discussed and outlined in the text.

With the exception of a few water quality parameters which were measured in the field (i.e. pH, temperature, dissolved oxygen and conductivity), all physical, chemical and microbiological analyses of waters were conducted in the laboratory.

The measurement of water quality parameters in the field and special methods employed to minimize sample degradation while in transit to the laboratory are discussed. Where applicable for example, the use of specially prepared sample containers and/or field filtration, chemical preservation and cold storage were employed to inhibit chemical reactions and microbial activity.

Every effort was made to deliver fresh samples to the laboratory but storage time did vary because of remote sample locations and local shipping arrangements. A supplementary monitoring exercise was initiated to investigate the effects of storage time. No significant changes in concentration were observed for conductivity, alkalinity, calcium, magnesium, sodium, potassium, sulphate and chloride. Significant changes in the measured forms of nitrogen and phosphorus were observed with storage time, even when the experimental sample was split under seemingly ideal conditions and stored at a temperature of 4^{O}C.

The procedures for collecting depth-integrated and grab samples in streams are reviewed in the text. Grab-sample techniques were used to collect surface-water samples only when field staff were not able to use depth-integrated techniques as a result of extreme flood conditions or during occasional equipment shortages.

Four percent of the PLUARG surface-water samples collected manually by the Ontario Ministry of the Environment were replicated to measure data reproducibility by obtaining two different samples taken as close to the same time and place as possible, using routine, manual sample collection methodology. In addition, laboratory staff randomly selected and split three to five samples daily for replicate analyses to determine differences attributable to the variables inherent in the laboratory test procedures. These data suggest that the effects of manual sample collection and sample handling techniques are negligible.

Automatic samplers were installed to permit the unattended sample collection of surface water at monitoring sites where streamflow response to surface runoff occurs relatively quickly (i.e. small drainage area). The construction and programming for sample frequency during high-flow and low-flow periods are discussed.

A comparison sample program was undertaken to delineate the representativeness of the automatically collected samples with the manually collected samples at each monitoring site. In general, the analytical results indicated that the comparison sample concentration differences are small. Variables unique to each monitoring site such as drainage area, mean annual streamflow, stream velocities and less representative fixed-point sampling with automatic samplers account for much of the variability measured in the comparison sample program.

Ground-water samples intended for water quality analyses were collected regularly from a network of drilled wells. To ensure the collection of a fresh, representative sample, all ground-water wells were flushed prior to sampling using pumps or bailers to minimize contamination of the sample from the casing materials. Procedures and equipment used for flushing the wells are outlined in the text. Sample containers, preservation and storage techniques, and field-filtration procedures used for the collection of surface-water samples were used for the collection of ground-water samples as well.

Samples of fluvial sediments (suspended sediment and bed material) and soil were collected to supplement data collected in the water quality program and also to quantify the attenuation of nutrients, inorganic trace contaminants and organic trace contaminants in the ground-water flow systems. Suspended-sediment quality was measured seasonally to determine the percentage of contaminants carried by sediment and to estimate the loading of some contaminants (i.e. PCBs) which often occur in water samples below the analytical detection limit. In order to obtain sufficient quantity of sediment for chemical analyses, large volumes of water (600 to 1200 L) were centrifuged to extract the suspended sediment from the water. Bed-material samples were collected to confirm by laboratory analyses, the identity of contaminants contributed by land-use activities in the pilot watersheds. Procedures and equipment for obtaining sediment samples are outlined in the text.

Every effort was made to maintain a consistently high standard of data quality. The activities of field staff were co-ordinated from a central location (Toronto). In addition, field staff were provided with identical monitoring equipment and instruction in its use. Close liaison was maintained between field staff and laboratory staff to provide warning of irregular sample load thereby minimizing the delay between sample collection and analysis.

The clear identification of monitoring program objectives and data requirements prior to initiating data collection are recommended as essential prerequisites for future monitoring programs. Flexibility of the data systems is essential for the efficient storage and retrieval of the data. Uniform sampling techniques and equipment are necessary to permit data comparison. Replicate sampling programs must be maintained to ensure data quality control. The development of specific ion electrodes for in-situ measurements of nutrients is recommended.

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9.0 INTRODUCTION

As a result of the Great Lakes Water Quality Agreement of April 15, 1972, the International Joint Commission (IJC) established the Pollution from Land Use Activities Reference Group (PLUARG). The Reference Group was requested to enquire into and report to the two governments upon the following questions:

> "1. Are the boundary waters of the Great Lakes System being polluted by land drainage from agriculture, forestry, urban and industrial land development, recreational and parkland development, utility and transportation systems, and natural sources?
>
> 2. If the answer to the foregoing question is in the affirmative, to what extent, by what causes, and in what localities is the pollution taking place?
>
> 3. If the Commission should find that pollution of the character just referred to is taking place, what remedial measures would in its judgement be most practicable, and what would be the probable cost thereof?"

In February 1974 the PLUARG prepared a "Detailed Study Plan" to assess Great Lakes pollution from land-use activities. The "Detailed Study Plan" emphasized four main tasks consisting of an assessment of management and research information (Task A), an inventory of land-use activities and analyses of land-use trends (Task B), detailed watershed studies (Task C) and Great Lakes studies (Task D).

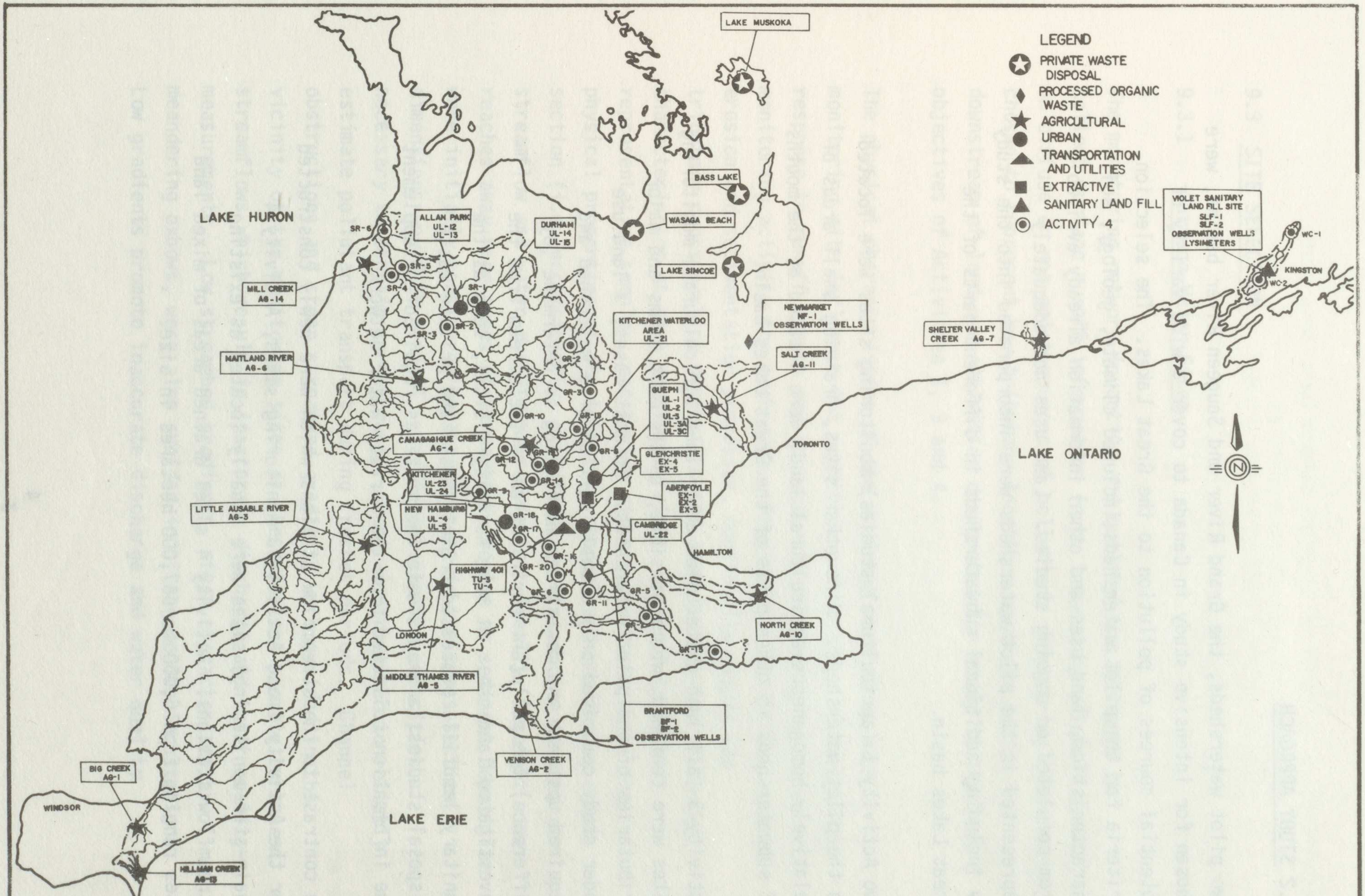


FIGURE # 1

CANADIAN TASK C MONITORING NETWORK

9.2 STUDY APPROACH

Two pilot watersheds, the Grand River and Saugeen River basins, were chosen for intensive study in Canada to cover a wide variety of potential sources of pollution to the Great Lakes. The selection criteria for the pilot watersheds included climate, geology, soil characteristics, land uses and other information already available from completed or ongoing studies. Land uses not adequately represented in the pilot watersheds were incorporated into the study by including additional subwatersheds in different parts of the Great Lakes basin.

Two Activity 1 (agricultural studies) monitoring sites were located in the pilot watersheds. Nine other sites, draining small areas of relatively homogeneous agricultural land, were located at the mouths of subwatersheds in other parts of the Great Lakes basin.

Activity 3 (all land-use studies other than agricultural) monitoring sites were confined, where possible, to the main stems and major tributaries of the pilot watersheds. In most cases, a land use under study comprised only a small portion of a watershed and required upstream and downstream monitoring to determine (by difference) the pollutant contribution to the stream from the investigated land use. At some Activity 3 sites, such as the sanitary landfill, processed organic waste and private waste disposal studies, a ground-water network was required to supplement the information collected from the surface-water network.

In contrast to the streamflow stations which were newly constructed for the Activity 1 and Activity 3 monitoring sites, Activity 4 (main-stem monitoring) sites were usually located at existing streamflow stations. Activity 4 sites drained areas of mixed land uses ranging from 6,000 to 667,000 hectares in size.

9.3 SITE SELECTION

9.3.1 Surface-Water Sites

The monitoring network (quantity and quality) was designed to collect surface runoff information (e.g. induced by rainfall events) on diffuse or non-point sources of pollution. Monitoring sites were chosen to represent key tributary locations upstream and/or downstream of land-use activities designated for study in the Task C objectives of Activities 1, 3 and 4.

The physical characteristics of the drainage area above each monitoring site influence the magnitude and duration of streamflow response to runoff events and consequently the timing and order of monitoring activity for each site. Physical variabilities, such as erosion and sedimentation processes, continually change the tributary cross-section dimensions and consequently the discharge characteristics at each monitoring site. In order to collect representative samples, monitoring sites were chosen where the physical properties of the tributary channel and monitoring cross-section (i.e. accessibility, stability) were conducive to accurate streamflow and water quality measurements. Ideally, straight river reaches away from zones of streambank erosion or sediment deposition were initially considered because changes in the cross-section dimensions would be minimal. Sufficient channel capacities, necessary to contain spring runoff, were also required to reliably estimate pollutant transport during freshet periods. Channel obstructions and steep streambed gradients were avoided in the vicinity of the monitoring sites as these factors promote turbulent streamflows which result in inaccurate discharge and water quality measurements. Low streambed gradients, often characterized by meandering oxbows, were also avoided in siting monitoring stations. Low gradients promote inaccurate discharge and water quality measurements as a result of sluggish streamflows, deep cross sections and poorly defined velocity profiles.

Existing highway and secondary road bridges were used wherever possible to permit easy accessibility throughout the year and to allow field staff to safely perform suspension measurements during high-flow periods. Readily available electrical supply, which is necessary to power heating cables for stilling-well intakes and submersible pumps for automatic samplers, was also a consideration in locating each monitoring site.

9.3.1.1 Agricultural Sites (Activity 1): As part of Activity 1 under the PLUARG study, Agriculture Canada (CDA) inventoried all types of agricultural practices common to the Lower Great Lakes basin and pinpointed areas with potential to pollute surface and ground waters (Coote et al, 1974). Cropping and fertilizer practices, drainage, soil, livestock density and pesticide usage were some of the considerations in designating these regions. From this inventory, eleven small subwatersheds were selected as representative of the major agricultural regions in the Great Lakes basin. Streamflow monitoring sites were established at the downstream outlet of each of the agricultural subwatersheds under investigation to provide base-line information for upstream studies (Figure 1).

9.3.1.2 Other Land-Use Sites (Activity 3): As part of Activity 3, monitoring sites were located upstream and downstream of a variety of urban centres, a major highway with routine maintenance operations, two extractive industries (a sand and gravel pit and a limestone quarry) and a sanitary landfill (Figure 1). Monitoring of surface-water runoff from two agricultural plots used for spreading of processed organic waste (sewage sludge) was also studied. Specific field studies were not undertaken to measure the water quality of waste-water lagoons and irrigation systems, used to dispose of municipal and industrial liquid waste; however, the locations of irrigation systems in the Grand River and Saugeen River pilot watersheds and the Lower Great Lakes basin were inventoried and the contaminant contribution was estimated from existing information.

9.3.1.3 Main-Stem Sites (Activity 4): After the land-use areas had been chosen for study in support of Task C Activities 1 and 3, the monitoring network was expanded to unmonitored areas of the Grand River and Saugeen River pilot watersheds to trace the movement of pollutants from the study areas to the boundary waters. The locations of existing streamflow stations were utilized as part of the Activity 4 study. Monitoring sites were located at both pilot watershed outlets above the back-water effects of lakes Erie and Huron, respectively.

9.3.2 Ground-Water Sites

The ground-water monitoring networks were designed to obtain data on the impairment of ground-water quality in the vicinity of waste disposal sites. Monitoring sites (observation wells, lysimeters, etc.) were established up and down gradient of the land-use study to delineate the extent of ground-water contamination. Monitoring networks were established for the sanitary landfill, processed organic waste disposal and private waste disposal studies under Task C.

Precipitation infiltrating into the ground recharges the ground-water system directly and ultimately controls the amount of ground-water discharge. The amount of infiltration will determine, in part, the amount of leachate that will be generated as a result of the infiltrating water mixing and reacting with the waste material (i.e. sanitary landfills). Water levels were used to determine the direction of ground-water movement and to monitor the changes in the hydraulic gradient. The amount of ground-water flow was estimated from Darcy's Law $Q = TIL$

where:

Q = quantity of water in imperial gallons per day (IGPD)
T = transmissivity (IGPD/ft)
I = hydraulic gradient feet per foot, dimensionless
L = width of cross section (feet)

10.0 DATA COLLECTION METHODOLOGY

All investigators conducting field measurements in the PLUARG program were required to document their field methodology and forward that documentation to the IJC Regional Office at Windsor. In fulfillment of that obligation, Ontario Ministry of the Environment (MOE) staff prepared a "Work Plan, January, 1976", to provide the working details for the PLUARG studies in which the Ministry was involved under Task C. However, the data collection methodologies were not sufficiently described in the "Work Plan" to permit comparison and evaluation of these data with data from other studies. Consequently this technical report has been prepared to facilitate data comparisons with other studies (ongoing or future).

10.1 WATER QUANTITY MEASUREMENT

10.1.1 Surface Water

A conventional streamflow gauging station consists of an artificial or naturally rated control (stream cross section where the stage height is proportional to flow), a stilling well with intake pipe, a water-level recorder and a recorder shelter (Figure 2). Continuous streamflow measurements were maintained at most monitoring sites under Task C Activities 1, 3 and 4. Field staff installed, calibrated and maintained streamflow gauging stations constructed for the PLUARG program.

10.1.1.1 Construction: After selecting a monitoring site (Section 9.3), the streambank was surveyed to determine the dimensions necessary for a stilling well and adjoining intake pipe. A 10-gauge, steel bulkhead was welded to the bottom of the required

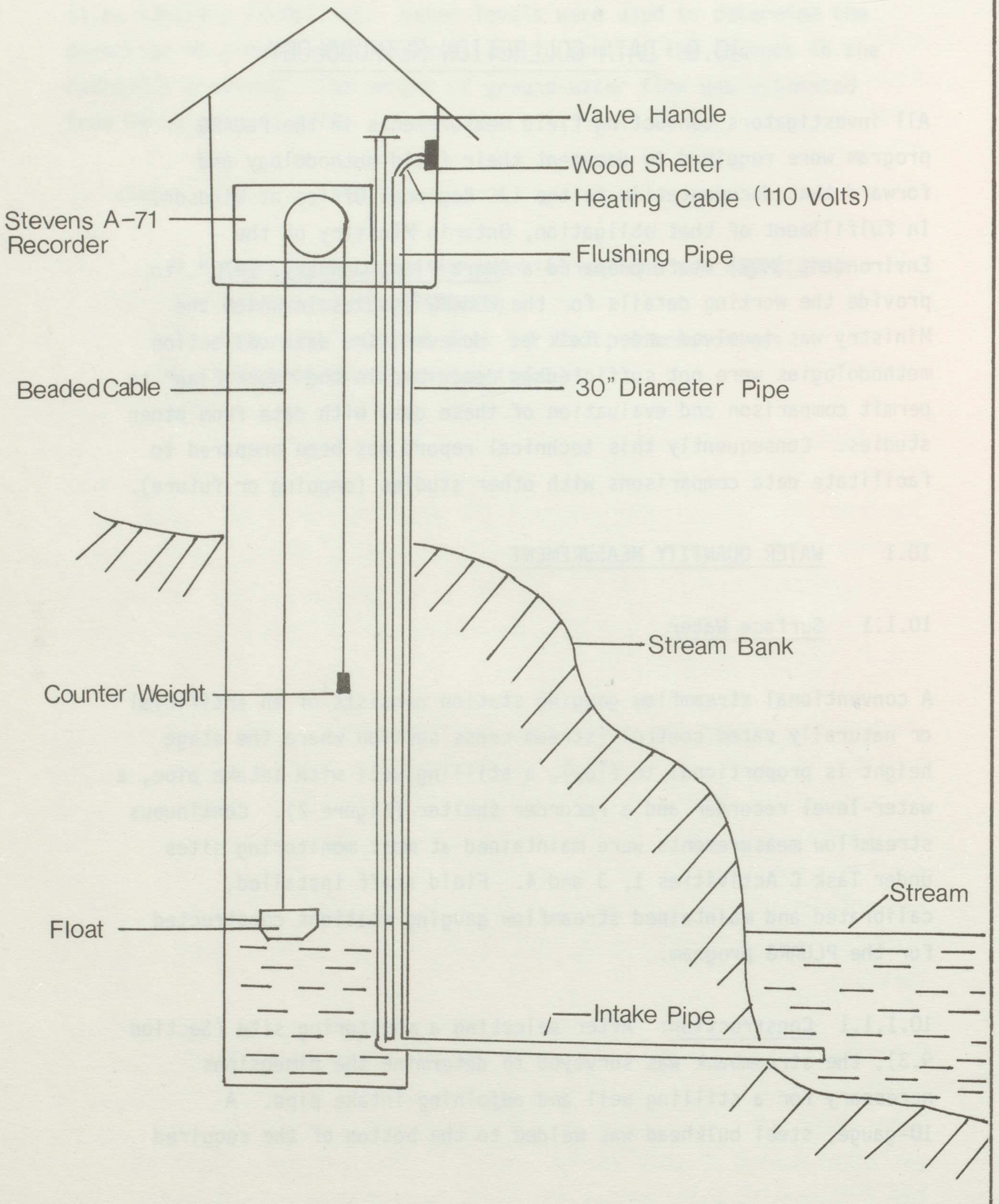
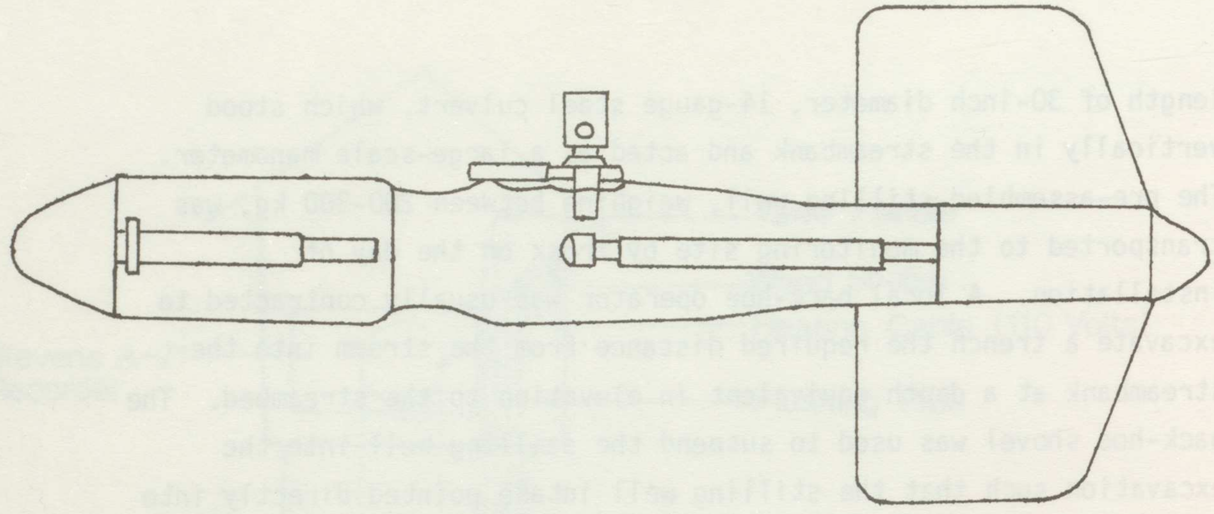


FIGURE # 2

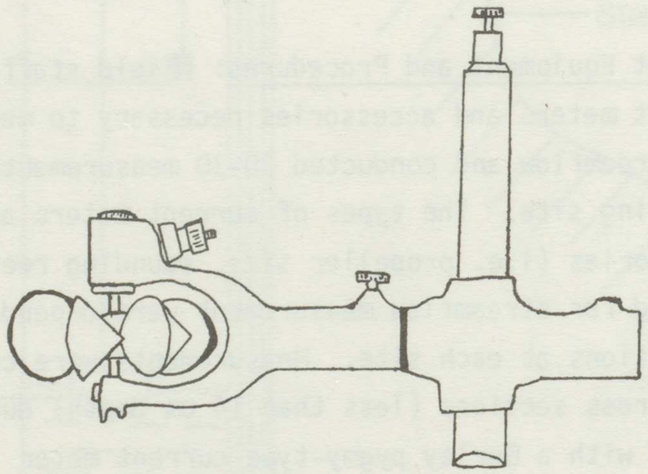
STILLING WELL INSTALLATION

length of 30-inch diameter, 14-gauge steel culvert, which stood vertically in the streambank and acted as a large-scale manometer. The pre-assembled stilling well, weighing between 200-300 kg, was transported to the monitoring site by truck on the day of installation. A local back-hoe operator was usually contracted to excavate a trench the required distance from the stream into the streambank at a depth equivalent in elevation to the streambed. The back-hoe shovel was used to suspend the stilling well into the excavation such that the stilling well intake pointed directly into the stream. Field staff threaded appropriate lengths of 2-inch diameter, steel pipe from the stilling well to the stream (along the trench excavation) to act as a water intake. The stilling well was then lowered the remaining distance into the excavation and held in a vertical position by ropes while the excavation was backfilled. A Leupold and Stevens A-71 stage recorder was mounted on top of the stilling well in a wooden shelter constructed to fit the top of the steel culvert (Figure 2).

10.1.1.2 Measurement Equipment and Procedures: Field staff were equipped with current meters and accessories necessary to measure all magnitudes of streamflow and conducted 20-30 measurements per year at each monitoring site. The types of current meters and current meter accessories (i.e. propeller size, sounding reel support devices) used for streamflow measurement were dependent upon the streamflow conditions at each site. Measurements were conducted in shallow, stream cross sections (less than 14 cm depth) during low-flow conditions with a Gurley pygmy-type current meter No.625-F. All other streamflow measurements were conducted with an OTT universal current meter No.C-31 (Figure 3) connected either to appropriate lengths of wading rod during low-flow conditions or to a sounding reel for suspension from a bridge when the stream was too deep to wade. The sounding reel was secured to either a wooden sounding board (Figure 4) and supported by field staff against the bridge railing or it was secured to an aluminium "A" frame device



OTT Universal Current Meter No. C-31



GURLEY Pygmy-type Current Meter No. 625-F

FIGURE # 3

STREAM FLOW METERING EQUIPMENT

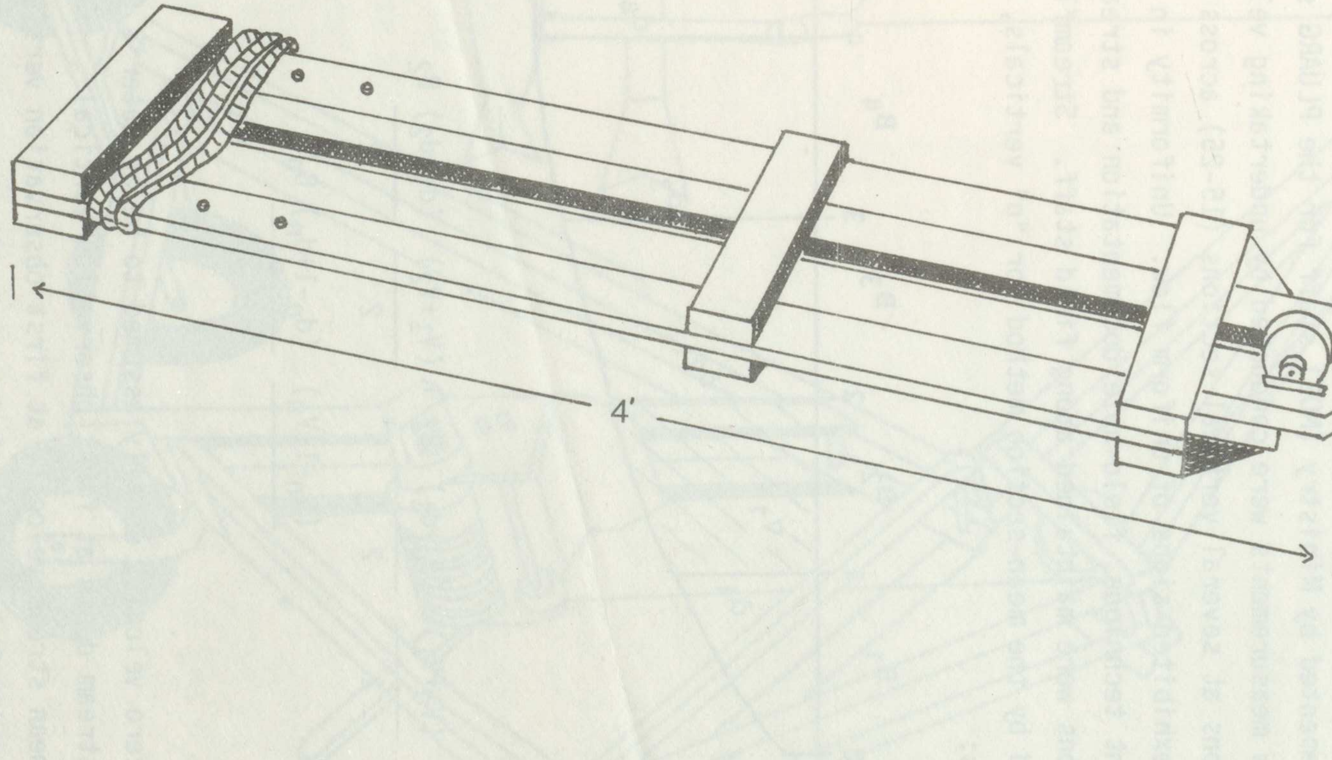
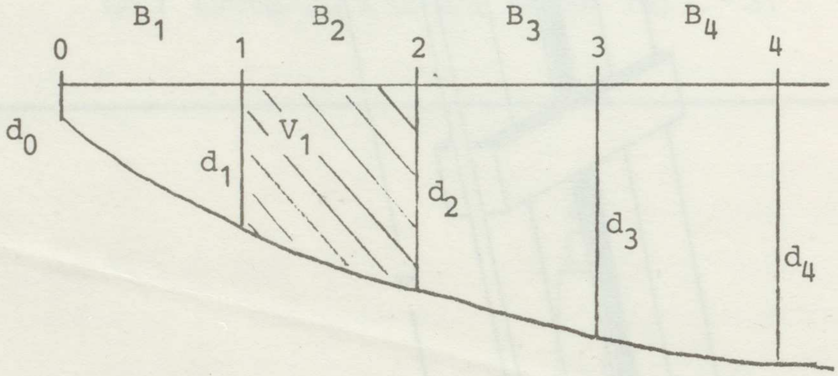


FIGURE #4 WOODEN SOUNDING-REEL SUPPORT FOR SUSPENSION STREAMFLOW MEASUREMENT

(Figure 5) to ensure more support and safer operation during flood conditions.

Standard procedures for discharge measurement and rating of controls, outlined in the United States Geological Survey (USGS) publication "Stream Gauging Procedure" (Corbett and Others 1962), were implemented by Ministry (MOE) staff for the PLUARG studies. Streamflow measurements were conducted by undertaking velocity observations at several vertical sections (15-25) across the stream where it exhibited signs of uniform flow. Uniformity in streamflow measurement technique, field-note documentation and streamflow calculations were maintained among field staff. Streamflow was calculated by the mean-section method for "n" verticals, described as follows:



$$Q = \frac{(V_o+V_1)}{2}\,\frac{(d_0+d_1)}{2}\,B_1 + \frac{(V_1+V_2)}{2}\,\frac{(d_1+d_2)}{2}\,B_2$$

$$+ \frac{(V_n-1+V_n)}{2}\,\frac{(d_n-1+d_n)}{2}\,B_n$$

V_o = zero velocity usually assumed to be at water's edge
d_1 = stream depth at first observation vertical
V_1 = mean stream velocity at first observation vertical
B_2 = horizontal distance between the first and second observation verticals
Q = discharge expressed as stream volume divided by time

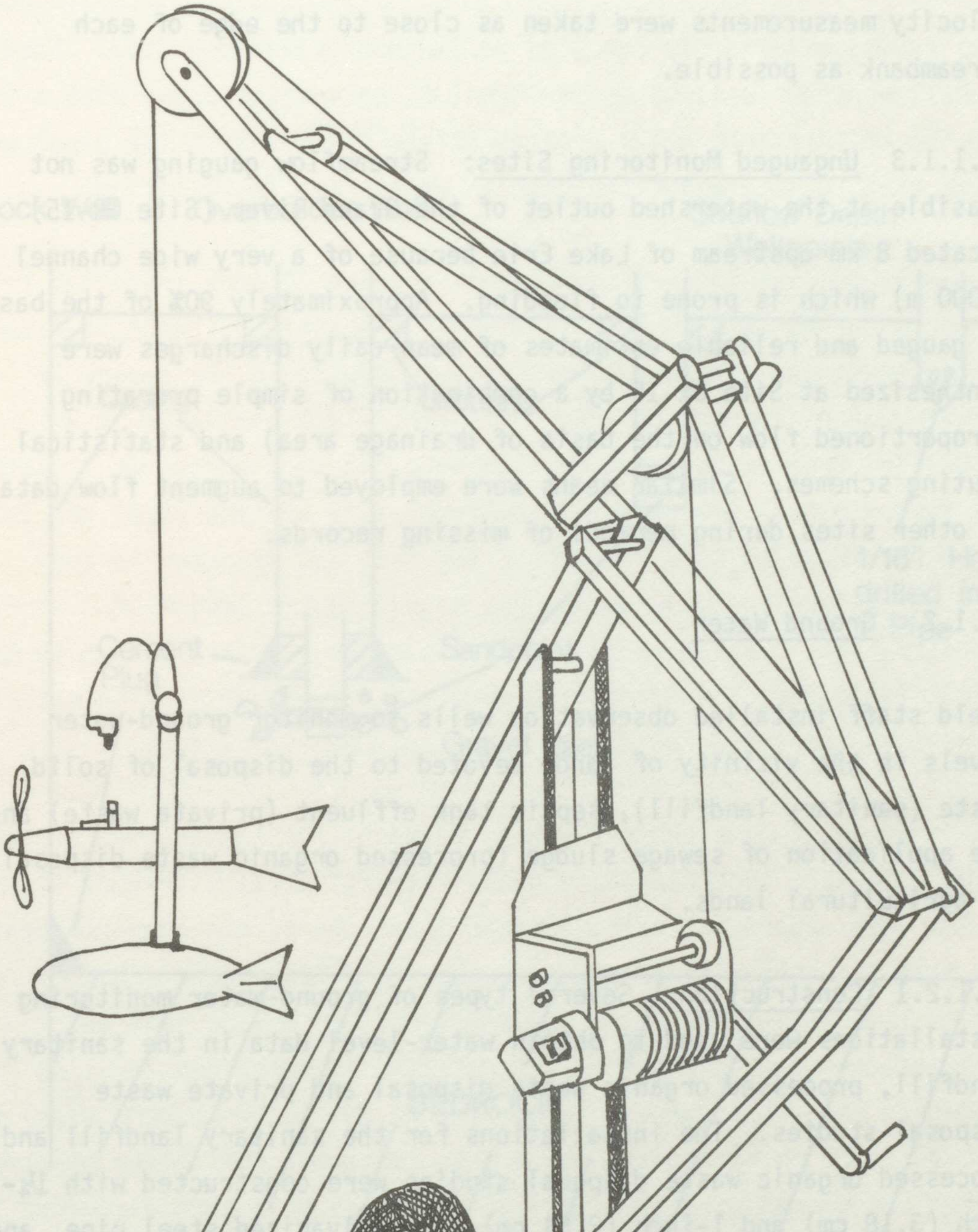


FIGURE #5

ALUMINIUM "A" FRAME SUPPORT FOR SUSPENSION STREAMFLOW MEASUREMENT

The depth of the stream at the water's edge was always measured and velocity measurements were taken as close to the edge of each streambank as possible.

10.1.1.3 Ungauged Monitoring Sites: Streamflow gauging was not feasible at the watershed outlet of the Grand River (Site GR-15) located 8 km upstream of Lake Erie because of a very wide channel (1000 m) which is prone to flooding. Approximately 90% of the basin is gauged and reliable estimates of mean daily discharges were synthesized at Site GR-15 by a combination of simple prorating (proportioned flow on the basis of drainage area) and statistical routing schemes. Similar means were employed to augment flow data at other sites during periods of missing records.

10.1.2 Ground Water

Field staff installed observation wells to monitor ground-water levels in the vicinity of lands devoted to the disposal of solid waste (sanitary landfill), septic tank effluent (private waste) and the application of sewage sludge (processed organic waste disposal) on agricultural lands.

10.1.2.1 Construction: Several types of ground-water monitoring installations were used to obtain water-level data in the sanitary landfill, processed organic waste disposal and private waste disposal studies. The installations for the sanitary landfill and processed organic waste disposal studies were constructed with 1¼-inch (3.18 cm) and 1-inch (2.54 cm) I.D. galvanized steel pipe, and 2½-inch (6.35 cm) I.D. steel casing by a combination of driving, jetting and rotary drilling (Figure 6). In all bedrock wells, the casing was seated into the bedrock and the wells were completed as open holes, by drilling several feet into the bedrock. Overburden installations were completed with 2-foot (61.0 cm) long by 1¼-inch (3.18 cm) I.D. sandpoints which were either sealed at the bottom of

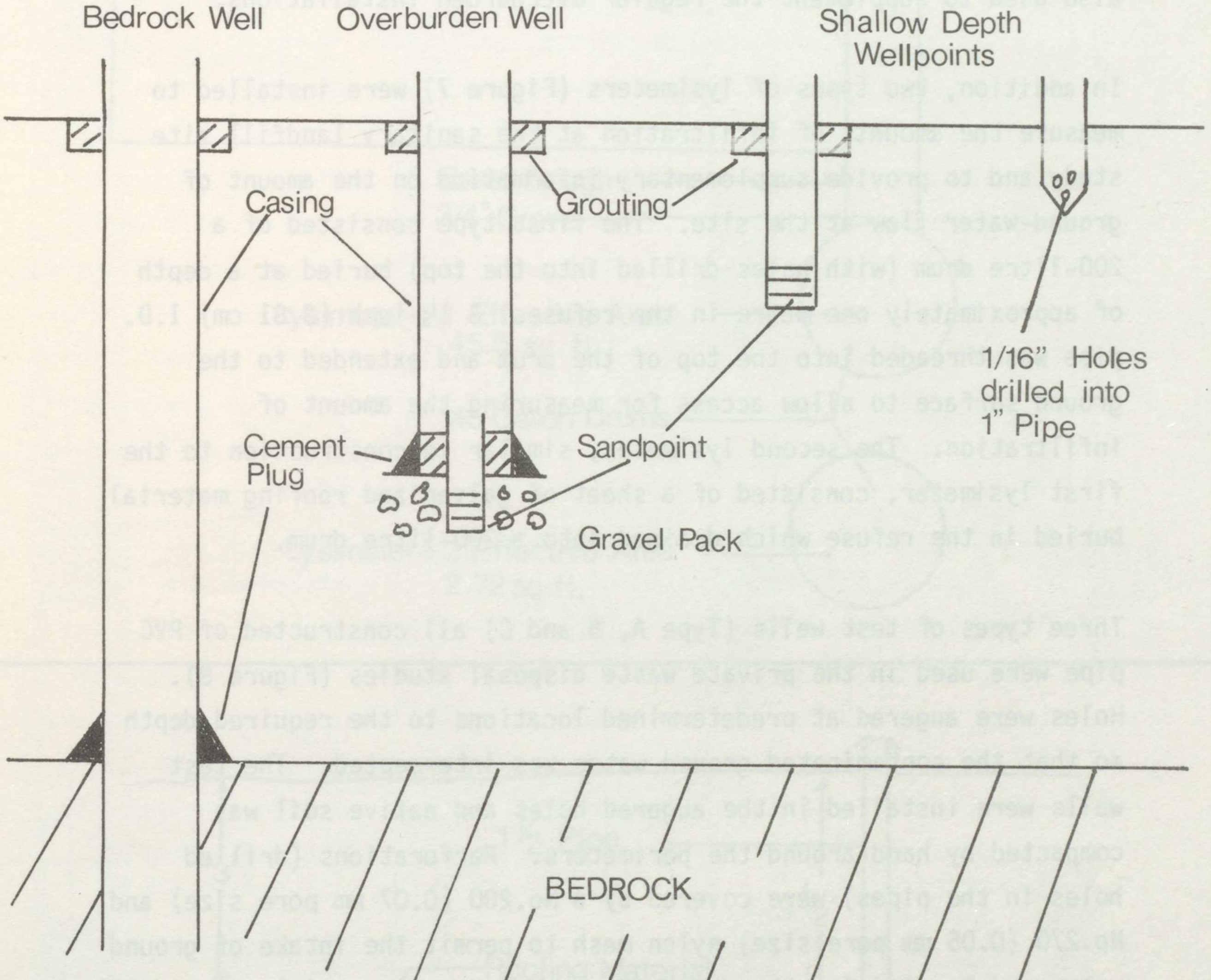


FIGURE # 6

TEST WELLS CONSTRUCTED FOR THE SANITARY LANDFILL AND PROCESSED ORGANIC WASTE STUDIES the casing or directly threated to 1¼-inch galvanized pipe. Some "shallow depth" wellpoints (1-inch I.D. galvanized pipes with a series of 1/16-inch holes drilled at the lower end of the pipe) were also used to supplement the regular overburden installations.

In addition, two types of lysimeters (Figure 7) were installed to measure the amounts of infiltration at the sanitary landfill site study and to provide supplementary information on the amount of ground-water flow at the site. The first type consisted of a 200-litre drum (with holes drilled into the top) buried at a depth of approximately one metre in the refuse. A 1½-inch (3.81 cm) I.D. pipe was threaded into the top of the drum and extended to the ground surface to allow access for measuring the amount of infiltration. The second lysimeter, similar in construction to the first lysimeter, consisted of a sheet of galvanized roofing material buried in the refuse which drained into a 200-litre drum.

Three types of test wells (Type A, B and C) all constructed of PVC pipe were used in the private waste disposal studies (Figure 8). Holes were augered at predetermined locations to the required depth so that the contaminated ground water was intercepted. The test wells were installed in the augered holes and native soil was compacted by hand around the perimeters. Perforations (drilled holes in the pipes) were covered by a No.200 (0.07 mm pore size) and No.270 (0.05 mm pore size) nylon mesh to permit the intake of ground water and to minimize the entry of suspended soil particles.

In cohesionless soils (i.e. sand, sandy silt) where cave-ins of soil developed upon augering holes into the saturated zone (i.e. below water table) of the soil, Type "A" well points were installed. Type "A" well points varied in diameter from 2.5 to 5 cm and from 1.2 to 3 m in length. Because of the nature of the sandy soils and the narrow diameter of the well point it was a simple matter to push or hammer these well points into the augered holes.

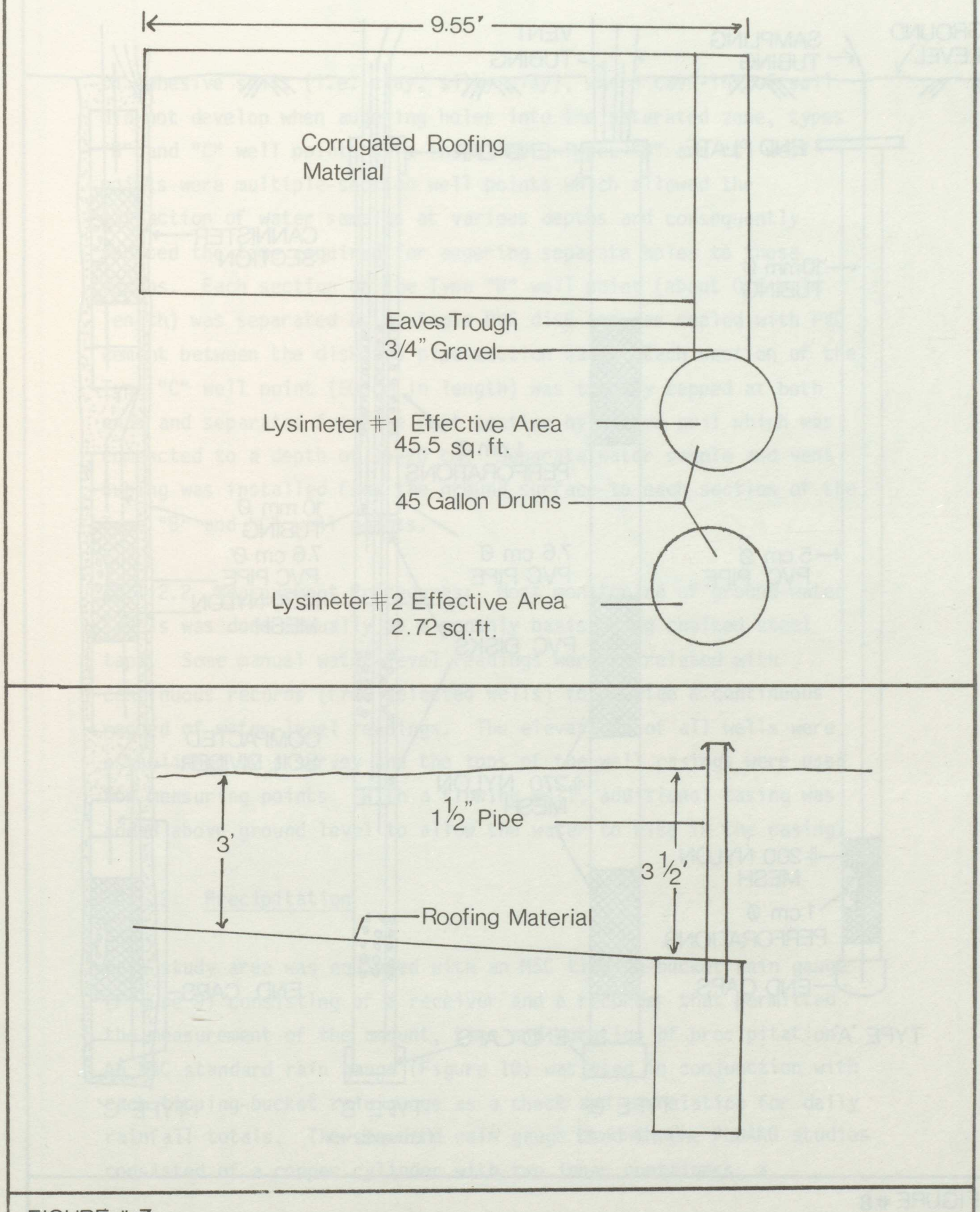


FIGURE #7
INFILTRATION LYSIMETERS CONSTRUCTED FOR SANITARY LANDFILL STUDIES

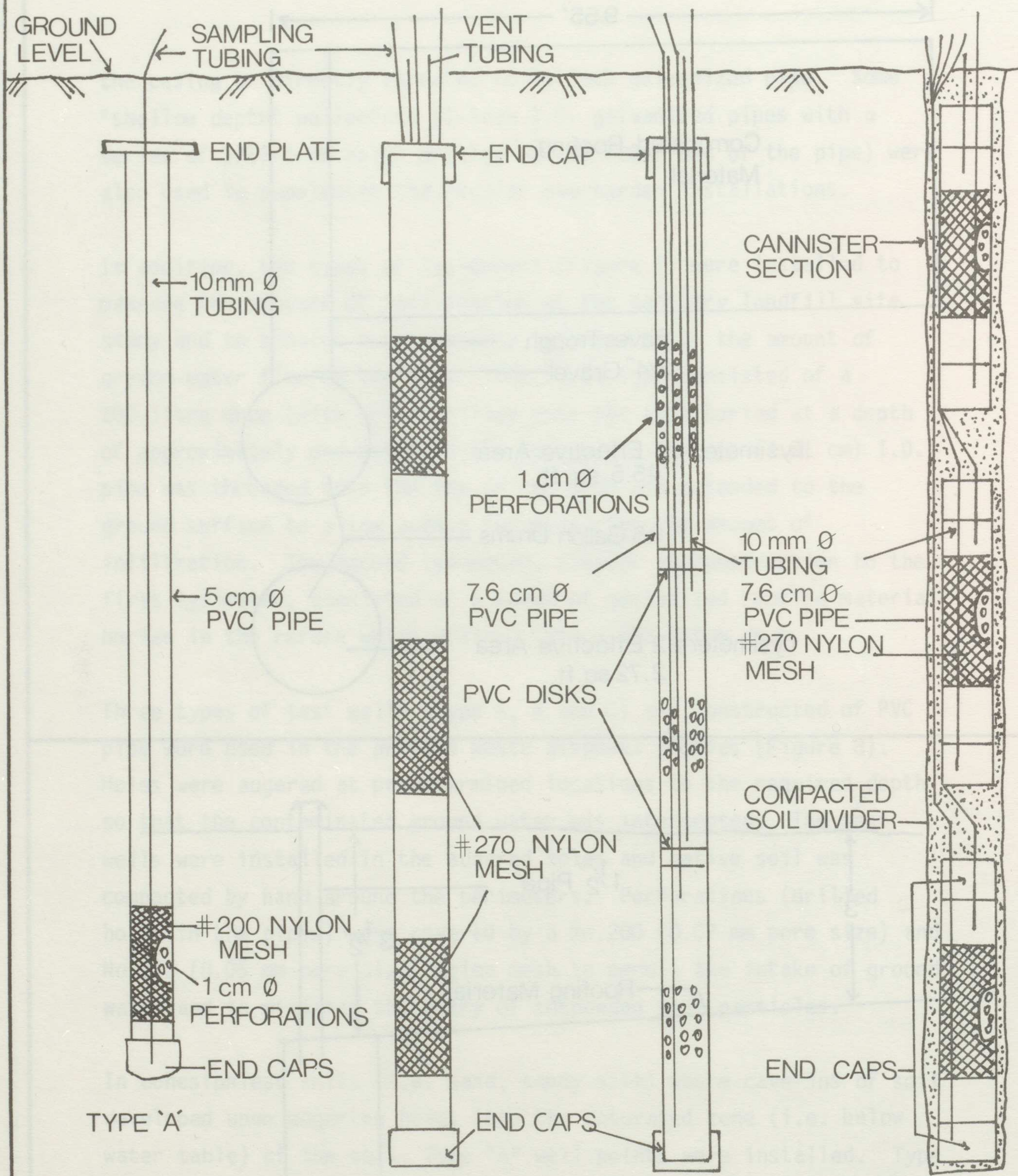


FIGURE #8

TEST WELLS CONSTRUCTED FOR THE PRIVATE WASTE DISPOSAL STUDIES

In cohesive soils (i.e. clay, silty clay), where cave-ins of soil did not develop when augering holes into the saturated zone, types "B" and "C" well points were installed. Types "B" and "C" well points were multiple-section well points which allowed the extraction of water samples at various depths and consequently reduced the time required for augering separate holes to those depths. Each section of the Type "B" well point (about 0.6 m in length) was separated by a single PVC disk and was sealed with PVC cement between the disk and pipe-section wall. Each section of the Type "C" well point (50 cm in length) was tightly capped at both ends and separated from the next section by native soil which was compacted to a depth of 15-20 cm. Separate water sample and vent tubing was installed from the ground surface to each section of the Type "B" and "C" well points.

10.1.2.2 Measurement Procedures: Most monitoring of ground-water levels was done manually on a monthly basis using chalked steel tape. Some manual water-level readings were correlated with continuous records (from selected wells) to provide a continuous record of water-level readings. The elevations of all wells were established by a survey and the tops of the well casings were used for measuring points. With a flowing well, additional casing was added above ground level to allow the water to rise in the casing.

10.1.3 Precipitation

Each study area was equipped with an MSC tipping-bucket rain gauge (Figure 9) consisting of a receiver and a recorder that permitted the measurement of the amount, time and duration of precipitation. An MSC standard rain gauge (Figure 10) was used in conjunction with each tipping-bucket rain gauge as a check and correlation for daily rainfall totals. The standard rain gauge used in the PLUARG studies consisted of a copper cylinder with two inner containers, a

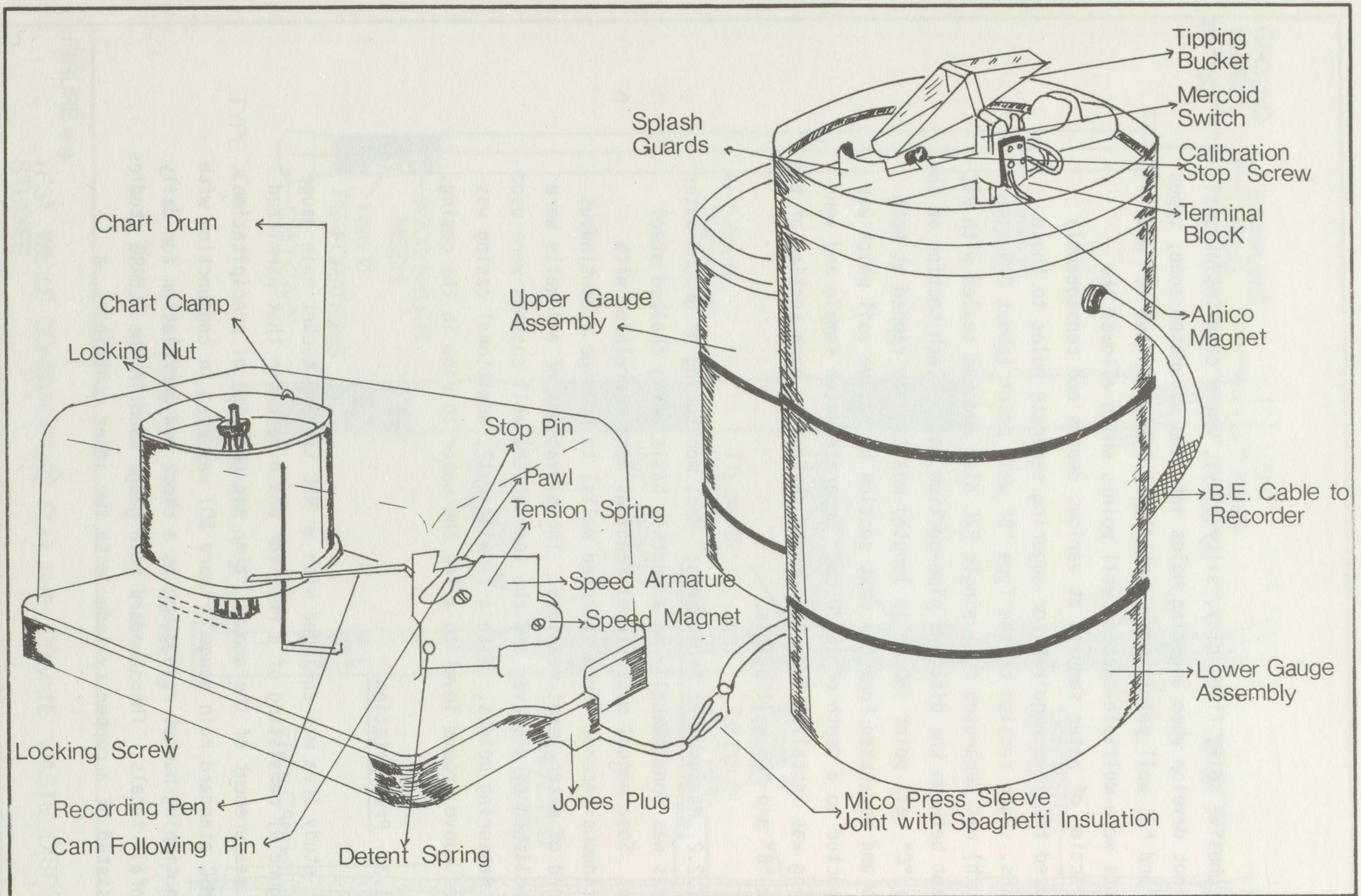


FIGURE #9

M S C TIPPING BUCKET RAIN GAUGE

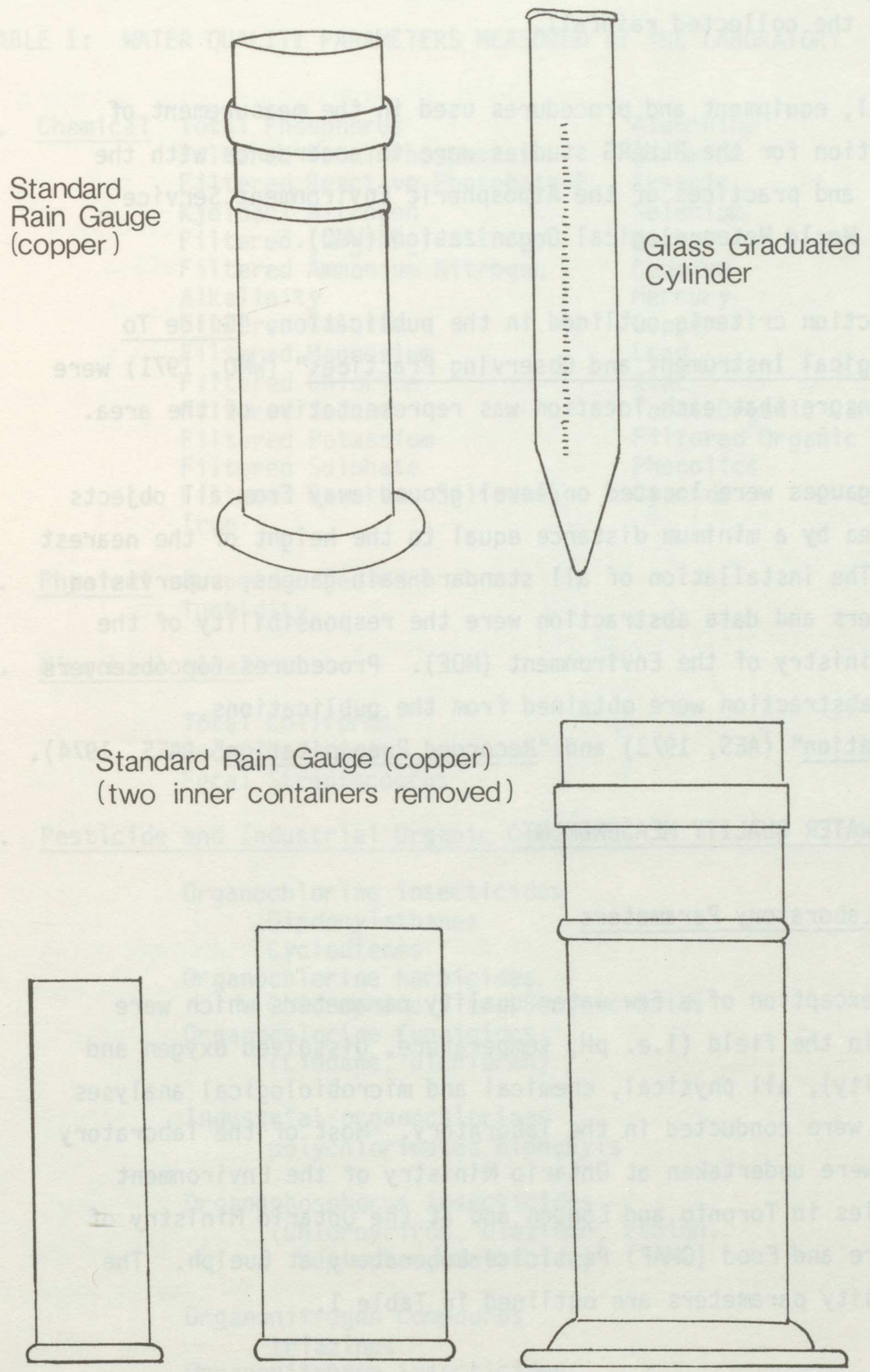


FIGURE #10

MSC STANDARD RAIN GAUGE

funnel-shaped collector, and a graduated glass cylinder for measuring the collected rainfall.

In general, equipment and procedures used in the measurement of precipitation for the PLUARG studies were in accordance with the standards and practices of the Atmospheric Environment Service (AES) and World Meteorological Organization (WMO).

Site-selection criteria outlined in the publication, "Guide To Meteorological Instrument and Observing Practices" (WMO, 1971) were used to ensure that each location was representative of the area.

All rain gauges were located on level ground away from all objects in the area by a minimum distance equal to the height of the nearest object. The installation of all standard rain gauges, supervision of observers and data abstraction were the responsibility of the Ontario Ministry of the Environment (MOE). Procedures for observers and data abstraction were obtained from the publications, "Precipitation" (AES, 1973) and "Recorded Precipitation" (AES, 1974).

10.2 WATER QUALITY MEASUREMENT

10.2.1 Laboratory Parameters

With the exception of a few water quality parameters which were measured in the field (i.e. pH, temperature, dissolved oxygen and conductivity), all physical, chemical and microbiological analyses of waters were conducted in the laboratory. Most of the laboratory analyses were undertaken at Ontario Ministry of the Environment laboratories in Toronto and London and at the Ontario Ministry of Agriculture and Food (OMAF) Pesticide Laboratory at Guelph. The water quality parameters are outlined in Table 1.

TABLE 1: WATER QUALITY PARAMETERS MEASURED AT THE LABORATORY

1. Chemical
    - Total Phosphorus
    - Filtered Total Phosphorus
    - Filtered Reactive Phosphate-P
    - Kjeldahl Nitrogen
    - Filtered (NO_3+NO_2)-Nitrogen
    - Filtered Ammonium Nitrogen
    - Alkalinity
    - Filtered Calcium
    - Filtered Magnesium
    - Filtered Chloride
    - Filtered Sodium
    - Filtered Potassium
    - Filtered Sulphate
    - Filtered Reactive Silicates
    - Iron
    - Aluminium
    - Chromium
    - Arsenic
    - Selenium
    - Nickel
    - Cadmium
    - Mercury
    - Copper
    - Lead
    - Zinc
    - Total Organic Carbon
    - Filtered Organic Carbon
    - Phenolics
    - Cyanide

2. Physical
    - Suspended Sediment
    - Turbidity

3. Microbiological
    - Total Coliforms
    - Fecal Coliforms
    - Fecal Streptococcus

4. Pesticide and Industrial Organic Compounds
    - Organochlorine insecticides
        - Dipdenylethanes
        - Cyclodienes
    - Organochlorine herbicides
        - Chlorophenoxy and Benzoic acids
    - Organochlorine fungicides
        - (Lindane, Dichloran)
    - Industrial organochlorines
        - polychlorinated biphenyls
    - Organophosphorus insecticides
        - (Chlorpyrifos, Diezinon, Ethion, Leptophos, Malathion)
    - Organonitrogen Compounds
        - triazines
    - Organonitrogen insecticides
        - methylcarbamates
    - Organonitrogen herbicides
        - thiocarbamates
        - (Alachlor)

10.2.2 In-Situ Parameters

Rapid changes in pH, dissolved oxygen and temperature occur within a short period of sample storage time. Tributary samples for these parameters were collected from the surface of the stream at the centre of flow with a stainless-steel sampling bucket (Figure 11). Measurements and analyses were conducted by field staff, where possible, immediately upon sample collection. Conductivity of selected ground-water samples was also measured in the field to determine the periods when more extensive monitoring was required to delineate changes in ground-water quality.

Field pH measurements were made using Leeds and Northrup (Model 7417) portable field pH meters with a "Combined pH Electrode" encased in a protective plastic shell. To minimize the error associated with the temperature-slope compensator, buffer solutions used for calibration were brought to the temperature of the sample in a sample-water bath. This instrument was calibrated twice daily by the field technicians to ensure accurate results. In addition to those measurements of pH made in the field, the pH of many samples were also measured at the laboratory.

Dissolved-oxygen concentrations in the stream were determined using a dissolved-oxygen test kit, (Model OX-2P), manufactured by the Hach Chemical Company. Samples intended for dissolved-oxygen analyses were collected from the centre of flow with a stainless-steel sampling bucket. Care was taken to fill the sampling bucket slowly to prevent bubbling which could result in elevated levels of dissolved oxygen. These measurements were time-consuming and were conducted primarily during the first year of study as the monitoring schedule was modified to collect the maximum number of samples each day.

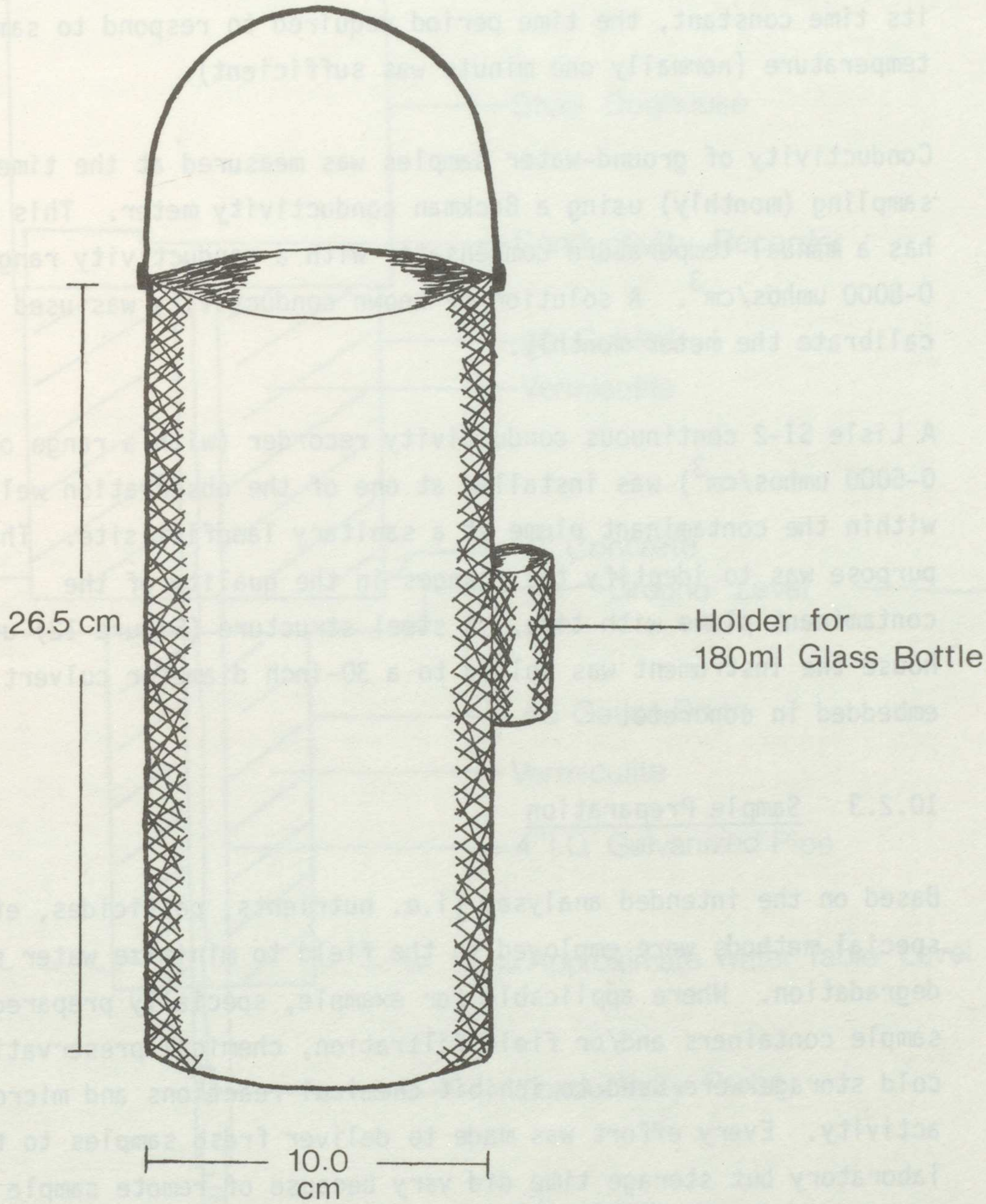


FIGURE # 11

STAINLESS-STEEL SAMPLING BUCKET

The stream water temperature was measured near the surface of flow using a mercury and glass immersion thermometer graduated from -10^{o}C to 110^{o}C. A reading to the nearest 0.5^{o}C was taken after the thermometer had been immersed for a period in excess of its time constant, the time period required to respond to sample temperature (normally one minute was sufficient).

Conductivity of ground-water samples was measured at the time of sampling (monthly) using a Beckman conductivity meter. This meter has a manual temperature compensator with a conductivity range of 0-8000 umhos/cm^3. A solution of known conductivity was used to calibrate the meter monthly.

A Lisle SI-2 continuous conductivity recorder (with a range of 0-5000 umhos/cm^3) was installed at one of the observation wells within the contaminant plume at a sanitary landfill site. The purpose was to identify the changes in the quality of the contaminant plume with time. A steel structure (Figure 12) used to house the instrument was bolted to a 30-inch diameter culvert embedded in concrete.

10.2.3 Sample Preparation

Based on the intended analyses (i.e. nutrients, pesticides, etc.), special methods were employed in the field to minimize water sample degradation. Where applicable for example, specially prepared sample containers and/or field filtration, chemical preservation and cold storage were used to inhibit chemical reactions and microbial activity. Every effort was made to deliver fresh samples to the laboratory but storage time did vary because of remote sample locations and local shipping arrangements.

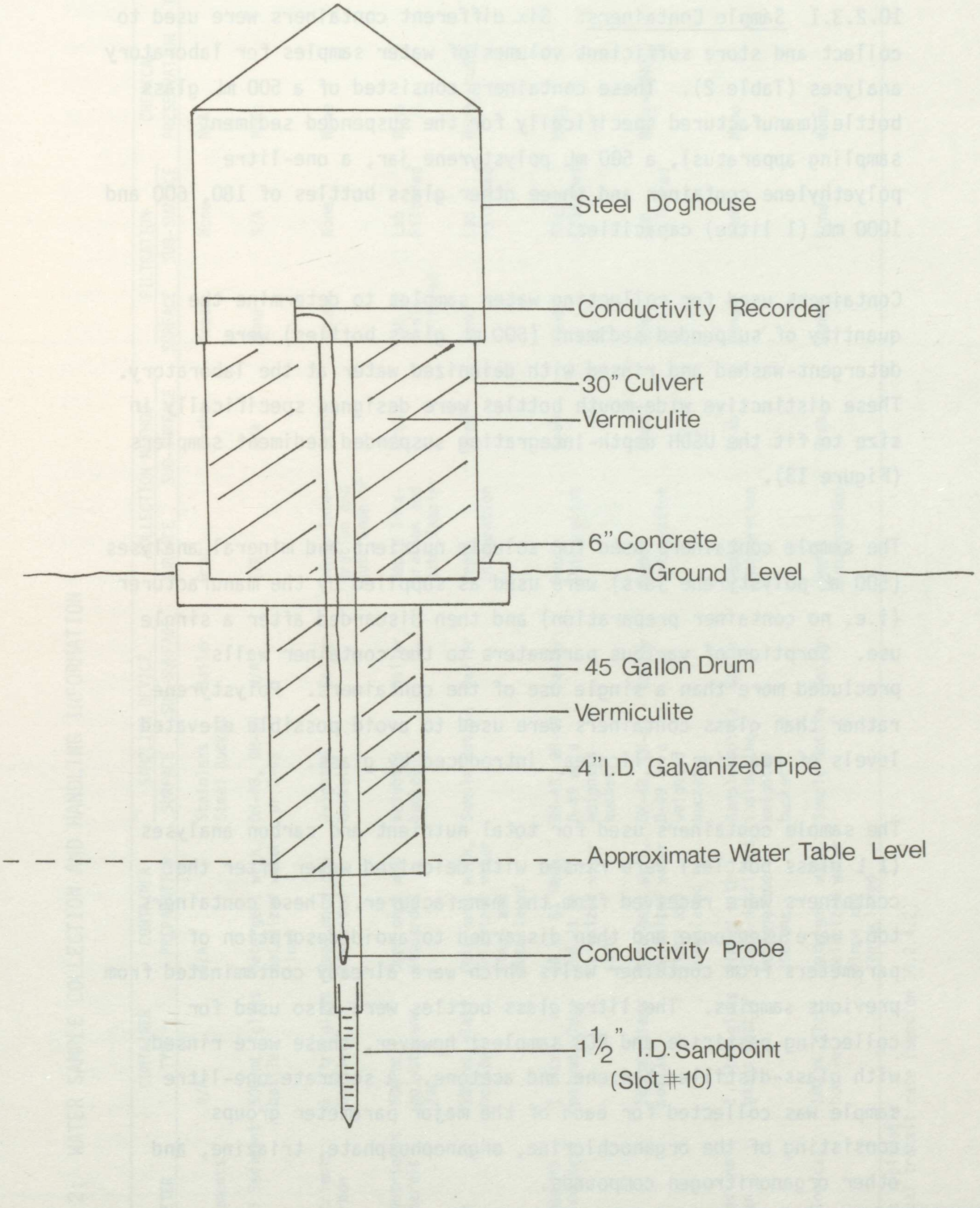


FIGURE #12

LAYOUT FOR CONTINUOUS CONDUCTIVITY RECORDER OF GROUND WATER IN THE SANITARY LANDFILL STUDIES

10.2.3.1 Sample Containers: Six different containers were used to collect and store sufficient volumes of water samples for laboratory analyses (Table 2). These containers consisted of a 500 mL glass bottle (manufactured specifically for the suspended sediment sampling apparatus), a 500 mL polystyrene jar, a one-litre polyethylene container and three other glass bottles of 180, 600 and 1000 mL (1 litre) capacities.

Containers used for collecting water samples to determine the quantity of suspended sediment (500 mL glass bottles) were detergent-washed and rinsed with deionized water at the laboratory. These distinctive wide-mouth bottles were designed specifically in size to fit the USDH depth-integrating suspended sediment samplers (Figure 13).

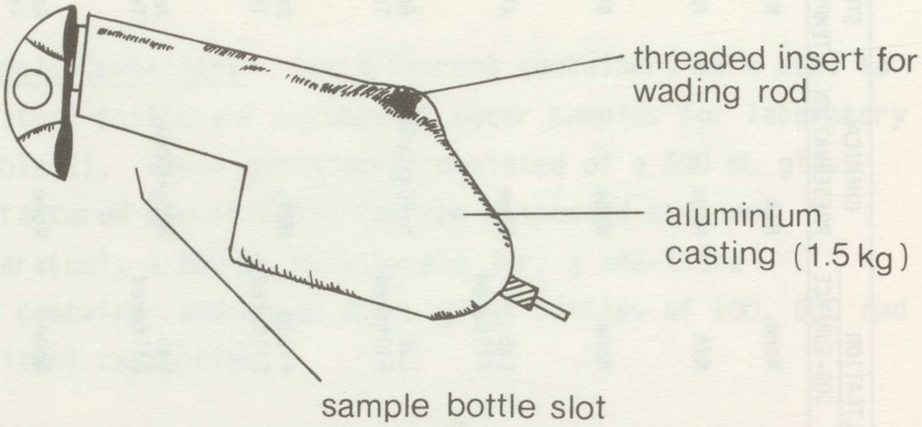
The sample containers used for soluble nutrient and mineral analyses (500 mL polystyrene jars) were used as supplied by the manufacturer (i.e. no container preparation) and then discarded after a single use. Sorption of various parameters to the container walls precluded more than a single use of the containers. Polystyrene rather than glass containers were used to avoid possible elevated levels of reactive "silicates" introduced by glass.

The sample containers used for total nutrient and carbon analyses (1 L glass bottles) were rinsed with deionized water after the containers were received from the manufacturer. These containers too, were used once and then discarded to avoid desorption of parameters from container walls which were already contaminated from previous samples. The litre glass bottles were also used for collecting pesticide and PCB samples; however, these were rinsed with glass-distilled benzene and acetone. A separate one-litre sample was collected for each of the major parameter groups consisting of the organochlorine, organophosphate, triazine, and other organonitrogen compounds.

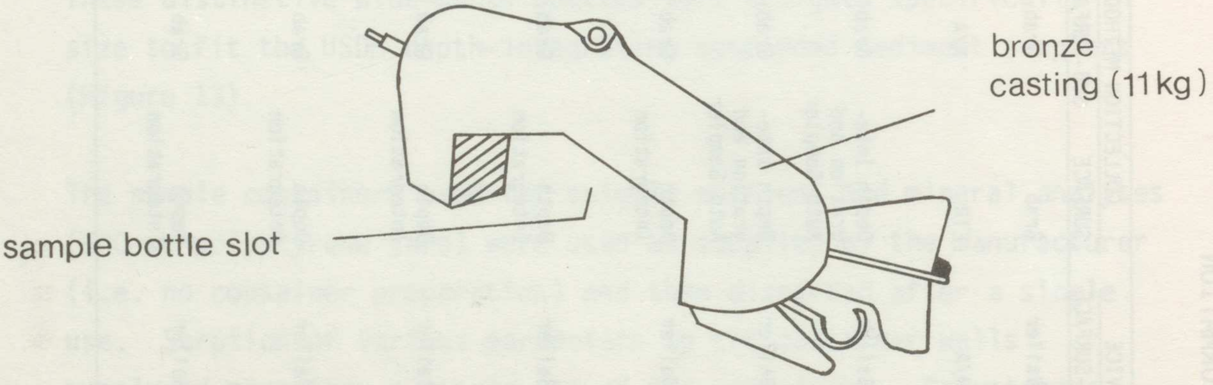
TABLE 2: WATER SAMPLE COLLECTION AND HANDLING INFORMATION

PARAMETER	CONTAINER TYPE	CONTAINER PREPARATION	SAMPLING DEVICE		COLLECTION METHOD		FILTRATION		CHEMICAL PRESERVATION	STORAGE TEMPERATURE
			SURFACE	SUB-SURFACE	SURFACE	SUB-SURFACE	SURFACE	SUB-SURFACE		
In Situ Measurements	N/A	N/A	Stainless Steel Bucket	Bailer	Grab	Grab	None	None	N/A	N/A
Suspended Sediment	500 mL glass bottle	Detergent wash, deionized water rinse	DH-48, DH-59 or D-49	N/A	ETR	N/A	None	N/A	None	Ambient Temp.
Total Nutrients and Carbon	1 litre glass bottle	Used once and discarded	Weighted bucket	Bailer	Depth Integration and Auto Sampler	Grab	None	None	None	4°C
Soluble Nutrients and Minerals	500 mL polystyrene jar	Used once and discarded	Weighted bucket	Bailer	Depth Integration and Auto Sampler	Grab	Lab or Field Filtered	Lab Filtered	None	4°C
Phenolics	180 mL glass bottle	Detergent wash, deionized water rinse and autoclaved	Sample Bottle	Bailer	Depth Integration	Grab	None	Lab Filtered	H_3PO_3+$CuSO_4$	Ambient Temp.
Trace Elements except mercury	1 litre polyethylene	24 hr 5% HNO_3 and 24 hr deionized water soak	DH-48, DH-59 D-49 or a weighted bucket	Bailer	Depth Integration	Grab	None	Field Filtered	HNO_3	Ambient Temp.
Mercury	180 mL glass bottle	Detergent wash, deionized water rinse and autoclaved	DH-48, DH-59 D-49 or a weighted bucket	Bailer	Depth Integration	Grab	None	Lab Filtered	HNO_3+$KMNO_4$	Ambient Temp.
Pesticides and PCB Scan	1 litre glass glass bottle	Rinsed with glass-distilled benzene and acetone	Sample Bottle inside the weighted bucket	Bailer	Depth Integration	Grab	None	None	None	Ambient Temp.
Microbiological	180 mL glass bottle	Detergent wash, deionized water rinse and autoclaved	Sample Bottle	Bailer	Depth Integration	Grab	None	None	None	4°C

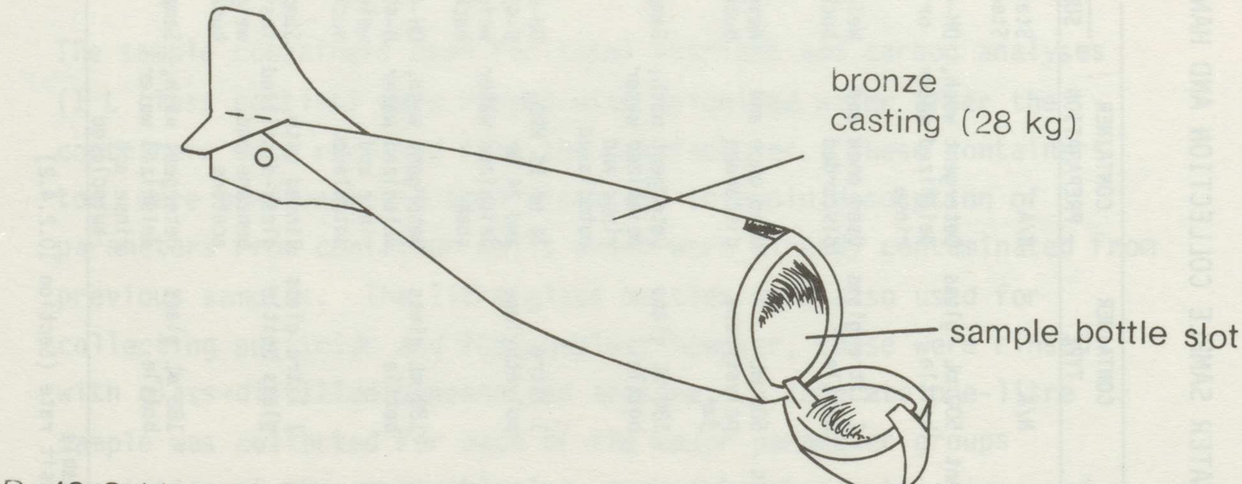
N/A - not applicable
ETR - equal transit rate (Section 10.2.4.2)



DH-48 Hand-Held Sampler



DH-59 Hand Line Sampler



D-49 Cable and Reel Sampler

FIGURE # 13

USDH DEPTH-INTEGRATING SUSPENDED SEDIMENT SAMPLERS

The one-litre polyethlene containers used for collection and delivery of trace-element samples were soaked for 24 hours with a 5% nitric acid solution followed by a further 24-hour soak with deionized water.

Upon receipt from the manufacturer, the 180 mL glass bottles were washed at the laboratory with a low-phosphate detergent, rinsed with deionized water and autoclaved. The sample bottles used for bacteriological analyses were also used to collect mercury samples. These bottles were discarded after each use because of their potential to contaminate a second sample; however, those bottles used for phenol analyses were recycled.

10.2.3.2 Sample Storage Time: Storage time is an important factor that affects all water samples removed from their natural environment. All samples were delivered to the laboratory as soon as was possible after collection to minimize the extent of changes in parameter concentrations occurring with time as a a result of chemical reactions and/or microbial activity. Distances between the laboratory and monitoring sites varied from 10 to 250 km. Approximately 80% of the routine samples were delivered to the laboratory less than 48 hours after collection. Delivery delays involving the remaining samples ranged from 3 to 7 days because of remote monitoring site locations and local shipping problems. Microbiological samples which were not delivered to the laboratory within 48 hours were discarded.

A supplementary monitoring exercise was initiated to investigate the effects of storage time on nutrient samples which are especially sensitive to analytical delays. Field staff collected a single 20 L sample downstream of a municipal discharge and split the sample into ten routine sample containers, stored them at 4^{o}C and shipped them to the laboratory on ten consecutive week days. It was anticipated that the individual sets of analytical results from these ten samples (high nutrient concentrations and varying sample-shipping intervals) would delineate trends in nutrient concentration changes occurring with sample storage time.

Changes in daily measured concentrations are shown in Figure 14 for phosphorus and in Figure 15 for nitrogen. Conductivity, alkalinity, calcium, magnesium, sodium, potassium, sulphate and chloride were also measured, and no significant changes in concentration were observed over the period of study. However, initial concentration values prior to sample storage were not measured, as the first analyses were initiated twenty-four hours after sample collection.

Concentrations of total phosphorus measured in ten consecutive analyses deviated unexpectedly from the mean total phosphorus concentration of 0.100 mg/L. These analytical results suggest that field staff were unsuccessful in attempting to recover equal quantities of suspended sediment in each of the ten sample containers when splitting the 20 L sample.

Filtered reactive phosphorus concentrations progressively increased with storage time (from 0.10 to 0.25 mg/L) which directly influenced the increase witnessed in the filtered total phosphorus concentration (from 0.017 to 0.037 mg/L). Complex phosphates tied up in the particulate phosphorus fraction of the sample hydrolize with time and revert to the reactive phosphate form as shown by the above-mentioned increases in concentration.

Analytical results from the same experimental sample show that the total nitrogen concentrations (Kjeldahl nitrogen and nitrate + nitrite-nitrogen) remain constant with storage time (2.70 mg/L). The concentrations of filtered (nitrate + nitrite)-nitrogen increase (from 1.7 to 2.0 mg/L) and Kjeldahl nitrogen and ammonium nitrogen decrease (from 0.75 to 0.50 mg/L and from 0.126 to 0.004 mg/L, respectively). The concentration changes outlined above result from bacterial decomposition of organic nitrogen and subsequent bacterial oxidation of ammonium nitrogen to the nitrite and nitrate-nitrogen forms.

In conclusion, significant changes in the measured forms of nitrogen and phosphorus were observed with storage time, even when the experimental sample was split under seemingly ideal conditions and stored at a temperature of 4°C. The variability measured in the total phosphorus concentrations re-emphasizes the need to collect representative quantities of suspended sediment in river water where phosphorus analyses are requested. These data also suggested that although all of the routine nutrient samples collected in the PLUARG program were stored at 4°C, the concentrations determined for filtered total phosphorus, filtered reactive phosphorus and filtered (nitrate + nitrite)-nitrogen (figures 14 and 15) represent a slight overestimation of actual in-stream quality. Conversely, the concentrations determined from routine samples for Kjeldahl nitrogen and filtered ammonium nitrogen represent a slight underestimation of actual in-stream quality. In-situ analyses would yield better estimates of in-stream quality but are presently not practical unless reliable specific-ion electrodes are developed for the measurement of these parameters.

10.2.3.3 <u>Field Filtration</u>: Water samples which were filtered in the field were first collected into two narrow-neck glass bottles (600 mL capacity each) to ensure that sufficient volume of sample was obtained for the field filtration procedure and subsequent analyses of the filtrate. In the case of surface-water samples, these containers were filled directly from the stream. Ground-water samples could not be collected directly into the sample containers but were transferred after the sample was collected by means of a bailer or a centrifugal pump.

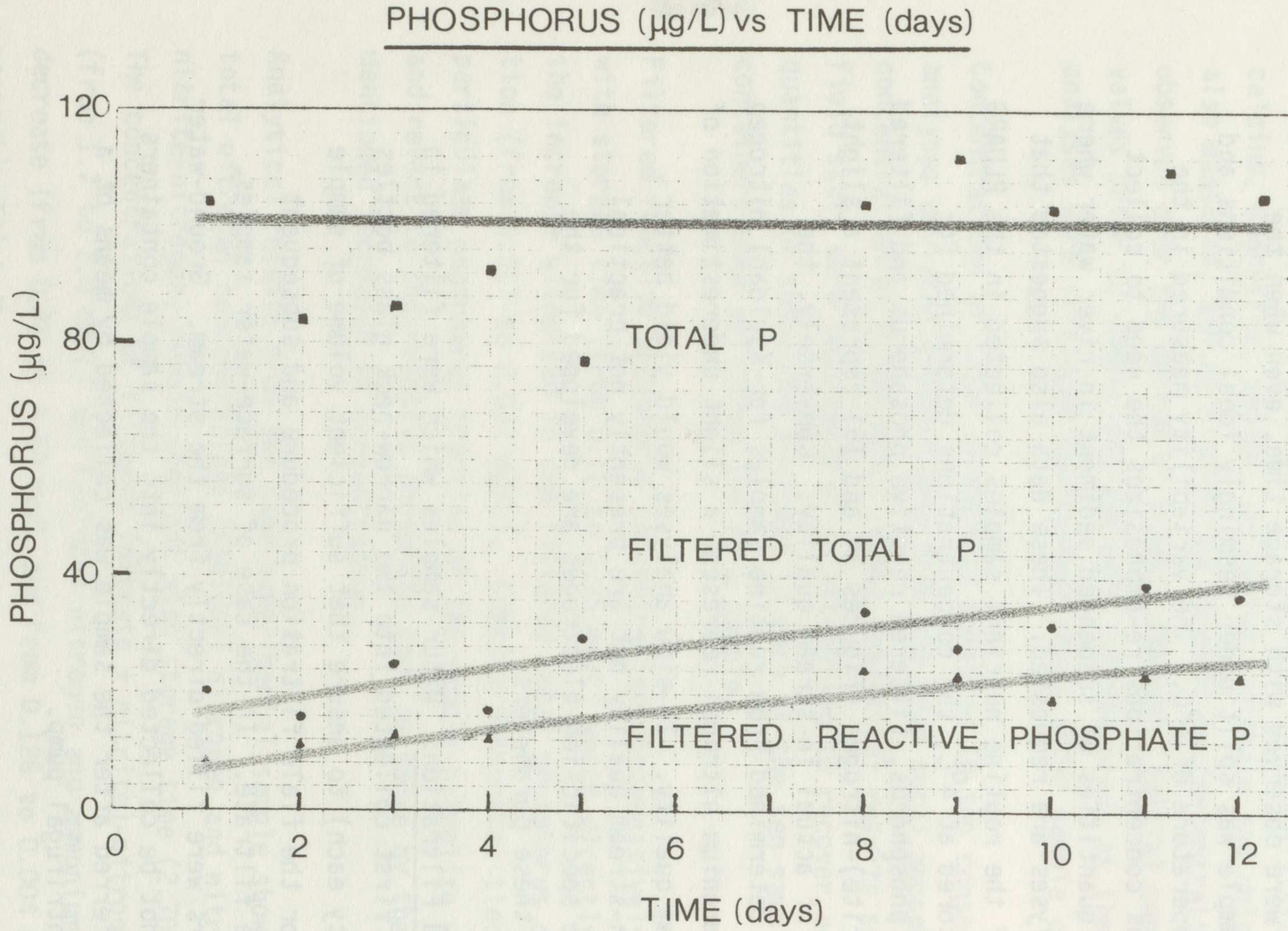


FIGURE # 14

PHOSPHORUS CONCENTRATION CHANGES WITH SAMPLE STORAGE TIME

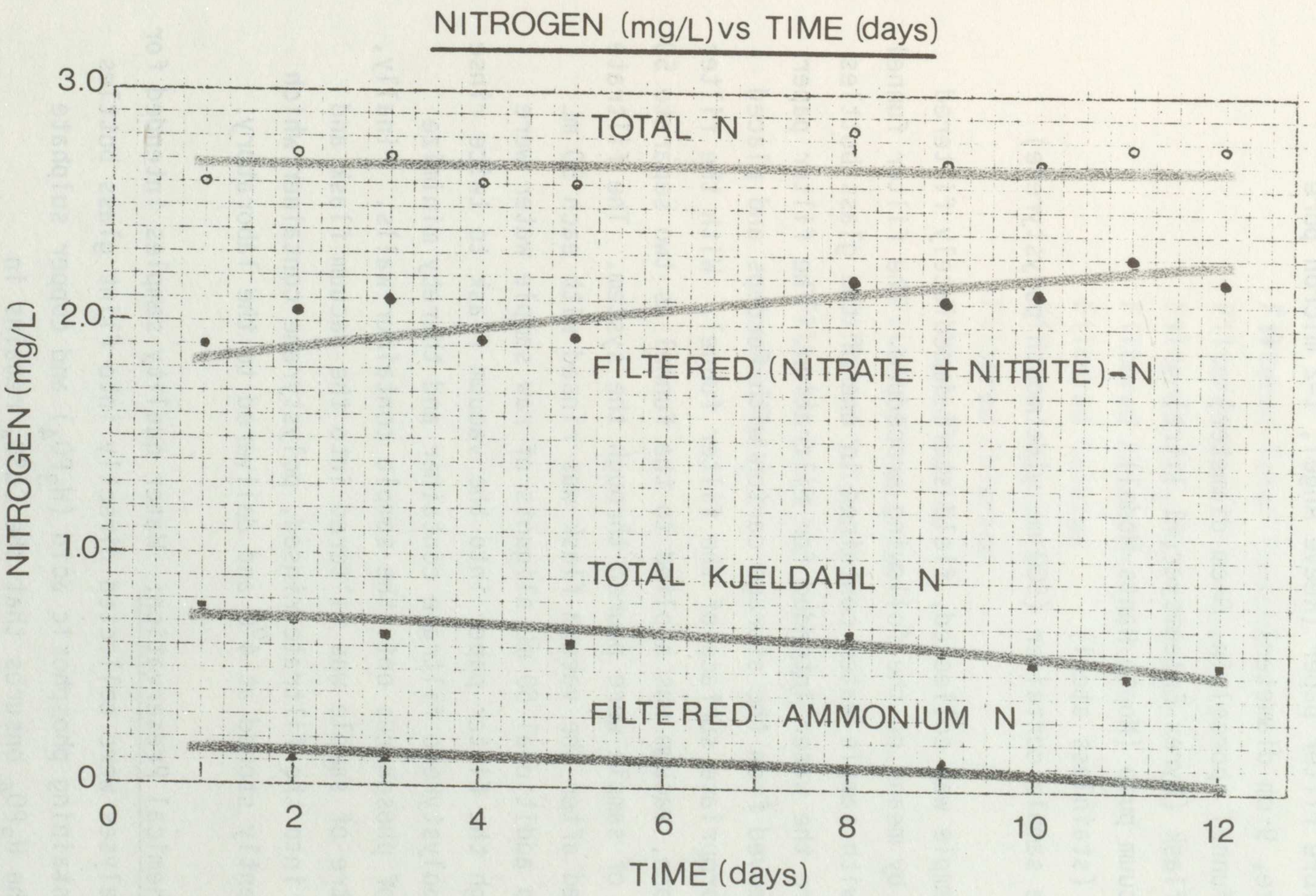


FIGURE # 15

NITROGEN CONCENTRATION CHANGES WITH SAMPLE STORAGE TIME

The following list of equipment was used for field filtration of samples analysed for the soluble water quality parameters listed in Table 3:

glass-fibre filter paper (Reeve Angel, 1-2 micron pore size, 9-cm diameter)
filter funnel (porcelain, 9-cm diameter)
vacuum flask (Pyrex Erlenmeyer, 1 litre)
hand vacuum pump (North Hants Model)
forceps (stainless steel)
filtrate sample container (500 mL wide mouth polystyrene)

After the sample was collected, field staff immediately filtered that sample by means of the following procedure. The filter funnel was rinsed with sample water contained in one of the glass bottles used to store the water intended for filtration. The filter paper was then removed from the storage carton with forceps and placed onto the appropriate surface of the filter funnel. With the filter paper in place, vacuum was applied to the funnel as two separate 50 mL aliquots of sample were poured through the system. The filtrate was discarded after the vacuum flask was rinsed with each 50 mL sample. Two additional 50 mL aliquots of raw sample water were drawn through the filter paper into the vacuum flask to twice rinse the 500 mL polystyrene filtrate container and thereby minimize adsorption of phosphorus onto the sample container walls. Finally, one-half litre of sample was filtered into the vacuum flask and transferred into the filtrate rinsed, polystyrene container which was subsequently stored at $4^{o}C$ and delivered to the laboratory.

10.2.3.4 <u>Chemical Preservation</u>: Water quality samples intended for phenolic analyses were collected directly into flint glass bottles (180 mL) containing phosphoric acid (H_3PO_4) and copper sulphate ($CuSO_4$). The H_3PO_4 ensures that the $CuSO_4$ remains in solution during the time when the sample is in transit to the

TABLE 3: WATER QUALITY PARAMETERS MEASURED IN THE FIELD-FILTERED SAMPLES

Filtered Total Phosphorus
Filtered Reactive Phosphate-P
Filtered (NO_3+NO_2)-Nitrogen
Filtered Ammonium Nitrogen
Filtered Calcium
Filtered Magnesium
Filtered Chloride
Filtered Sodium
Filtered Potassium
Filtered Sulphate
Filtered Reactive Silicates
Conductivity

laboratory. The $CuSO_4$ inhibits any Pseudomonas population which, given time, can degrade phenolic compounds in the sample.

Water quality samples intended for most trace-elements analyses (Cu, Pb, Zn, Cr, Ni, Cd, As) were submitted to the laboratory in one-litre polyethylene containers (Table 2). Concentrated nitric acid (HNO_3) was added to the sample in the field (1 mL HNO_3 per litre of sample) to minimize adsorption of metals onto the container walls. The same chemical preservation technique was used for water samples intended specifically for mercury analysis. In addition, sufficient saturated potassium permanganate ($KMnO_4$) solution was added to sustain a faint pink colour in the sample and thereby prevent the loss of elemental mercury during the time of sample storage or concentration (boiling) by the analyst. Because of the unique chemical preservation technique for mercury samples, they were collected and stored in a separate container (180 mL flint glass bottle).

10.2.3.5 Sample Storage Temperature: Sample containers used to store waters intended for nutrient, mineral and microbiological analyses were immersed entirely in ice to sustain a sample temperature near 4^oC. All other water quality samples were stored at ambient temperatures except during the winter season when care was taken to ensure that none of the samples were allowed to freeze.

10.2.4 Manual Surface-Water Samples

10.2.4.1 Grab Samples: The grab-sample technique employed the use of a stainless-steel bucket (Figure 11) suspended from a bridge by rope to collect water samples from the surface of the stream at the centre of flow. A sample obtained in the stainless-steel bucket was transferred into the appropriate containers. Grab-sample techniques were seldom used because the quantity of suspended sediment near the surface of the stream is usually not representative of in-stream quality (i.e. particle-size distribution varies vertically).

Grab-sample techniques were used only when field staff were not able to use depth-integrated techniques as a result of extreme flood conditions or during occasional equipment shortages.

10.2.4.2 Depth-Integrated Samples: Representative samples of suspended sediment and water quality parameters which have a strong affinity for sediment (phosphorus, metals, pesticides and PCBs) were collected by depth-integration techniques. Depth-integrated samples were collected by raising and lowering the sample container or the sample collection apparatus at a constant velocity through one or more sampling verticals. One sampling vertical was designated at the centre of flow. Additional sampling verticals were located at equally spaced intervals along the tributary cross-section (imaginary line at right angles to the direction of streamflow). The number of sampling verticals varied at each monitoring site because of the seasonal variability in the magnitude of streamflow and the width of each tributary cross-section (Table 4).

Depth-integrated samples were collected in some cases by hand directly from the stream into the sample containers. Alternatively, sample collection apparatus were used as an aid to collect depth-integrated samples. A simple weighted bucket (Figure 16) was designed to accommodate the standard one-litre glass and polyethylene sample containers. Sample collection by means of the weighted bucket eliminated the possibility of contamination (i.e. direct collection into the sample container). Three models of depth-integrating suspended-sediment samplers (DH-48, DH-59 and D-49) which were developed by the Federal Inter-Agency Sedimentation Project (Figure 13) were also used to collect depth-integrated samples. The sample collection apparatus and technique used in the collection of any one given sample was dependent upon the intended analyses and the streamflow conditions at the time of sample collection.

TABLE 4: MONITORING SITE LOCATIONS AND THE NUMBER OF CROSS-SECTION VERTICALS USED IN THE COLLECTION OF DEPTH-INTEGRATED WATER SAMPLES

RIVER BASIN	STREAM	SAMPLE POINT DESCRIPTION	MILEAGE	LOCATION CODE	PLUARG CODE	SAMPLE VERTICALS
AUSABLE RIVER	L.AUSABLE R.	AT CONC. NO.5 USBORNE TOWNSHIP	75.0	08 0022 014 02	AG-3	1-3
BIG CREEK	VENISON CREEK	WEST OF WALSINGHAM	12.2	16 0124 005 02	AG-2	1-3
GRAND RIVER	ABERFOYLE CR.	AT HWY. 6 SOUTH OF ABERFOYLE	103.6	16 0184 059 02	EX-1	1-3
	ABERFOYLE CR.	AT TOWNLINE RD. S-W OF ABERFOYLE	102.5	16 0184 060 02	EX-2	1-3
	ABERFOYLE CR.	PRIVATE RD. W. OF HWY.6 IN ABERFOYLE	103.4	16 0184 061 02	EX-3	1-3
	CANAGAGIGUE CR.	AT WATERLOO-WELLINGTON CO. LINE	132.7	16 0184 053 02	AG-4	1-3
	CANAGAGIGUE CR.	WEST OF WATERLOO CO. ROAD NO. 22	124.4	16 0184 079 02	GR-19	1-3
	CEDAR CREEK	AT HWY. 401 N. OF ROSEVILLE ROAD	109.3	16 0184 064 02	TU-3	1-3
	CEDAR CREEK	AT HWY. 401 S. OF ROSEVILLE ROAD	108.7	16 0184 065 02	TU-4	1-3
	CONESTOGO R.	AT WELLINGTON ST. DRAYTON	149.0	16 0184 075 02	GR-10	1-3
	CONESTOGO R.	AT GLEN ALLAN	138.6	16 0184 077 02	GR-12	1-3
	CONESTOGO R.	AT HWY. NO. 85 IN ST. JACOBS	122.6	16 0184 078 02	GR-14	1-3
	ERAMOSA RIVER	AT VICTORIA ROAD GUELPH	110.2	16 0184 054 02	UL-1	1-3
	GRAND RIVER	AT 1ST.BR.DNSTR.FROM GALT STP	86.5	16 0184 011 02	UL-22	3-5
	GRAND RIVER	BRIDGE AT DUNNVILLE	4.8	16 0184 035 83	GR-15	3-10
	GRAND RIVER	1ST.CONC. DNSTR.BELLWOOD L.OUTLET	138.3	16 0184 037 02	GR-13	1-3
	GRAND RIVER	AT HWY.89 BRIDGE IN KELDON	171.4	16 0184 066 02	GR-2	1-3
	GRAND RIVER	AT CONC.RD. 13 N-W OF MARSVILLE	151.5	16 0184 067 02	GR-3	1-3
	GRAND RIVER	AT BRIDGE WEST OF WINTERBOURNE	122.1	16 0184 069 02	UL-21	3-5
	GRAND RIVER	AT HWY.NO.6 IN CALEDONIA	31.4	16 0184 070 02	GR-5	1-3
	GRAND RIVER	MOUNT PLEASANT ST. BRANTFORD	56.9	16 0184 076 02	GR-11	3-5
	LUTTERVAL CR.	ERAMOSA TWP.LINE 3 N.OF ROCKWOOD	121.2	16 0184 073 02	GR-8	1-3
	McKENZIE CR.	ONEIDA-McKENZIE RD.S.OF CALEDONIA	30.6	16 0184 072 02	GR-7	1-3
	McKENZIE CR. TRIB.	AT SIX NATIONS CORNERS	35.7	16 0184 089 02	FR-1	1-3
	MONTGOMERY CR.	AT VANIER & SHELLEY DR. KITCHENER	101.6	16 0184 086 02	UL-24	1-3
	NITH RIVER	AT 1ST. BR. UPSTR.OF NEW HAMBURG	134.4	16 0184 057 02	UL-4	1-3
	NITH RIVER	AT HWY.7-8 SOUTH OF NEW HAMBURG	130.1	16 0184 058 02	UL-5	1-3
	NITH RIVER	AT DAM IN NEW HAMBURG	131.2	16 0184 068 02	GR-18	1-3
	NITH RIVER	PERTH TWP.RD.9 N. OF SHAKESPEARE	152.2	16 0184 074 02	GR-9	1-3
	NITH RIVER	AT BRIDGE DNSTRM. OF CANNING	85.3	16 0184 080 02	GR-20	3-5
	NITH RIVER	AT HWY.NO. 97 PLATTSVILLE	114.4	16 0184 083 02	GR-17	1-3
	NITH RIVER	AT 1ST.BRIDGE WEST OF AYR	96.1	16 0184 084 02	GR-16	1-3

Table 4 Continued

RIVER BASIN	STREAM	SAMPLE POINT DESCRIPTION	MILEAGE	LOCATION CODE	PLUARG CODE	SAMPLE VERTICALS
	SCHNEIDER CR.	AT HAYWARD AVE.KITCHENER	101.7	16 0184 085 02	UL-23	1-3
	SPEED RIVER	AT WOODLAWN ROAD GUELPH	111.9	16 0184 043 02	UL-2	1-3
	SPEED RIVER	AT HANLON EXPRESSWAY BRIDGE	106.7	16 0184 056 02	UL-3	1-3
	SPEED RIVER	AT GUELPH RD.32 N.OF GLENCHRISTIE	101.7	16 0184 062 02	EX-4	1-3
	SPEED RIVER	DOWNSTREAM OF LIMESTONE QUARRY	101.0	16 0184 063 02	EX-5	1-3
	SPEED RIVER	DOWNSTREAM OF GUELPH STP	105.5	16 0184 082 02	UL-3C	1-3
	WHITMANS CR.	AT BURFORD-CLEAVER RD.N. OF HWY.53	73.1	16 0184 071 02	GR-6	1-3
HILLMAN CREEK	HILLMAN CR. TRIB.	AT CONC.NO.15 MERSEA TOWNSHIP	4.6	16 0030 002 02	AG-13	1-3
HUMBER RIVER	SALT CREEK	AT CONC. NO.8 2.6 MI.N. OF HWY.7	21.7	06 0083 017 02	AG-11	1-3
LYNN RIVER	DAVIS CR.TRIB.	AT NORFOLK ST.NORTH OF SIMCOE	10.2	16 0159 006 02	UL-17	1-3
	KENT CREEK	SOUTH OF CEDAR STREET SIMCOE	9.9	16 0159 005 02	UL-19	1-3
	LYNN RIVER	AT DE COU ROAD SIMCOE	7.1	16 0159 003 02	UL-20	1-3
	LYNN R.TRIB.	AT QUEENSWAY EAST. HWY.3 SIMCOE	9.7	16 0159 004 02	UL-18	1-3
	PATTERSON CR.	AT NORFOLK CO.RD. NO.34 SIMCOE	10.2	16 0159 007 02	UL-16	1-3
MAITLAND R.	MAITLAND R.TRIB.	1.6 MILES NORTH OF FORDWICH	68.2	08 0056 025 02	AG-6	1-3
SAUGEEN RIVER	CAMP CREEK	AT ROAD SOUTH OF ALLEN PARK	65.8	08 0123 026 02	UL-12	1-3
	CAMP CREEK	NORTH OF HWY.NO.4 IN ALLAN PARK	66.3	08 0123 027 02	UL-13	1-3
	MILL CREEK	AT CONC.NO.12 BRUCE TOWNSHIP	22.5	08 0123 035 02	AG-14	1-3
	N.SAUGEEN R.	AT CONC.RD.6-7 ELDERSLIE TWP.	26.1	08 0123 031 02	SR-5	1-3
	SAUGEEN RIVER	BENTINCK TWP.CONC.2-3 N.OF HWY.4	76.7	08 0123 029 02	SR-1	1-3
	SAUGEEN RIVER	AT BRUCE CO.RD.3 N. OF BURGOYNE	7.4	08 0123 030 02	SR-6	3-10
	SAUGEEN RIVER	AT BRUCE CO.ROAD NO.19	52.9	08 0123 032 02	SR-3	1-3
	SAUGEEN RIVER	AT HIGHWAY NO.6 DURHAM	81.2	08 0123 033 02	UL-14	1-3
	SAUGEEN RIVER	AT R.R.BRIDGE S-E OF DURHAM	80.6	08 0123 034 02	UL-15	1-3
	S. SAUGEEN R	AT NORMANDY TWP.ROAD NO.17-18	63.2	08 0123 012 02	SR-2	1-3
	TEESWATER R.	AT CO.RD.NO.3 S-W OF PAISLEY	24.2	08 0123 008 02	SR-4	1-3

Table 4 Continued

RIVER BASIN	STREAM	SAMPLE POINT DESCRIPTION	MILEAGE	LOCATION CODE	PLUARG CODE	SAMPLE VERTICALS
SHELTER VALLEY	SHELTER VALLEY CR.	AT 1ST.BRIDGE NORTH OF HWY.401	4.8	06 0142 002 02	AG-7	1-3
SYDENHAM RIVER	UNNAMED DITCH	RD.BETWEEN CONC.9 & 10 N-E OF HWY.81	88.8	04 0027 013 02	TU-5	1-3
THAMES RIVER	BIG CREEK	AT CONC.NO.10 TILBURY WEST TWP.	10.4	04 0013 033 02	AG-1	1-3
	MIDDLE THAMES	AT CONC.NO.14 EAST NISSOURI TWP.	157.2	04 0013 034 02	AG-5	1-3
TWENTY MILE CR.	NORTH CREEK	AT SHURIE RD.S-E OF SMITHVILLE	16.5	06 0024 003 02	AG-10	1-3
WILTON CREEK	WILTON CREEK	WEST OF HARROWSMITH	17.0	17 0037 002 02	WC-1	1-3
	WILTON CREEK	AT HWY.NO.2 MORVEN	5.5	17 0037 003 02	WC-2	1-3
	WILTON CREEK	UPSTREAM OF LANDFILL IN VIOLET	9.9	17 0037 004 02	SLF-1	1-3
	WILTON CREEK	AT RD.N-W FROM STORMS CORNER	8.0	17 0037 005 02	SLF-2	1-3
	WILTON CREEK	AT CONC.4-5 3MI.S-W OF MORVEN	3.4	17 0037 006 02	WC-3	1-3

AG	monitoring site in the vicinity of agricultural land use
BR	bridge
DNSTR.	downstream
EX	monitoring site in the vicinity of extractive industry land use
FR	monitoring site in the vicinity of forested land use
GR	monitoring site on the mainstem or tributaries of the Grand River
MILEAGE	distance from the monitoring site location to the junction of the terminal stream and terminal basin
R.R.	railroad
SLF	monitoring site in the vicinity of land used for sanitary landfill
SR	monitoring site on the mainstem or tributaries of the Saugeen River
STP	sewage treatment plant
TRIB.	tributary
TU	monitoring site in the vicinity of a transportation and utility corridor
UL	monitoring site in the vicinity of urban land use
UPSTR.	upstream
WC	monitoring site on the mainstem of Wilton Creek

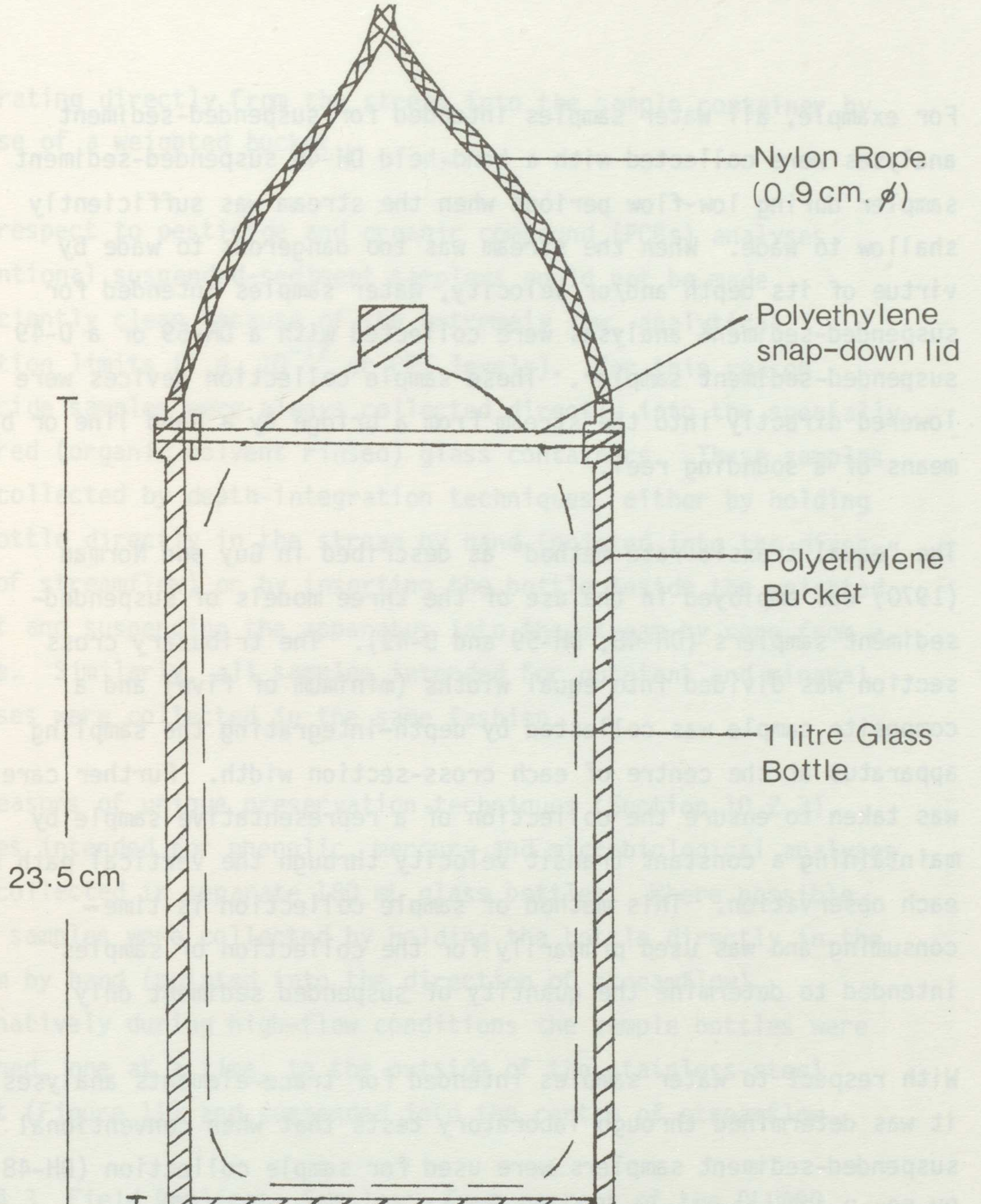


FIGURE #16

WEIGHTED BUCKET WATER QUALITY SAMPLER

For example, all water samples intended for suspended-sediment analyses were collected with a hand-held DH-48 suspended-sediment sampler during low-flow periods when the stream was sufficiently shallow to wade. When the stream was too dangerous to wade by virtue of its depth and/or velocity, water samples intended for suspended-sediment analyses were collected with a DH-59 or a D-49 suspended-sediment sampler. These sample collection devices were lowered directly into the stream from a bridge by a hand line or by means of a sounding reel.

The "equal transit rate method" as described in Guy and Norman (1970) was employed in the use of the three models of suspended-sediment samplers (DH-48, DH-59 and D-49). The tributary cross section was divided into equal widths (minimum of five) and a composite sample was collected by depth-integrating the sampling apparatus at the centre of each cross-section width. Further care was taken to ensure the collection of a representative sample by maintaining a constant transit velocity through the vertical path of each observation. This method of sample collection is time-consuming and was used primarily for the collection of samples intended to determine the quantity of suspended sediment only.

With respect to water samples intended for trace-elements analyses, it was determined through laboratory tests that when conventional suspended-sediment samplers were used for sample collection (DH-48, DH-59, D-49), the brass intake supplied by the manufacturer introduced significant quantities of zinc and lead. The suspended-sediment samplers were modified by replacing the brass intake with a teflon intake manufactured to the sampler specifications. Teflon washers were also manufactured to insert between the mouth of the sample bottle and the body of the sampler, to ensure that water quality samples collected for trace-elements analyses contacted only the teflon material and the sample vessel. In the absence of the modified sampling apparatus, contamination was avoided by depth-integrating directly from the stream into the sample container by the use of a weighted bucket.

With respect to pesticide and organic compound (PCBs) analyses, conventional suspended-sediment samplers could not be made sufficiently clean because of the extremely low, analytical detection limits (i.e. 10^{-12} or PPT levels). For this reason pesticide samples were always collected directly into the specially prepared (organic solvent rinsed) glass containers. These samples were collected by depth-integration techniques, either by holding the bottle directly in the stream by hand (pointed into the direction of streamflow) or by inserting the bottle inside the weighted bucket and suspending the apparatus into the stream by rope from a bridge. Similarly, all samples intended for nutrient and mineral analyses were collected in the same fashion.

For reasons of unique preservation techniques (Section 10.2.3), samples intended for phenolic, mercury and microbiological analyses were collected in separate 180 mL glass bottles. Where possible, these samples were collected by holding the bottle directly in the stream by hand (pointed into the direction of streamflow). Alternatively during high-flow conditions the sample bottles were attached, one at a time, to the outside of the stainless-steel bucket (Figure 11) and suspended into the centre of streamflow.

10.2.4.3 Field Replicate Samples: Four percent of the PLUARG surface-water samples collected manually by the Ontario Ministry of the Environment were replicated to measure data reproducibility. Two different samples (i.e. volume not split) were taken as close to the same time and place as possible, using routine, manual sample-collection methodology. Large volumes of sample were not collected and split in the field since decanting turbid samples from one vessel would leave behind much of the sediment fraction. Replicate samples were collected on a random basis at all PLUARG monitoring

TABLE 5: STANDARD DEVIATION OF POLLUTANT CONCENTRATIONS MEASURED IN THE LABORATORY SPLIT-SAMPLE AND FIELD REPLICATE SAMPLE PROGRAMS

PARAMETER	Full Scale (FS) Calibrated Concentration Range (mg/L)	"LAB EFFECT" STANDARD DEVIATION computed from analytical results of "single samples split in the lab"			"LAB + FIELD EFFECT" STANDARD DEVIATION computed from analytical results of "replicate samples, collected in the field by manual sampling methods"		
		Low Lev. 0-20% FS	Mid-Lev. 21-50% FS	High Lev. 51-100% FS	Low Lev. 0-20% FS	Mid-Lev. 21-50% FS	High Lev. 51-100% FS
Susp. Solids							
(Low Range)	0-20	-	-	.69	.73	.80	.87
(High Range)	0-100	.69	.69	-	.87	-	-
Tot. Phosphorus	0-.20	.002	.004	.004	.003	.009	.011
Filtered Total Phosphorus	0-.10	.002	.004	.004	.002	.002	.002
Filtered Reactive Phosphate-P	0-.10	.0011	-	.0021	.0007	.0012	.003
Total Nitrogen (calculated)	0-2	-	-	-	-	.0310	.051
Total Kjeldahl-N	0-2	.026	.035	.037	.030	.038	.051
Filt.(NO_3 + NO_2)-N	0-2	.011	.022	.039	.012	.009	.058
Filtered Ammonia-N	0-.5	.004	.008	.009	.006	.011	.012
Calcium	0-100	.260	.72	1.2	-	.34	1.60
Magnesium	0-50	.040	.26	.40	-	.17	.50
Sodium							
(Low Range)	0-10	.048	.123	.17	.06	.15	.170
(High Range)	0-50	.17	-	.48	-	-	.5
Potassium	0-6	.037	.084	.097	.10	.03	.029
Alkalinity	0-250	.38	.40	.80	-	.40	.620
Chloride							
(Low Range)	0-10	.05	.07	.16	-	.120	.140
(High Range)	0-50	.16	.19	.43	-	.19	.29
Sulphate	0-100	.80	1.0	.92	.43	.49	-
Conductivity(umho/cm^3)	0-1000	3.0	2.3	5.5	-	2.4	5.5

sites through a full range of stream discharge, to ensure that a wide range of pollutant concentrations and flows were sampled. All field personnel participated in collecting replicate samples so that the daily monitoring performance of each individual could also be evaluated. Replicate samples were collected, stored, preserved and delivered to the laboratory in the same manner as all routine water samples.

Analytical results from field replicate samples (pairs of data) were used to compute a standard deviation for a list of routine chemical parameters (Table 5). Citing the parameter total phosphorus as an example in Table 5, the analytical differences obtained from all replicate samples were used to compute a standard deviation (by averaging) that applied to the entire calibrated concentration range (.0 to 0.2 mg/L). In addition, the analytical differences from replicate samples (see Section 10.2.4.4), were used to compute separate standard-deviation values for concentrations occurring in the low level 0-20% (0 to .04 mg/L), mid level 21-50% (.041 to .10 mg/L) and the high level 51-100% (.101 to 0.2 mg/L) of the calibrated concentration range. The breakdown of the standard deviations outlined above provides a convenient way to show the distribution of sample concentrations and to assess the effects of pollutant concentrations on data variability. Selection of concentration-level divisions by percentage of the calibrated concentration range (0-20, 21-50 and 51-100%) were chosen to be consistent with the concentration-level divisions used by the Minstry's analysts to evaluate the analytical performance (i.e. laboratory split-sample program).

10.2.4.4 Laboratory Split Samples: Differences attributable to the variables inherent in the laboratory test procedure can be quantified by replicate analyses of one sample from a given sampling run (within-run replicate analyses).

Laboratory staff randomly selected and split 3 to 5 samples daily for replicate analyses. Analytical results from split samples (pairs of data) were used to compute a standard deviation for each water quality parameter. The standard deviation of the split sample measures the routine effects of laboratory analyses on data reproducibility. "Section 1-B, Data Quality Report Series" (King and Fellin, 1976), contains laboratory performance reports on the analyses of water quality parameters studied under PLUARG. Standard-deviation values appear in this publication as a measure of the reproducibility of single samples that were re-analysed.

The standard deviation computed for each water quality parameter from the laboratory split samples is also shown in Table 5. These data suggest that the effects of the field activity (manual sample collection techniques and sample handling techniques adopted for the PLUARG field program) on the quality of data derived from the routine tributary samples are negligible.

10.2.4.5 Frequency: During non-runoff periods, the locations of point sources were a key factor in establishing a sample collection frequency at each monitoring site. Sites draining areas without any point sources were sampled 4 to 12 times per month. More frequent sampling was unnecessary as ground water constitutes the principal supply of streamflow during these periods and the ground-water quality is relatively constant. Monitoring sites draining areas influenced by point sources (i.e. urban land use) were sampled more often, 12 to 20 times per month, in anticipation of variable waste inputs from these areas.

The frequency and timing of sample collection were determined by the magnitudes and fluctuations of streamflows as well as by the runoff characteristics of the drainage basins (i.e. drainage area, soil type, soil cover and the presence of tile drains or storm sewers, etc.). In order to provide reliable pollutant loading estimates, the time interval between sample collections was shortest at those monitoring sites where streamflow responded to surface runoff in the least amount of time (usually small drainage areas and/or areas with a large portion of the area in impervious cover).

During the spring freshet, additional Ministry staff (approximately 20), not routinely involved in PLUARG monitoring, were recruited to increase sample frequency at the monitoring sites (approximately 50) not instrumented with automatic sampling equipment. Field staff monitored water quality in the direction of flow from the headwater areas of the tributary, downstream to the pilot watershed outlet, as frequently as possible. After the initial streamflow response to runoff, the rising limb of the streamflow hydrograph was sampled once or twice per hour until the peak flow was reached. The sample collection interval then diminished from one-to four-hour intervals and finally twice daily throughout the falling limb of the hydrograph. Local observers were hired to ensure that the watershed outlets were monitored adequately throughout the entire year.

The parameters analyzed at each monitoring site were dependent on potential or suspected pollutants, land use and temporal aspects such as low-flow or high-flow period. The land uses as well as the streamflow conditions dictated the sample collection frequency. With respect to land use for example, collection of pesticide samples from agricultural areas were emphasized while trace-elements samples were collected more frequently from monitoring sites in the vicinity of urban areas. Only the suspended-sediment, nutrient and mineral (i.e. major anions and cations) analyses were conducted on all samples. During runoff events however, all water quality analyses (parameters listed in Table 1) were conducted in anticipation of detecting the pollutants which otherwise might occur below the analytical detection limits.

10.2.5 Surface-Water Samples from Automatic Samplers

Automatic samplers were installed to permit the unattended sample collection of surface water at monitoring sites where streamflow response to surface runoff occurs relatively quickly (i.e. small drainage area). The CAE submersible-pump sampler and the SIRCO vacuum sampler were the two types of automatic samplers (Figure 17) used exclusively in the field program.

Eight CAE submersible-pump samplers were installed at the outlets of small watersheds (Figure 18) chosen for the study of runoff from agricultural and urban land uses (Activities 1 and 3). Historic streamflow hydrographs indicated that approximately sixty surface-runoff events per year resulted in temporary increases of streamflow at these monitoring sites (drainage area from 900-5600 ha.). Approximately ten to fourteen of these surface-runoff events resulted in streamflow peaks which exceeded 50 cfs (1.42 m^3/s). These samplers were designed to operate all year and were programmed to respond to the larger variety of surface-runoff events in anticipation of the most significant periods of pollutant transport.

Two SIRCO vacuum samplers (Figure 19) were also installed, at the surface drainage outlets of small agricultural plots (three to eight hectares) to measure brief periods of surface runoff (one or two days per year) from agricultural lands used for processed organic waste disposal.

10.2.5.1 Construction: A concrete pad was poured around the perimeter of a conventional stilling well, to support a steel building in which the CAE submersible-pump sampler was housed. The

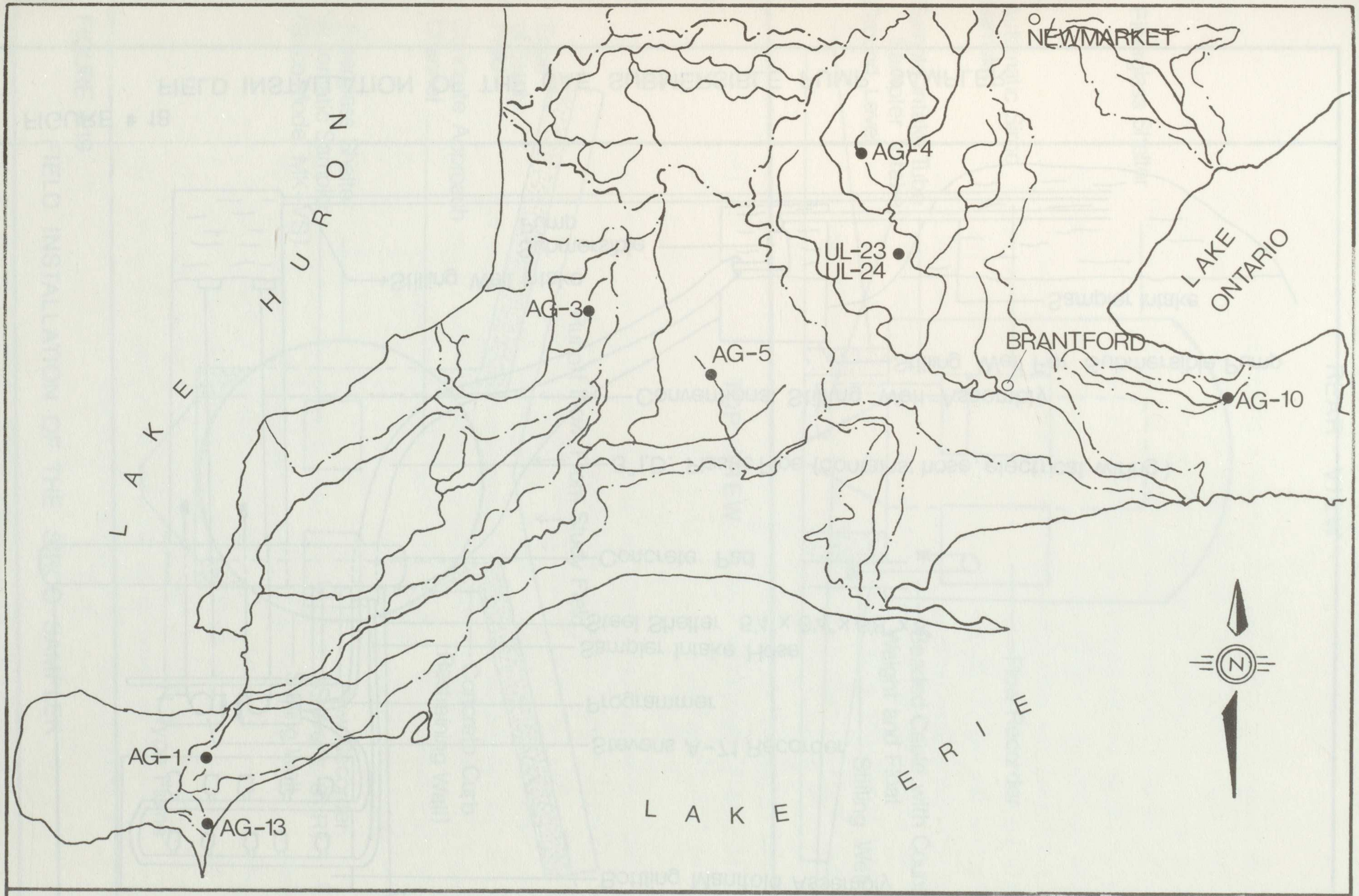


FIGURE #17

LOCATIONS OF AUTOMATIC SAMPLERS

● CAE PUMPING SAMPLER

○ SIRCO VACUUM SAMPLER

*see Table 4 for description of monitoring locations

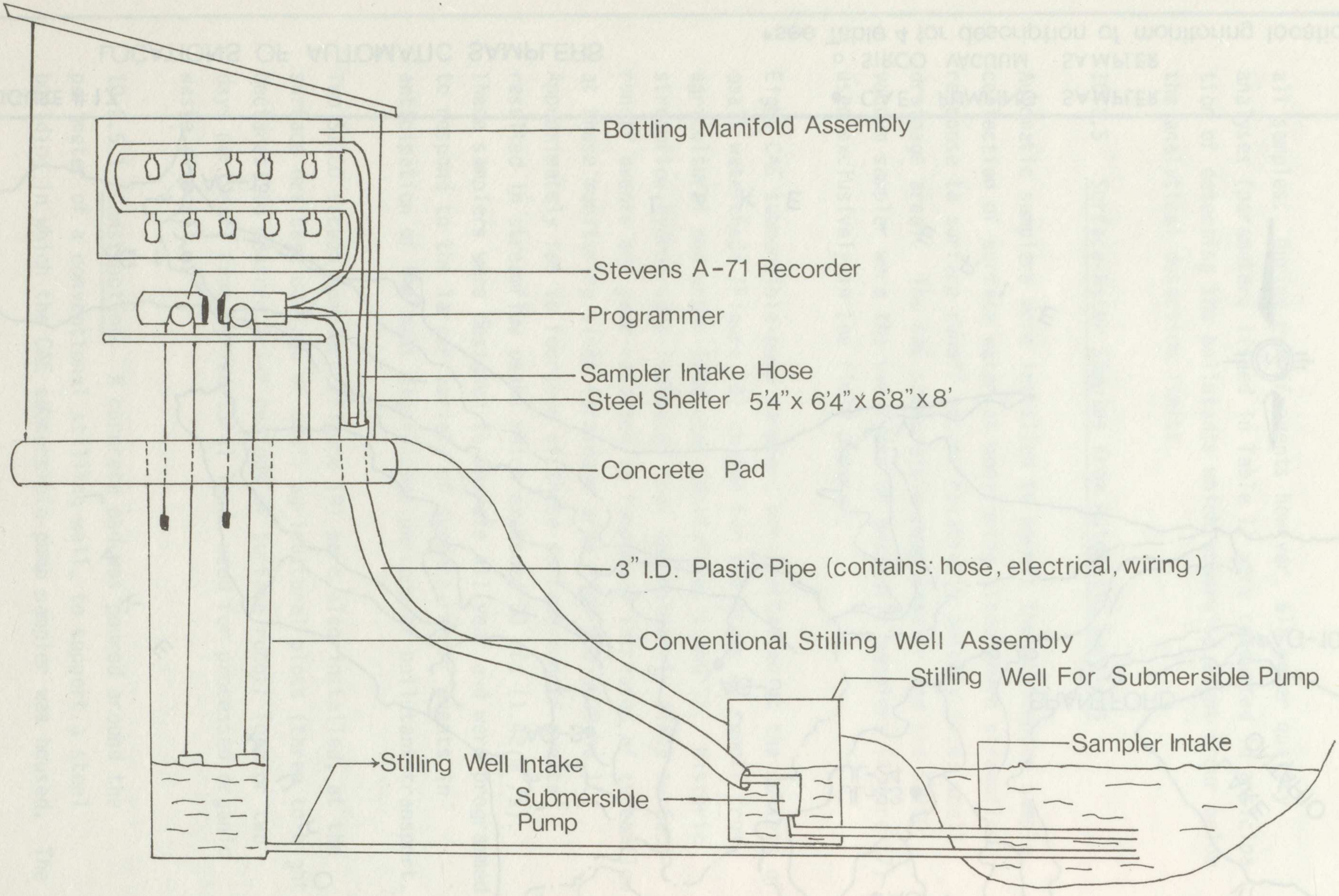


FIGURE # 18

FIELD INSTALLATION OF THE CAE SUBMERSIBLE PUMP SAMPLER

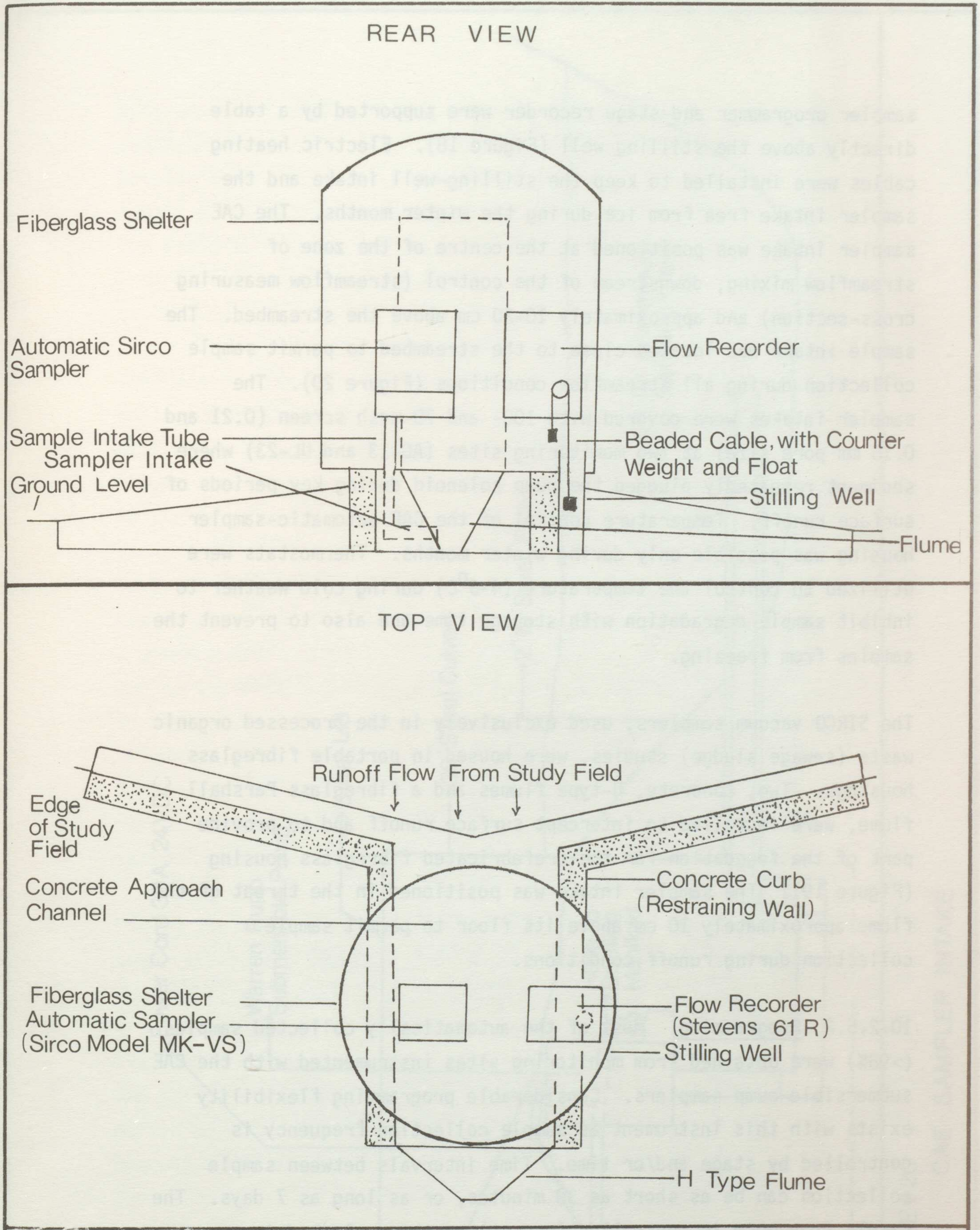


FIGURE #19

FIELD INSTALLATION OF THE SIRCO SAMPLER

sampler programmer and stage recorder were supported by a table directly above the stilling well (Figure 18). Electric heating cables were installed to keep the stilling-well intake and the sampler intake free from ice during the winter months. The CAE sampler intake was positioned at the centre of the zone of streamflow mixing, downstream of the control (streamflow measuring cross-section) and approximately 10-20 cm above the streambed. The sample intake was located close to the streambed to permit sample collection during all streamflow conditions (Figure 20). The sampler intakes were covered with 100- and 70-mesh screen (0.21 and 0.15 mm pore size) at two monitoring sites (AG-13 and UL-23) where sediment repeatedly plugged the pump solenoid during key periods of surface runoff. Temperature control of the CAE automatic-sampler housing was possible only during winter months. Thermostats were utilized to control the temperature (4-6°C) during cold weather to inhibit sample degradation with storage time and also to prevent the samples from freezing.

The SIRCO vacuum samplers, used exclusively in the processed organic waste (sewage sludge) studies, were housed in portable fibreglass housings. Two, concrete, H-type flumes and a fibreglass Parshall flume, were installed to intercept surface runoff and to provide part of the foundation for the prefabricated fibreglass housing (Figure 19). The sampler intake was positioned in the throat of the flume approximately 10 cm above its floor to permit sample collection during runoff conditions.

10.2.5.2 <u>Programming</u>: Most of the automatically collected samples (>98%) were obtained from monitoring sites instrumented with the CAE submersible-pump samplers. Considerable programming flexibility exists with this instrument as sample collection frequency is controlled by stage and/or time. Time intervals between sample collection can be as short as 30 minutes, or as long as 7 days. The sample frequency is controlled (preset) by three clock-driven

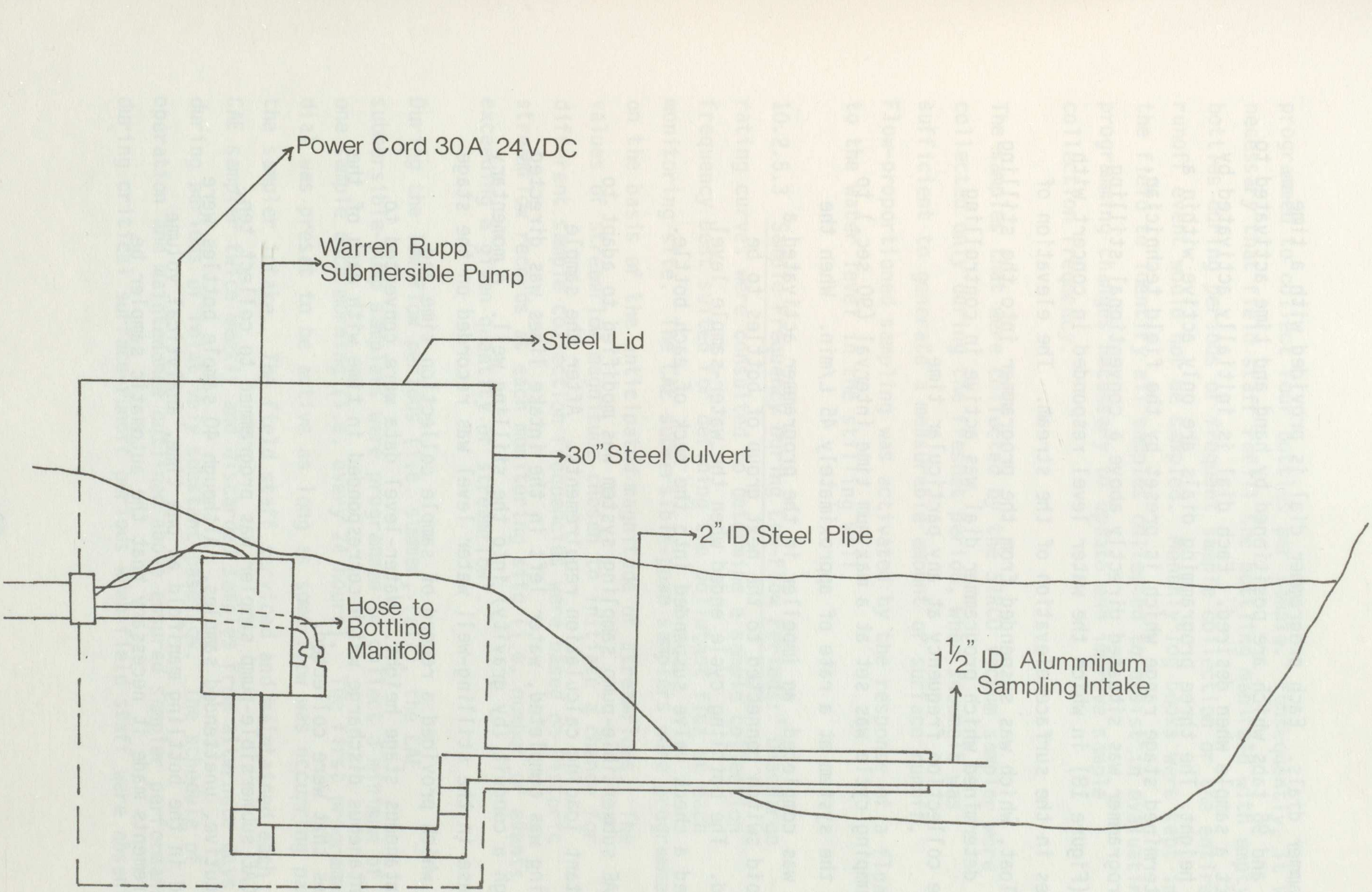


FIGURE # 20

CAE SAMPLER INTAKE

programmer dials. Each programmer dial is provided with a time scale and 96 tabs which are positioned by hand and time activated to collect a sample when desired. Each dial is initially activated by stage height. The three programming dials are only active within a predetermined stage range which is preset by the field technician. The programmer was situated directly above a conventional stilling well (Figure 18) in which the water level responded in concert with changes in the surface elevation of the stream. The elevation of the float, which was suspended from the programmer into the stilling well, determined which programmer dial was active in controlling sample collection frequency at any particular time.

The pumping cycle was set at a maximum time interval (90 sec.) to purge the system at a rate of approximately 45 L/min. When the purge was completed, an impeller in the programmer activated a solenoid switch connected to the next group of bottles to be filled. The bottling cycle ended when the water-sample level reached a check valve suspended into the neck of each bottle.

The CAE submersible-pump sampling system was modified to adapt to pollutant loading calculation requirements. After the sample bottling was completed, water left in the intake lines was directed through a conduit (by gravity) into the stilling well. A momentary increase in the stilling-well water level was recorded on the stage chart which provided a record of sample collection time and instantaneous stage height. Water-level data were converted to instantaneous discharge which corresponded in time with each of the samples that were collected.

Each CAE submersible-pump sampler was programmed to collect ten, consecutive, unattended samples. Although 40 sample bottles were housed in the bottling manifold at one time, analytical volume requirements made it necessary that the automatic sampler be programmed to collect four bottles per sample. Consequently, it was necessary that field staff refill the bottling manifold with empty bottles during periods of frequent sample collection or the entire runoff event would not be sampled. Monthly log books were kept in the field to identify all samples collected to assist in evaluating programming changes necessary to update and improve sample collection frequency.

The samples that were collected by the SIRCO vacuum sampler were collected only during the freshet period, when snowmelt was sufficient to generate a measurable amount of surface runoff. Flow-proportioned sampling was activated by the response of a float to the water level in the stilling well.

10.2.5.3 Sample Frequency During Low-Flow Periods: Discharge rating curves were consulted to determine a sample collection frequency best suited for defining the pollutant flux at each monitoring site. The CAE submersible-pump samplers were programmed on the basis of the anticipated magnitude of streamflows. The values of streamflow magnitude chosen to initiate a change for different sample collection frequencies were based on historic streamflow records at each monitoring site (i.e. number of events exceeding a given quantity of streamflow).

During the low-flow periods (i.e. summer, fall), the CAE submersible-pump samplers were programmed to collect a minimum of one sample each morning (i.e. every 24 hours). The first programmer dial was preset to be active as long as some flow was occurring past the sampler intake. The field staff serviced and maintained each CAE sampler twice weekly and discarded samples from alternate days during periods of relatively constant baseflow. The schedule of operation and maintenance outlined above ensured sampler performance during critical surface-runoff periods when field staff were absent.

Depending upon the runoff characteristics of the drainage basin, sample collection frequency was increased from once daily to between three and six times daily when the stream stage height exceeded a predetermined level, usually equivalent to 5 to 10 cfs (.14 to .28 m^3/s). This sampling cycle was controlled by the second programmer dial. Most frequent sample collection was reserved for two urban subwatersheds (UL-23, UL-24) and two agricultural subwatersheds (AG-1, AG-10), where surface runoff influenced streamflow for the shortest period of time (i.e. flashy runoff). Runoff duration at each site was found to be variable because of the unique watershed characteristics which prevailed upstream of the monitoring sites (i.e. relative imperviousness, storm sewer and/or tile-drainage network).

Sample collection frequency was again increased by the third programmer dial when the stream stage height exceeded a level which was equivalent to 30 to 50 cfs (.8 to .14 m^3/s). Streamflows during the low-flow periods of the year exceeded these arbitrarily chosen values usually for only short periods of time (one to six hours) during significant runoff events. Samples during this period were collected at or near the maximum of one to two samples per hour.

10.2.5.4 <u>Sample Frequency During High-Flow Periods</u>: The sample collection frequency was modified for the spring freshet period in anticipation of exceptionally high streamflows. The service and maintenance schedule (visits by field staff) for each CAE submersible-pump sampler was increased from twice weekly to three or four times per week.

A minimum of one sample per day was collected automatically during periods of streamflow less than 30 cfs (0.84 m^3/s) while awaiting significant runoff events (first programmer dial). Again, depending upon the runoff characteristics of the drainage basin, the sample collection frequency was increased (second programmer dial) from once daily to between three and six times daily when the stream stage exceeded a level which was equivalent to 30 to 50 cfs (.8 to 1.4 m^3/s). Sample collection frequency was increased by the third programmer dial when the stream exceeded a stage level which was equivalent to 60 to 90 cfs (1.6 to 2.5 m^3/s). Streamflows exceeding these values were considered to be exceptionally high and samples were collected at or near the maximum of one to two per hour, where possible.

10.2.5.5 Comparison Samples: Because the CAE sampler intake was positioned at a fixed point in the cross section of the stream (i.e. automatic sample not depth-integrated), water quality samples collected by manual techniques were assumed to be more representative of the in-stream quality than samples collected by automatic techniques.

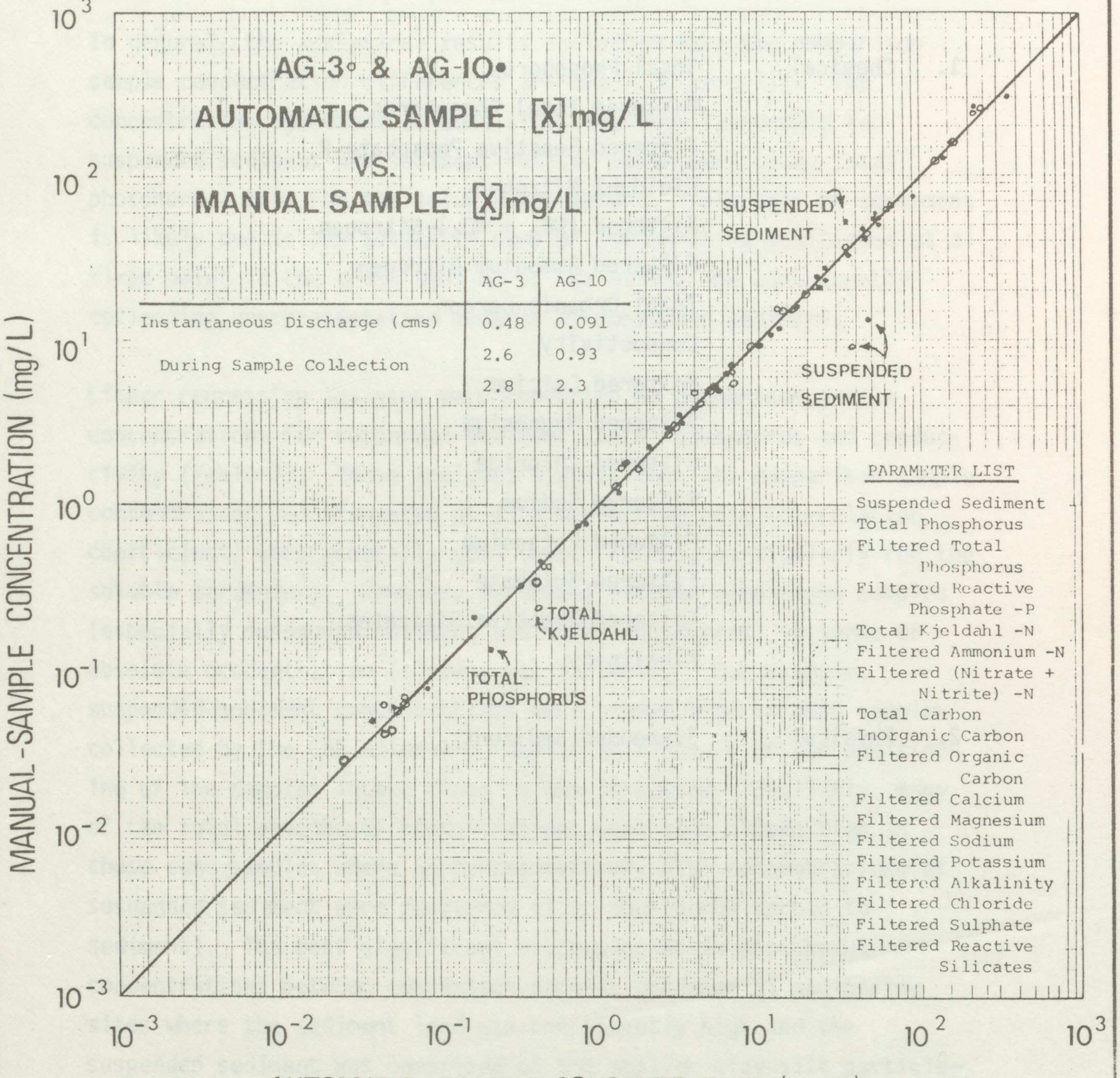
A comparison sample program was undertaken to delineate the representativeness of the automatically collected samples at each monitoring site. Water quality samples were collected by both manual and automatic techniques (paired samples) at all monitoring sites instrumented with the CAE submersible-pump samplers. Immediately after collecting a manual sample at a predetermined cross section, an automatic sample was collected by manually triggering the sampler programming device. Comparison samples were collected on a weekly basis, emphasizing collection during all streamflow conditions, to ensure that a wide range of pollutant concentrations were sampled. Comparison samples were submitted to the laboratory in the same manner as routine samples (i.e. containers, storage temperature, storage time, etc.). Parameters introduced into solution from the surfaces of the components in the automatic sampler (i.e. copper, and lead) were excluded from the routine PLUARG list of parameters. Samples intended for microbiological analyses, trace elements, pesticide and PCB analyses were collected by manual sampling techniques only at these sites. The parameters analysed routinely on those samples collected by the CAE automatic samplers are listed in Table 6.

In general, the analytical results indicated that the comparison sample concentration differences are small (Figure 21). The concentration agreement at some sites was less favourable for suspended sediment and sediment-related parameters (i.e. total phosphorus) than for the soluble parameters. This lack of agreement is likely due to the automatic sampler intake being positioned at a fixed point in the cross section of the stream and consequently collecting unrepresentative amounts of suspended sediment.

Linear regression analyses were conducted on comparison sample concentrations for suspended sediment, total phosphorus and conductivity (Table 7). These analyses suggest that the comparison sample concentration relationships at each monitoring site (correlation coefficient) were generally good (most >0.70), particularly for the soluble parameters. However, agreement between comparison samples (especially suspended sediment and total phosphorus) in terms of absolute concentration (slope), was variable. For example, suspended-sediment concentrations were biased high in most samples collected by the CAE automatic sampler as a result of the positioning of the sampler intake close to the streambed. Similarly, many of the total phosphorus concentrations were also biased high in those same samples where unrepresentatively high concentrations of suspended sediment were recovered (i.e. phosphorus sorbed to sediment). The most significant discrepancies in phosphorus concentrations between comparison samples occurred at monitoring sites where the sediment load was consistently high and the suspended sediment was comprised of the smaller clay-silt particle-size range (UL-23). Conductivity concentration comparisons (Table 7) confirmed that the dissolved components (anions and cations) were approximately equal using either sample collection technique.

TABLE 6: WATER QUALITY PARAMETERS ANALYSED ON A ROUTINE BASIS FROM SAMPLES COLLECTED BY THE CAE AUTOMATIC SAMPLERS

1.	Chemical	Total Phosphorus
		Filtered Total Phosphorus
		Filtered Reactive Phosphate-P
		Kjeldahl Nitrogen
		Filtered $(NO_3 + NO_2)$-Nitrogen
		Filtered Ammonium Nitrogen
		Total Organic Carbon
		Conductivity
		Filtered Calcium
		Filtered Magnesium
		Filtered Chloride
		Filtered Sodium
		Filtered Potassium
		Filtered Sulphate
		Filtered Reactive Silicates
		Alkalinity
2.	Physical	Suspended Sediment



	AG-3	AG-10
Instantaneous Discharge (cms)	0.48	0.091
During Sample Collection	2.6	0.93
	2.8	2.3

FIGURE # 21
POLLUTANT CONCENTRATIONS MEASURED IN COMPARISON SAMPLES OBTAINED FROM TWO MONITORING SITES

TABLE 7: COMPARISON SAMPLE CONCENTRATION RELATIONSHIPS (BEST FIT LINE) FOR CONDUCTIVITY, SUSPENDED SEDIMENT AND TOTAL PHOSPHORUS

MONITORING SITE	CONDUCTIVITY	r	SUSPENDED SEDIMENT	r	TOTAL PHOSPHORUS	r
UL-24 (10)	Y = 44. + 0.97 X	.98	Y = -14. + 1.1 X	.97	Y = .002 + 1.1 X	.94
AG-13 (17)	Y = -6.3 + 1.0 X	.99	Y = -6.1 + 0.9 X	.99	Y = -.005 + 0.97 X	.98
AG-4 (37)	Y = 9.5 + 0.95 X	.73	Y = 0.6 + 0.7 X	.74	Y = -.001 + 0.93 X	.92
AG-5 (55)	Y = -9.9 + 1.0 X	.99	Y = 5.7 + 0.5 X	.86	Y = .014 + 0.82 X	.62
AG-10 (50)	Y = 46. + 0.86 X	.98	Y = -0.9 + 0.98 X	.93	Y = .040 + 0.97 X	.60
UL-23 (58)	Y = 150. + 0.92 X	.92	Y = 1.9 + 0.7 X	.75	Y = .064 + 0.48 X	.68
AG-1 (26)	Y = -15. + 1.0 X	.99	Y = 5.6 + 1.0 X	.89	Y = .005 + 0.93 X	.94
AG-3 (45)	Y = -5.8 + 1.0 X	.99	Y = 5.2 + 0.6 X	.70	Y = .001 + 0.95 X	.95

X is the concentration of the automatic sample

Y is the concentration of the manual sample

r is the correlation coefficient

( ) is the number of comparison (paired) samples

Variables unique to each monitoring site such as drainage area and mean annual streamflow (Table 8) probably account for much of the variability measured between monitoring sites in the comparison sample program (i.e. regression equations, Table 7). In addition, the baseflow period was sampled more successfully (greater number of comparison samples) than any other period of flow. Low streambed gradients (1.7 to 3.7 m/km at AG-1, AG-3, AG-10 and AG-13) results in lower stream velocities, poor mixing and less representative fixed-point sampling with automatic samplers. Samples were also found to be less representative where the efficiency of the purging cycle was reduced by long intake-conduit lengths resulting in large, inside surface areas contacting the sample (37 m and 0.70 m^2, respectively at AG-4). In addition, differential compaction and settling of the earth material in the vicinity of the intake conduit could create depressional areas in the flexible conduit which would trap sufficient sample to contaminate subsequent samples. Screens installed on the intakes of two CAE submersible-pump samplers to circumvent solenoid plugging prevented the collection of suspended-sediment particles larger than the pore size of the screen (AG-13, UL-23).

10.2.6 Ground-Water Samples

Ground-water samples intended for water quality analyses were collected regularly (one or two times per month) from a network of drilled wells. These wells were located in the vicinity of land-use studies related to the disposal of solid waste (sanitary landfill) and septic-tank effluent (private waste) and the application of sewage sludge (processed organic waste) on agricultural lands. A summary of sample collection and handling information are presented in Table 2. Sample containers, preservation and storage techniques and field-filtration procedures previously outlined (Section 10.2.3) were used for the collection of ground-water samples as well.

TABLE 8: CAE AUTOMATIC MONITORING SITE CHARACTERISTICS

MONITORING SITE	DRAINAGE AREA (ha)	MEAN ANNUAL STREAM FLOW (m^3/s)	STREAMBED GRADIANT (m/km)	LENGTH OF INTAKE CONDUIT (m)	AREA OF INTAKE CONDUIT (m^2)	INTAKE SCREEN PORE SIZE (mm)
UL-24	1,000	0.096	8.8	12.	0.23	none
AG-13	2,100	0.23	3.4	7.6	0.15	0.21
AG-4	2,500	0.25	17.	37.	0.70	none
AG-5	3,000	0.42	13.	15.	0.29	none
AG-10	3,000	0.38	2.1	9.1	0.17	none
UL-23	3,600	0.49	8.2	11.	0.20	0.15
AG-1	5,000	0.44	1.7	12.	0.23	none
AG-3	5,600	0.95	3.7	15.	0.29	none

The depth of monitoring wells varied from approximately 1½ to 12 metres. All well casings used in water-well construction were sealed at the surface with concrete or bentonite (natural clay) and left capped. Well casings were sealed at the surface to prevent contamination by direct surface-water infiltration down the outside of the casing into the ground-water system. Prior to sampling, all ground-water wells were flushed by use of a gas-driven centrifugal pump, a hand vacuum pump or a bailer to minimize contamination of the sample from the casing materials and to ensure collection of fresh sample. Wells were flushed until they no longer yielded water or until field staff succeeded in displacing a volume of water at least twice the volume of the well casing. Sampling was undertaken after ground-water levels recovered which varied from 5 minutes to 24 hours depending on the permeability of the earth materials in which the wells were completed.

10.2.6.1 Bailing: After a well was flushed, a bailer (250 mL) approximately 60 cm in length (aluminium pipe) and 1.9 to 2.5 cm in diameter with a check valve at the bottom was lowered into the well using a nylon rope. The first sample was discarded and served to rinse the bailer apparatus. The bailer was than repeatedly lowered and raised until sufficient sample volume was obtained by transfering water directly from the bailer into the appropriate sample containers.

10.2.6.2 Pumping: Samples were also collected by means of a hand vacuum pump from observation wells in the private waste disposal (septic-tank tile fields) studies. The polyethylene tubing and vacuum receiving flask which were attached to the hand pump, were rinsed with sample before the final sample was collected and transferred into the appropriate containers.

10.3 SEDIMENT QUALITY MEASUREMENT

The sediment quality monitoring program was designed to measure the quality of fluvial sediments (suspended sediment and bed material) and soils. Soil analyses were undertaken to quantify the attenuation rates of nutrients, inorganic trace contaminants and organic trace contaminants on lands used for sanitary landfill, private waste disposal and the application of processed organic waste as fertilizer. Bed-material samples were collected to confirm by laboratory analyses, the identity of contaminants contributed by each of the investigated land-use activities. Suspended-sediment quality was measured to determine the percentage of contaminants carried by sediment and to estimate the mass transport of some contaminants (i.e. PCBs) which often occur in water below the analytical detection limit.

The sediment quality parameters measured at the laboratory are listed in Table 9 and the sediment sample collection and handling information (i.e. containers, sampling device, etc.) are outlined in Table 10.

10.3.1 Bed Sediment

Samples of streambed sediment were collected by the multi-vertical composite method. A minimum of five subsamples were collected from the top five to ten cm of bed material. These subsamples were collected at equally spaced intervals along the sampling cross section and were then composited to form a sample of at least 500 g. On larger streams (greater than 250 m cross-section width) a greater number of subsamples were collected at equally spaced intervals (50 m) to ensure that the cross section was sampled representatively.

TABLE 9: SEDIMENT QUALITY PARAMETERS MEASURED AT THE LABORATORY

1.	Chemical	Non-Apatite Inorganic Phosphorus
		Apatite Phosphorus
		Organic Phosphorus
		PO_4 Isotherm Test
		Kjeldahl Nitrogen
		Calcium
		Magnesium
		Sodium
		Potassium
		Iron
		Manganese
		Aluminium
		Chromium
		Arsenic
		Selenium
		Nickel
		Cadmium
		Mercury
		Copper
		Lead
		Zinc
		Cobalt
		Tin
		Total Carbon
		Organic Carbon
2.	Physical	Cation Exchange Capacity
		Total Carbonates
		Clay Mineralogy
		Loss on Ignition/COD
		Particle Size Distribution
3.	Microbiological	Total Coliforms
		Fecal Coliforms
		Fecal Streptococcus
		Pseudomonas aeruginosa
		Salmonella
		Heterotrophic bacteria
		Nitrifying bacteria
4.	Pesticides and Industrial Organic Compounds*	

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* See Table 1 for full list of parameters

TABLE 10: SEDIMENT SAMPLE COLLECTION AND HANDLING INFORMATION

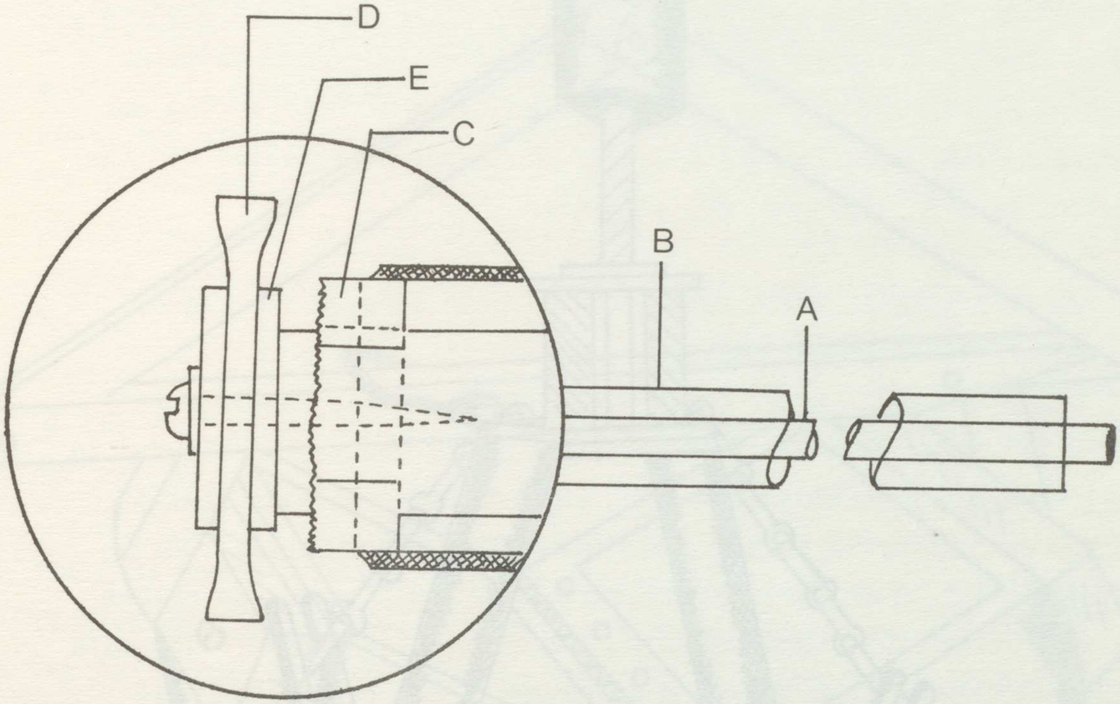
			SAMPLING DEVICE			COLLECTION METHOD				
PARAMETER GROUP	CONTAINER TYPE	CONTAINER PREPARATION	BED SEDIMENT	SUSPENDED SEDIMENT	SOILS	BED SEDIMENT	SUSPENDED SEDIMENT	SOILS	CHEMICAL PRESERVATION	STORAGE TEMPERATURE
Pesticides & PCB Scan	500 mL. wide mouth glass jar	Detergent wash, deionized water rinse and rinse with distilling glass benzene and acetone	Aluminium corer, Ekman Dredge or Ponar	Submersible pump	None	Multi-vertical composite	Centrifuged	None	None	Ambient Temp
All other chemical analyses including nutrients, minerals and metals	500 mL. wide mouth glass jar	Detergent wash, deionized water rinse	Plexiglass corer, Ekman Dredge or Ponar	Submersible pump	Auger Spade or Drill	Multi-vertical composite	Centrifuged	Composite	None	Ambient Temp
Microbiological	125 mL. wide mouth Nalgene jar	Autoclaved	Sample Container or Ethanol rinsed Ponar	none	None	Multi-vertical composite	None	None	None	$4^{o}C$

Bed-material samples were collected in a one and one-half inch I.D. (3.81 cm) coring device (Sutton, 1974). The sampler (Figure 22) consists of a clear acrylic or aluminium tube 1 metre in length with a piston constructed out of a sponge and 3/4-inch (1.91 cm) wooden dowel. The purpose of the piston is to keep the sediment sample in place while the sampler is being raised out of the stream. In streams that were too deep to wade, an Ekman dredge (Figure 23) or Ponar dredge (Figure 24) was suspended by a rope and utilized in the collection of bed-material samples. Relatively few bed-material samples were collected in this fashion.

To prevent contamination from the samplers, bed-material samples were collected in the aluminium tube for pesticide analyses and the acrylic tube for other analyses (i.e. trace elements, nutrients and particle size).

Bed-material samples were also collected for microbiological analyses in a special study along the lower 34-km reach of the Grand River. In this case an ethanol-rinsed Ekman dredge was used for sample collection.

Bed-material samples were transferred from the collection device to containers for storage and shipment to the laboratory. A 500 mL glass bottle rinsed with organic solvent was used as a container for bed sediments intended for pesticide and PCB analyses. A 125 mL autoclaved nalgene jar was used as a container for bed sediments intended for microbiological analyses. All other analyses (i.e. heavy metals, nutrients, particle size) were conducted on a single bed-material sample stored in a 500 mL. detergent washed, deionized, water-rinsed glass jar.



Longitudinal view of corer with piston head magnified.

Parts are: Dowling (A) , Plastic Core Liner (B), Metal Cutter (C)

Cellulose Sponge (D), and Rubber Washer (E)

FIGURE # 22

BED-MATERIAL SAMPLER

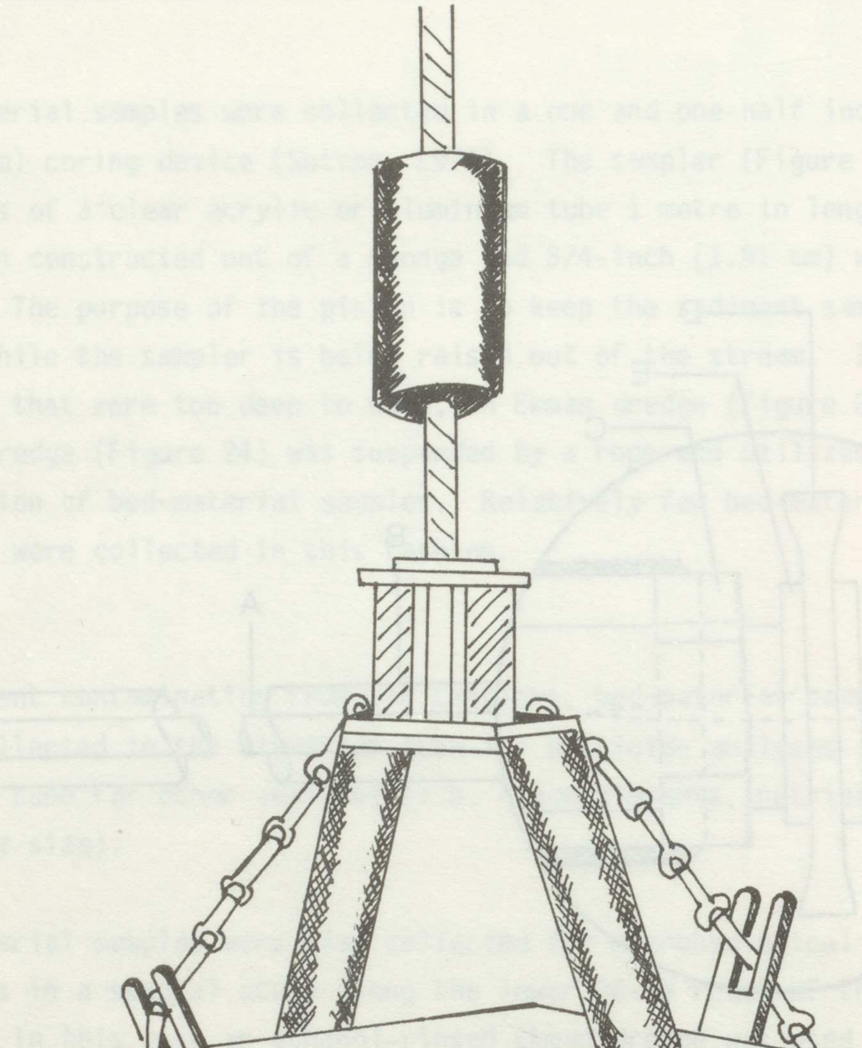


FIGURE # 23

EKMAN DREDGE

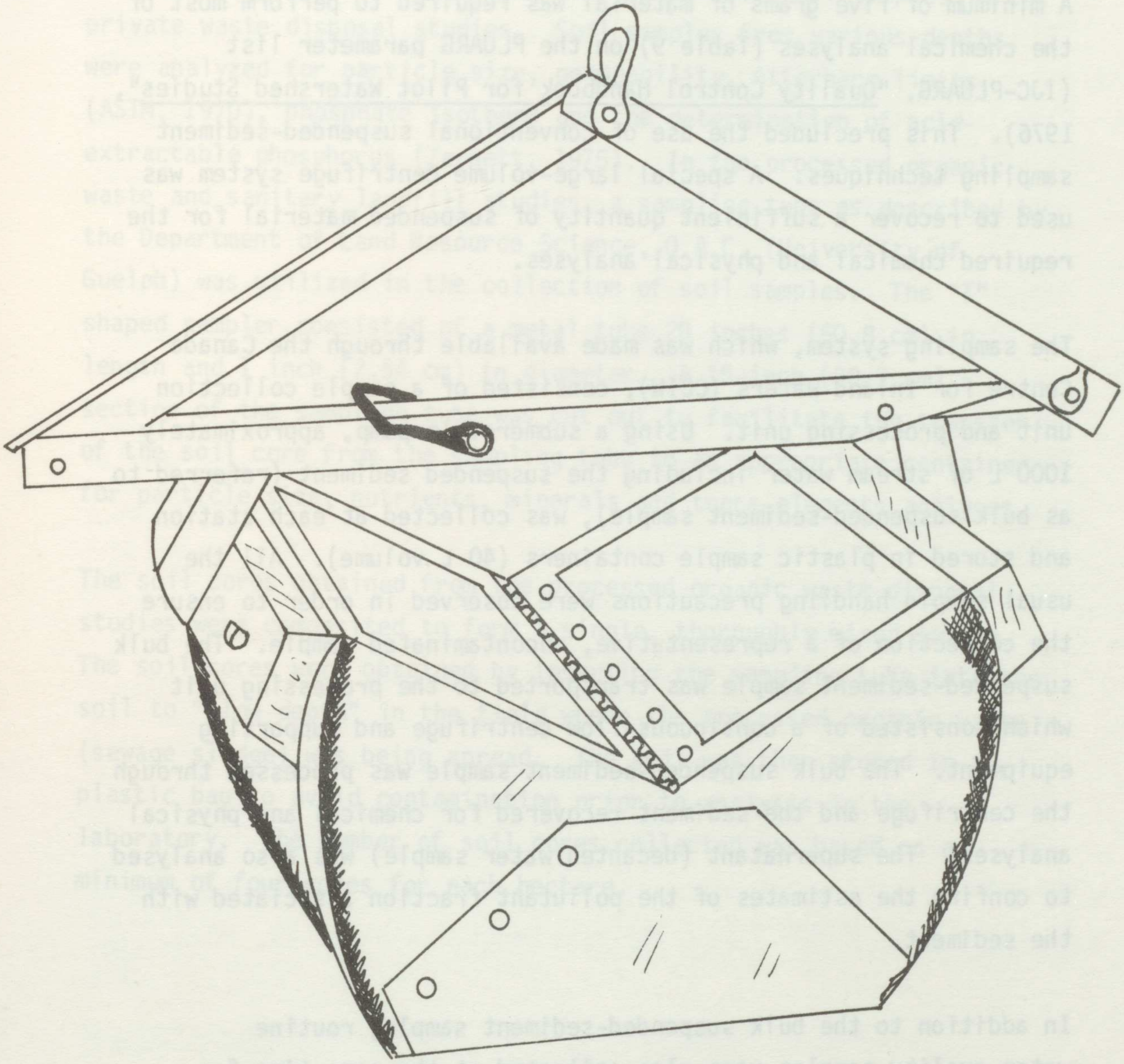


FIGURE # 24

PONAR DREDGE

10.3.2 Bulk Suspended Sediment

A minimum of five grams of material was required to perform most of the chemical analyses (Table 9) on the PLUARG parameter list (IJC-PLUARG, "Quality Control Handbook for Pilot Watershed Studies", 1976). This precluded the use of conventional suspended-sediment sampling techniques. A special large-volume centrifuge system was used to recover a sufficient quantity of suspended material for the required chemical and physical analyses.

The sampling system, which was made available through the Canada Centre for Inland Waters (CCIW), consisted of a sample collection unit and processing unit. Using a submersible pump, approximately 1000 L of stream water including the suspended sediment (referred to as bulk suspended-sediment sample), was collected at each station and stored in plastic sample containers (40 L volume). All the usual sample handling precautions were observed in order to ensure the collection of a representative, uncontaminated sample. The bulk suspended-sediment sample was transported to the processing unit which consisted of a continuous-flow centrifuge and supporting equipment. The bulk suspended-sediment sample was processed through the centrifuge and the sediment recovered for chemical and physical analyses. The supernatant (decanted water sample) was also analysed to confirm the estimates of the pollutant fraction associated with the sediment.

In addition to the bulk suspended-sediment sample, routine water quality samples were also collected at the same time for chemical analyses to verify those concentrations derived from the bulk suspended-sediment and supernatant samples.

10.3.3 Soil

A small, hand-operated auger was used to collect soil samples in the private waste disposal studies. Soil samples from various depths, were analyzed for particle size, permeability, Atterberg limits (ASTM, 1970), phosphate isotherm and the determination of acid-extractable phosphorus (Zarnett, 1975). In the processed organic waste and sanitary landfill studies, a sampling tube as described by the Department of Land Resource Science, O.A.C. (University of Guelph) was utilized in the collection of soil samples. The "T" shaped sampler consisted of a metal tube 20 inches (50.8 cm) in length and 1 inch (2.54 cm) in diameter. A 15-inch (38.1 cm) section of the sampling tube was cut out to facilitate the transfer of the soil core from the sampling tube to an appropriate container for particle size, nutrients, minerals and trace-elements analyses.

The soil cores obtained from the processed organic waste disposal studies were composited to form a single, thoroughly mixed sample. The soil cores were obtained by inserting the sampling tube into the soil to "plow depth" in the field where the processed organic waste (sewage sludge) was being spread. The soil was then stored in a plastic bag to avoid contamination prior to analysis in the laboratory. The number of soil cores collected was based on a minimum of four cores for each hectare.

11.0 LABORATORY MEASUREMENTS

This technical report is not intended to explore the variability in water or sediment quality data resulting from the effects of laboratory measurements; however, for the sake of completeness the quantitative analytical techniques employed by the analyst for waters and sediments are summarized in tables 11 and 12.

Analysts from all participating laboratories conducting water and sediment quality analyses of PLUARG samples were obliged to document analytical methodologies employed in the determination of each parameter. This documentation was forwarded to the IJC Regional Office at Windsor. Involvement of the analysts was encouraged and regular meetings were conducted during the PLUARG planning phase and later during the quality-control program (IJC-PLUARG, 1976: "Quality Control Handbook for Pilot Watershed Studies").

In addition to the split, replicate and comparison sample programs, reference and natural samples were distributed among laboratory participants ("round robins") to intercompare performance on routine water quality determinations. A full-scale exchange of sediment samples was not arranged. Instead, details of analytical methodology were exchanged among a smaller group of analysts active in that field (PLUARG Task C Analysts Meeting, October 28, 1976).

TABLE 11: ANALYTICAL TECHNIQUES USED TO MEASURE WATER QUALITY

CHEMICAL PARAMETER	ANALYTICAL TECHNIQUE
ALKALINITY	Fisher Titralizer; Radiometer A.T.S.
AMMONIUM NITROGEN (FILTERED)	Technicon AutoAnalyzer
ARSENIC	Flameless A.A.S.*; Colorimetry
CADMIUM	A.A.S.*
CALCIUM	Manual EDTA Titration; A.A.S.*
CARBON	Beckman Infrared Analyzer
CHLORIDE	Radiometer ATS: Fisher Titralyzer; Techicon AutoAnalyzer
CHROMIUM	A.A.S.*; Colorimetry
CONDUCTIVITY	Radiometer CDM3
COPPER	A.A.S.*
IRON (TOTAL)	Technicon AutoAnalyzer; A.A.S.*
LEAD	A.A.S.*
MAGNESIUM	A.A.S.*; calculated
MANGANESE	Technicon AutoAnalyzer; A.A.S.*
MERCURY	Flameless A.A.S.*
NICKEL	A.A.S.*
NITRATE + NITRITE -N (FILTERED)	Technicon AutoAnalyzer
KJELDAHL -N	Technicon AutoAnalyzer
REACTIVE PHOSPHATE -P (FILTERED)	Technicon AutoAnalyzer
PESTICIDES (chlorinated HYDROCARBONS)	Solvent Extraction & Gas Chromatography
pH	Radiometer
PHENOLICS-REACTIVE	Technicon AutoAnalyzer (4AAP)
PHOSPHORUS-TOTAL	Technicon AutoAnalyzer
PHOSPHORUS-FILTERED TOTAL	Technicon AutoAnalyzer
POTASSIUM	A.A.S.*
SELENIUM	Fluorometric
SILICATES-REACTIVE	Technicon AutoAnalyzer
SODIUM	A.A.S.*
SOLIDS-SUSPENDED	Gravimetric
SULFATE	Technicon AutoAnalyzer
TURBIDITY	Nephelometric (HAC 1300 or 1300A)
ZINC	A.A.S.*

Microbiological Parameter	Analytical Technique
TOTAL COLIFORMS	Membrane Filtration
FECAL COLIFORMS	Membrane Filtration
FECAL STREPTOCOCCUS	Membrane Filtration

TABLE 12: ANALYTICAL TECHNIQUES USED TO MEASURE SEDIMENT QUALITY

SEDIMENT PARAMETER	PREPARATION	ANALYTICAL TECHNIQUE
ALUMINIUM	Aqua Regia Digestion	A.A.S.*
ARSENIC	Aqua Regia Digestion	Flameless A.A.S.*
CALCIUM	Aqua Regia Digestion	A.A.S.*
CHROMIUM	Aqua Regia Degestion	A.A.S.*
COBALT	Aqua Regia Digestion	A.A.S.*
CHEMICAL OXYGEN DEMAND	H_2SO_4 - Dichromate Digestion	Manual Titration
COPPER	Aqua Regia Digestion	A.A.S.*
IRON	Aqua Regia Digestion	A.A.S.*
LEAD	Aqua Regia Digestion	A.A.S.*
MAGNESIUM	Aqua Regia Digestion	A.A.S.*
MANGANESE	Aqua Regia Digestion	A.A.S.*
MERCURY	Aqua Regia Digestion	Flameless A.A.S.*
NICKEL	Aqua Regia Digestion	A.A.S.*
NITROGEN (TOTAL)	H_2SO_4 - Persulphate Digestion	Automated Colourimetric
PHOSPHORUS (TOTAL)	H_2SO_4 - Persulphate Digestion	Automated Colourimetric
POTASSIUM	Hot HCL Digestion	A.A.S.*
SODIUM	Hot HCL Digestion	A.A.S.*
TIN	Aqua Regia Digestion	A.A.S.*

* Atomic Absorption Spectrophotometry

12.0 RECOMMENDATIONS FOR FUTURE MONITORING

12.1 MONITORING PROGRAM OBJECTIVES

Monitoring program objectives and specific data needs for each monitoring site should be identified before undertaking surveillance. A cost-efficient monitoring strategy should be formulated to meet the objectives of all monitoring programs. Field staff should be acquainted with the operation and maintenance of all monitoring equipment and execute data-collection methods uniformly.

12.2 FIELD PROGRAMS

Field programs should meet the requirements of both the data user and the analyst. The data user should define data requirements to the laboratory support staff as they relate to specific research needs and the laboratory should produce data of a defined quality. Quality-assurance audits for each parameter should be routinely produced by the analyst to document the changes in analytical performance.

12.3 DATA SYSTEMS

Data systems should be flexible to accept changing reporting practices with minor modification. Data systems should be designed to include confidence limits for each parameter as a part of the printout. Coding systems should be instituted to deal with "criterion of detection" so that "less than" values are not included in pollutant loading calculations.

12.4 SEDIMENT QUALITY MEASUREMENT

It is desirable that all sediment quality measurements be performed uniformly with respect to sampling equipment, containers, preservation, storage and collection techniques. Emphasis on uniform sediment quality measurements should be placed upon those commonly measured parameters such as nutrients, mineralogy, trace elements, pesticides and PCBs. Data variability should be measured by undertaking replicate sediment sample programs to examine the effects of sample collection techniques on data quality. During periods of high streamflow, bulk suspended-sediment samples should be collected at those monitoring sites where sediment is enriched with organic and inorganic trace contaminants.

12.5 WATER QUALITY MEASUREMENT

It would be desirable that all water quality measurements be performed uniformly with respect to sampling equipment, containers, preservation, storage and collection technique. Since specific data needs vary among monitoring programs, emphasis on uniform water quality measurements should be placed upon those parameters most commonly measured such as suspended sediment, nutrients and minerals.

The need exists for the development of specific-ion electrodes for in-situ water quality measurements of dissolved phosphorus, reactive phosphorus, Kjeldahl nitrogen, nitrate nitrogen, nitrite nitrogen and ammonium nitrogen. Further refinement of automatic samplers designed for tributary surveillance is necessary to ensure the collection of representative, uncontaminated samples.

12.6 SURFACE WATER

Frequent sample collection, during periods of highest streamflow, should be ensured at monitoring sites selected to estimate annual pollutant loads. Data variability should be measured by undertaking replicate and comparison water-sample collection programs to examine manual and automatic-sample collection effects on data quality.

12.7 GROUND WATER

The need exists for demonstration projects to examine ground-water sample collection apparatus and techniques for the collection of representative, uncontaminated samples.

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