ASSESSMENT OF SURFACE AND GROUND WATERS, STREAM AND ESTUARY SEDIMENTS AND OTHER ECOSYSTEM RECEPTORS TO DETERMINE LONG TERM IMPACTS OF SURFACE PCB AND HEAVY METAL RELEASES, MAKINSONS, NEWFOUNDLAND

JASON BOURGEOIS

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BY

JASON BOURGEOIS

A thesis submitted to the School of Graduate Studies in partial fulfilment
of the requirements for the degree of Master of Science

Department of Earth Science
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ABSTRACT

As part of a National Contaminated Sites Remediation Program (NCSRP), FFC/BEAK (1992*d*) identified polychlorinated biphenyl (PCB) and heavy metal contamination from an old salvage yard at the top of a small drainage basin located in Makinsons, Newfoundland. Given the lack of understanding of how PCBs and heavy metals are distributed and attenuated in small drainage basins that consist of thin overburden underlain by fractured bedrock, a study was undertaken with the main objective of determining how PCBs and heavy metals are distributed in the surface waters, ground waters, soils, sediments within the stream and estuary, and bivalve bioreceptors (*Mercenaria mercenaria*). It was necessary to describe the spatial distribution of PCBs and heavy metals in order to determine the role that these waters, sediments, and bioreceptors, play in contaminant transport within this small drainage basin.

There is evidence that the salvage yard is contributing PCBs, Cr, As, MnO, Fe_2O_3, and Pb to the Makinsons drainage basin. The major pathway is believed to be surface runoff carrying contaminants adsorbed on sedimentary and particulate matter from the salvage yard to the stream. However, PCBs were unexpectedly detected in stream sediments and soils located upgradient from the salvage yard, suggesting an additional source of PCB contamination. This additional source probably relates to the oiling of roads to control dust before they were paved.

Based on the surface water and ground water chemistry described in this study, mobilization of dissolved metals from the salvage yard-bog area was found to be negligible. Relatively neutral pH (> 6) conditions detected in drainage basin ground waters most likely limited the aqueous solubility of metals and resulted in the predominant species being adsorbed to the soil framework. An additional source of contamination to the drainage basin is suspected to include domestic septic effluent. *M. mercenaria* collected from the South River estuary were enriched in Fe, Ni, Mn, Cd, Cr, and Pb, relative to average concentrations of *M. mercenaria* collected along the Atlantic coast of the US. However, PCBs were not present ≥ 0.05 ppm (wet weight) in *M. mercenaria* from the estuary. Therefore, PCBs adsorbed on suspended material are either being deposited closer to the salvage yard or are being diluted by uncontaminated suspended matter. Regardless, PCBs are not available to these relatively immobile bioreceptors in the estuary.

ACKNOWLEDGEMENTS

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Many thanks and apologies to Graham Dillabough and Sandy Archibald whom I incessantly badgered for the use of their school supplies. Terry Christopher generously provided the use of sediment coring equipment and crucial advice on core collection. Special thanks to Mr and Mrs. Hector Belbin of Clarke's Beach for the cake and coffee after a few hard days of rowing.

I would also like to thank my homes away from home: especially the Molloys in St. John's and also the Buckles in St. John's and Jackmans in St. Phillips. My entire family never ceased in their encouraging support throughout this ordeal. Moire Wadleigh deserves a special thanks for a loan of $5 the very first time I met her. She surely must have thought, "What in the world am I getting involved with". Special thanks to John and Colin at Discovery Graphics and the staff at St. Stephen's Elementary School in Stephenville who were very helpful with the final drafts of the thesis.

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Chapter 1. INTRODUCTION

1.1 Background

Since the 1930s, polychlorinated biphenyls (PCBs) have been utilized as dielectric materials in electrical capacitors and transformers, plasticizers in certain waxes, in paper manufacturing, and for various industrial purposes (Addison, 1983 and Menzer and Nelson, 1986). PCBs refer to biphenyl molecules containing 1-10 chlorine atoms (McDonald and Tourangeau, 1986) (Figure A.1), of which 80 congeners are commonly produced (Abarnou *et al.*, 1987). Their extreme resistance to degradation makes them very useful in the electrical industry and also contributes to their environmental persistence (Hutzinger *et al.*, 1974). The exclusive manufacturer of PCBs in North America (Monsanto Company) (Nisbet and Sarofim, 1972) voluntarily restricted their production in 1970 when they were recognized as persistent and possibly hazardous environmental contaminants (Addison, 1983). Concern over the introduction of PCBs into the environment is based on the fact that biological organisms tend to accumulate these compounds even when ambient levels in water and sediments are below critical concentrations. Experimental studies have shown that high levels of PCBs cause cancer in laboratory animals and it is suspected they promote cancer in humans (McDonald and Tourangeau, 1986).

PCBs can migrate along atmospheric, ground water, and surface water pathways. The relatively high vapour pressures of PCBs allow them to be released into the atmosphere by evaporation from exposed, contaminated soils or electrical containers

(Oloffs *et al.*, 1972; Standley and Hites, 1991; and Strachan, 1988). Most airborne PCBs will be adsorbed on particulates which may contain PCB concentrations of up to 80 ppm. They are transported by wind, and deposited on land and water within 2 or 3 days (Nisbet and Sarofim, 1972). The extremely low aqueous solubility of PCBs (approximately 50 to 200 ppb, Nisbet and Sarofim, 1972) limits the possibility for substantial migration of large quantities in ground water (Freeze and Cherry, 1979). In addition, when the positively charged PCBs are transported by ground water they bind to the negatively charged clay particles that form the soil framework (Nisbet and Sarofim, 1972). In contrast to ground waters, flowing surface waters, with their greater load of negatively charged suspended and particulate matter, are assumed to be the main mode of PCB transport within aquatic environments (Dexter and Pavlou, 1978; Nisbet and Sarofim, 1972; and Pavlou and Dexter, 1979). It is proposed (Nisbet and Sarofim, 1972), that approximately 60 % of PCBs released to the environment are deposited with the fine grained sediments at the bottom of rivers or lakes near their point of release. Increases in salinity is also known to reduce concentrations of dissolved and particulate phase PCBs in estuarine waters (Dexter and Pavlou, 1978; Duinker *et al.*, 1982; and Latimer, 1989). The fine grained particles flocculate into large aggregates and sink (Dyer, 1979 and Latimer *et al.*, 1991). Consequently, PCBs display non-conservative behaviour in estuarine systems since colloidal bound contaminants destabilize when salt and fresh waters mix.

1.2 Previous Work

Large scale, compartmental studies on the distribution of PCBs in *terrestrial* (Anderson and Pankow, 1986; Atwater, 1984; Boyd and Sun, 1990; Roberts *et al.*, 1982; and Schwartz *et al.*, 1982), *coastal* (Brownawell and Farrington, 1986; Greig and Sennefelder, 1985; Harvey and Steinhauer, 1976; and Weaver, 1984), *estuary* (Abarnou *et al.*, 1987; Bopp *et al.*, 1981; Herrmann et al., 1984; and Latimer *et al.*, 1991), and *river* systems (Law *et al.*, 1991) are numerous throughout the literature. Also the distribution of PCBs among specific bioreceptors has been thoroughly investigated (Courtney and Denton, 1976; Farrington *et al.*, 1983; Hargrave *et al.*, 1992; and Langston, 1978). Few, if any, of these studies involve a complete investigation into the migration of PCBs in surface waters and ground waters, their deposition in stream and estuary sediments, and accumulation by other ecosystem receptors.

Environmental concerns have led to the implementation of programs such as the National Contaminated Sites Remediation Program (NCSRP) that are designed to identify and remediate old contaminated sites. As part of the NCSRP program, FFC/BEAK (1992*d*) identified PCB and heavy metal contamination from an old salvage yard at the top of a small drainage basin located in Makinsons, Newfoundland, Canada (Figure 1.1). The drainage basin includes a stream approximately 3 km in length that flows into South River (approximately 1/2 km wide and 4 km in length) (Figure 1.2). Operations at the salvage yard consisted of recovering metal from old electrical transformers containing PCB

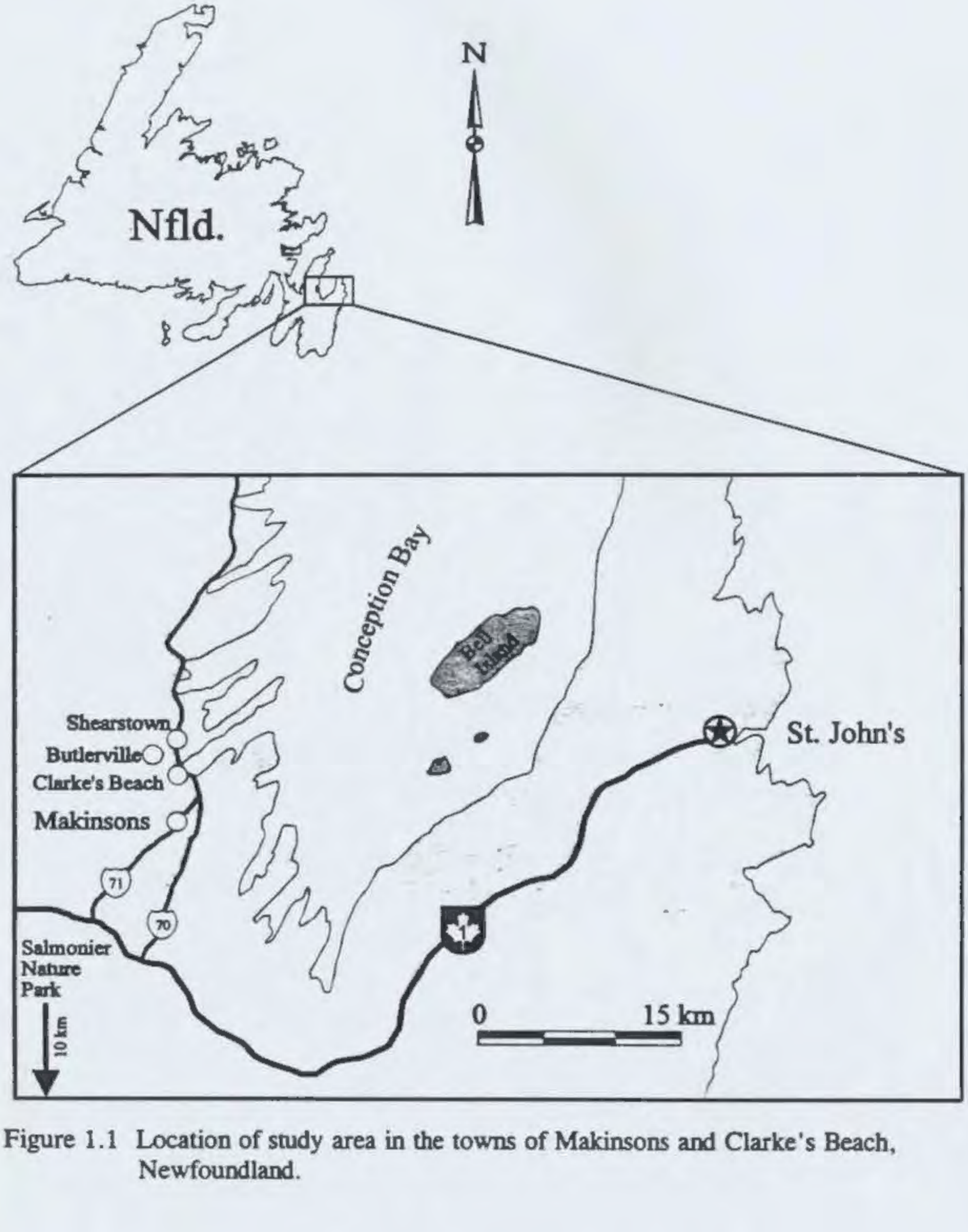


Figure 1.1 Location of study area in the towns of Makinsons and Clarke's Beach, Newfoundland.

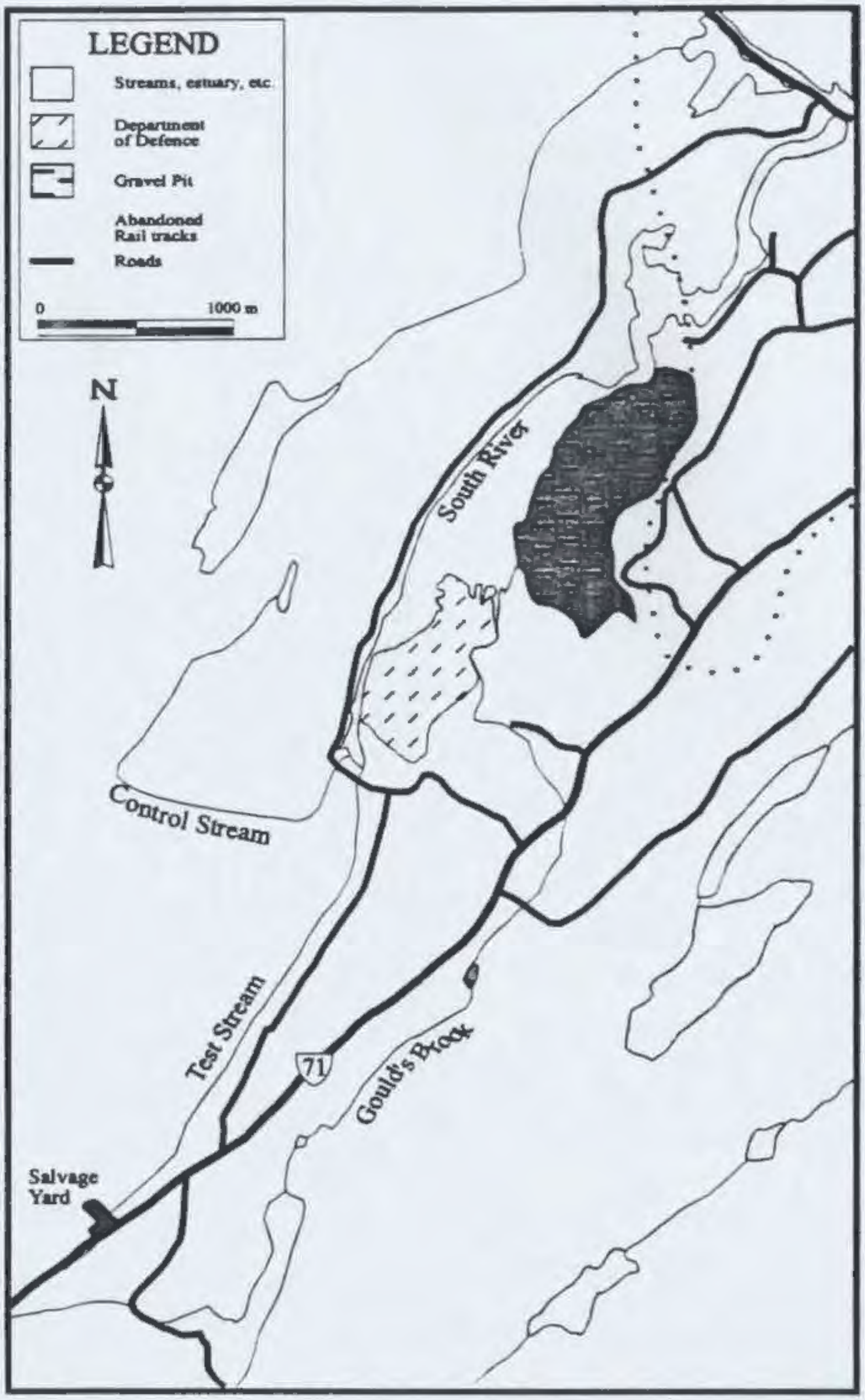


Figure 1.2 Regional map of study area indicating the salvage yard, test stream, estuary, additional streams and ponds, roadways, etc.

contaminated oil. Most of the salvage work was performed during the period of 1975-1985 and all operations were suspended by 1989 (FFC/BEAK, 1992*d*).

The detailed work within the salvage yard identified PCB concentrations of up to 470 ppm in soil. In addition, FFC/BEAK (1992*d*) detected 7 metals (Sb, Ba, Cd, Pb, Sn, V, and Zn) whose median concentrations in salvage yard soil samples were present above remediation criteria set by the Canadian Council of Ministers of the Environment (CCME), 1991). Median concentrations ($n = 10$) of all metals investigated within the salvage yard (FFC/BEAK, 1992*d*) are displayed in Figure 1.3. However, the primary focus of the NCSRP program was remediation of contaminated sites and the detailed investigations by FFC/BEAK, (1992*d*) were not extended to the lower part of the stream and the estuary.

Reconnaissance work was performed within the drainage basin (FFC/BEAK, 1992*d*) and PCB concentrations of up to 29 ppm were discovered in stream sediments within 100 m downstream of the salvage yard, which decreased to 0.1 ppm approximately 1.5 km downstream (Figure 1.4). The results of this reconnaissance work (FFC/BEAK, 1992*d*) and the duration of salvage activity (approximately 25-30 years), suggest that PCBs have been migrating from the salvage yard-bog area into the downstream ecosystem for a significant period of time. However, there have been no detailed investigations to determine how the PCBs and heavy metals are distributed in the downstream basin or whether they are available to bioreceptors in the South River estuary.

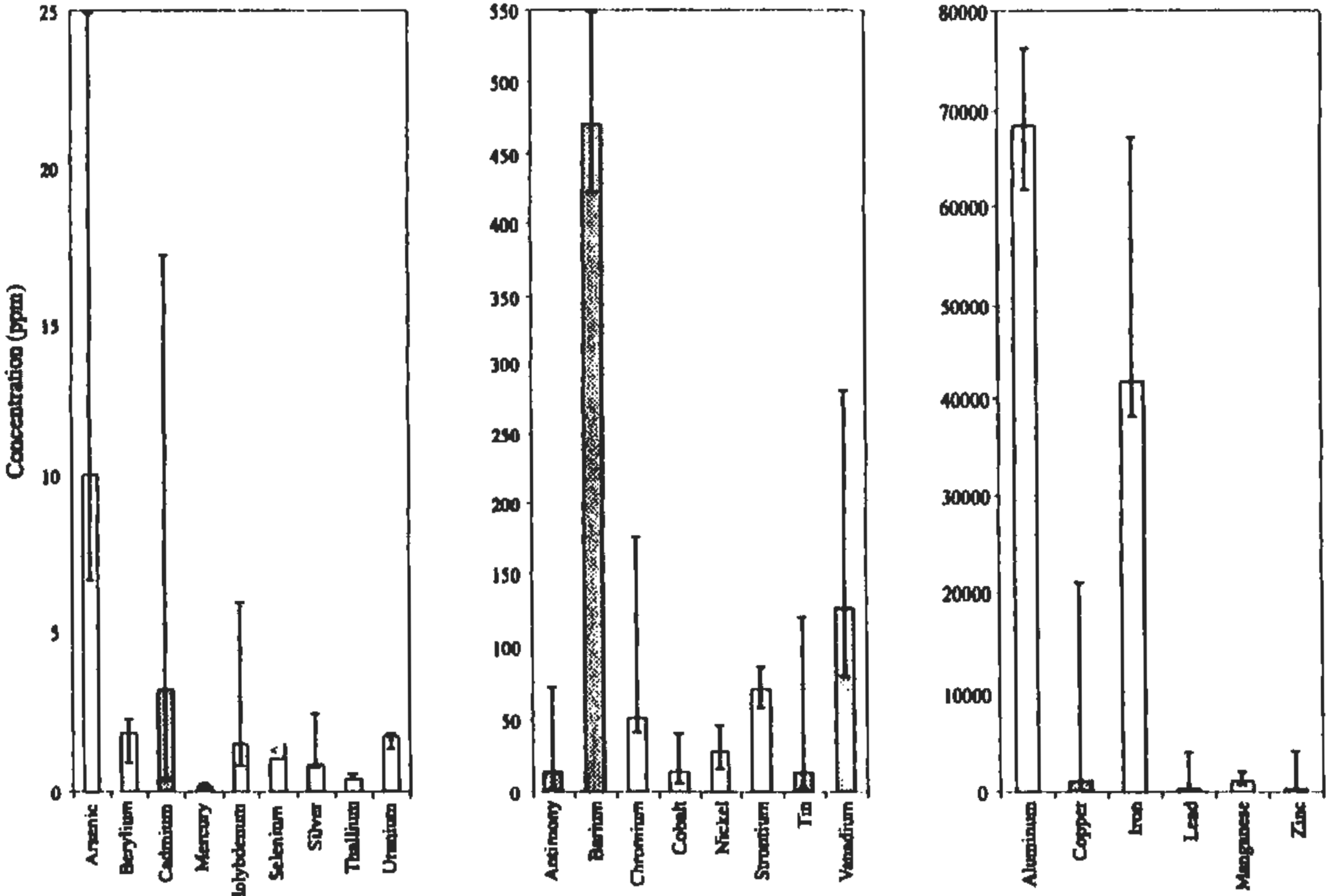


Figure 1.3 Median metal concentrations (bars) detected in salvage yard soils (FFC/BEAK, 1992*d*). The concentration range of each metal (i.e. minimum and maximum values) is included as a vertical bracket. Median metal concentrations detected above remediation criteria (CCME, 1991) are included as shaded bars.

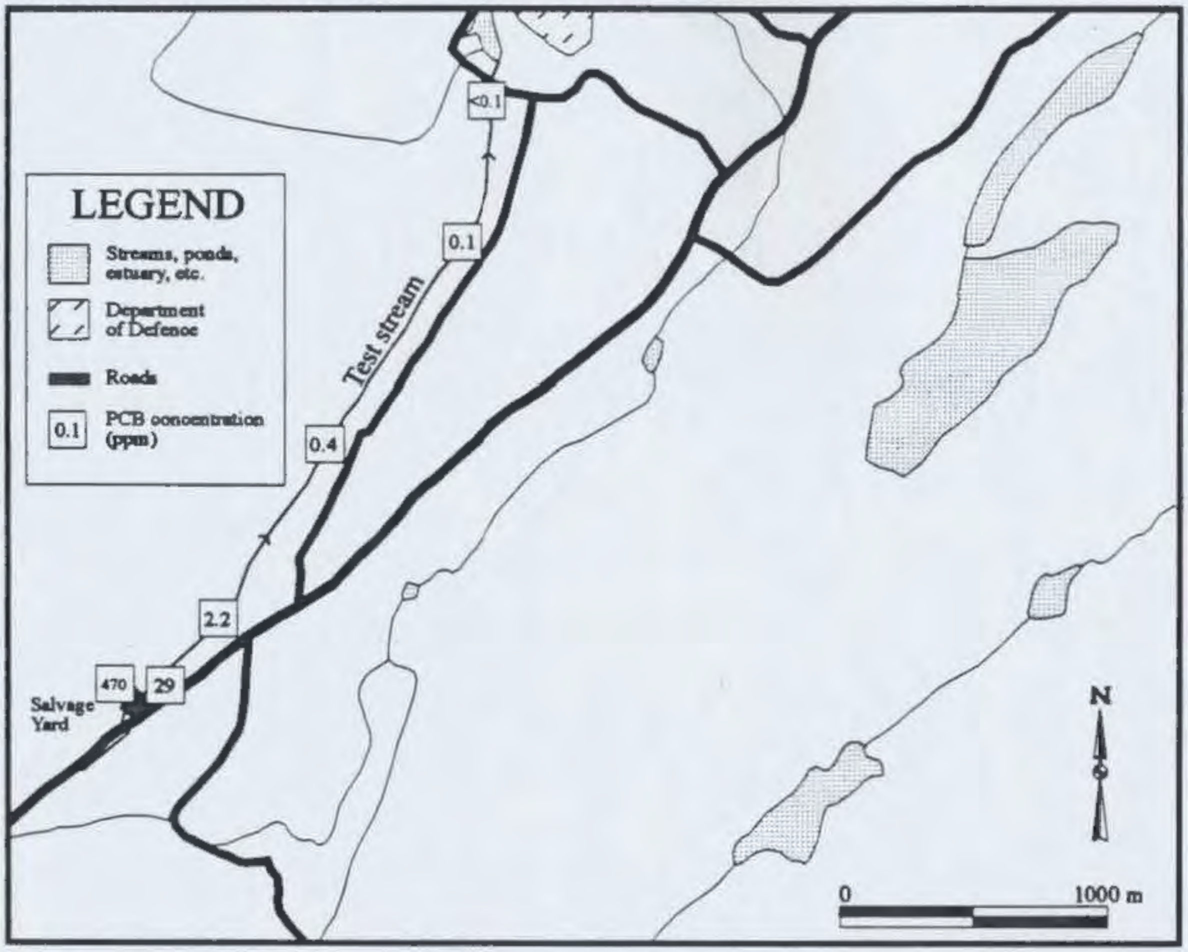


Figure 1.4 Maximum PCB concentrations detected in salvage yard and stream sediments (modified from FFC/BEAK 1992*d*). Arrows indicate direction of stream flow.

1.3 Objectives and Scope

Numerical simulation of surface water / ground water interaction, including the response of drainage basins to precipitation, has become increasingly important in order to determine the influence of physical hydrogeology on contaminant migration. Given the lack of understanding of how PCBs and heavy metals are distributed downstream from contaminant releases in small drainage basins consisting of thin overburden underlain by fractured bedrock, a study was undertaken with 2 main objectives. The first objective, was to determine how PCBs and heavy metals are distributed in the surface waters, ground waters, sediments within the stream and estuary, and other ecosystem receptors (i.e. clams). This objective was intended to document the extent of contamination downstream from the salvage yard-bog area. The second objective was to identify the roles that surface waters and ground waters, sediments within the stream and estuary, and other ecosystem receptors, play in the attenuation and migration of PCB and heavy metal releases. Based on similar investigations in the literature, the spatial distribution of PCBs and heavy metals in the Makinsons study area, and the hydrogeological and geochemical framework, these roles were considered as major or minor pathways, and / or major or minor receptors.

In order to accomplish these goals, a variety of techniques were employed. Firstly, the MODFLOW three-dimensional finite-difference code was used to numerically simulate ground water flow within the Makinsons drainage basin. These simulations were aimed at estimating the distribution of discharge and recharge areas in order to determine the potential for contaminant migration. Next, the spatial distribution of PCBs and heavy metals within the Makinsons drainage basin was described. This was made possible through a sampling / analytical program consisting of ground water samples, surface water samples, stream sediment samples, soil samples, and bedrock samples, collected from the Makinsons drainage basin. In addition, sediment cores and homogenized clam (*Mercenaria mercenaria*) samples were collected from South River. Any relationships observed in the data sets were corroborated using the SYSTAT statistical computer package. Finally, the MINTEQA2 geochemical speciation model was used to calculate mineral saturation indices for all the surface water and ground water samples. This technique was valuable in determining whether precipitation of dissolved metals was a significant influence on sediment and soil chemistry.

Chapter 2. HYDROGEOLOGICAL FRAMEWORK

2.1 Background

The Makinsons drainage basin is underlain by two major bedrock units of Hadrynian age (Late Precambrian) (Hutchinson, 1953 and McCartney, 1954). The oldest unit is the Conception Group which is overlain conformably by the St. John's Group (Williams and King, 1979) (Figure 2.1.1). The Conception Group includes a 2 to 5 km thick series of rocks that represent extensive turbidite and pelagic sedimentation (Williams and King, 1979). The bulk of the Conception Group consists of the lowermost Drook Formation, characterized by green siliceous siltstone and sandstone with some silicified tuff (King, 1980). The Mistaken Point Formation marks the top of the Conception Group (Williams and King, 1979) and contains bedded tuffaceous siltstones and sandstones (gray to pink), shales (green to purple and red), some minor tuff horizons, and metazoan fossils (King, 1988). The St. John's Group consists of a 2 km thick deltaic series of marine shales and interbedded sandstones (Williams and King, 1979) that progrades and thickens southward (King, 1988). The lowermost Trepassey Formation consists of medium to thinly bedded, graded, gray sandstone and shale, with some minor tuffaceous rocks (King, 1988). This formation constitutes a transitional zone into the underlying Mistaken Point Formation (Conception Group). The Fermeuse Formation is the middle unit of the St. John's Group (Williams and King, 1979) and consists of shale (gray to black) containing lenses of buff-weathering sandstone and siltstone, and mainly light gray, thinly bedded, contorted shale and sandstone at the base (Williams and King, 1979).

The Conception Group aquifer has been found to yield between 0.6 and 136.5 L/min (ave.= 20.1 L/min) whereas the St. John's Group yields 1.1 to 364 L/min (ave.= 27.4 L/min)

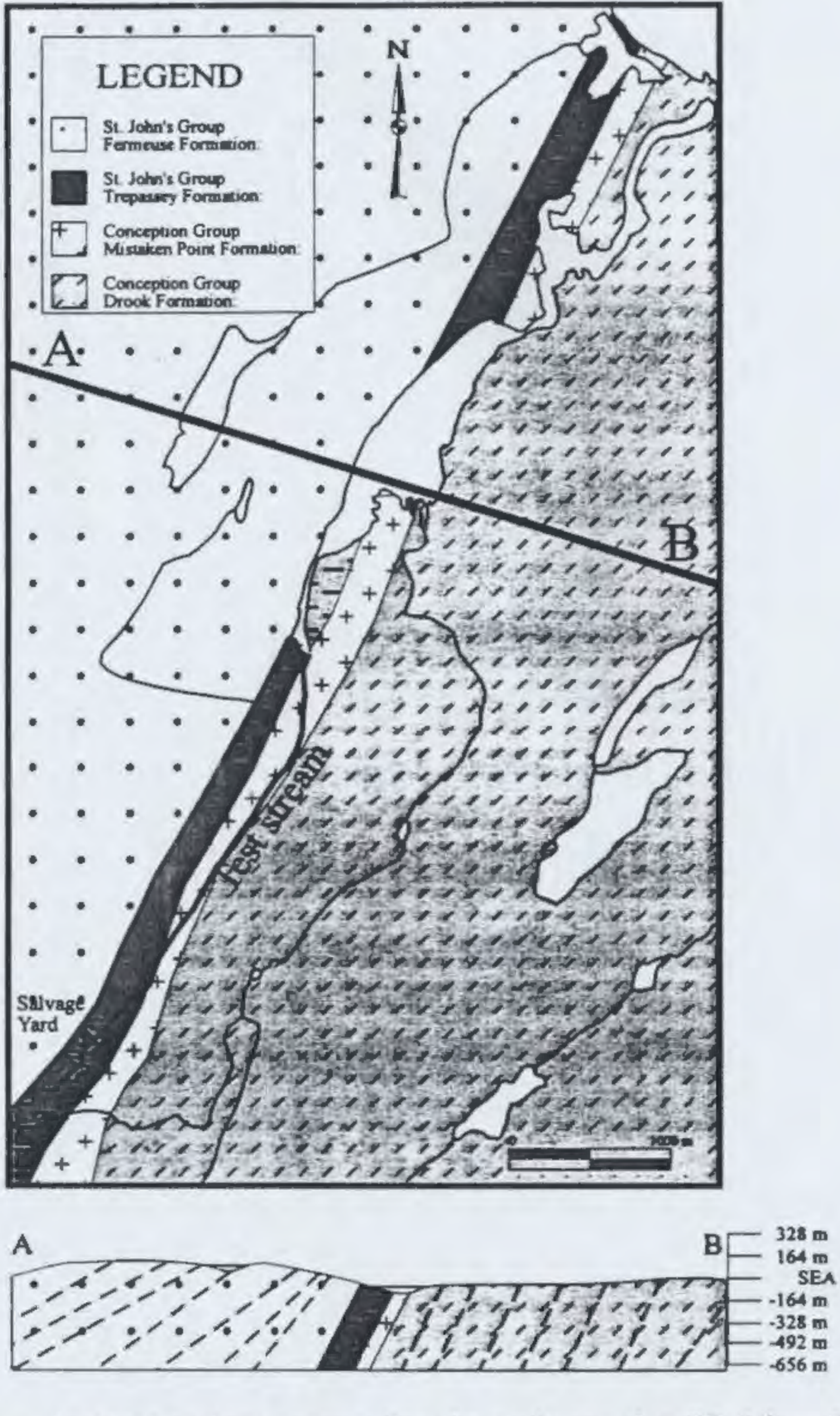


Figure 2.1.1 Regional geology surrounding the study area (modified from King, 1988). Cross section (looking north-northeast) indicates thickness of formations and orientation of bedding.

(Gale *et al.*, 1984). Therefore, the Conception Group is classified as an aquifer of low to moderate yield whereas the St. John's Group is an aquifer of moderate yield (Gale *et al.*, 1984). Flow in the bedrock aquifer most likely occurs through fractures because matrix porosity and permeability are too low to contribute to the yield of the wells completed in these rock groups. FFC/BEAK (1992*d*) detected weathered and / or fractured green siltstone beneath the overburden in the salvage yard and the upper 4 to 5 m of the bedrock is probably more intensely fractured than at depth. Matrix diffusion involving microcracks and fissures, however, may also play a role in determining the fate and transport of contaminants.

Surficial geology of the Makinsons drainage basin consists of four different types of glacially derived material (Henderson, 1972) (Figure 2.1.2). The surficial geology around and east of the salvage yard includes mostly ground moraine (continuous cover) and stony till 1.5 to 6 m thick. The area west and north of the salvage yard contains ground moraine (discontinuous cover) and a thin till cover with some ledges and knobs of rock outcrop. Small areas adjacent to the streams are underlain by modern stream deposits. Closer to the coast (Clarke's Beach), the surficial geology consists mainly of outwash deposits (gravel, sand, silt), kames, outwash plain, valley train and delta (Henderson, 1972). Based on the grain size distribution, the overburden in the salvage yard is estimated to have a low hydraulic conductivity (10^{-7} to 10^{-10} m/s) (FFC/BEAK, 1992*d*). The overburden and fractured bedrock most likely act as two separate, but coupled, aquifer systems with the overburden behaving as heterogeneous porous media while the fractured bedrock would follow typical fracture flow and transport processes. The dominant soil type in the drainage basin is Cochrane soil

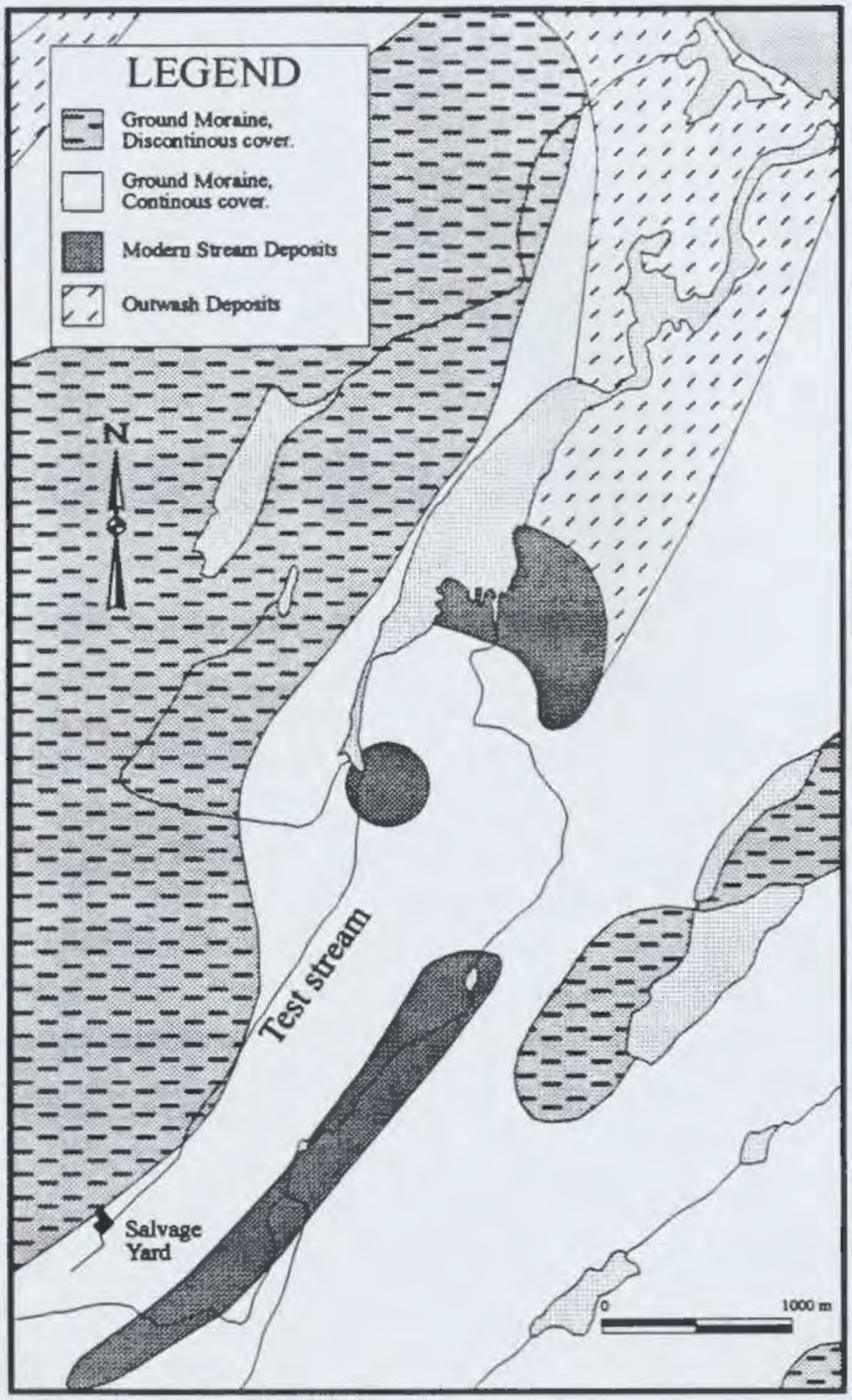


Figure 2.1.2 Surficial geology surrounding the study area (modified from Henderson, 1972).

(Heringa, 1981). Its color is dark olive gray and the parent material is medium textured, dark olive gray glacial till derived mainly from gray slate and some siltstone.

Surface water hydrology in the Makinsons drainage basin was inferred from 1:5000 topographical map and 1:3750 aerial photograph review. The salvage yard is located just below the headwaters of a small, intermittent stream containing several smaller tributaries and ditches which all drain the same basin (Figure 2.1.3). The stream bed consists of gravel, fine sand, silt, clay, and organic materials. It is rocky in most places but sometimes includes sediment between boulders and in small calm eddies. A small valley, detected using a Geonics EM31 electromagnetic instrument, in the bedrock topography just below the salvage yard (FFC/BEAK, 1992*d*), appears to coincide with the stream course and suggests that bedrock may play a role in the development of surface drainage. However, surface topography is considered to be the major factor controlling surface hydrology in the study area. The steep topography (sloping up to 30 %) west of the salvage yard (Heringa, 1981) together with the paved surface of Hodgewater Line (Route 71), most likely channel surface water and local ground waters into the relatively flat bog area just below the salvage yard. The stream originates at approximately 70 m (above mean sea level) and flows into South River approximately 3000 m downstream. Generally, the water table is less than 0.5 m below ground surface within 5 m of the stream, and approximately 1 m below ground surface at 20 m from the stream (FFC/BEAK, 1992*d*). The local aquifer is most likely discharging to the stream since ground water recharge is expected in topographic highs and discharge in topographic lows (Figure 2.1.4). Considering these surface water-ground water interactions,

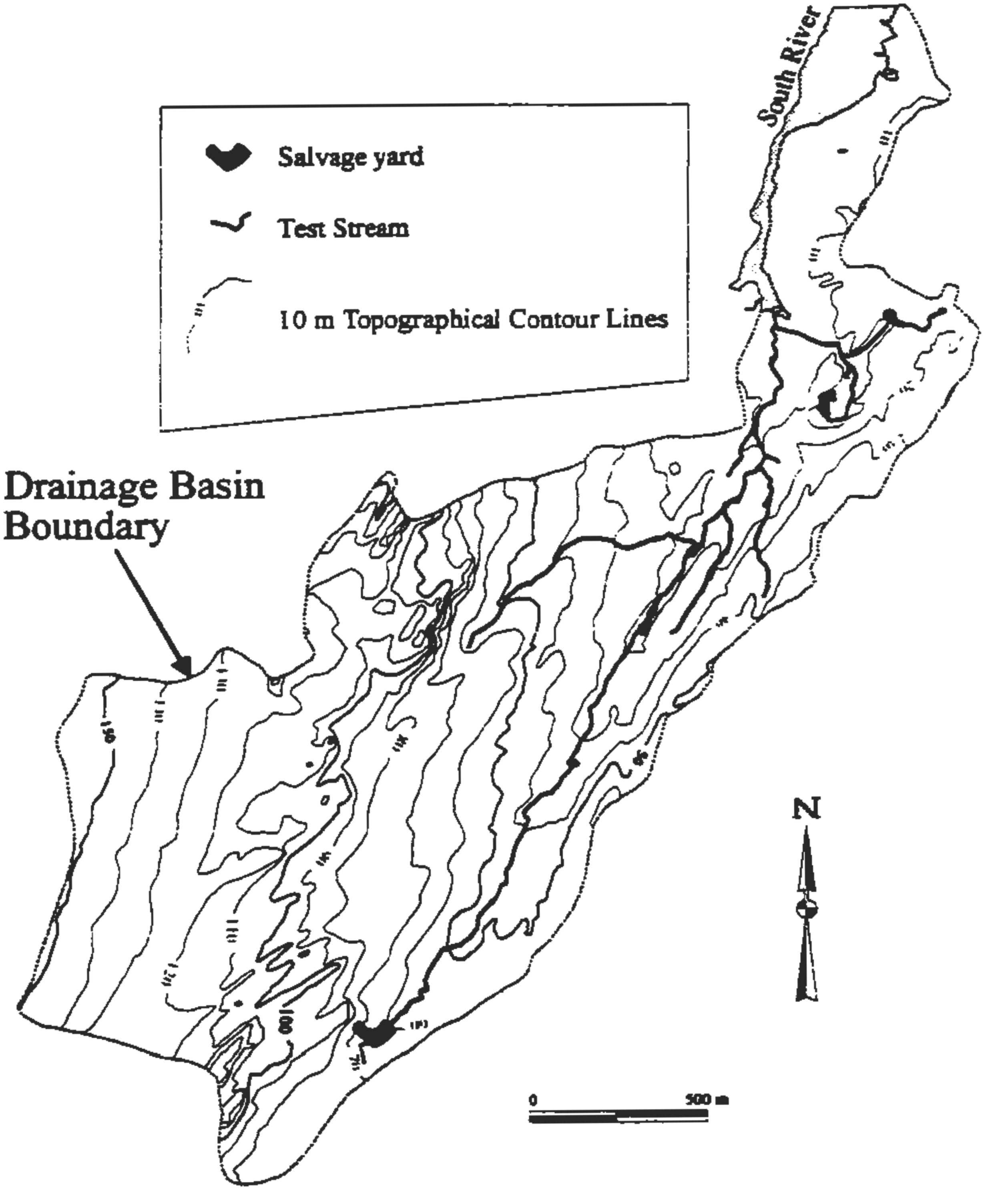


Figure 2.1.3 Drainage basin, stream, and topographic contours.

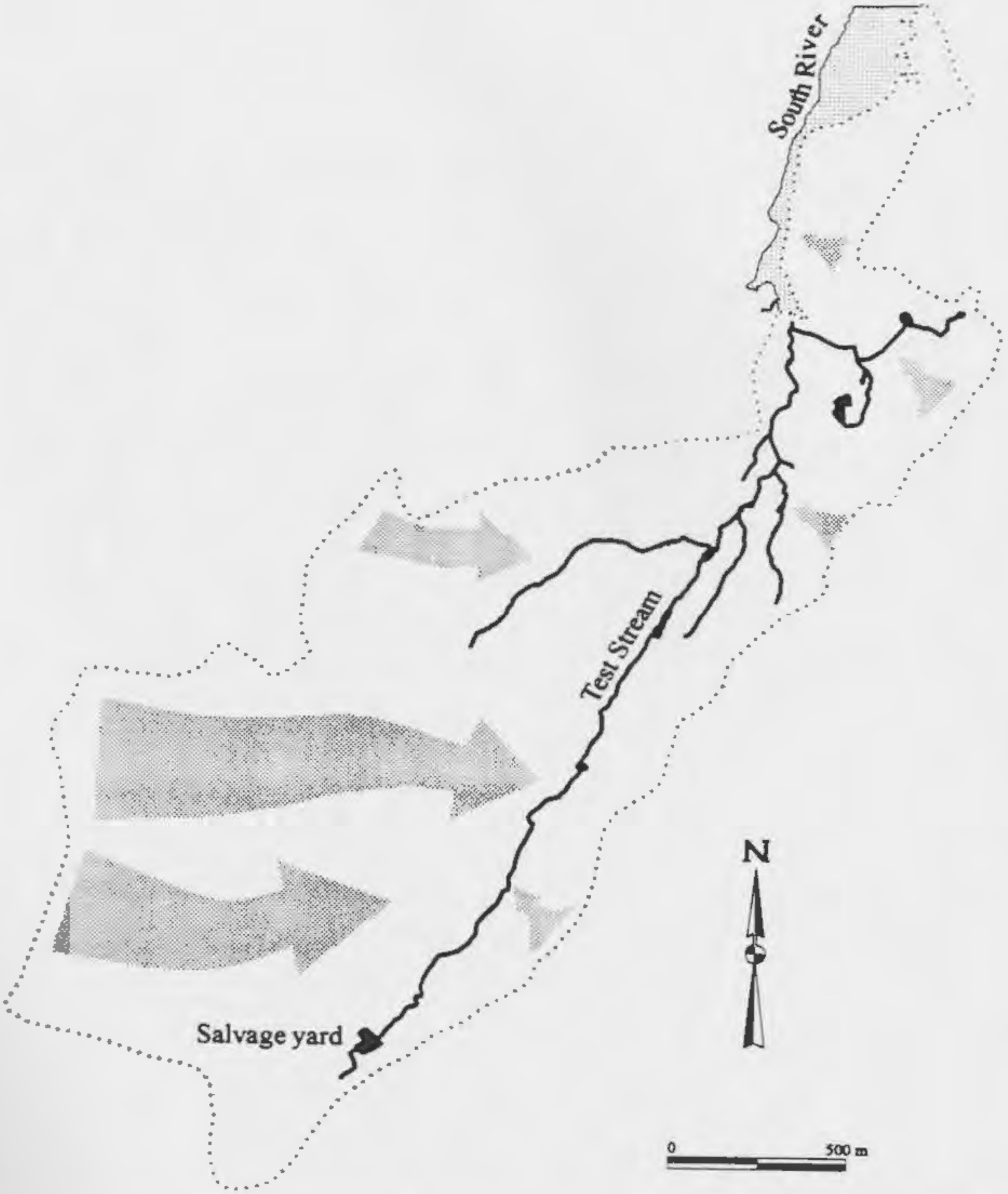


Figure 2.1.4 Drainage basin (dotted line) and stream outlines (dark solid lines), and inferred direction of ground water flow.

it is expected that surface flow rate will increase along the test stream as it flows through the basin. Flow rates were estimated by measuring the surface velocity and cross sectional area of the stream at 13 locations where surface water samples were collected. Flow rate generally increased downstream, yet variations were observed at different points along the stream. This may suggest that flow occurs through the gravel in the stream bed at certain locations.

Additional fresh water sources to South River include a small stream (control stream) draining a different basin northwest of the test stream and a larger stream (Gould's Brook) entering approximately 1 km further seaward (see Figure 1.2). South River is essentially an inlet of the sea and can be described as a region of mixing of fresh and salt waters (i.e. estuary).

2.2 Field Investigation

Figure 2.2.1 includes the topographic gradient and the relative stream flow (L/min) along the test stream. The headwaters of the stream originate at 70 m (above mean sea level) and flow into South River approximately 3 km downstream. The general pattern is one of increasing flow as the stream flows through the basin. Ground water flow is perpendicular to the potentiometric contours (towards stream) (Figure 2.2.2) and was inferred from water table elevations measured in the mini-piezometers. Therefore, the stream is "gaining" (Fetter, 1988) at both locations since ground water is being discharged to the stream. Hydraulic gradients at the four piezometer locations (i.e. SOW1 to 3, SOW4 to 6, SOW7 to 9, and SOW10 to 12) are estimated to be 0.006, 0.008, 0.03, and 0.009, respectively. Figure 2.2.3 is a three-dimensional perspective view of the Makinsons drainage basin topography and highlights the location of the small valley where the test stream flows.

Stream dimensions vary along the course with small "waterfalls" in areas of steeper gradient and small "steadies" in areas with shallow gradient. In some locations, the stream is barely visible through the rocks, and flow appears to be diverted under or adjacent to the stream bed. This is most likely the reason for the significant variation in stream flow between 2000 and 3000 m (Figure 2.2.1). Flow ranged from approximately 1 L/min near the headwaters (STW1) to over 1000 L/min near the bottom of the basin (STW12). The ditches and tributaries appear to contribute very little to the total volume of water flowing in the stream (Figure 2.2.1). At each location, the cross sectional area of the stream displayed irregular geometry, therefore the flow rates are not exact but provide sufficient insight in

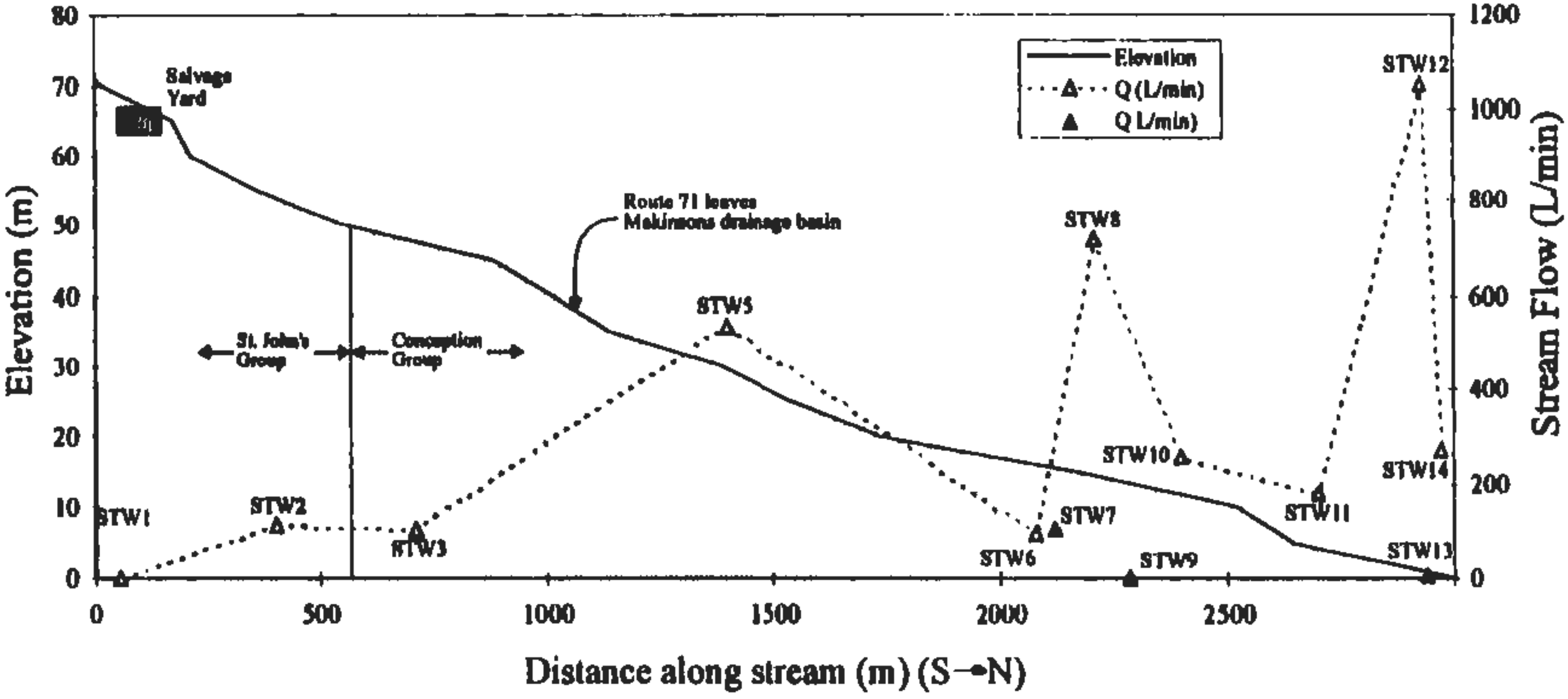


Figure 2.2.1 Topographic gradient (m) and relative stream flow (Q) (L/min) along test stream. The hollow triangles indicate locations along the main course while the solid triangles are tributaries. Vertical exaggeration is 10X.

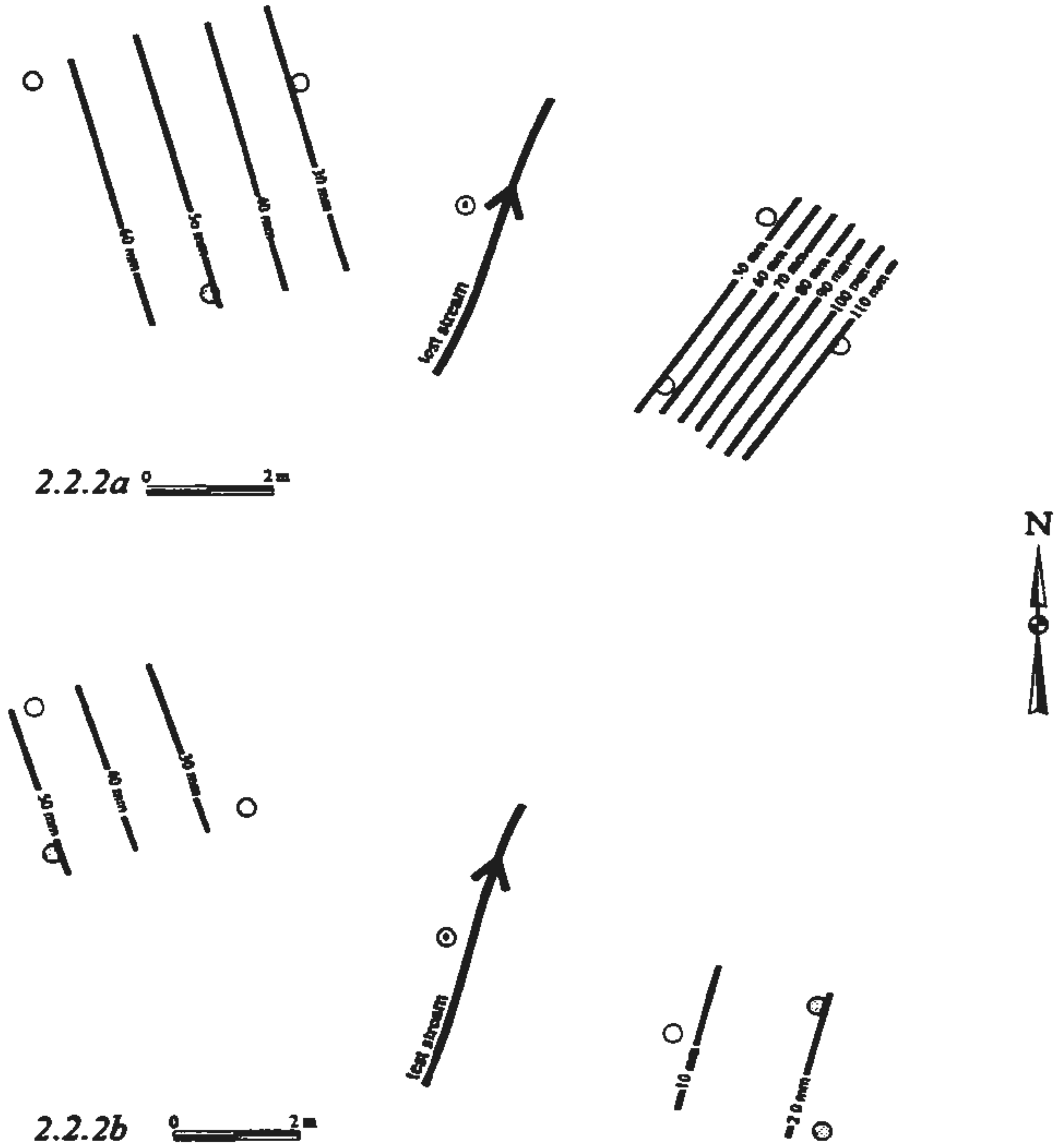


Figure 2.2.2 Potentiometric surfaces (mm) at each of the four locations of "mini" piezometers. The hydraulic head of the stream is arbitrarily defined as zero and the heads in the piezometers are calculated relative to the stream. a) is located approximately 200 m upstream from the top of South River and *b)* is located approximately 175 m downstream from the salvage yard. The arrows indicate direction of surface water flow.

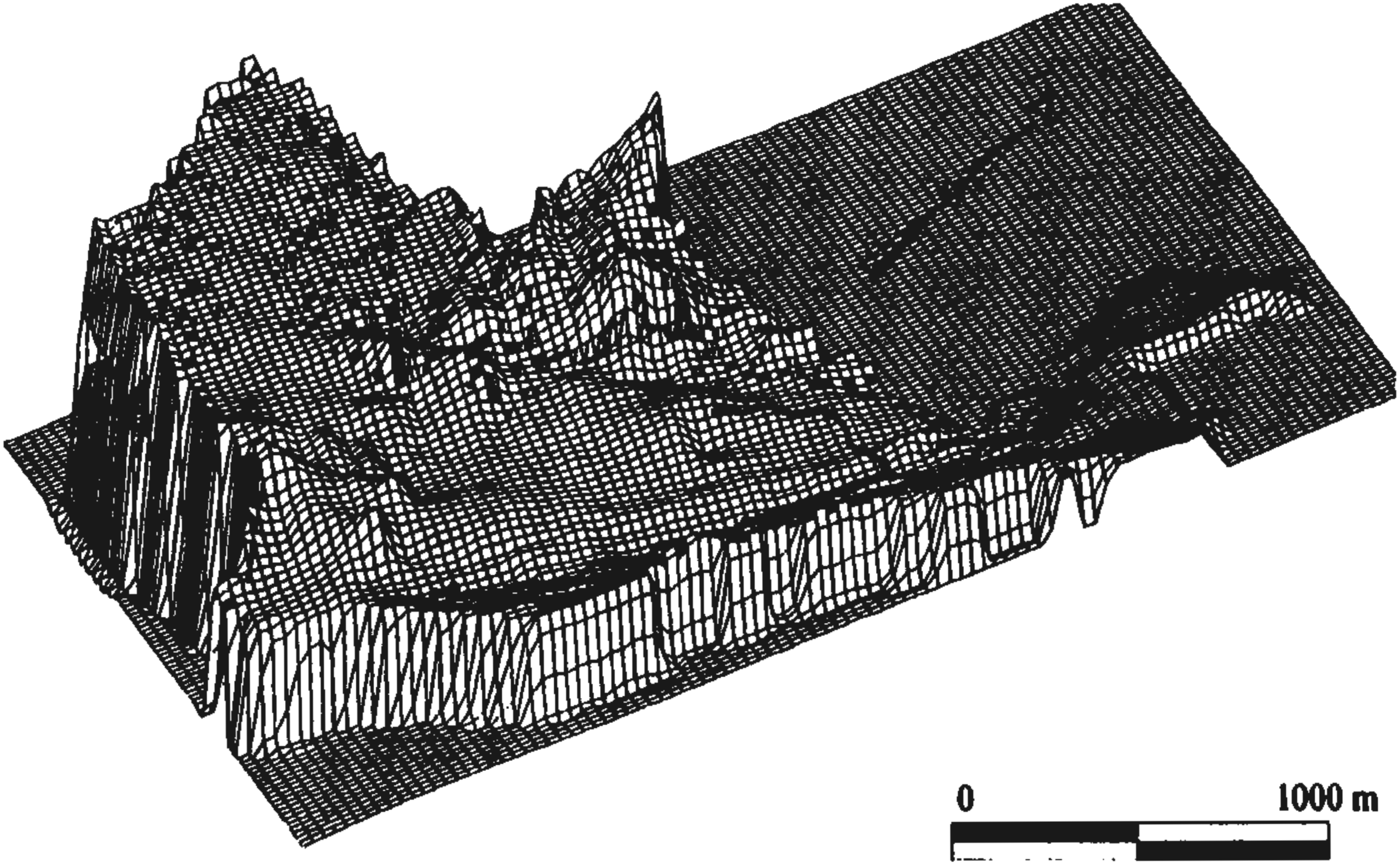


Figure 2.2.3 Perspective view of the topography in the Makinsons drainage basin. The view is towards the north-east and vertical exaggeration is 2X.

order to describe variation in flow conditions along the stream. Unfortunately, these stream flow measurements were collected on July 13, 1995 and it should be noted that the water table conditions were the lowest observed throughout the entire period of study (1993-1995). It was assumed that relative stream flow varied consistently during different hydrologic conditions, therefore the time of year when measurements were collected was irrelevant.

Any seasonal variation in stream flow is most likely influenced by precipitation and temperature. Figure 2.2.4 contains the monthly variation in precipitation, recorded at the nearest Environment Canada station (Butlerville), over the sampling period (1994). Butlerville is located approximately 7 km north-west of Makinsons (see Figure 1.1) and provides a history of precipitation in the area during 1994. Figure 2.2.5 includes daily variation in precipitation at Butlerville and also daily variation in stream flow from the nearest Newfoundland Department of Environment station at Shearstown. Shearstown is located approximately 8 km north of Makinsons (see Figure 1.1) and should provide insight into variation in stream flow conditions in the general area during 1994.

August was subject to the greatest temperature, least precipitation, and relatively lowest stream flow (Figures 2.2.4 and 2.2.5). Temporal variation of salinity throughout the upper portion of the South River estuary corresponds to Figures 2.2.4 and 2.2.5 (see Figure B.1). Salinity increases in South River from June to August but decreases significantly in November. This pattern is most likely due to minimal rainfall and increased evaporation during the summer (Figure 2.2.4).

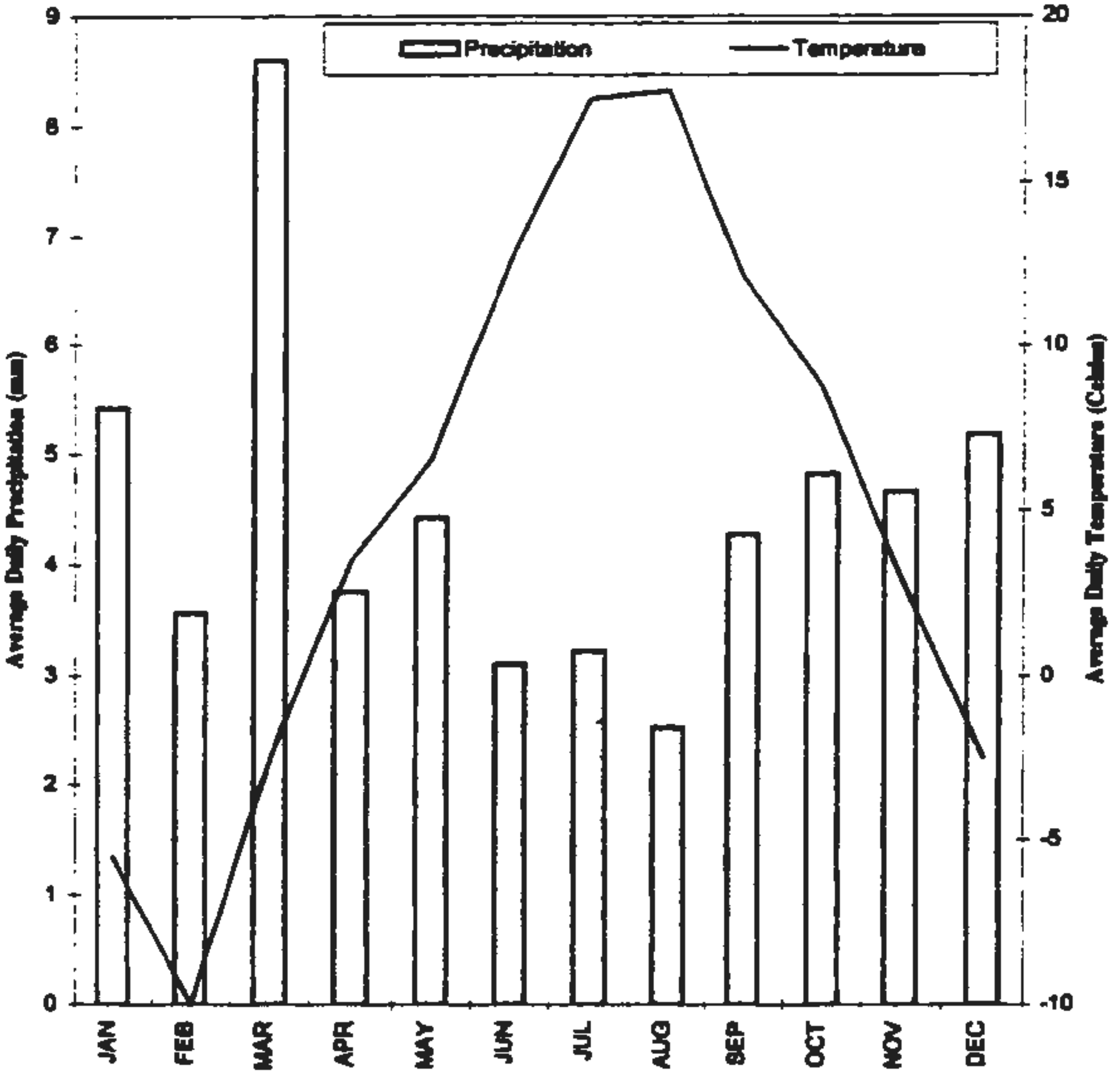


Figure 2.2.4 Monthly variation in precipitation and temperature recorded at Butlerville, Newfoundland (1994).

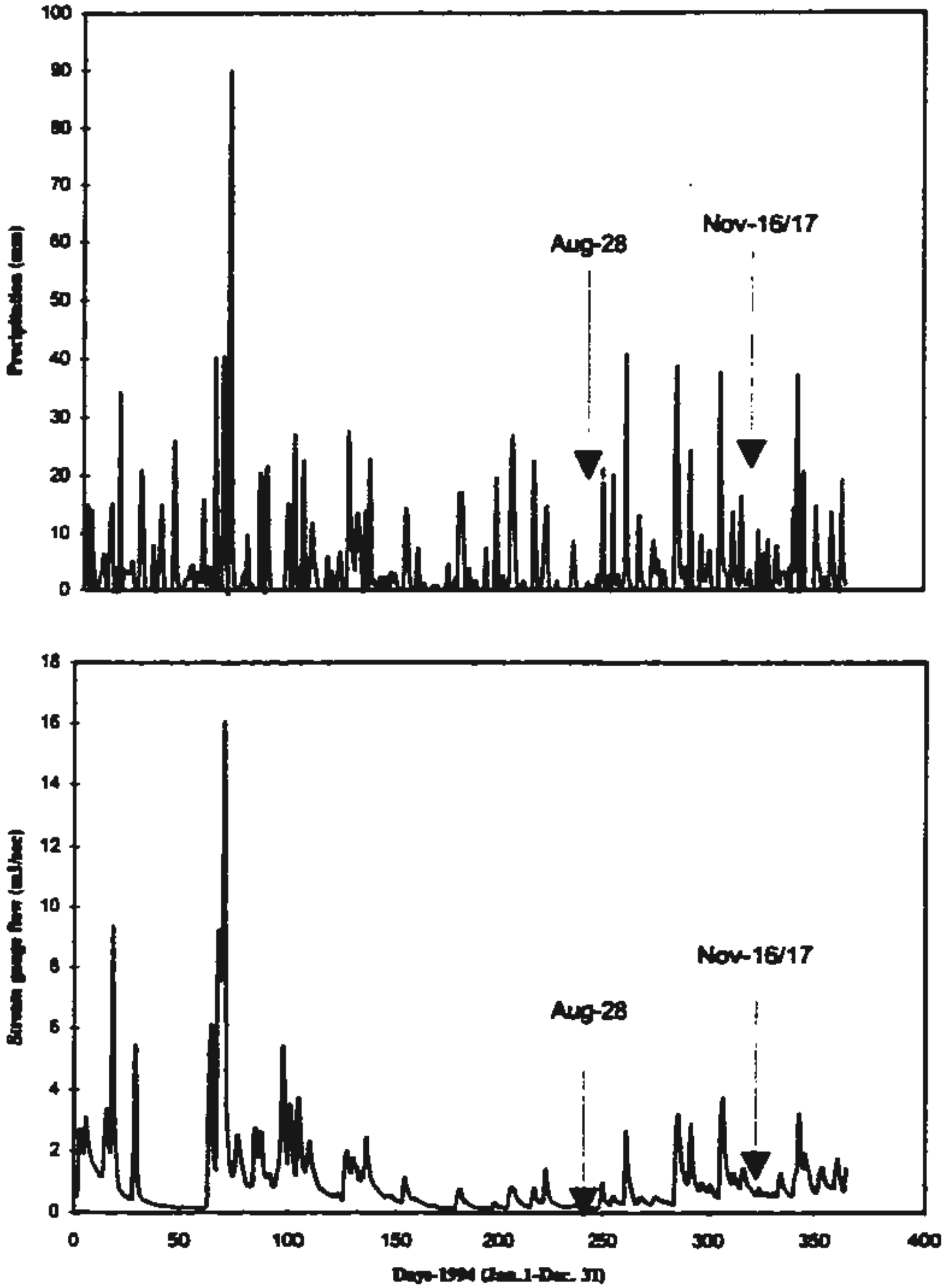


Figure 2.2.5 Daily variation in precipitation (Butlerville, Newfoundland) and stream flow (Shearstown, Newfoundland) during 1994. These stations were the most proximate to the study area at Makinsons, Newfoundland. The two sampling periods (August 28 and November 16/17, 1994) are indicated.

2.3 Three-Dimensional Numerical Simulation of Ground Water Flow

2.3.1 Model Construction and Input Parameters

A modular three-dimensional finite-difference ground water flow model (MODFLOW) (McDonald and Harbaugh, 1988), was used for numerical simulations. MODFLOW has been extensively used and tested against a suite of analytical solutions. The ground water flow model of the Makinsons drainage basin was produced and operated using the "Visual MODFLOW" v1.1 computer package (Guiguer and Franz, 1995). Visual MODFLOW allows the user to work in a more "user friendly" environment and makes changing / adjusting model parameters easier. These simulations were aimed at estimating the distribution of discharge and recharge areas in the Makinsons drainage basin.

The 3D model grid used here (Figure 2.3.1) contains 53 rows and 126 columns. The dimensions of the model are 4250 m (south-west to north-east) x 2050 m (south-east to north-west). For greater head resolution, column widths were narrowest (25 m) in the two areas where piezometers were installed and 50 m elsewhere. Row widths were narrowest (12.5 m and 25 m) along the main course of the test stream and were 50 m elsewhere. The 3D mesh contains six layers. Layer 1 includes the soil horizon and glacial till (5 m) whereas layer 2 only includes glacial till (5 m). Layers 3 (20 m), 4 (50 m), 5 (50 m), and 6 (45 m) include fractured bedrock. The total thickness of the model is 175 m. In order to avoid confusion between positive and negative elevations (with respect to mean sea level (msl)), the lowest point in layer 6 was assigned an elevation of 0 m. Therefore, 0 m elevation in the model corresponds to -175 m (msl). Also, the maximum elevation in layer 1 (i.e. 170 m msl)

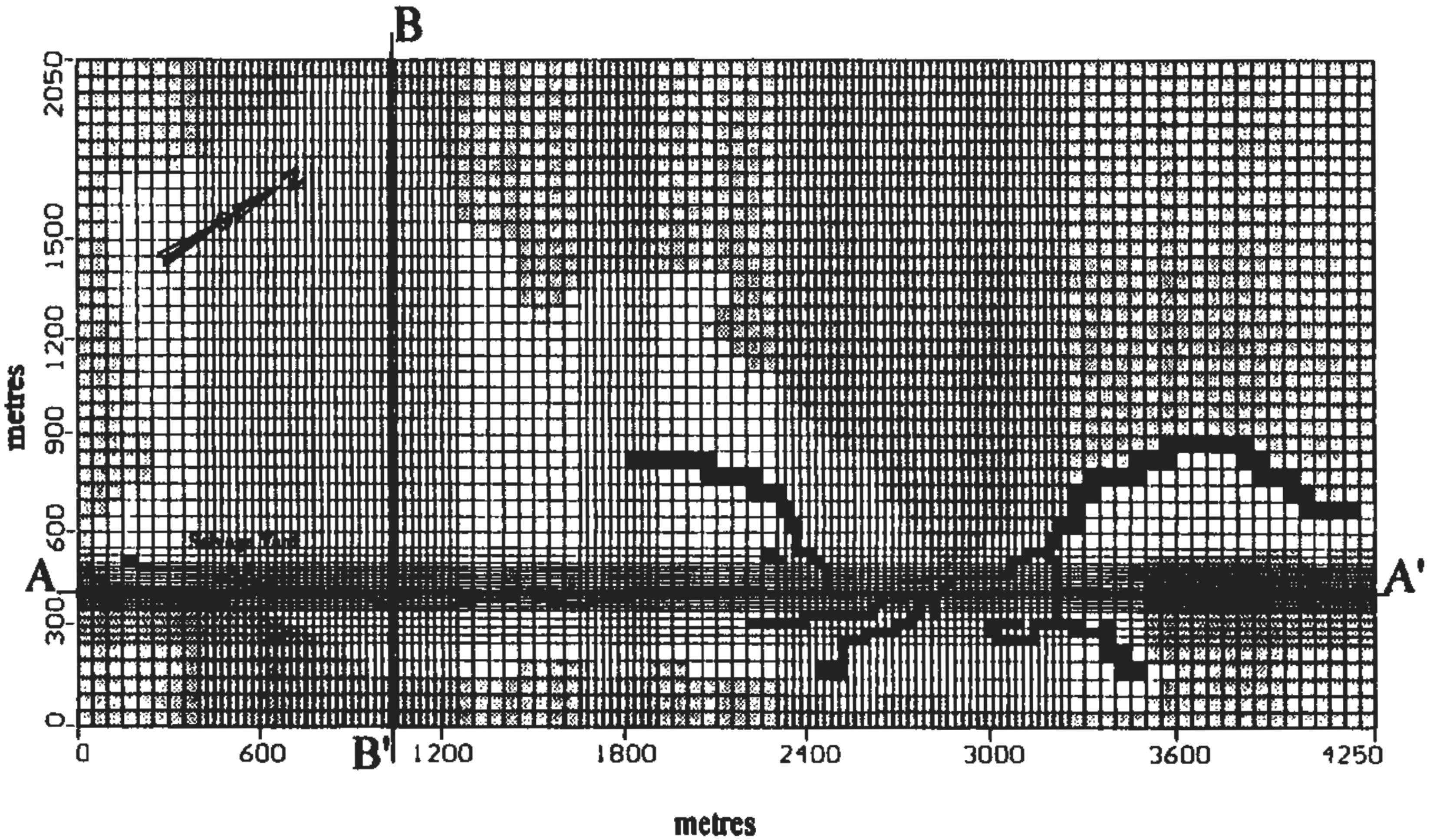


Figure 2.3.1 Configuration of 3D model grid over the Makinsons drainage basin. Grey-shaded cells are no-flow cells, white cells are active cells, and the black cells are constant head cells where the stream is located. Locations of cross-sections (A-A' and B-B') and the salvage yard are indicated.

is assigned an elevation of 345 m (170 m + 175 m). Thicknesses for layers 1 and 2 were based on results from FFC / BEAK, 1992*d*) who detected overburden up to 8 m deep. MODFLOW cannot properly function if the aspect ratio is greater than 10. As a consequence the dimensions of a cell (i.e. x,y,z) cannot differ by a factor of 10. Due to these constraints, the thinnest allowable layer was 5 m. Therefore, the overburden was modeled as 10 m instead of 8 m. This is a difference of only 25 % and is acceptable for these purposes. Thicknesses of layers 3 to 6 in the bedrock were assigned for convenience and do not reflect any hydrostratigraphic divisions. Surface elevation in each cell was recorded (±1 m) from a 1:5000 topographic map. This surface was considered the top of layer 1. The bottom of layer 1 was simply 5 m below the value in each cell so that the layer topography was geometrically irregular but a constant layer thickness was maintained. This procedure was repeated for all the layers and is better illustrated in Figures 2.3.2 and 2.3.3.

Boundary conditions for the model were intended to reflect the local hydrogeologic conditions as close as possible. The perimeter and bottom of the drainage basin are designated as no-flow boundaries (gray shaded cells) (Figure 2.3.1). The perimeter of the drainage basin was established from careful inspection of 1:5000 topographic maps. In addition, layer 1 cells containing the test stream and tributaries, as well as boggy areas, were assigned constant head values. Each constant head value was equal to the cell centered elevation in that cell.

Recharge rates are difficult to specify over an entire drainage basin. In the Makinsons drainage basin, the recharge rate was estimated using total annual precipitation data (1635.2

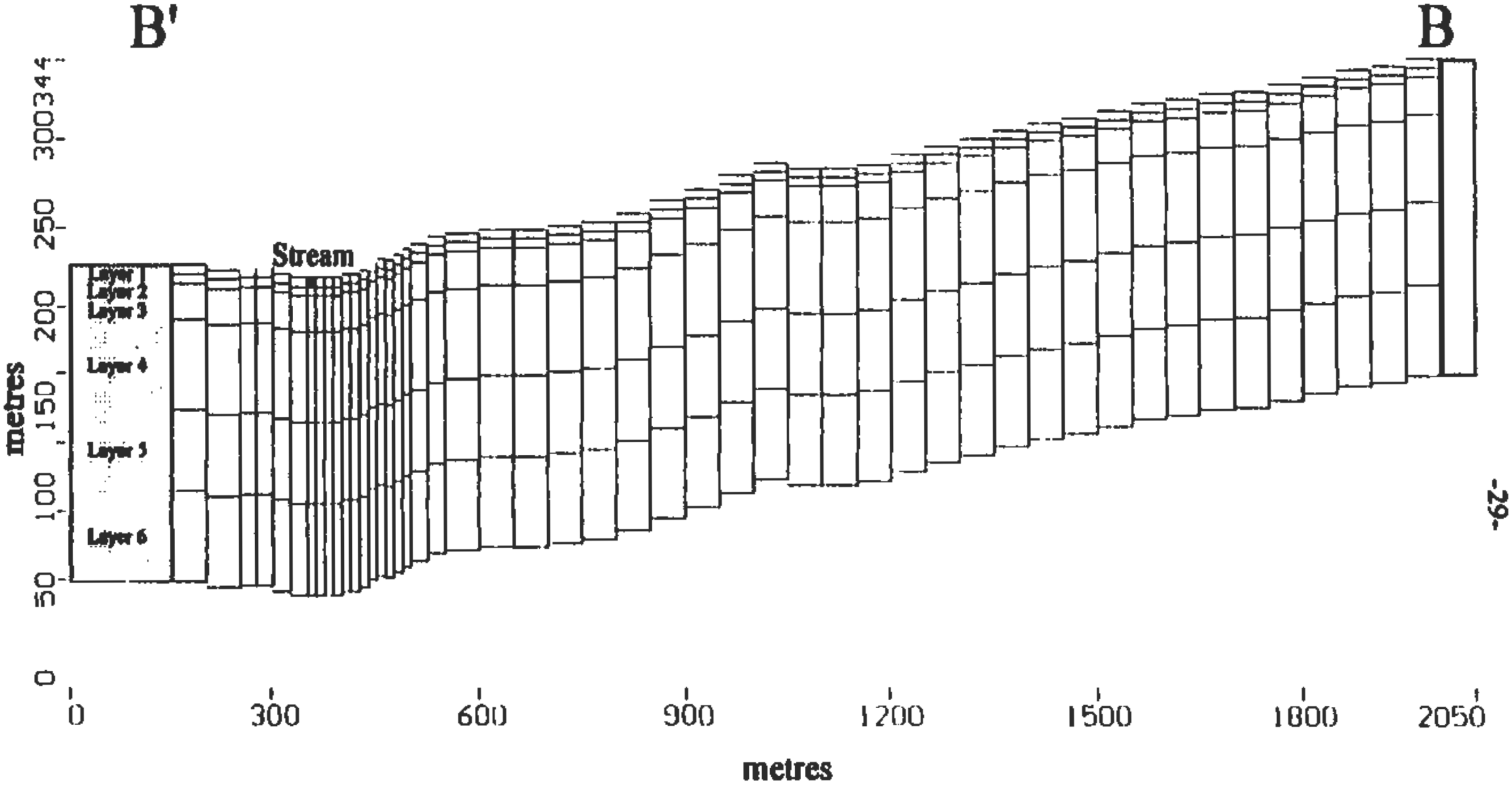


Figure 2.3.2 Configuration of model layers for profile B'-B. Layers 1 through 6, as well as the location of the stream are indicated. Vertical exaggeration is 2.5X.

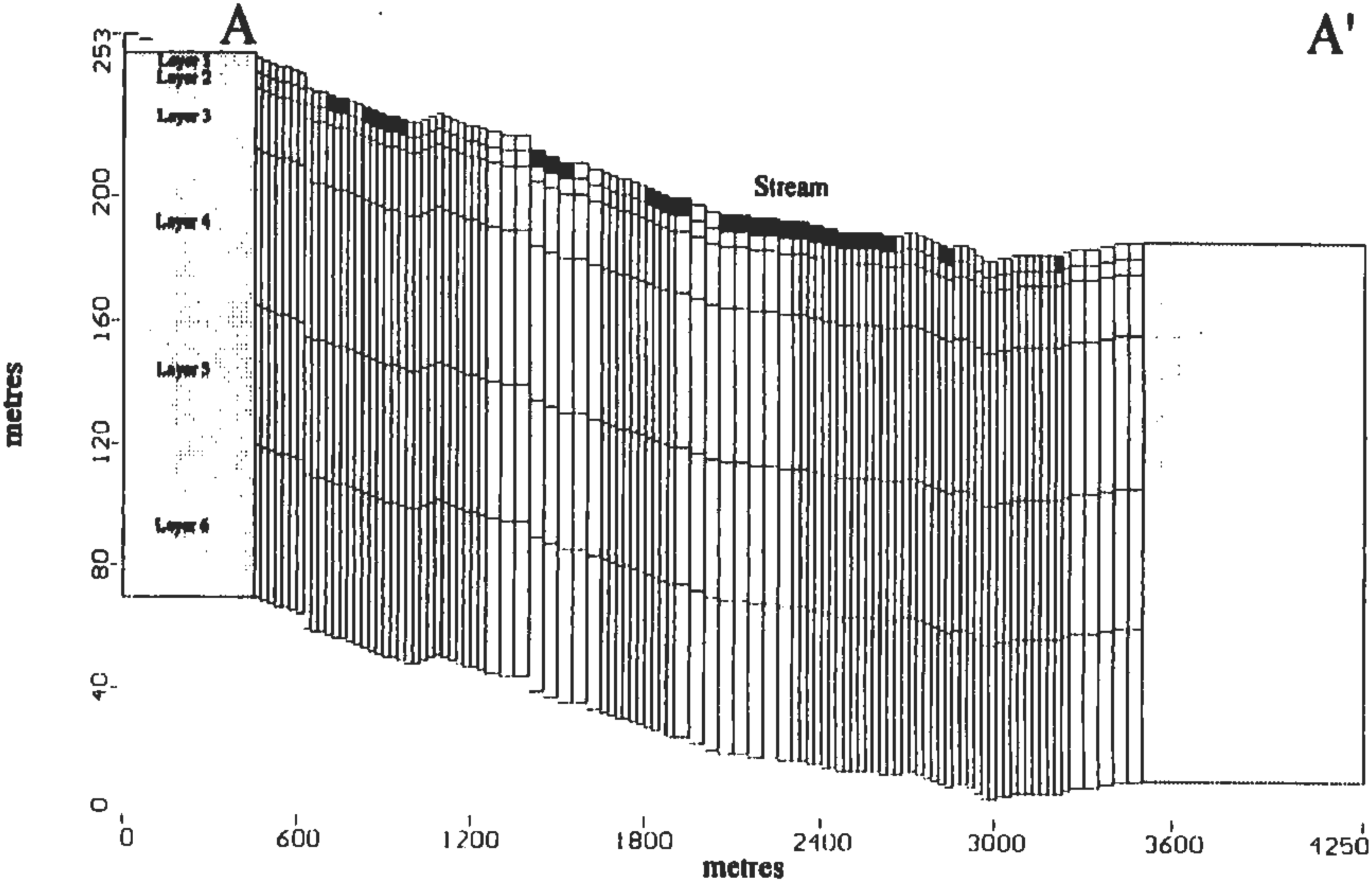


Figure 2.3.3 Configuration of model layers for profile A'-A. Layers 1 through 6, as well as the location of the stream are indicated. Vertical exaggeration is 10X.

mm) from 1994, measured at the nearest station in Butlerville. Usually, approximately 5 % of total average runoff in a drainage basin occurs as aquifer recharge or infiltration. This leaves 81.76 mm/year as a possible recharge rate for the Makinsons drainage basin. For this specific model, 1.6 % of total average runoff (26.16 mm/year) performed as the best estimate of the annual recharge rate.

Equivalent porous media conductivities were used in the simulation. Layer 1 was modeled as a Type 1 layer (McDonald and Harbaugh, 1988) and is suitable where unconfined conditions are expected to persist in the layer throughout the entire period of simulation. Layers 2 through 6 were modeled as a Type 3 layer and incorporate all of the Block-Centered-Flow options associated with water table conditions (McDonald and Harbaugh, 1988). As well, several small areas of exposed fractured bedrock in layer 1 were assigned hydraulic properties of layer 3. Table 2.1 includes the hydraulic properties assigned to each layer.

2.3.2 Numerical Simulation and Results

Steady state modeling was performed using the Strongly Implicit Procedure Package (SIP). SIP is a method of solving a large system of simultaneous equations (40,068 in this case) by iteration (McDonald and Harbaugh, 1988). The general concepts of the linear algebra and numerical analyses are outlined in Weinstein *et al.* (1969). The acceleration factor was assigned the default value of 1 and the rate of convergence was controlled using the seed value. A relatively high seed value of 0.1 (default seed of 0.01) was used during the

Table 2.1 Hydraulic parameters used in numerical simulation of ground water flow in the Makinsons drainage basin.

Layer	Hydraulic Conductivity	Specific Storage	Specific Yield	Porosity
1	1.25 e-7 m/sec	0.001 / m	0.16	0.2
2	1.25 e-8 m/sec	0.001 / m	0.1	0.15
3	1.25 e-7 m/sec	0.0001 / m	0.04	0.05
4	1.25 e-9 m/sec	0.0001 / m	0.0009	0.001
5	1.25 e-11 m/sec	0.0001 / m	0.00009	0.0001
6	1.25 e-11 m/sec	0.0001 / m	0.00009	0.0001

iterations in order to slow the rate of convergence. The rate of convergence was slowed in order to minimize oscillations of computed heads during iterations. Extreme computational oscillation causes head values to drop erroneously below the bottom of the cell and results in cells changing to no-flow for all succeeding iterations. Therefore, starting heads were set at 350 m in each layer and were slowly brought down to achieve steady state conditions. The result of the high seed value is an increase in number of iterations in order for the simulation to converge and reach steady state. The simulation was assumed to have converged and steady state conditions were met when the maximum change in head was less than ±0.01 m.

A water budget (volumetric) of all inflows and outflows into the Makinsons drainage basin was calculated. This estimation of a water budget acts as a check on the acceptability of the solution, and provides summary information on the flow system. In MODFLOW, the water budget is calculated independently of the equation solution process, and provides independent evidence of a valid solution. In this case, the % difference between inflow and outflow was -0.76 % and is within the traditional acceptable level of ±1 % (Guiguer and Franz, 1995).

Figure 2.3.4 displays the equipotential contours (hydraulic heads) in layers 1 and 2. The equipotential surface roughly reflects the topography in the Makinsons drainage basin. The surface is east-dipping, west of the stream and west-dipping, east of the stream. Therefore, ground water flow is channeled towards the valley where the stream runs and would appear to limit any significant lateral dispersion of contaminants from the salvage yard. Figures 2.3.5 and 2.3.6 contain head values from layers 3 - 6. The pattern is similar but smoother and less pronounced than layers 1 and 2. This trend of decreasing complexity in simulated head patterns with depth has been observed in other regional ground water flow studies (Gale *et al.*, 1987). Again, ground water flow is channeled under the valley.

Figure 2.3.7 is a cross section at column 34 and includes equipotential lines. Ground water flow is perpendicular to the equipotential lines and is generally horizontal from the mountain (west of the stream) into the valley where the stream runs. Ground water is also shown to be discharging into the stream. Figure 2.3.8 is a cross section at row 40 and also includes equipotential lines. In Figures 2.3.7 and 2.3.8, ground water flow is near horizontal at depth. However, in the upper layers, ground water appears to be continuously discharging to the stream. To better illustrate the distribution of recharge and discharge areas in the Makinsons drainage basin, a plan view of the basin was created to map the hydraulic gradient between layers 1 and 2 (Figure 2.3.9). Vertical hydraulic gradients (m/m) were calculated by dividing the simulated heads in layer 1 by the simulated heads in layer 2. A head difference

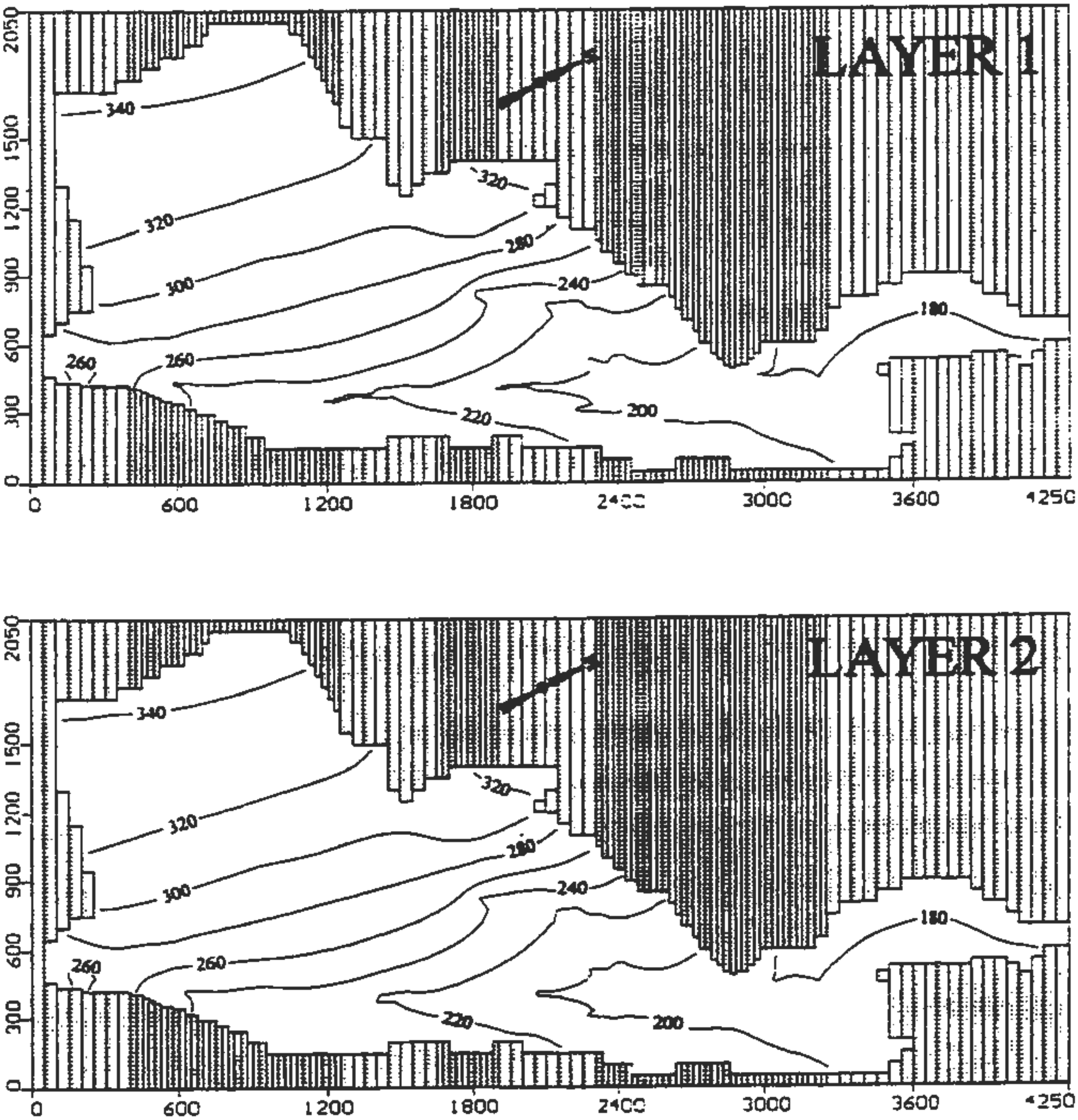


Figure 2.3.4 Simulated hydraulic heads for layers 1 and 2. Heads are in metres above sea level (+ 175 m).

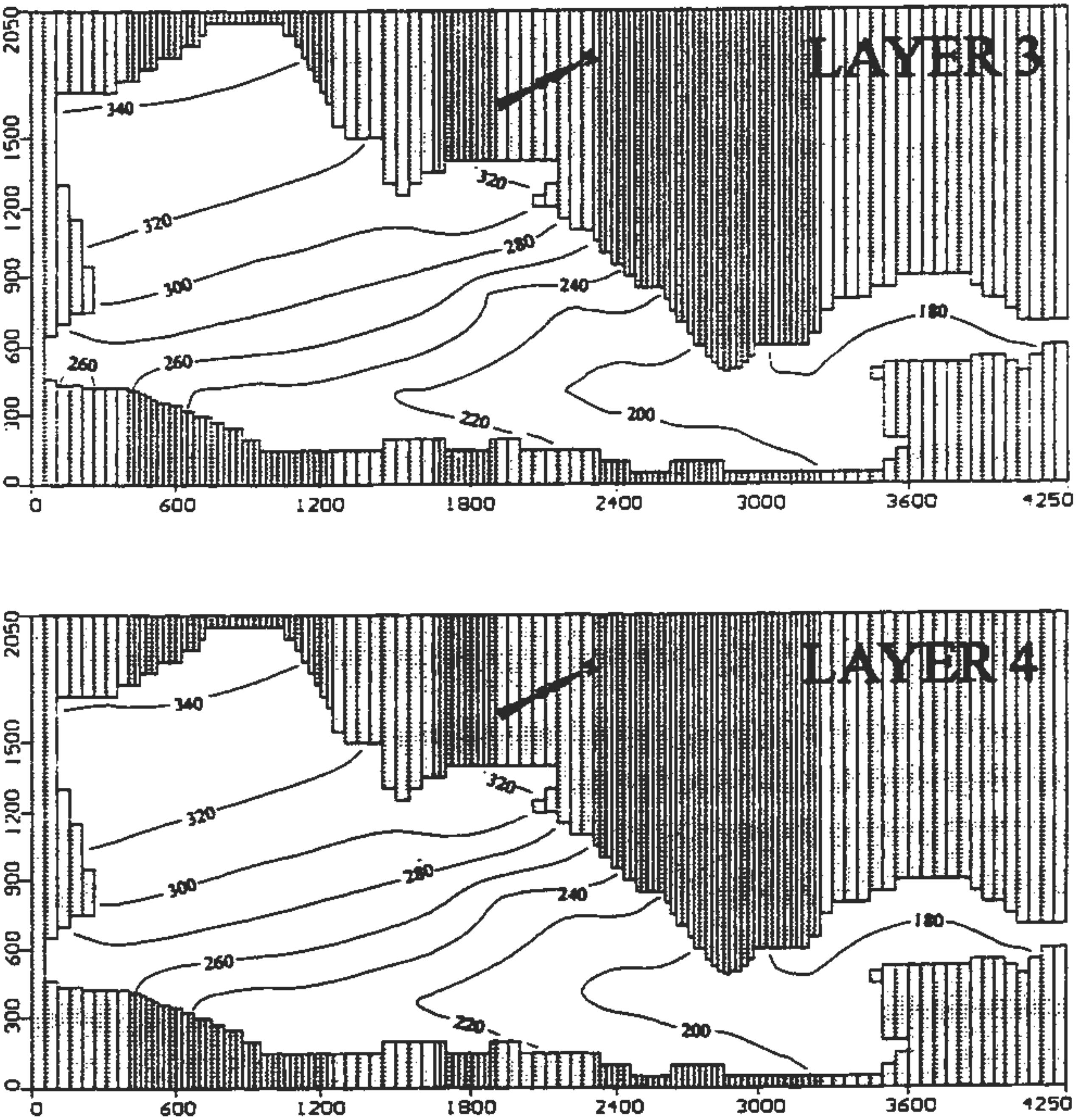


Figure 2.3.5 Simulated hydraulic heads for layers 3 and 4. Heads are in metres above sea level (+ 175 m).

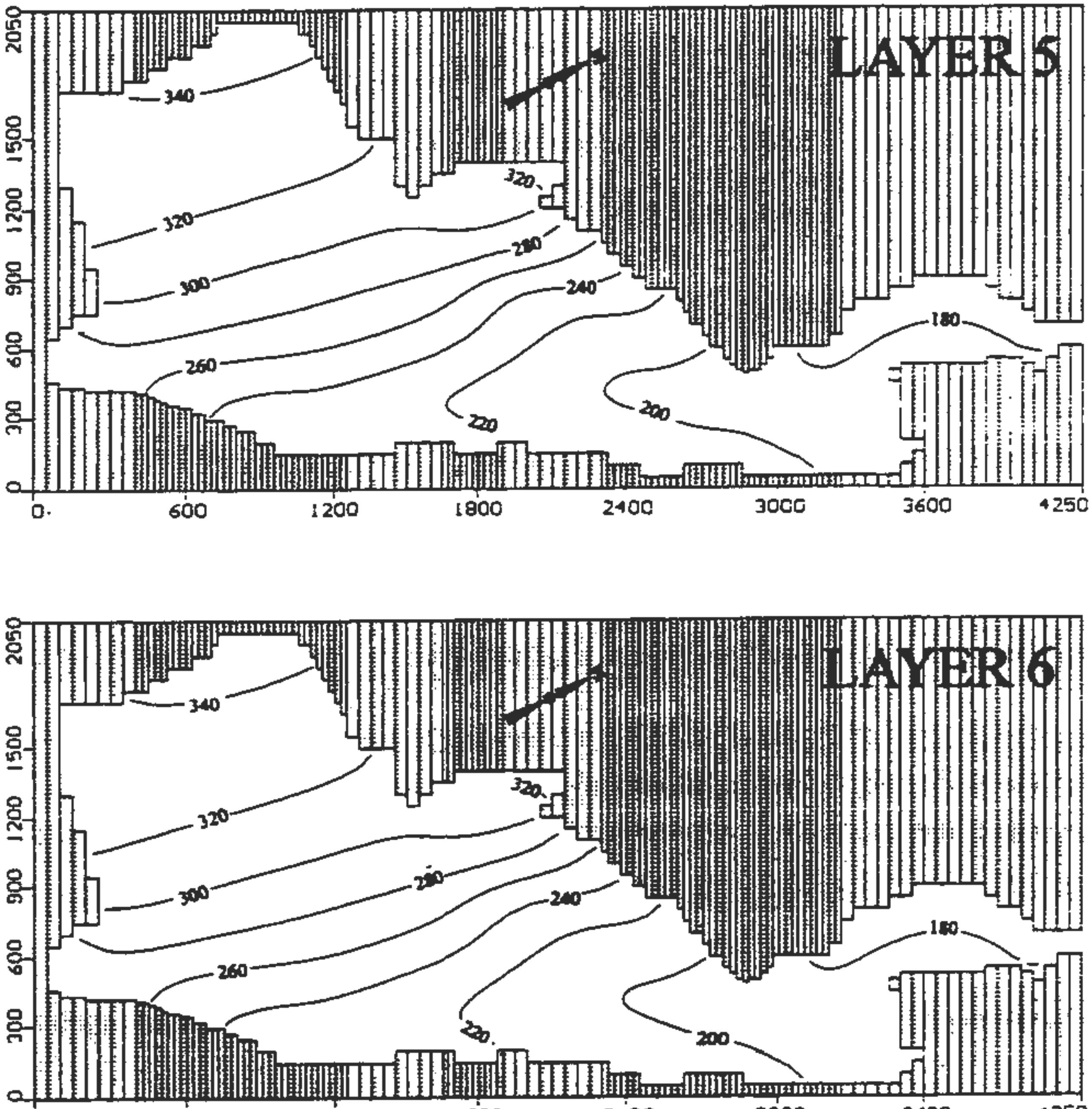


Figure 2.3.6 Simulated hydraulic heads for layers 5 and 6. Heads are in metres above sea level (+ 175 m).

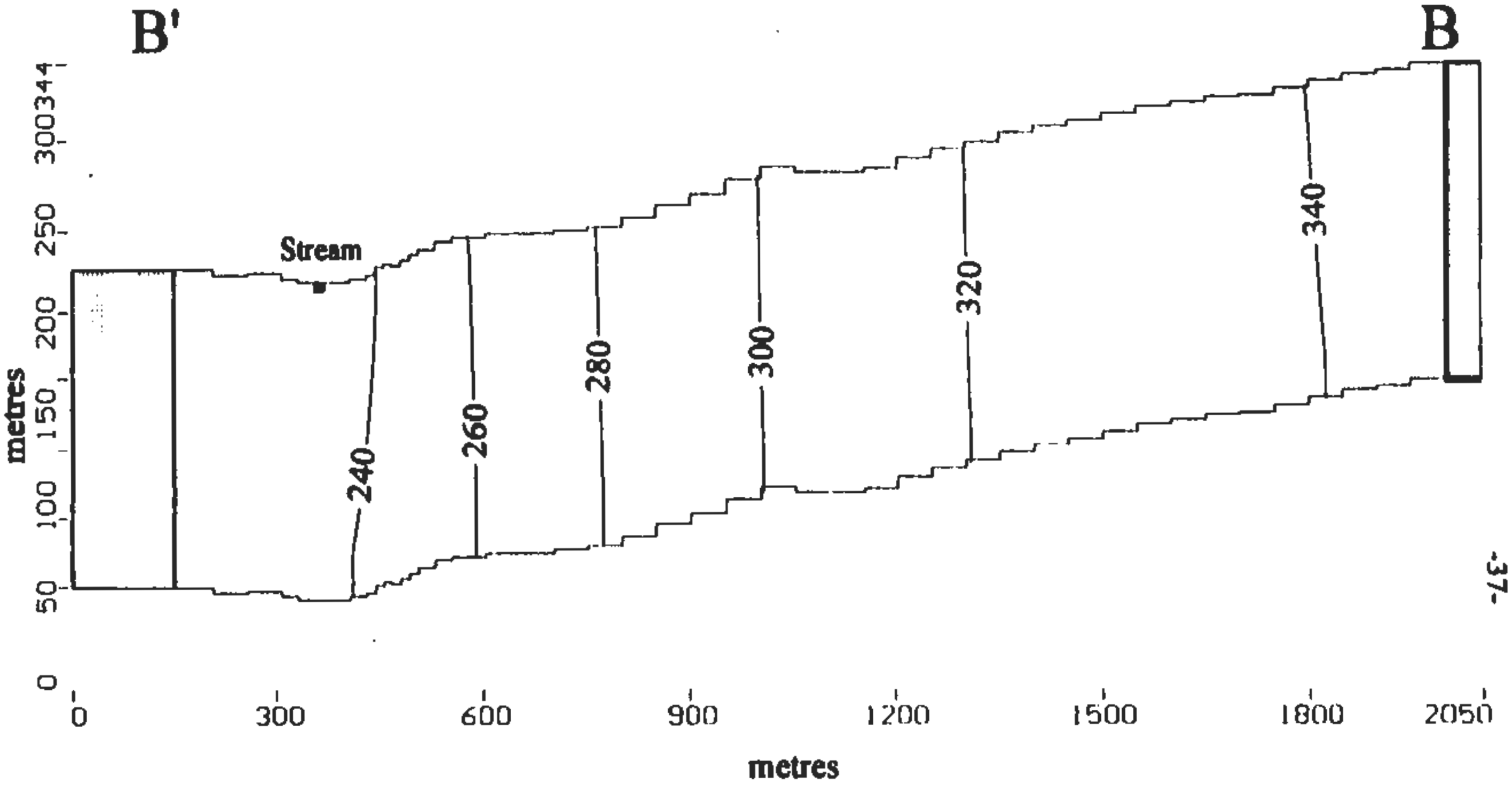


Figure 2.3.7 Simulated hydraulic heads for profile B'-B. Hydraulic heads are in meters above sea level (+175 m). Vertical exaggeration is 2.5X.

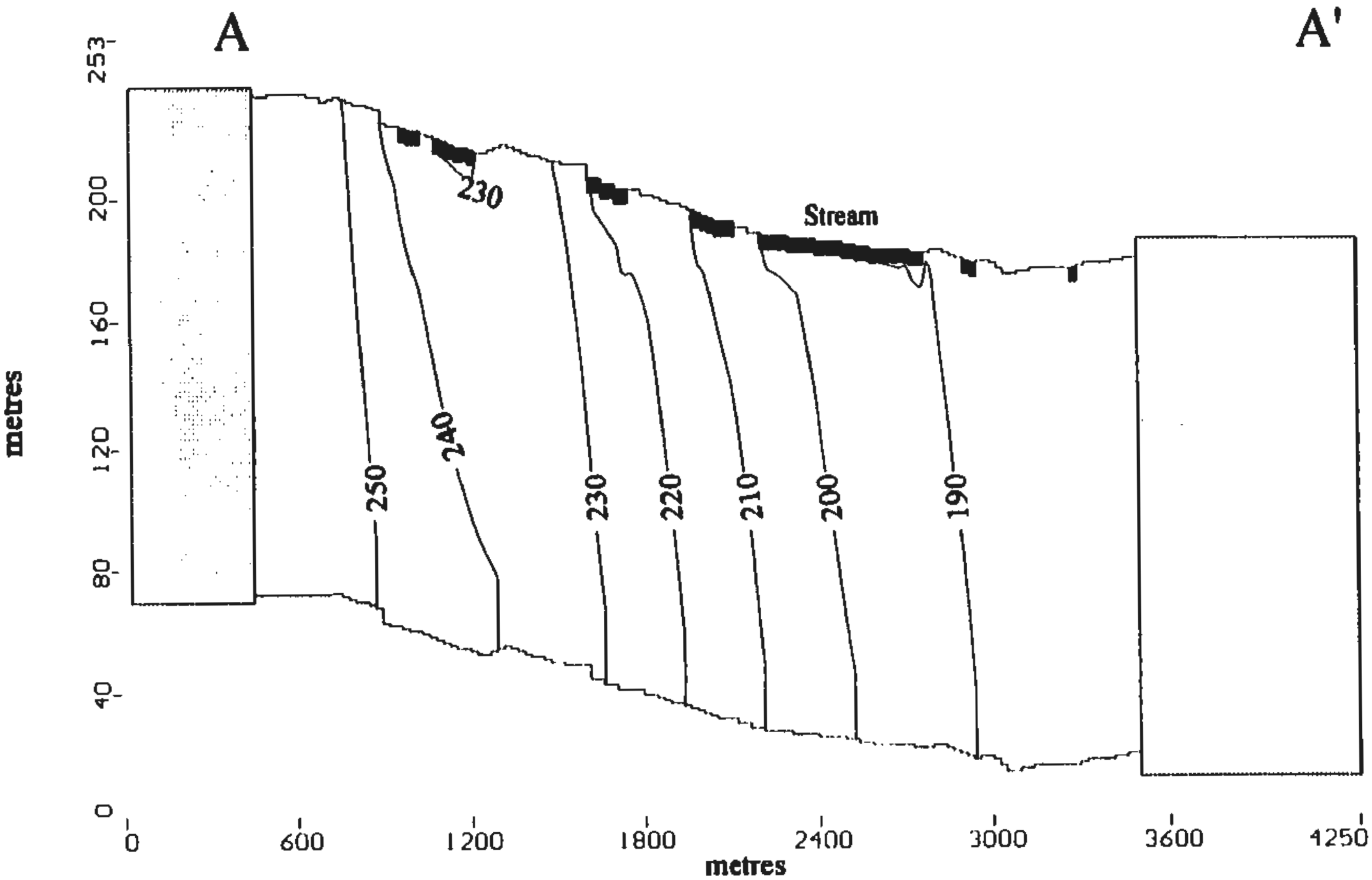


Figure 2.3.8 Simulated hydraulic heads for profile A-A'. Hydraulic heads are in meters above sea level (+175 m). Vertical exaggeration is 10X.

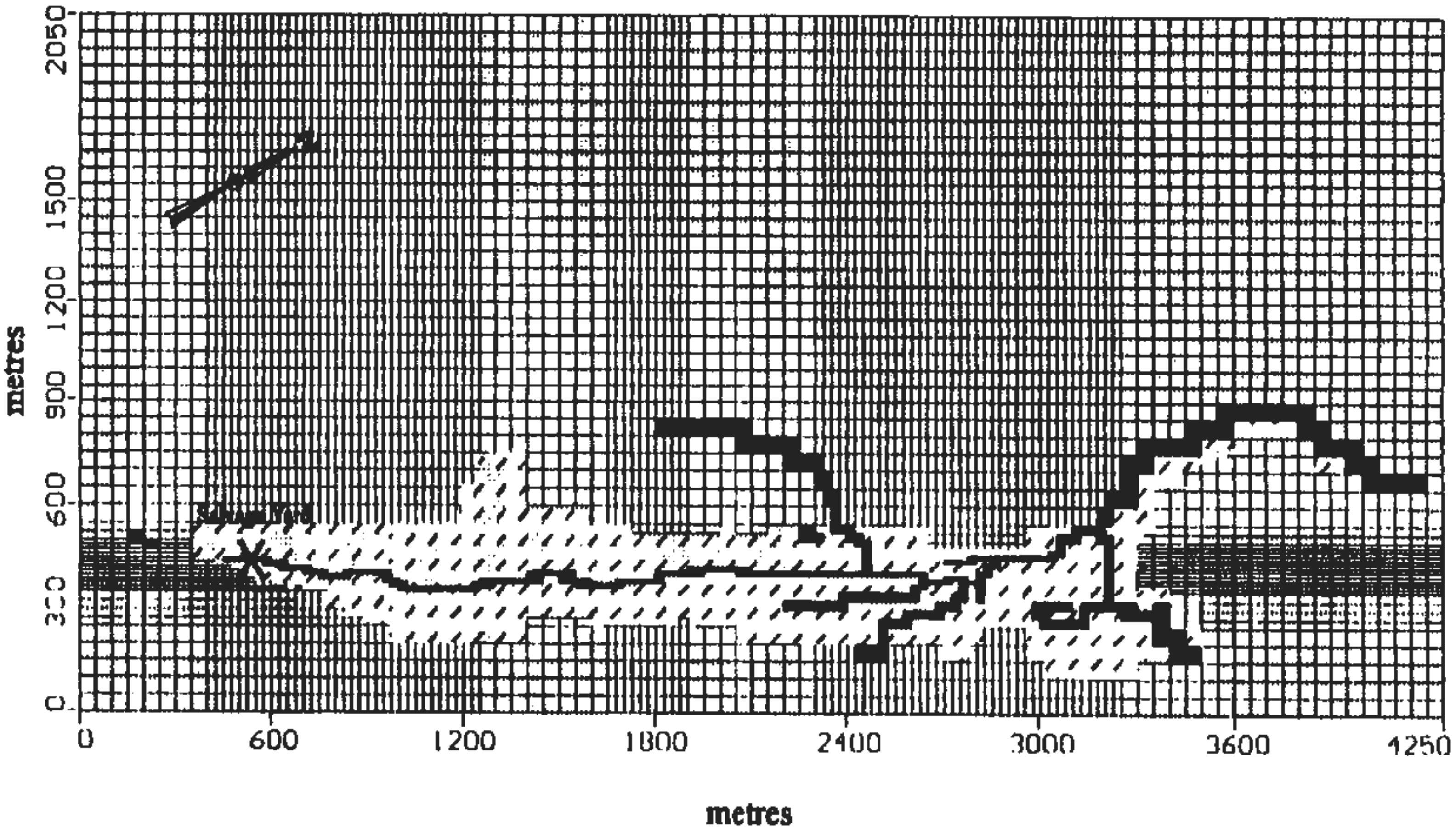


Figure 2.3.9 Distribution of discharge (hatched) and recharge areas in the Makinsons drainage basin. These areas are estimated based on differences in hydraulic heads between layers 1 and 2.

greater than 1 (decreasing head with depth) indicates a recharge area, while a head difference less than 1 (increasing head with depth) indicates a discharge area. The discharge areas (hatched) are confined to the north-eastern edge of the Makinsons drainage basin (Figure 2.3.9). This corresponds with the slight valley in the topography as well as the course of the stream. If in fact, ground water flow in the aquifer follows 2 different patterns (upper and lower), it could be divided into two flow systems- a shallow and deep aquifer. Since the aquifer (s) appear to be consistently discharging to the stream, any surface releases of PCBs or heavy metals should remain at the surface and not be transported deep into the ground water system. In order to better describe this, a subroutine of MODFLOW, called MODPATH was performed to simulate pathlines of possible contaminants released in the salvage yard. Figure 2.3.10 shows that any ground water migration of contaminants would be quickly directed towards the stream.

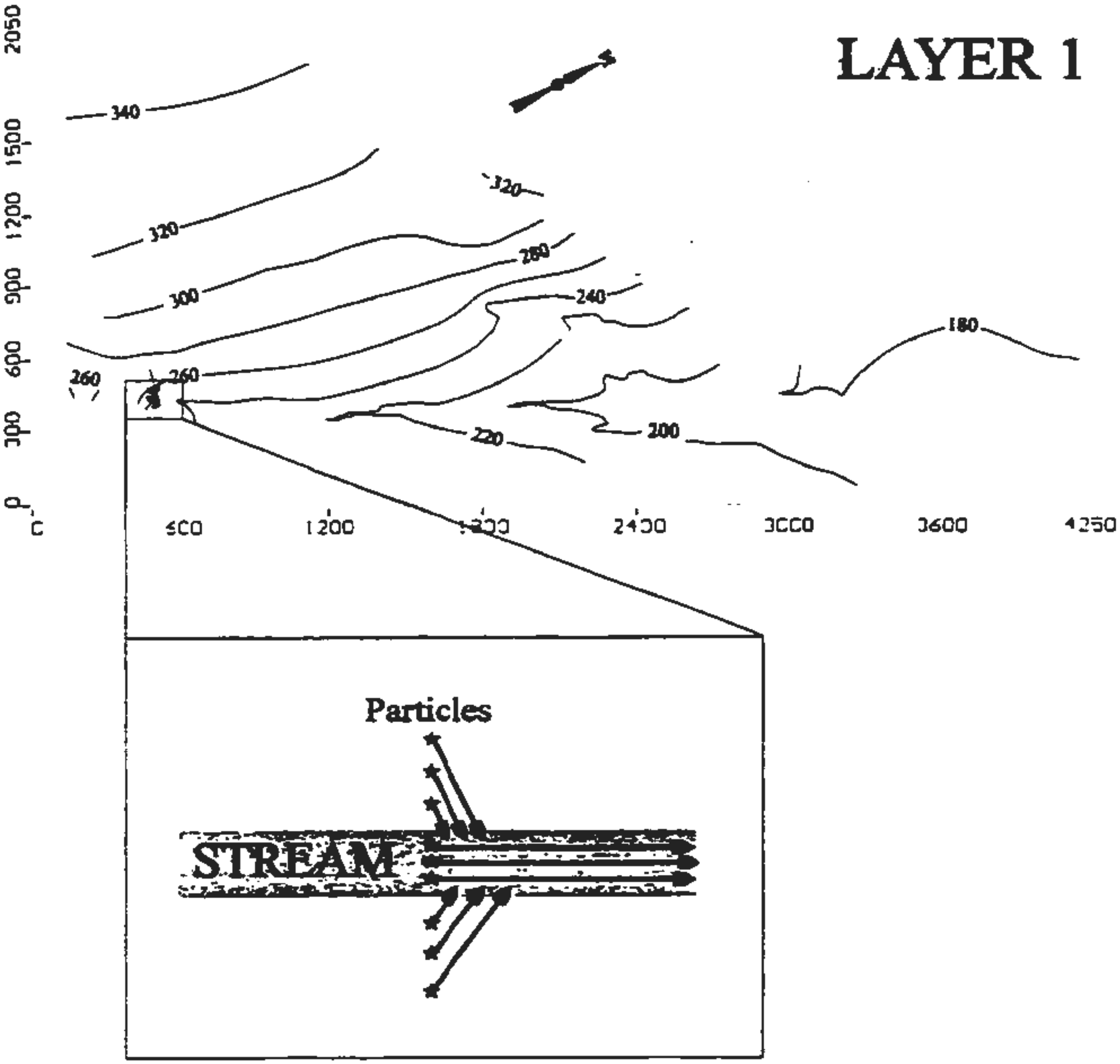


Figure 2.3.10 Simulated flow paths of particles, in layer 1, released from the salvage yard area.

Chapter 3. SAMPLING PROCEDURES AND ANALYSES

3.1 Sediment and Soil Sampling and Analysis

Sediment cores were collected from 27 sites in the South River estuary (Figure 3.1). Sampling was performed during March and April, 1994 since a layer of ice provided easy access to preferred coring locations. Sample sites were surveyed from landmarks in terms of distance and orientation to allow exact positioning on topographic maps and airphotos. At each site, three holes spaced approximately 0.50 m apart in a triangular configuration, were cut in the ice with a 100 mm diameter ice auger. A modified ball-valve coring device (Reasoner, 1986) was used to retrieve the upper 0.20-0.40 m of estuarine sediment. Two distinct core barrel attachments were employed to recover the sediment samples. An 87.5 mm diameter plexiglass barrel was used to collect cores for trace metal analysis and a 62.5 mm diameter steel barrel was used for PCB analysis. A third core was collected as a safety precaution in case of damage to cores during collection, transport, or storage. The procedure involved inserting the coring device to its maximum depth into the sediment, carefully retrieving the collected sediment sample, and quickly capping the bottom. The barrel was unscrewed from the coring device and any water trapped in the core barrel was siphoned out using a length of polyethylene tubing. The upper portions of the cores had a very high moisture content and could not be transported back to the laboratory intact. Therefore, the upper 20 mm of each core was sampled in the field and placed into clean glass jars. Sediment cores retrieved for trace metal analysis were immediately extruded into a "Saran Wrap" (polyethylene) lined, split

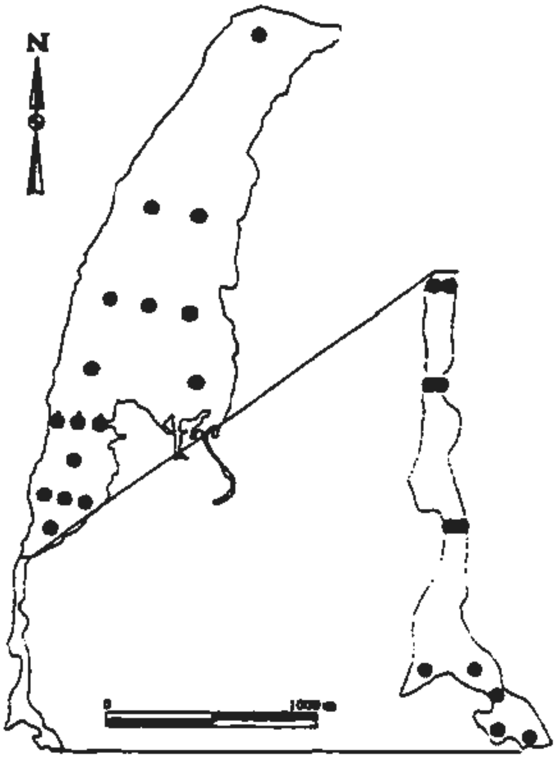


Figure 3.1 Locations of sediment cores collected from the South River estuary.

plexiglass tube to minimize possible contamination and aid in core handling. The extruded core was then wrapped in aluminum foil, labeled, and placed in a length of eaves trough to be transported back to the laboratory. Sediment cores retrieved for PCB analyses were extruded into a tin foil lined, split, plexiglass tube. These cores were then wrapped in plastic wrap, labeled, and placed in a length of eaves trough for transport.

Upon return to the laboratory, the cores were stored at 4° C and later split, photographed, and described (color, texture, etc.). The outer 3 mm of the core was discarded to minimize bias due to smearing. Reconnaissance work into the presence of

PCBs in the South River estuary, initially involved sampling the top 100 mm of 6 sediment cores (Figure 3.2). These samples consisted of approximately 50 g of wet sediment and were stored in pre-cleaned glass bottles suitable for trace organic analyses. These samples were shipped, by courier, to Fenwick Laboratories Limited (Halifax, NS). At Fenwick, the procedure for determining total PCB content includes extraction with methylene chloride, solvent exchange into isooctane and analysis using capillary gas chromatography coupled with dual electron capture detectors (detection limit = 0.1 ppm). Two additional sediment cores were sampled (Figure 3.2) at 50 mm intervals. Six samples (approximately 50 g wet), from these two cores, were shipped, by courier, to Environmental Protection Laboratories Inc. (EPL) (Mississauga, ON). The procedure at EPL consisted of solvent extraction followed by chromatographic clean up and analysis by capillary gas chromatography with dual electron detectors (detection limit = 0.05 ppm) with external standard area summation (according to U.S. EPA Methods No. 3550 / 3620 / 3630 / 3660 / 8080A /608).

Two sediment cores (Figure 3.2) analyzed for trace metals were sampled at 20 mm intervals and stored in acid-washed glass bottles. Samples were first oven dried at ≤ 40° C for 48 hours, weighed, and ignited at 450° C overnight to determine the loss on ignition (LOI). Approximately 3.2 g of sample was pulverized (≤ 75 μm) for 10 minutes using an alumina swing mill. The swing mill was carefully cleaned between samples by pulverizing clean silica sand and washing with methanol. Exactly 3.00 g of pulverized sample was

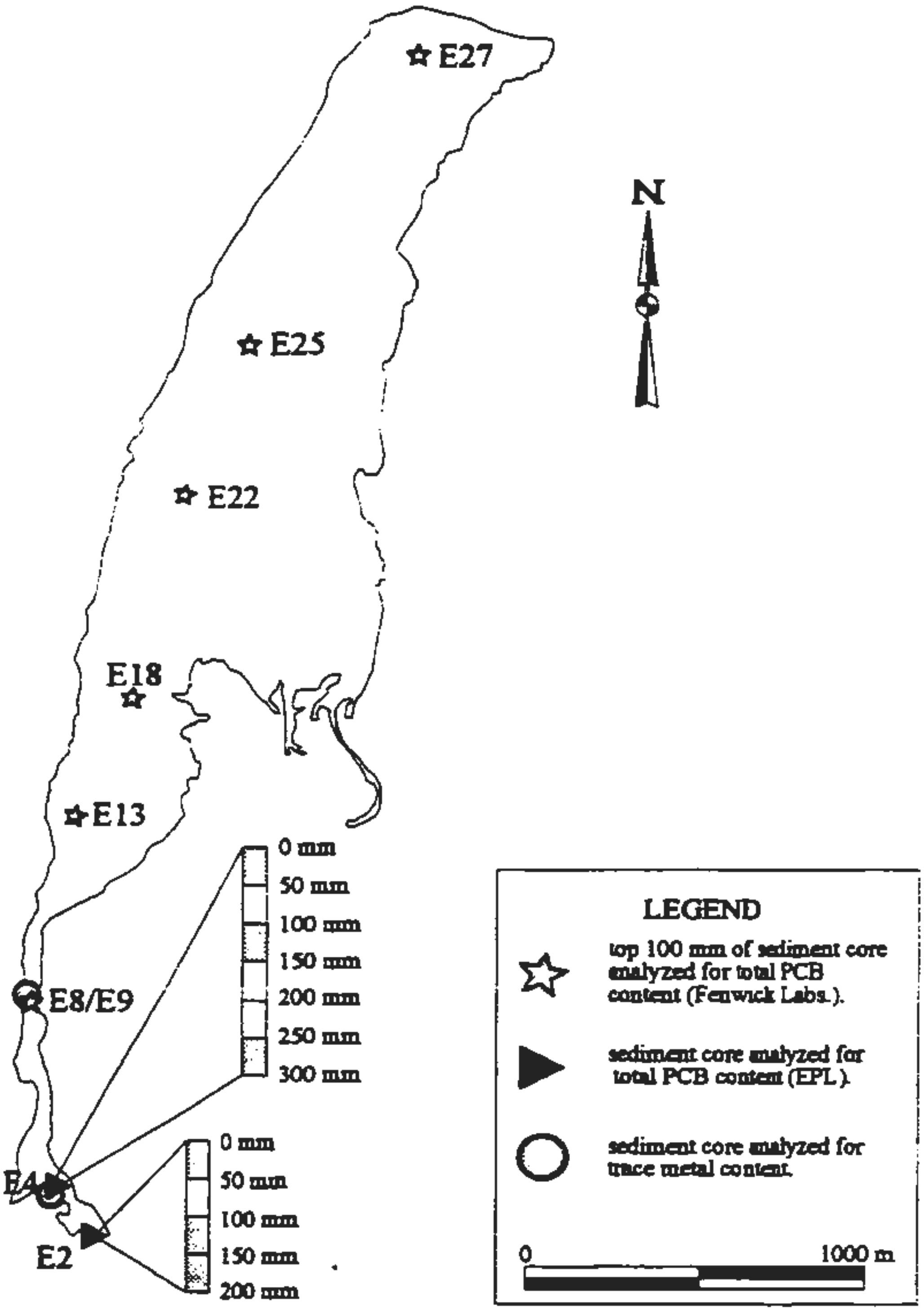


Figure 3.2 Locations of sediment cores analysed for PCBs and trace metals in the South River estuary.

carefully weighed, mixed with 0.42 g of phenolic resin and mixed on rotating drums for 10 minutes. The resulting mixture was pressed into pellets and heated at 115° C for 15 minutes. The pellets were subsequently analyzed using an Applied Research Laboratories (ARL) 8420^+ X-Ray Fluorescence instrument. The remaining sample that was not pulverized was wet sieved through a no. 230 sieve ($\leq 63\ \mu m$) in order to determine the silt + clay fraction.

Ten sediment samples were collected from the test stream and two from the control stream (Figure 3.3). It should be noted that samples STS7 and STS8 were not analyzed for total PCB content. The control stream is located in an adjacent basin, northwest of the Makinsons drainage basin (see Figure 1.2). The control stream was selected based on proximity to the Makinsons drainage basin and similarity of geology. The control stream drains a relatively undeveloped basin and is located entirely within the St. John's Group (see Figure 2.1.1). The sediment samples from the control stream were intended to represent background geochemistry of the area. Four soil samples were also collected from the Makinsons drainage basin (Figure 3.3). Soil samples were collected with a soil auger and were typically 0.30 m below ground surface and below the water table. After each sample was collected, the auger was carefully scrubbed to remove soil and was rinsed in methyl hydrate to prevent cross-contamination. In addition, 1 soil sample from the control basin and 2 tidal marsh samples from the South River estuary, were collected. Subsequent sample preparations and procedures for analyses were as described above.

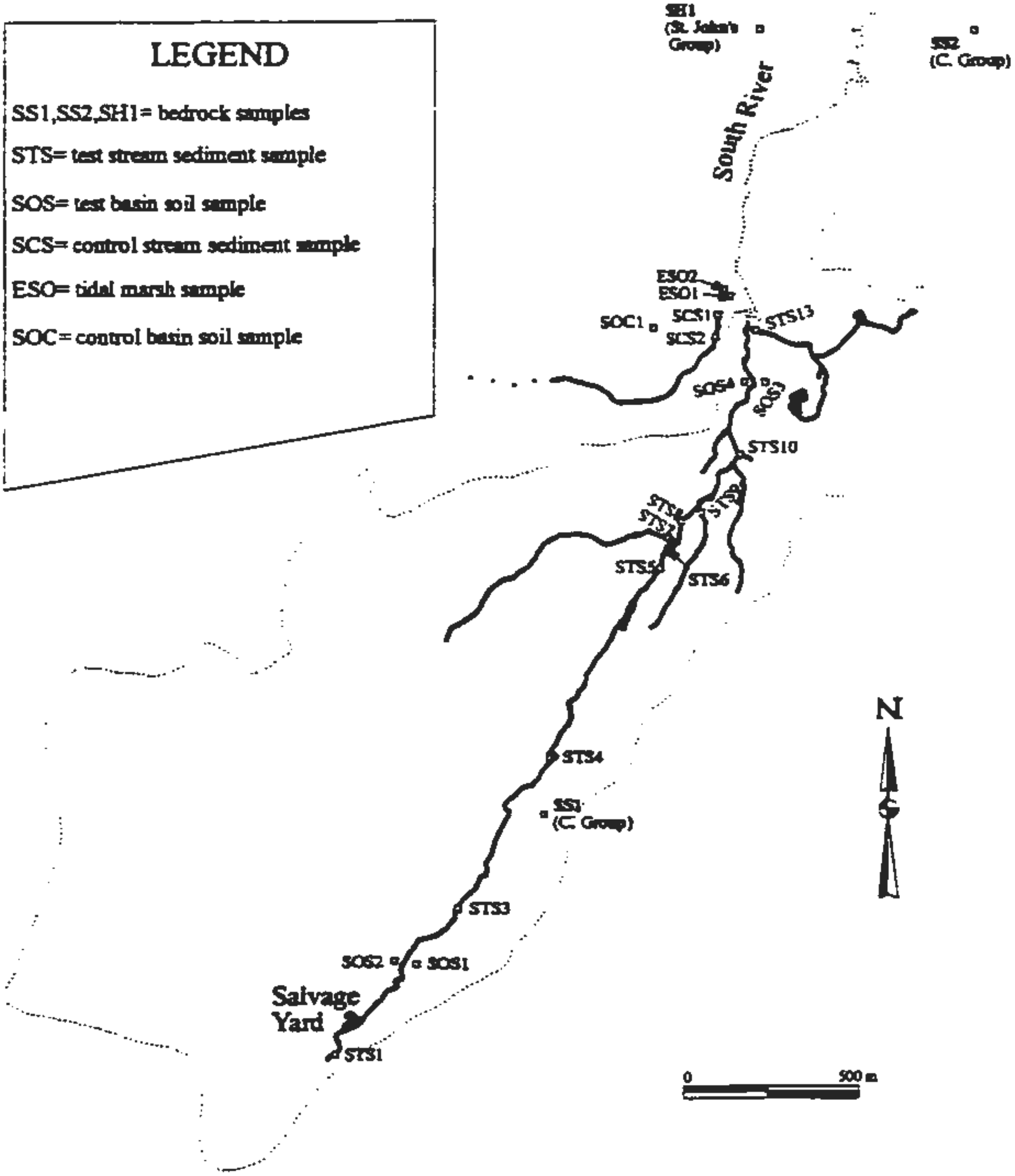


Figure 3.3 Locations of stream sediment, soil, and bedrock samples collected from the study area.

Description of sediment / soil sample locations is included as part of a sampling matrix (Table B.1).

3.2 Surface and Ground Water Sampling and Analysis

Polyethylene sample bottles (250 ml and 125 ml) were first scrubbed and soaked for 24 hours in 1.5 M HNO_3. The bottles were rinsed three times in deionized water (DIW), soaked for 24 hours in DIW, rinsed three more times in DIW and finally air dried in a fumehood. Fourteen water samples from the test stream and one from the control stream were collected on November 16/17, 1994 (Figure 3.4). The control stream and the test stream were visually observed to be roughly the same size, drain roughly the same area, and appeared to have similar flow rates. Included in the 14 test stream sites sampled on November 16/17, were 9 sites that had been previously sampled on August 28, 1994. Therefore, a surface water sample set was collected at 9 locations along the test stream on August 28, and again on November 16/17, 1994 (Figure 3.5). Description of the water sample sites is also included as part of the sampling matrix in Table B.1. Electrical conductivity and temperature were measured in the field using an Orion Model 122 conductivity meter. pH was also measured in the field using a μicropHep pH meter.

Twelve "mini" piezometers were constructed using 12.5 mm (inside diameter) PVC pipe. A 0.30 m screen was constructed from 0.5 mm NITEX netting which was fastened over holes drilled in the PVC pipe. The intention was to prevent sediments from clogging

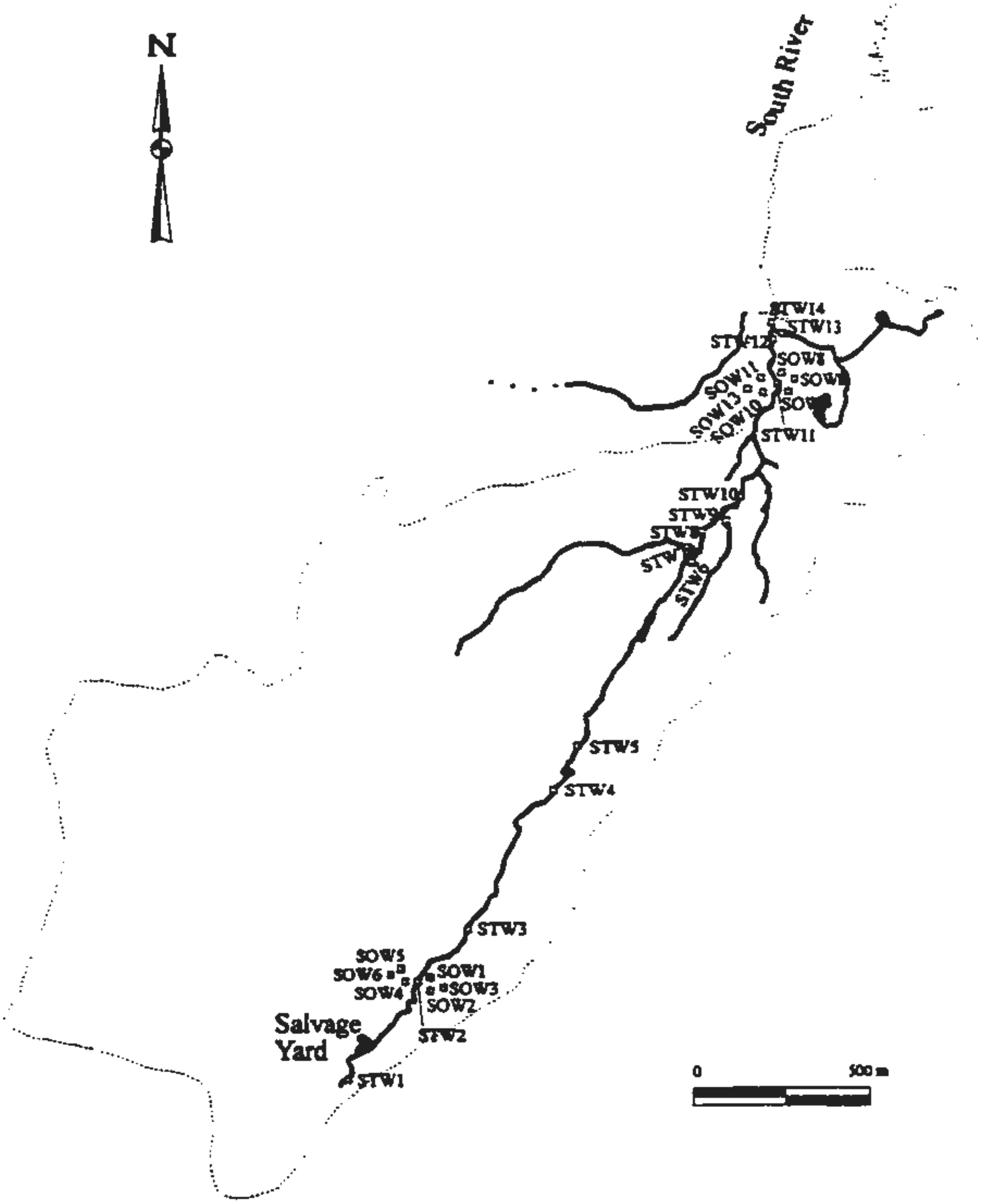


Figure 3.4 Locations of surface and ground water samples collected from the study area. SOW1 through SOW12 are ground water samples while the remaining locations are surface water samples.

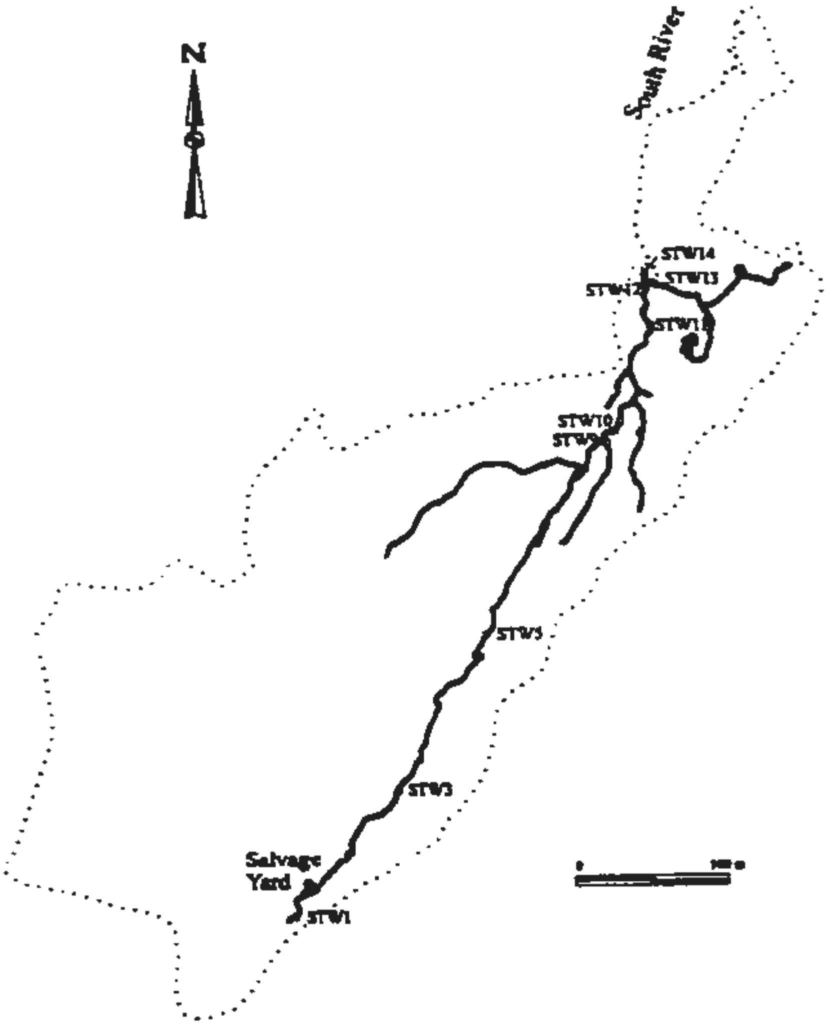


Figure 3.5 Locations of the two surface water sample sets collected on August 28 and again on November 16/17, 1994.

the piezometers and to minimize problems when filtering the ground water. The piezometers were installed at two different locations along the test stream: approximately 175 m downstream from the salvage yard and approximately 200 m upstream from the top of the South River estuary. At each location, three piezometers were installed in a triangular pattern on either side of the test stream (Figure 3.6). Figure 3.7 illustrates the geometry of the installed piezometers relative to the test stream.

The holes for the piezometers were dug using a soil auger. The water table was encountered 0.20-0.25 m below ground surface and the piezometers were installed at a depth that enabled the screens to be completely submerged. Native soil and rocks were used to fill the hole to the top of the screened portion of the piezometer. A 70-100 mm layer of bentonite chips was placed over the screen to prevent a hydraulic connection between the ground and surface waters. Native soil and rocks were again used to fill the remainder of the hole above the layer of bentonite. The piezometers were developed by repeatedly withdrawing ground water (60 cc. syringe and polyethylene tubing) to help the system achieve steady-state conditions and minimize bias due to the disturbance of installation. After each sample was collected, all equipment was scrubbed to remove soil and rinsed with methyl hydrate to avoid cross contamination.

Ground water was sampled on November 16/17, 1994 and was withdrawn from the piezometers using the 60 cc. syringe and polyethylene tubing. The water was stored in pre-washed polyethylene bottles and was treated and analysed as the previously mentioned surface waters. Depth to water level was measured (±2 mm) using a water level metre and the relative depths of the water table were calculated (±5 mm) using string and line levels.

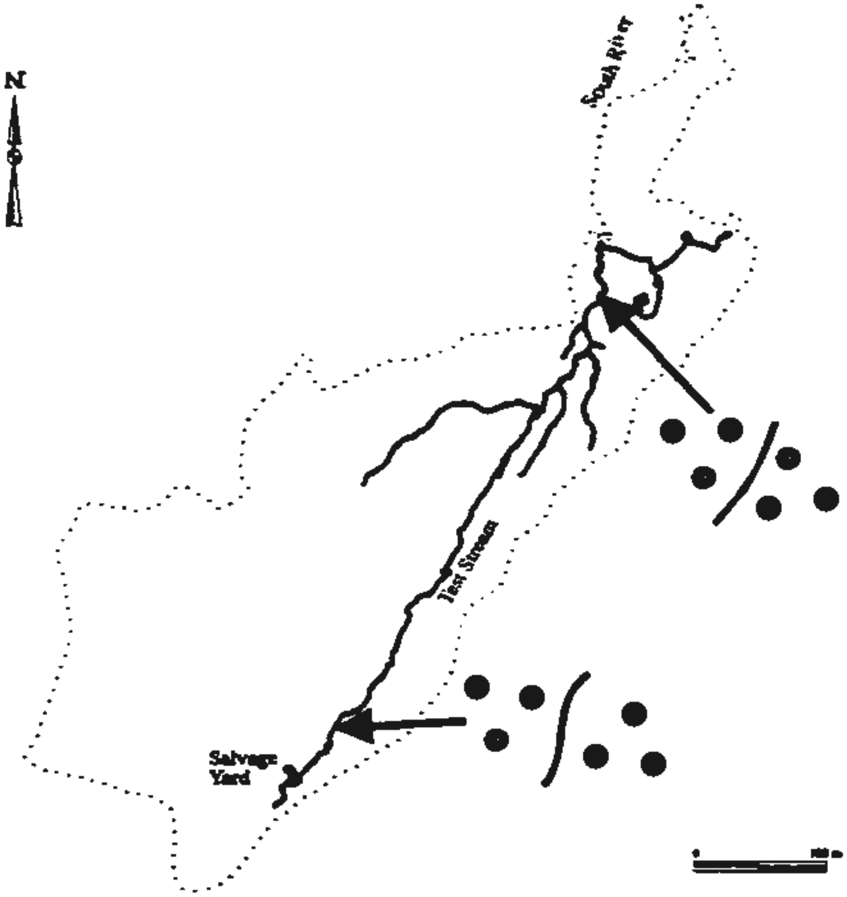


Figure 3.6 Triangular configurations and locations of installed "mini" piezometers in the drainage basin.

Water samples for minor and major cation analysis were filtered through Sartorius 0.45 μm cellulose acetate and acidified with distilled 8 N HNO_3 (2 ml acid:100 ml water) to prevent precipitation of metals and biological growth. Water samples for major anion analysis were filtered only. Water samples collected for alkalinity titrations were not filtered or acidified. For dissolved oxygen titrations, water samples were collected in 60 ml BOD bottles and preserved with Dissolved Oxygen 1 Reagent Powder Pillow 1 and

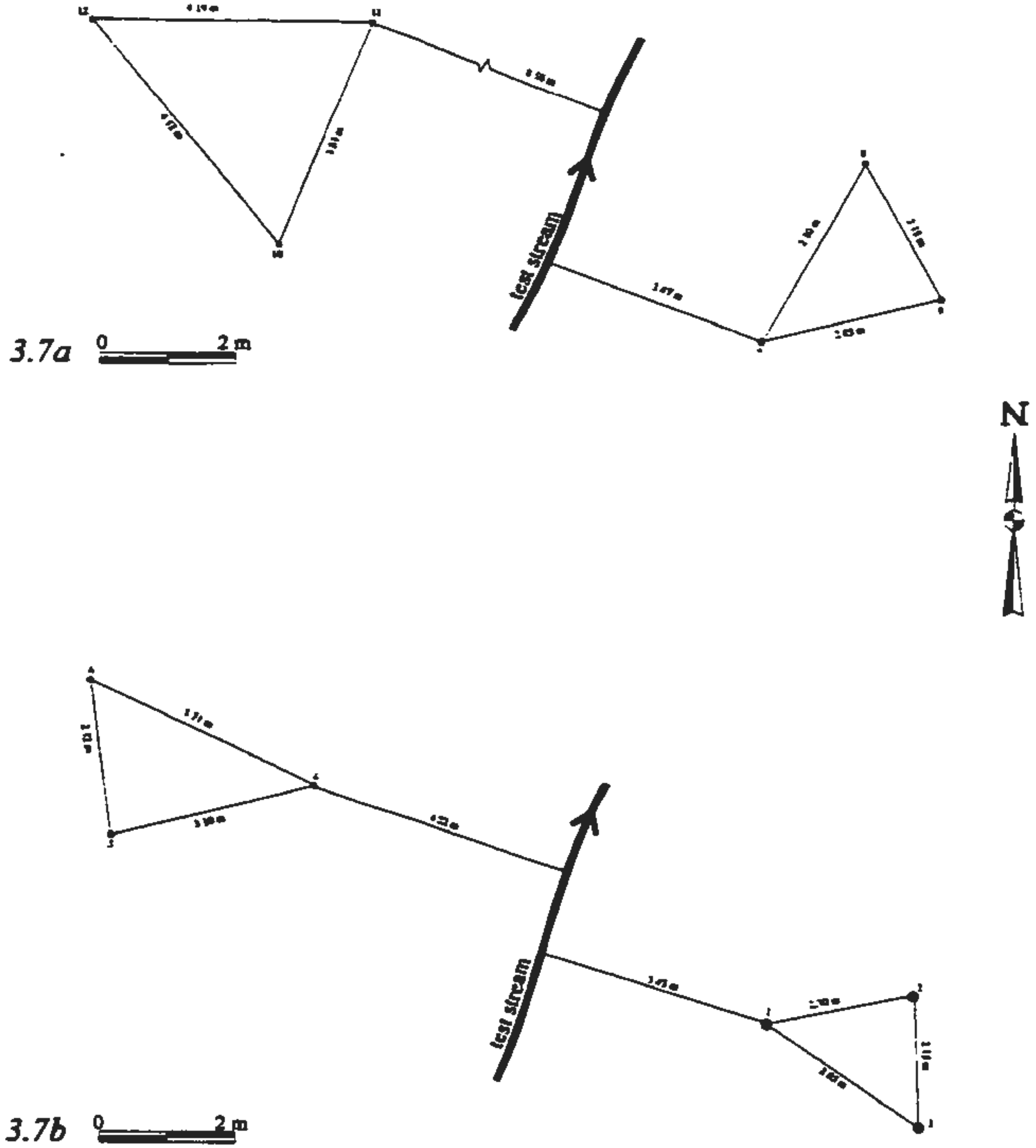


Figure 3.7 Geometry of installed piezometers relative to the test stream. Figure *3.7a* represents the piezometers installed 200 m upstream from the South River estuary and *3.7b* represents the piezometers installed 175 downstream from the salvage yard. Arrows indicate direction of stream flow.

Dissolved Oxygen 2 Reagent Powder Pillow (Hach, 1989). All water samples were transported back to the laboratory in a cooler and stored at 4° C until analysed.

Alkalinity, as HCO_3^- (ppm), was determined by titrating with 0.1600 N H_2SO_4 (Digital Titrator) and using a Bromocresol Green-Methyl Red Indicator Powder Pillow (Hach, 1989). In order to determine dissolved oxygen concentrations (ppm O_2), Dissolved Oxygen 3 Reagent Powder Pillow was first added to the bottle and allowed to mix (Hach, 1989). 20 ml of sample solution was then titrated to a colourless endpoint with 0.200 N Sodium Thiosulphate (Digital Titrator) (Hach, 1989). Alkalinity and dissolved oxygen titrations were performed upon return to the laboratory (< 4 hours).

Major anion (SO_4^{2-}, Cl^-, and NO_3^{2-}) concentrations were determined using a Dionex-DX 100 Ion Chromatograph (IC). Major cation (Na^+, Ca^{2+}, Mg^{2+}, K^+) concentrations were determined using a Perkin-Elmer model 2380 Atomic Absorption Spectrometer (AA). Samples were spiked with lanthanum oxide dissolved in HCl to reduce ionization interferences. Trace element concentrations were determined using a modified Perkin-Elmer SCIEX ELAN model 250 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS).

Relative surface water flow (L/min) was estimated, on July 13, 1995, at 13 locations along the test stream where water samples had been previously collected (Figure 3.4). Stream flow at site STS4 was omitted due to error in data collection. The cross sectional area of the stream was estimated by measuring the depth of water (±5 mm) at

0.20 m intervals across each location. Stream velocity was estimated by the time required for a float to travel 2 m at the approximate centre of each transect. The average of 5 trials was used as the best estimate of velocity. The average flow rate (L/min) at each location was calculated by simply multiplying the average surface water velocity by the cross-sectional area of the stream (Fetter, 1988). Unfortunately, current metres were not available at the time of data collection.

3.3 Bioreceptor Sampling and Analysis

Clams (*Mercenaria mercenaria*) were dredged from the upper 0.20-0.25 m of sediment at five locations in the South River estuary (Figure 3.8). At each location, the sample was divided into two sub-samples: one for PCB analyses and one for trace metal analyses. The clams were rinsed of loose sediment and stored in filtered ($\leq 45\ \mu m$) estuarine water for 48 hours to purge their digestive system contents and therefore, minimize bias from ingested sediment (Flegal and Martin, 1976). After 48 hours the soft portions were removed from the shells and frozen until analysed.

Samples for PCB analysis were stored in aluminum foil and plastic bags while the samples for trace metal analysis were stored in pre-washed plastic bottles. In most cases, 30 or more clams were combined to form a homogenized sample of the population. The frozen samples for PCB analysis were shipped by courier to Zenon Environmental Laboratories (Burlington, ON). Analyses were performed using gas chromatography with

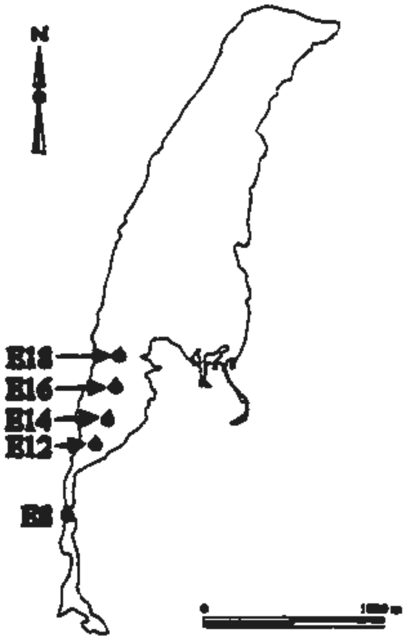


Figure 3.8 Locations of clam (*Mercenaria mercenaria*) samples collected from the South River estuary.

an electron capture detector (detection limit= 0.05 ppm) and concentrations were expressed relative to the wet weight of the sample.

The samples analysed for trace metals were first freeze dried and approximately 0.30 g of sample was added into the Teflon cup of a high-pressure acid-digestion bomb. Fifteen ml of doubly distilled 16 N HNO_3 was added to the dried tissue and the bomb was sealed. Samples were digested at 130 °C for 48 hours in a muffle furnace and transferred to 100 ml snap-top vials. The samples were heated on a hot-plate at 90 °C and evaporated to dryness. The samples were then made up to 20 ml with 0.2M HNO_3. Following this process, the samples were not completely digested and they had to be refluxed with HNO_3 and H_2O_2 (Friel *et al.*, 1990). The 20 ml solution was heated on a hot plate and evaporated to 1-2 ml. Two ml of concentrated HNO_3 and 2 ml of 15 % H_2O_2 were added and the solution was evaporated to dryness. One ml of concentrated HNO_3 and 1 ml of 15 % H_2O_2 were then added and the solution was refluxed for 1 hour, followed by evaporation to 1-2 ml. One ml of concentrated HNO_3 and 1 ml of 15 % H_2O_2 were added again and the solution was refluxed for 4 hours, followed by evaporation to near dryness. The samples were then made up again to 20 ml with 0.2 M HNO_3. This final solution was analysed for trace element content by ICP-MS.

3.4 Estuary characterization

Salinity influences the distribution of heavy metals and PCBs in the water column, therefore estuarine dynamics were characterized. Synoptic sampling of the estuary was not practical so a successive sampling program was performed. Sampling at the pre-selected sites was performed in as short a time as possible to best meet steady state conditions (Morris, 1978, 1985). As well as detecting spatial variation in salinity, temporal variation was also investigated during four different sampling periods. Electrical conductivity and temperature were measured within 2 hours after low tide at 9 locations along the western shore of South River on June 22, 1994 (Figure 3.9). Electrical conductivity and temperature values were used to calculate salinity by the method outlined

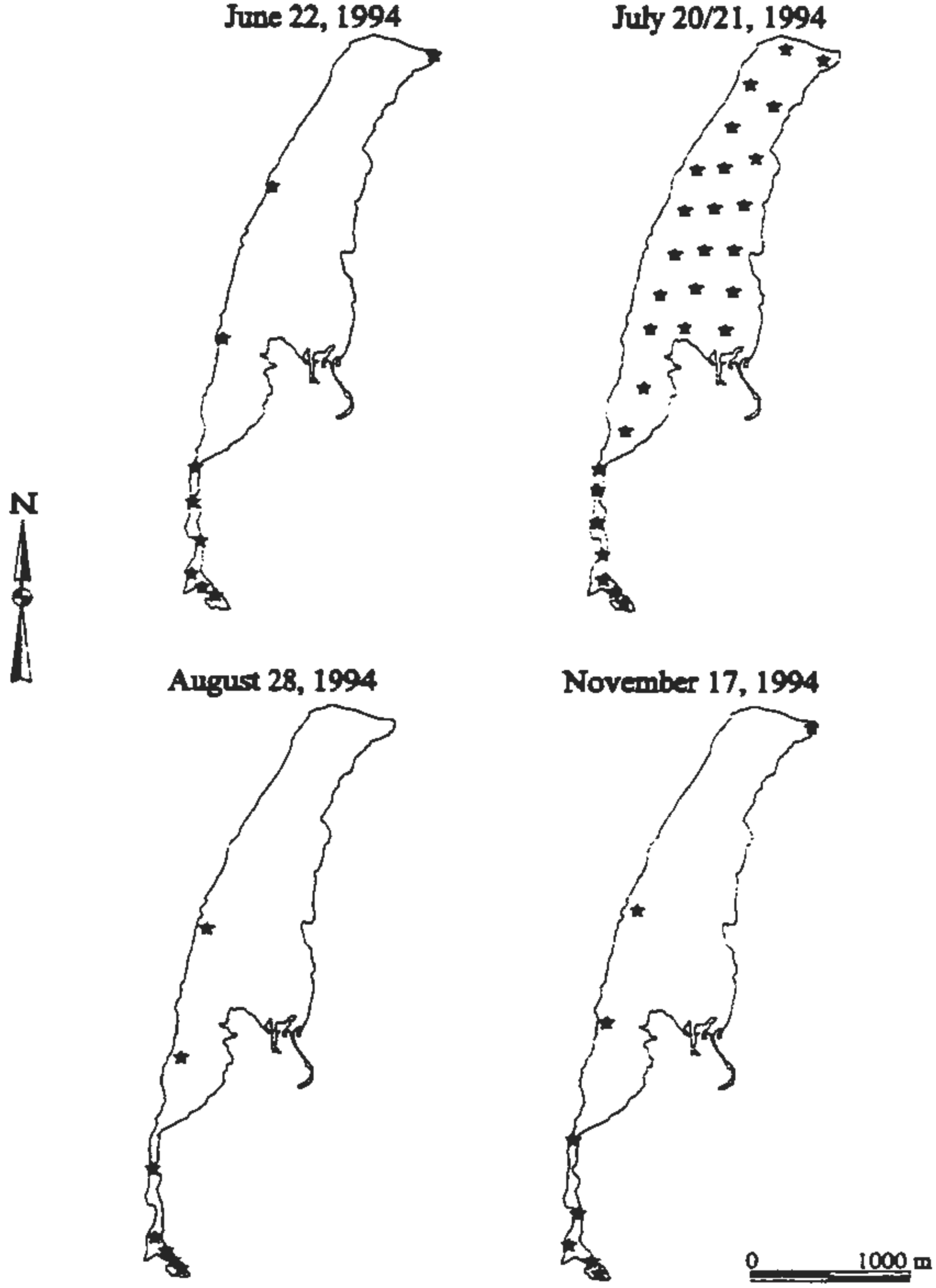


Figure 3.9 Locations of salinity determinations in the South River estuary (1994).

in Cox *et al.* (1967) (Appendix C). This method is accurate to ± 0.01 ‰ between 2.5-41.6 ‰ salinity.

A more complete investigation into the estuarine dynamics of South River was completed over July 20 and 21, 1994. Twenty-nine sampling sites were marked with floats and weights and were sampled for electrical conductivity, temperature, pH, and depth at, or near, low tide and high tide (Figure 3.9). The time required to sample all 29 sample sites by rowboat was 1 ½ hours. Sampling on July 20 was at or near high tide (1739 hrs at Holyrood), commenced at site #1 at 1700 hrs and concluded at site #29 at 1835 hrs. Sampling on July 21 was performed at or near low tide (1204 hrs at Holyrood), commenced at site #1 at 1155 hrs and concluded at site #29 at 1335 hrs. Equipment malfunction did not allow pH measurements to be collected in the field but values were obtained within 3-4 hours back at the laboratory. Bathymetry was measured (±30 mm) using a 2 m staff marked at 10 mm intervals. The maximum depth was approximately 2 m at the most northerly sample site (see Figure 3.9) and the average depth was approximately 0.90 m (n=30). On August 28, 1994, electrical conductivity and temperature were measured within 2 hours before low tide at 8 locations along the western shore of South River (Figure 3.9). Electrical conductivity and temperature were again measured (approximately low tide) at 6 locations along the west shore of South River on November 17, 1994 (Figure 3.9).

Chapter 4. RESULTS AND DISCUSSION

The main objectives of this study were to, first determine how PCBs and heavy metals are distributed in sediments, surface waters, ground waters, and ecosystem receptors (i.e. clams); and next to identify the roles that the sediments, surface waters, ground waters, and clams play in the transport of PCBs and heavy metals. This chapter is organized according to these objectives with section 4.1 containing the results of the sampling / analytical program within the Makinsons drainage basin and South River estuary. The spatial distribution of PCBs, elements, and oxides is first described in the soils and sediments within the stream and estuary. Next, the surface waters and ground waters are characterized and the spatial distribution of the major / minor ions are described. Finally in section 4.1, the spatial distribution of PCBs and trace elements in clams collected from the South River estuary is described.

In section 4.2, the geochemistry of the Makinsons drainage basin is assessed in order to distinguish between natural variation (i.e. background) and anthropogenic input. Describing the spatial distribution of PCBs and heavy metals was intended to document the extent of contamination within the basin. Therefore, it is important to determine whether concentrations are above background variation and indicative of contamination. This assessment is much simpler with respect to PCBs since they are synthetic and any quantity detected is direct evidence of contamination. However, the distribution patterns of heavy metals in the Makinsons drainage basin may be the result of background variation or anthropogenic input. Given that one of the main objectives of this study was to determine the roles that the waters, sediments, and clams play in contaminant migration, evidence of contamination must first be established before specific roles can be determined.

The roles (pathways / receptors) that sediments within the stream and estuary, surface waters and ground waters, and other ecosystem receptors play in migration of PCBs and heavy metals are addressed in section 4.3. These roles are determined after considering similar investigations in the literature, the hydrogeological framework, and the spatial distribution of the contaminants in the Makinsons drainage basin.

4.1 Geochemistry of the Makinsons Study Area

A problem facing the consolidation of results in this study, was the number of parameters available to describe each data set. There were 32 parameters available to describe sediment chemistry; 33 parameters for both ground water and surface water chemistry, and 38 for the clam samples. Therefore, it was not practical to present the spatial distribution of the parameters (i.e. elements) individually, and groupings of elements was opted for. The next issue to address was the criteria on which the elements should be grouped. Ideally, a multivariate statistical procedure (i.e. factor or cluster analysis) would be used to group the elements, but the data in this study were not suitable. First of all, many of the parameters were not normally distributed and contained outliers (Rollinson, 1993). Moreover, the number of parameters exceeded the number of observations in all the data sets and this created a problem with "dimensionality" (Garrett, 1993). This "dimensionality" problem is that in order for reliable results to be obtained from a correlation matrix, the number of observations must be at least 3 times as large as the number of parameters (Howarth and Sinding-Larsen, 1983). Factor analysis and cluster analysis both start from the computation of such a matrix, therefore the data in this study were not suitable for groupings based on multivariate statistics.

Given that one of the objectives of this study was to describe the spatial distribution of PCBs and heavy metals in the Makinsons drainage basin, it was decided that elements should be grouped according to similarity of their distribution patterns. In each of the 4 data sets (i.e. sediment, surface water, ground water, and clam), parameters were first compared, contrasted, and grouped according to their pattern of relative concentrations throughout the study area. For example, in the sediment data set, Na_2O, MgO, K_2O, and Rb, all displayed similar patterns within the Makinsons drainage basin and can be described as a group (Figure 4.1). As a further simplification, one element (i.e. Rb) is displayed as a representative of the group since all the elements display the same distribution pattern. Given that the metals suspected of representing contamination (i.e. anthropogenic input) are individually presented in section 4.2, this approach is considered acceptable. Greater emphasis will be eventually placed on these suspected contaminants since it is the roles that the sediments, waters, and bioreceptors play in their migration that is of concern in this study.

4.1.1 Sediments and Soils

In order to describe the spatial distribution of PCBs and heavy metals within the Makinsons drainage basin, a sampling / analytical program was performed. Seven stream

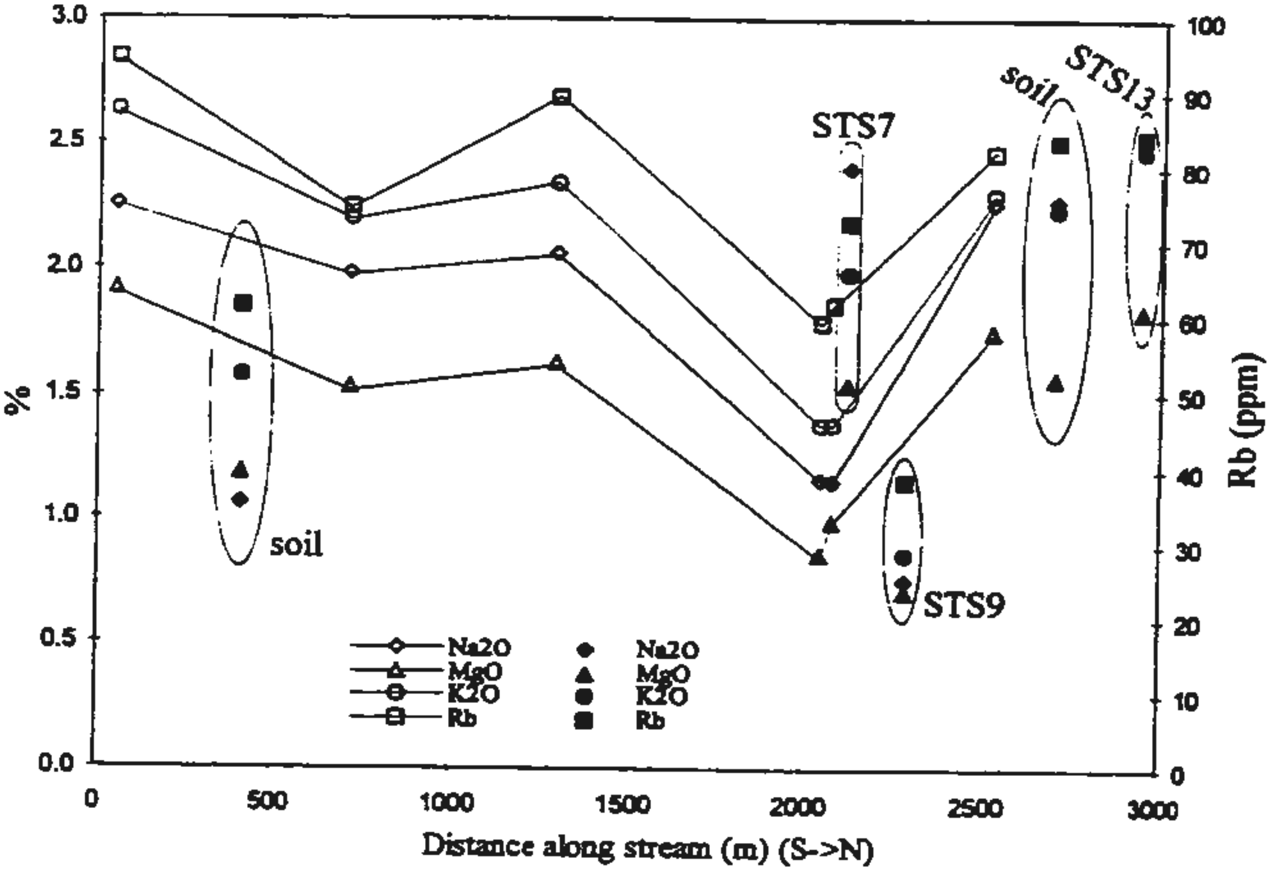


Figure 4.1 Concentrations of Group 1 parameters along the test stream. All four parameters display similar distribution patterns and can be described as a group. Na_2O, MgO, and K_2O are measured as % along the left axis, while Rb is measured as ppm along the right axis. The tributaries and soil samples (solid symbols) are labeled and the hollow symbols are samples along the main course of the test stream.

sediment samples were collected from the main course of the test stream and 3 from its tributaries. In addition, 4 shallow soil samples were collected within 10 m of the test stream. Locations of the sediment and soil sample sites are displayed in Figure 4.1.2. Based on XRF, LOI, grain size, and PCB analyses, a total of 32 parameters were available to describe the sediment and soil samples. Given that one of the main goals of this study was to determine the roles that sediments and waters play in contaminant migration, it was considered beneficial to include main stream and tributary sediment samples, as well as soil samples in the same geochemical profile. Based on the physical hydrogeology within the Makinsons basin (see Figure 2.3.4), surface water and ground water is channeled into the main course of the test stream. Therefore, the tributaries would not be subject to contamination from the salvage yard and should give a better estimate of background concentrations. Also, the soil samples are not subject to suspended material in the stream and should help distinguish between the roles that ground waters and surface waters play in the transport of PCBs and heavy metals. These issues will be discussed in sections 4.2 and 4.3.

According to the relative concentration patterns, the 32 parameters were arranged into 4 groups: *1)* Rb, Na_2O, MgO, and K_2O; *2)* SiO_2, Al_2O_3, Nb, Zr, Ga, Th, Sc, and TiO_2; *3)* Pb, Cu, Zn, S, Ce, Y, P_2O_5, organic content (LOI), CaO, and Sr; and *4)* Cr, Ni, As, MnO, Ba, Fe_2O_3, V, Cl, and PCBs. A representative of each group is displayed in Figure 4.1.3. Concentrations of the first group (Rb, Na_2O, MgO, and K_2O) are greatest upstream from the salvage yard (STS1), decrease downstream from the salvage yard, and increase again at site STS4 (see Rb in Figure 4.1.3). Concentrations decrease at sites STS5, STS6, and STS8 and

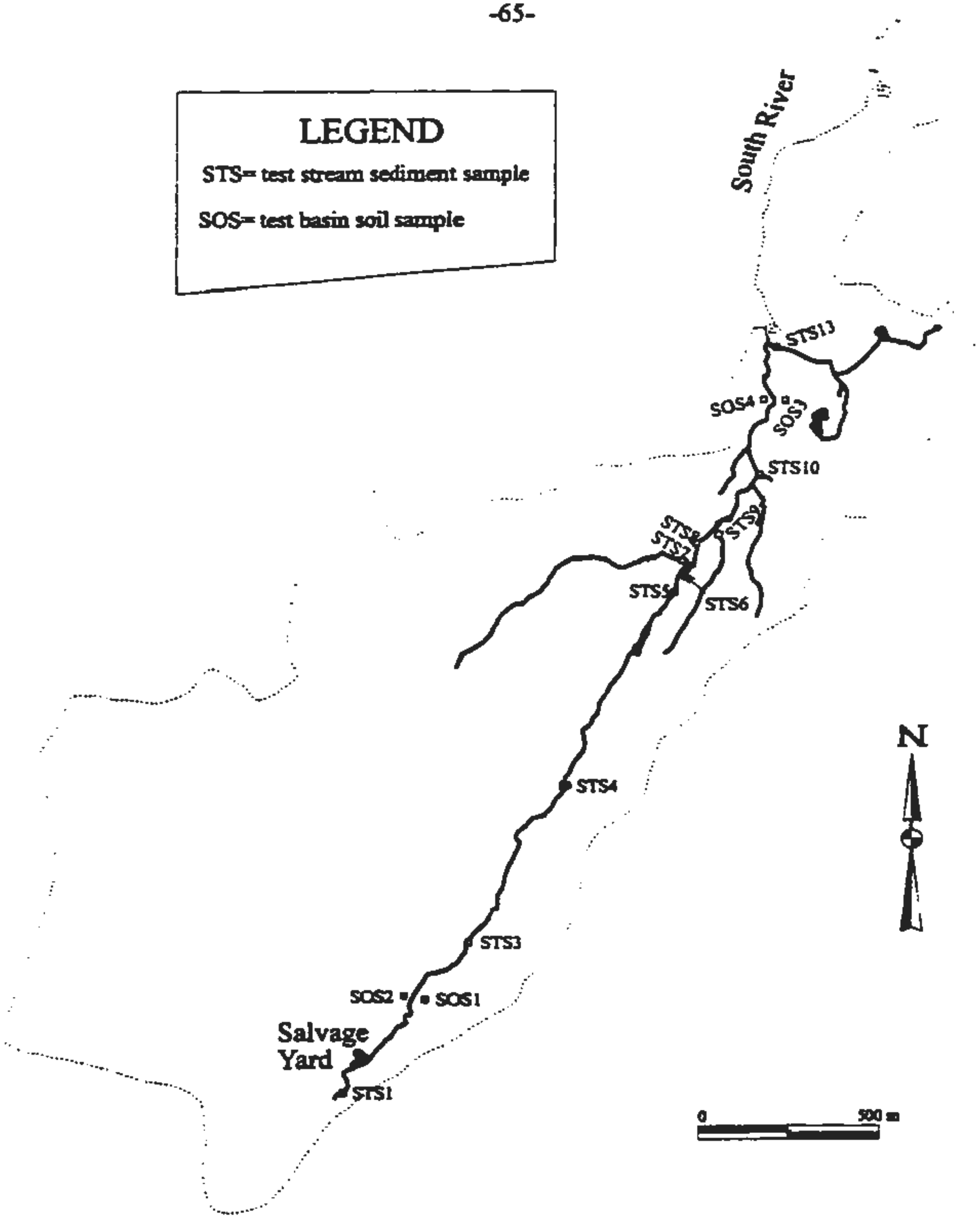


Figure 4.1.2 Locations of the stream sediments and soil samples collected from the Makinsons drainage basin.

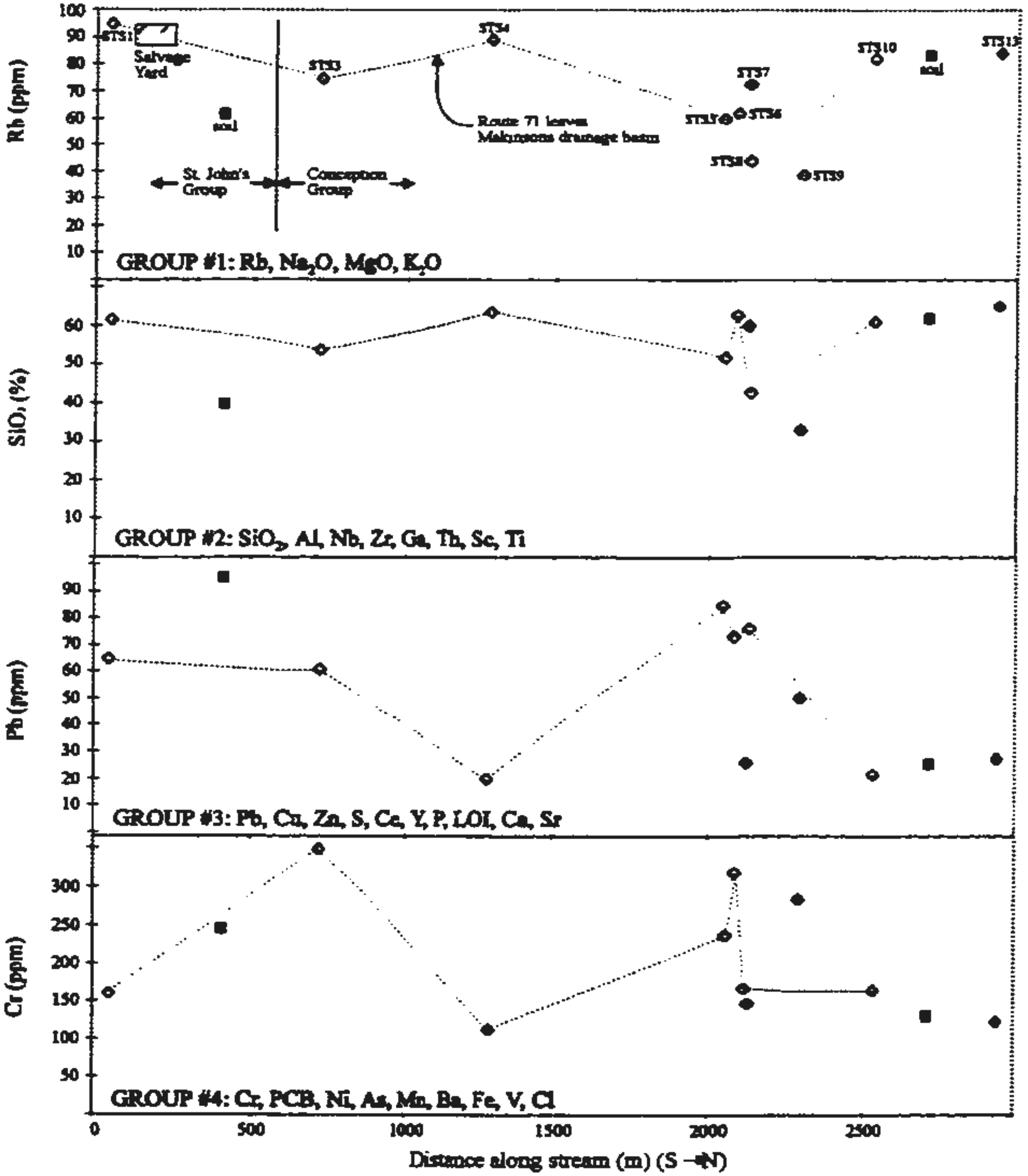


Figure 4.1.3 Groups 1, 2, 3, and 4 behaviour, shown by Rb, SiO_2, Pb, and Cr in sediments and soils versus distance along stream. Hollow diamonds are stream sediments along the test stream, solid diamonds are from the tributaries, and the solid squares are soil samples.

concentrations in upper basin soils are less than in the adjacent stream sediments. It should be noted that the soil samples were not collected at the exact location of stream sediments, but approximately 100 m upstream at the St. John's Group location and 100 m downstream at the Conception Group location (Figure 4.1.3). Compared to the main stream course, group 1 concentrations are higher in the tributary STS7 (draining an undeveloped portion of the basin) and lower in the tributary STS9. Elements and oxides of the second group (SiO_2, Al_2O_3, Nb, Zr, Ga, Th, Sc, and TiO_2) also display an increase in concentration upstream from the salvage yard and again at site STS4 (see SiO_2 in Figure 4.1.3). But there is also a slight increase at site STS6 and soil samples in the upper basin are depleted relative to all stream sediments. Relative to adjacent stream sediments, group 2 concentrations are depleted in tributary STS9. The differences between groups 1 and 2 are subtle and they could possibly be treated as the same group. Constituents of the third group (Pb, Cu, Zn, S, Ce, Y, P_2O_5, organic content (LOI), CaO, and Sr) decrease in concentration immediately downstream from the salvage yard and display peak concentrations at sites STS5 and / or STS6 (see Pb in Figure 4.1.3). In addition, grain size corresponds to this pattern; the silt + clay fraction decreases downstream from the salvage yard and increases at sites STS5 and STS6. Group 3 concentrations are enriched, relative to all stream sediments, in upper soil samples. Compared to the main course, the relative concentrations of group 3 are lower in sediments from tributary STS7 and greater in tributary STS9 (Figure 4.1.3). Constituents of the fourth group (Cr, Ni, As, MnO, Ba, Fe_2O_3, V, Cl, and PCBs) display an increase in concentration immediately downstream from the salvage yard (STS3) and again at sites STS5 and / or STS6 (see Cr in Figure 4.1.3). Compared to sediments along the main course, group 4 concentrations are lower in the tributary STS7 and greater in the tributary STS9. The distribution pattern of PCBs in the Makinsons drainage basin corresponds closest with the profile of group 4 elements and this group may reflect salvage yard contamination. This issue will be discussed in sections 4.2 and 4.3.

The spatial distribution of PCBs, within stream sediments and soils collected from the Makinsons drainage basin and control basin, are graphically depicted in Figure 4.1.4. Two stream sediment samples were collected from the control stream but PCBs were not present above the detection limit of 0.05 ppm. However, PCBs were detected (1.76 ppm) in a soil sample (SOC1) from the control stream basin (Figure 4.1.4). PCBs were also detected at two tidal marsh locations (ESO1 and ESO2) in the South River estuary at concentrations of 0.06 ppm. The entire stream sediment and soil data set is included in Table D.1.

The spatial distribution of PCBs and heavy metals within South River estuary sediment cores was also investigated in an attempt to determine the extent of migration from the salvage yard-bog area. South River sample sites are displayed in Figure 4.1.5. Reconnaissance work into the presence of PCBs in the South River estuary initially involved sampling the top 100 mm of 6 sediment cores. Two additional cores (E2 and E4) were sampled in greater detail (50 mm intervals) to a maximum depth of 300 mm. Reconnaissance work into the presence of trace metals in the South River estuary involved sampling 2 sediment cores (E4 and E9) at 20 mm intervals. Trace concentrations of PCBs (0.02 - 0.05 ppm) were detected but not quantified (EPL) from the upper 50 mm of cores E2 and E4

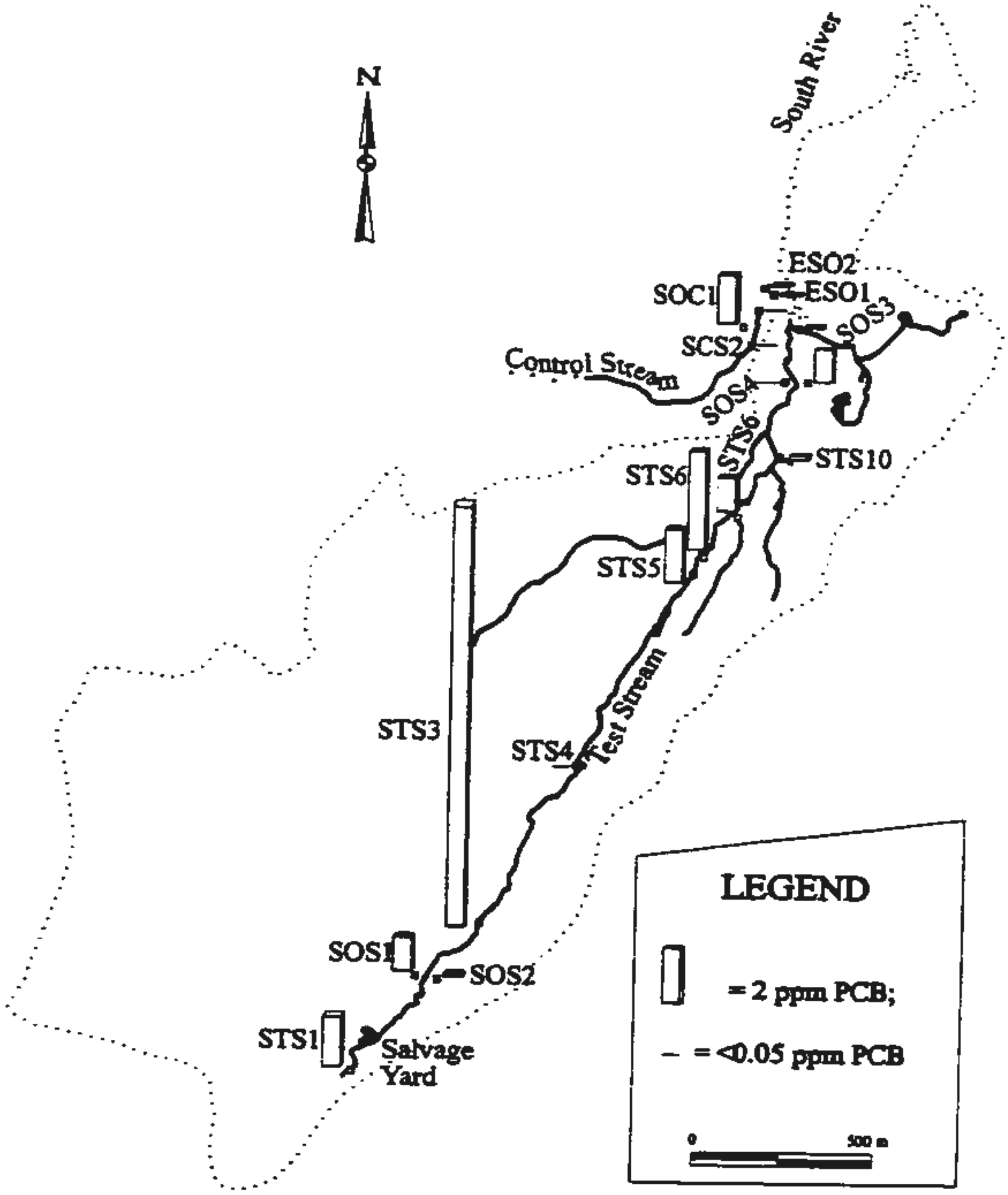


Figure 4.1.4 Entire stream sediment and soil sample set analysed for total PCB content. Note elevated PCBs in bog sample near control stream.

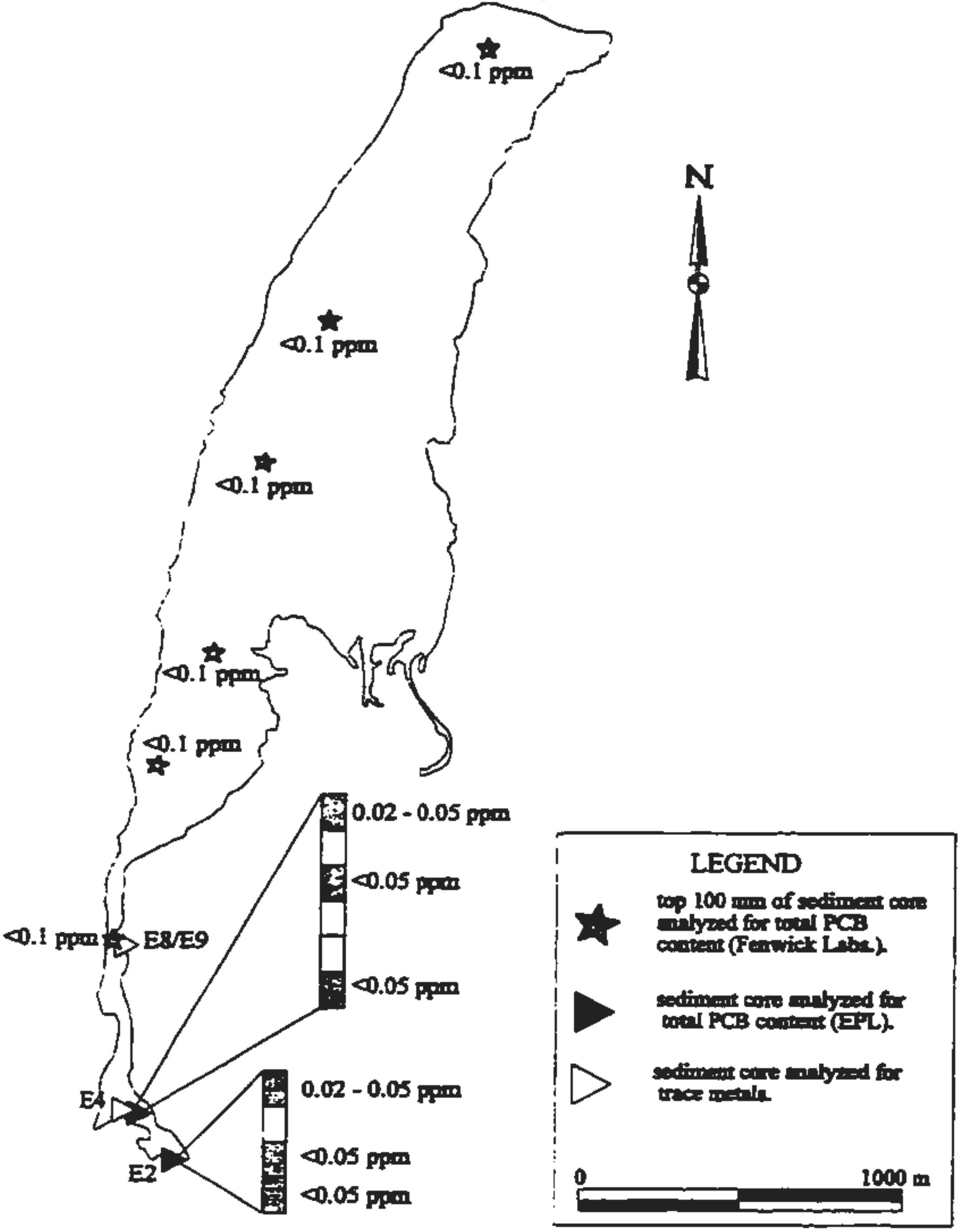


Figure 4.1.5 Entire South River sediment sample set that was analysed for total PCB and trace metal content. Each of the 50 mm intervals sampled for PCB content are shaded and the concentrations are marked.

collected in the South River estuary (Figure 4.1.5). However, PCBs were not detected (≥ 0.1 ppm) in the upper 100 mm of South River sediments north of these two locations.

Figures 4.1.6 and 4.1.7 present sediment chemistry from two cores (E4 and E9) in the South River estuary. Core E4 (Figure 4.1.6) consisted of dark yellowish brown (10 YR 4/2) (Canada Soil Survey Committee, 1978) organic sediment (LOI ranged from approximately 20 to 40 %). Apart from natural variations, few of the constituents appear to display any distinct trends from top to bottom. However, Pb displays an unexplained sharp peak in the top 20 mm of the core and again at 270 mm of depth and both LOI and Al display a peak at approximately 160 mm of depth (Figure 4.1.6). Core E9 (Figure 4.1.7) consisted of dark yellowish brown (10 YR 4/2) sediment in the upper 170 mm and olive gray (5 Y 3/2) (Canada Soil Survey Committee, 1978) sediment in the lower 40 mm. The boundary between the two sediment layers is characterized by a sharp drop in LOI (>20 % to <10 %). This was also observed in the laboratory since the olive gray layer appeared to be clean sand with little organic material. It should be noted that concentrations of Pb throughout both core E4 and E9 were consistently greater than concentrations reported from lake sediments in this region (Davenport *et al.*, 1992).

4.1.2 Surface Waters and Ground Waters

Eleven surface water samples were collected along the main course of the test stream and 3 from its tributaries to describe the evolution of surface waters from the top of the

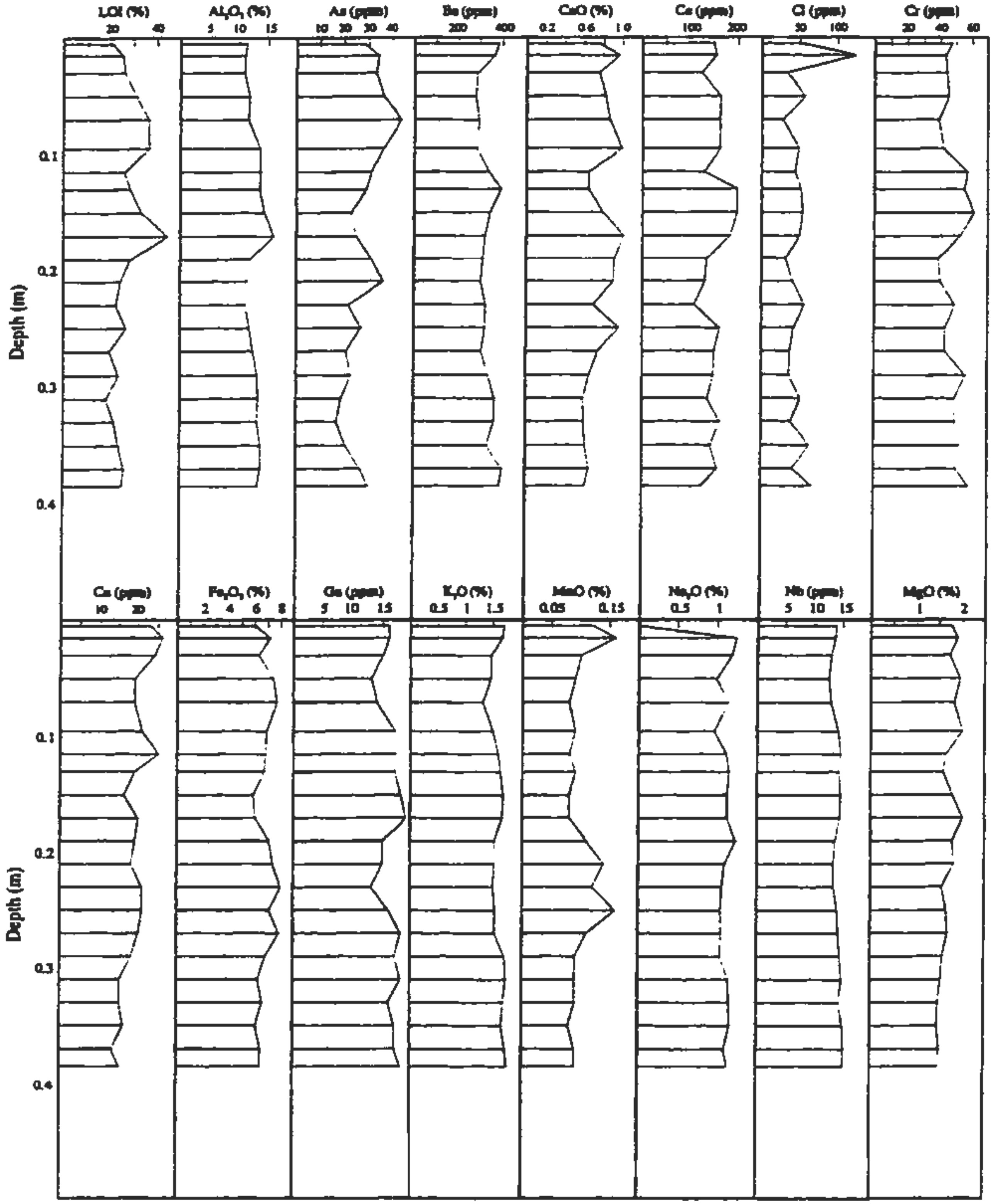
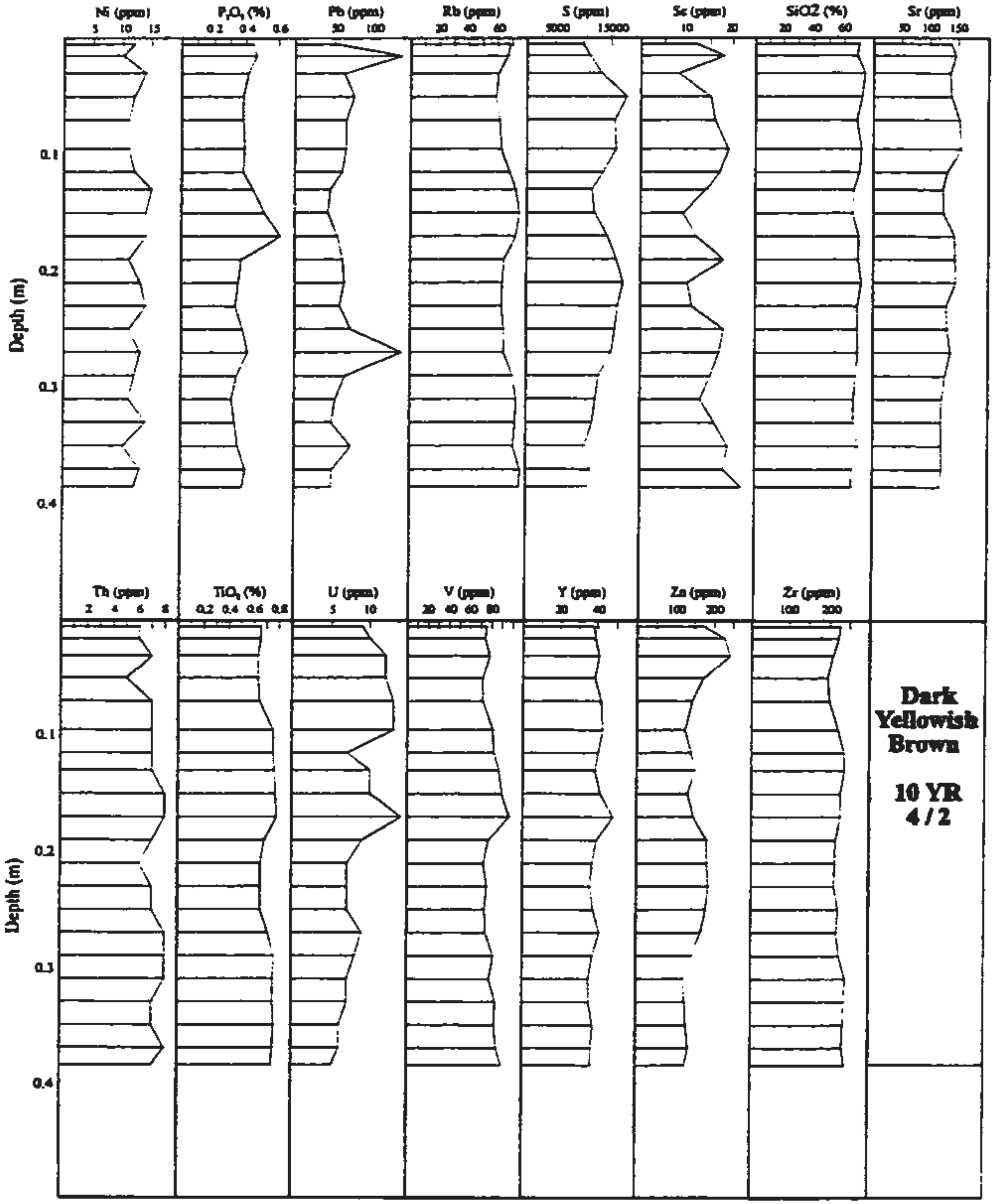


Figure 4.1.6 Sediment chemistry from core E4.



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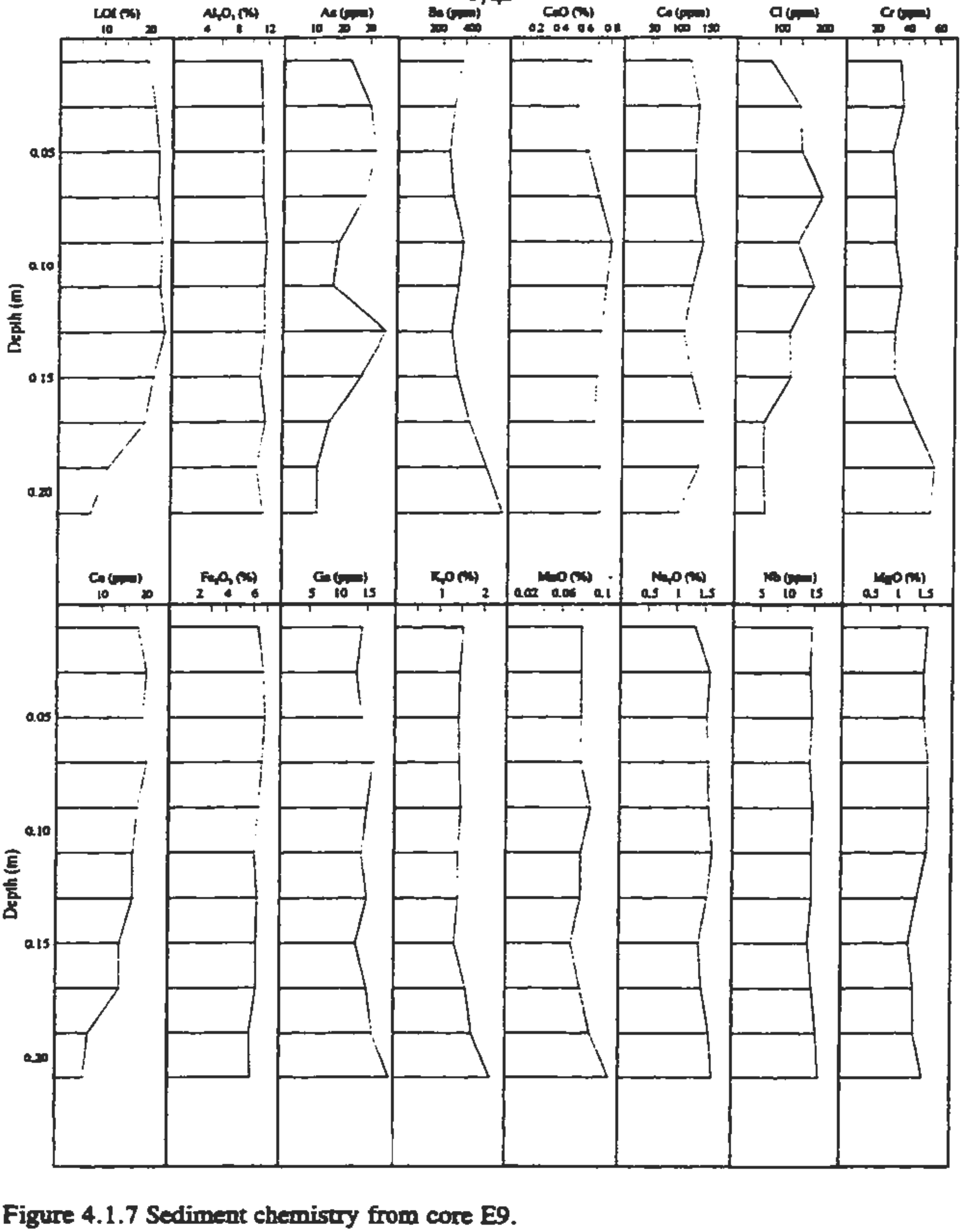

Figure 4.1.7 Sediment chemistry from core E9.

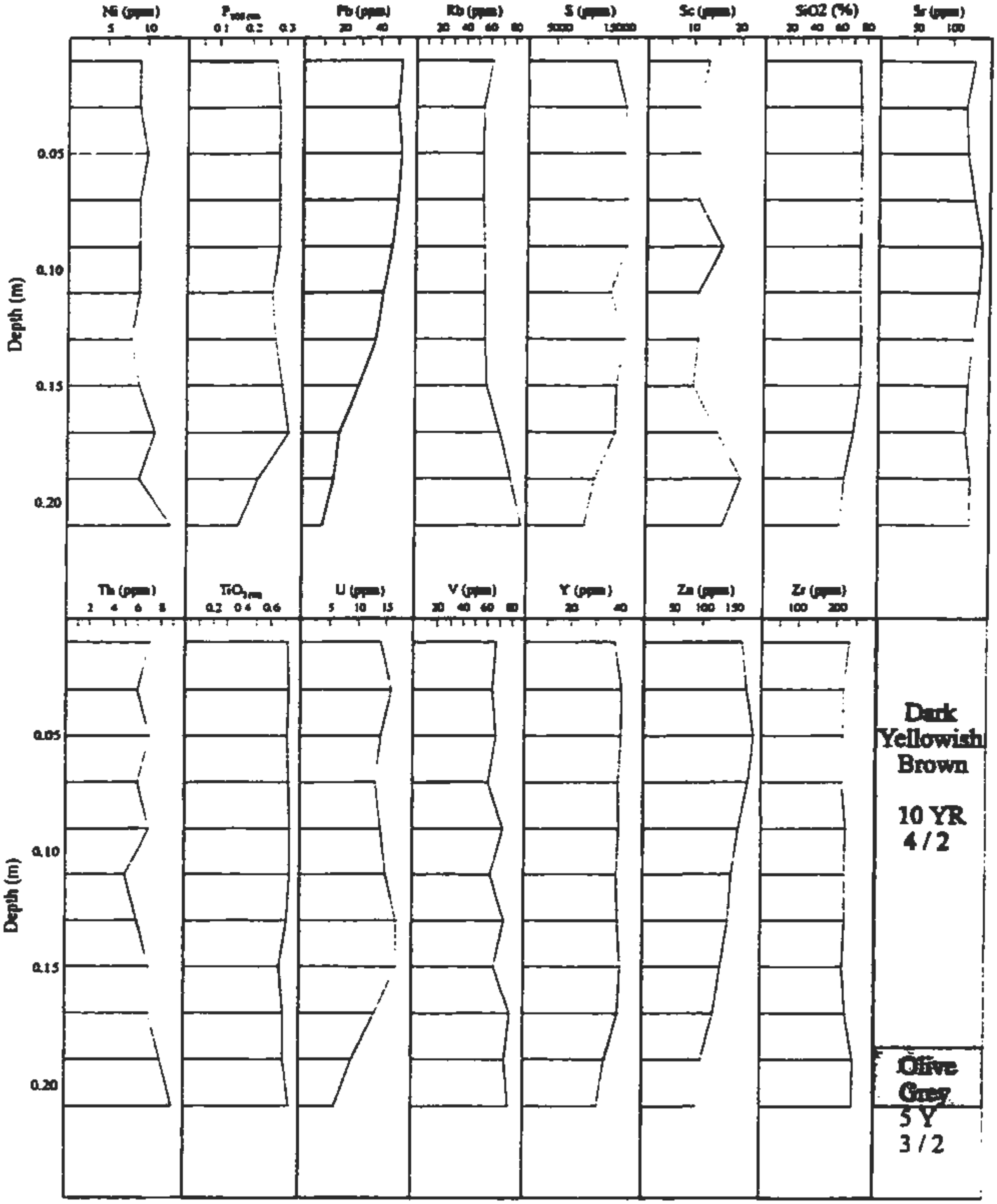

Figure 4.1.7 cont…

Makinsons drainage basin to the bottom (Figure 4.1.8). Ground water chemistry was also determined at two locations- samples were collected from 6 piezometers near the top of the basin and 6 near the bottom of the basin. Characterizing the surface waters and ground waters in the Makinsons drainage basin must take into account that the test stream crosses over two different bedrock units (see Figure 2.1). The headwaters originate in an area underlain by the St. John's Group and cross into the Conception Group approximately 550 m downstream. The dominant rock types of the St. John's and Conception Groups are shales and sandstones, respectively (King, 1988). The three southern-most surface water sample sites in Figure 4.1.8 are located within, or adjacent to, the St. John's Group and the remaining eight are in the Conception Group. Ground waters near the top of the basin are sampled on the St. John's Group whereas those near the bottom were sampled on the Conception Group. The entire control stream is located on the St. John's Group (see Figure 2.1).

Figure 4.1.9 is a Piper diagram (Piper, 1944) of the surface and ground waters collected in November, 1994. All samples are classified as sodium- and chloride-type waters except for SOW12 which is bicarbonate-type (Freeze and Cherry, 1979). The control stream sample is also classified as sodium- and chloride-type water but contains a lower proportion of Cl than surface waters from the Makinsons drainage basin (Figure 4.1.9). Surface water samples correspond closely with ground water collected near the top of the basin, whereas ground water samples collected near the bottom of the basin appear

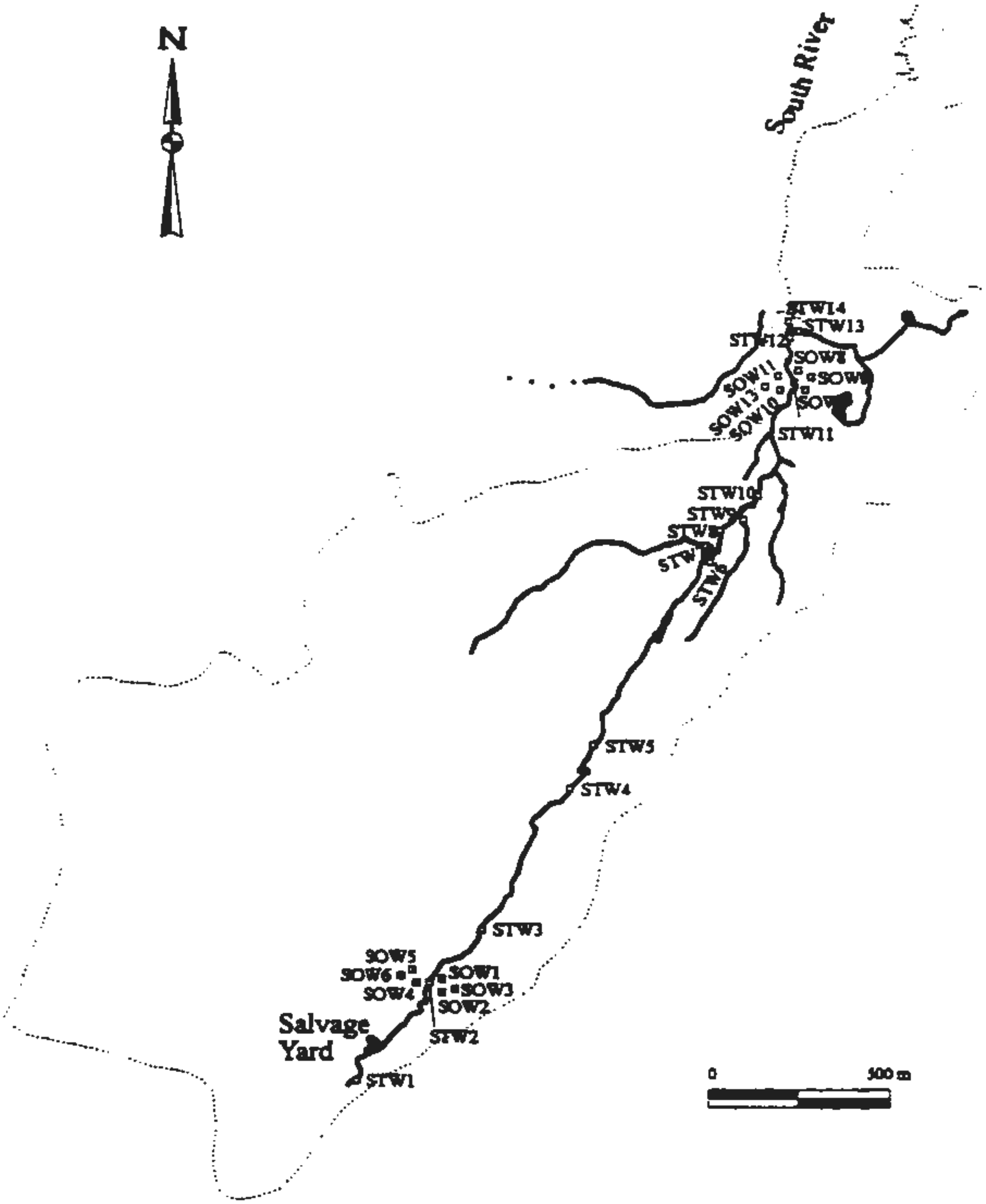

Figure 4.1.8 Locations of water samples collected from the Makinsons drainage basin. SOW1 through SOW12 are ground water samples and STW1 through STW14 are surface water samples.

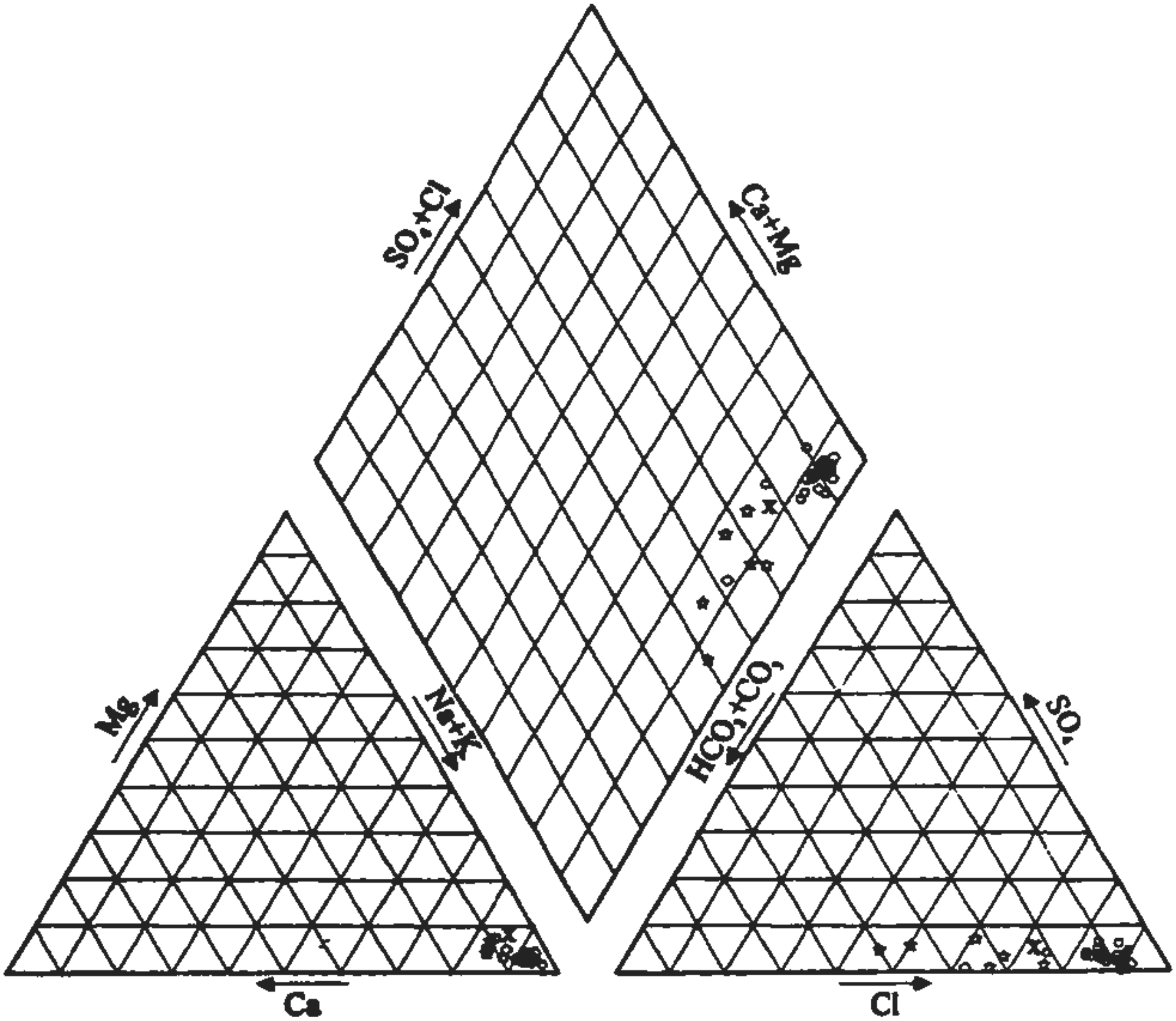

Figure 4.1.9 Piper diagram of the major cations and anions measured from the main course of the test stream and ground water samples collected on November 16/17, 1994. Surface water samples= ○, ground water samples from the upper portion of the basin=◇, ground water samples from the lower portion of the basin= ☆, and the control stream sample= X.

somewhat different than both upper basin ground waters and surface water samples. The lower basin ground water samples represent a trend towards bicarbonate-dominated ground water, which is more characteristic of shallow ground water (Freeze and Cherry, 1979 and Gale *et al.*, 1984). However, the average alkalinity remains constant at both locations and this apparent change in water type is most likely due to the lower concentrations of chloride in the lower basin ground waters. This trend may also reflect the change in lithology from the top of the basin to the bottom. Figures E.1, E.2, and E.3 contain temperature, conductivity, pH, dissolved oxygen, and major ion chemistry of the ground water samples collected at each of the twelve piezometers and also includes the corresponding surface water parameter for comparison.

In surface waters from the Makinsons drainage basin, the average pH and total dissolved solids (TDS) were approximately 7 and 60 mg/l, respectively, compared with 7.6 and 20 mg/l in the control stream. In both streams, alkalinity and dissolved oxygen are comparable (< 10 ppm and 7 -10 ppm, respectively). These values were compared with the average reported for selected drainage basins on the Avalon Peninsula (Gale *et al.*, 1984) and appear slightly different. The pH and TDS were both higher along the test stream than values (4-6.5 and < 25 mg/l, respectively) reported by Gale *et al.* (1984). The control stream sample was comparable to results from Gale *et al.* (1984), except its pH was slightly higher (pH= 7.6). Ground water quality from the 12 shallow "mini" piezometers was also compared with water quality of deeper wells completed in overburden at various locations around the Avalon Peninsula (Gale *et al.*, 1984). pH, alkalinity, sulfate, Ca, and K are comparable, but TDS, Cl, and Na concentrations in the shallow upper basin ground waters are greater than those detected by Gale *et al.* (1984) from the deeper wells. The source of these discrepancies will be discussed in sections 4.2 and 4.3.

Based on pH, ICP-MS, AA, and IC analyses, a total of 33 parameters were available to describe the water samples. These parameters were grouped according to the same criteria as the sediment parameters in section 4.1.1. The 33 parameters describing surface and ground water chemistry can be arranged into 3 groups according to their relative distribution patterns throughout the drainage basin: *1)* Si, SO_4, Zn, Sr, Ti, Ba, Ca, and conductivity; *2)* Cl, As, NO_3, Fe, K, La, Cd, HCO_3, Co, Mn, Na, Mg, and I; and *3)* Cu, Ce, Co, Pb, Sn, Ni, Sb, Rb, and Al. Constituents of the first group (Si, SO_4, Zn, Sr, Ti, Ba, Ca, and conductivity) display a general decrease in concentration downstream from the headwaters and are more concentrated in ground waters than surface waters (see Si in Figure 4.1.10). Ions of the second group (Cl, As, NO_3, Fe, K, La, Cd, HCO_3, Co, Mn, Na, Mg, and I) may increase in concentration upstream from the salvage yard but are highest in concentration at the site (STW3) downstream from the salvage yard (see Cl in Figure 4.1.10). The overall pattern of this group is decreasing concentration down through the basin and greater concentrations in ground waters than surface waters. Metals of the third group (Cu, Ce, Co, Pb, Sn, Ni, Sb, Rb, and Al) increase in concentration

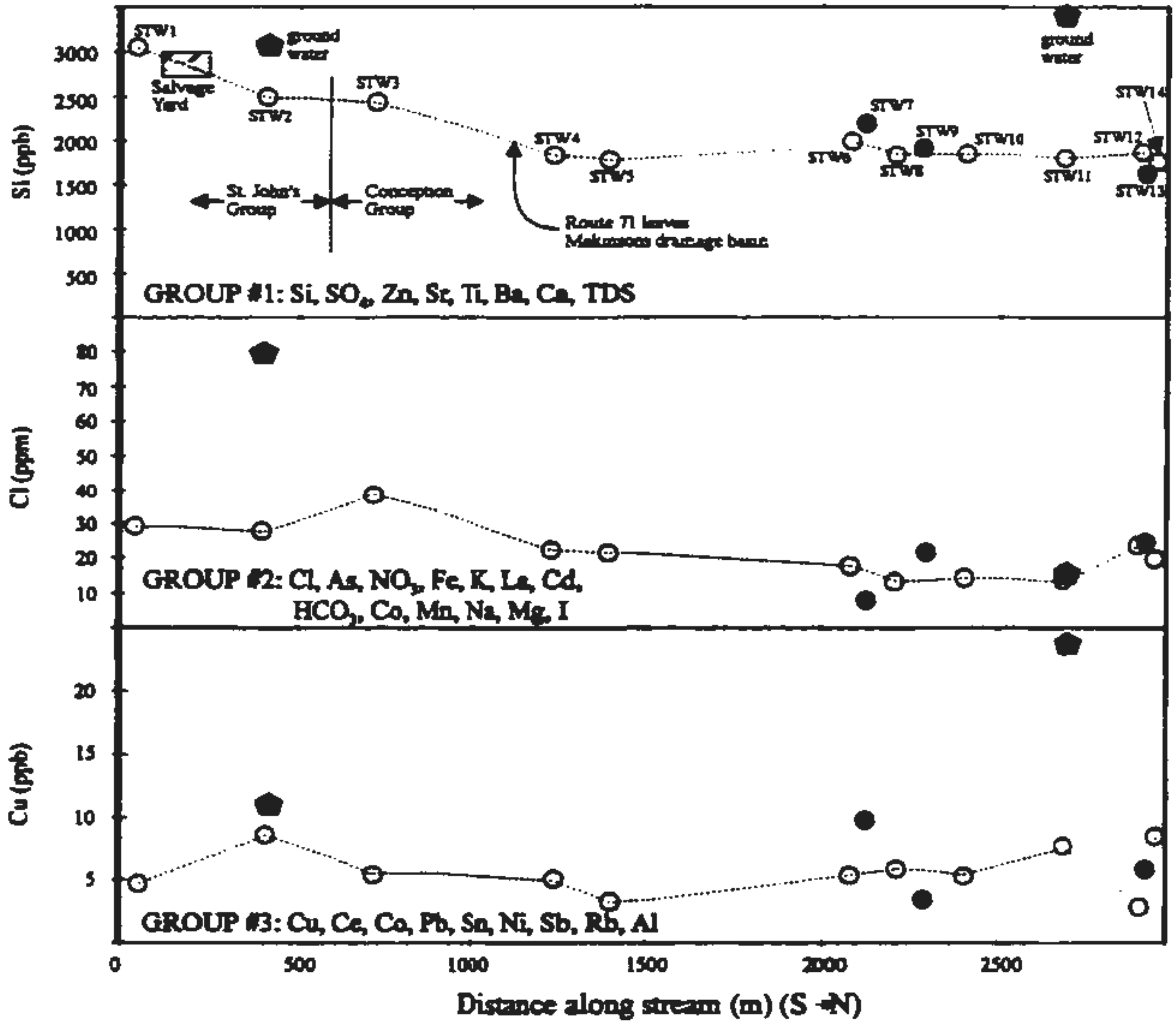

Figure 4.1.10 Group behaviour as shown by Si, Cl, and Cu in surface water samples versus distance along stream. Hollow circles are surface water samples along the main course of the test stream, solid circles are from the tributaries, and solid pentagons are ground water samples.

immediately downstream from the salvage yard (STW2) and increase again further downstream near STW11 (see Cu Figure 4.1.10). The overall pattern is still a general decrease in concentration down through the basin and greater concentrations in ground waters than surface waters. Apart from Ce, the ground water concentrations of this group are much higher in the lower basin waters than the upper basin. In all three groups (Figure 4.1.10), the pattern of decreasing dissolved load as the test stream flows through the basin, is opposite to the typical pattern of increased dissolved load as a river flows through a basin (Freeze and Cherry, 1979). The patterns of pH and dissolved oxygen along the test stream are erratic and could not be grouped with the other variables. However, it should be noted that pH and O_2 concentrations are lower in ground waters and tributaries than in surface waters along the main course of the stream. The entire water chemistry data set from the Makinsons drainage basin is included in Table F.1

Temporal Variation

Seven surface water samples were collected from the main course of the test stream on August 28, 1994 and a second set was collected on November 16/17, 1994 (see Figure 3.5). Comparison of these two data sets was included to assess whether there was seasonal influence on the solubility and subsequent migration of metals in the Makinsons drainage basin. Stream gauge flow measured at Shearstown on August 28 was 0.181 m^3/sec and 0.750 m^3/sec over November 16 and 17 (see Figure 2.2.5). This variation in stream flow is likely due to the fact that August was hotter and drier (17.7 °C and 2.5 mm/day) than

November (3.0 °C and 4.7 mm/day) (Figure 2.2.4). Summer samples, therefore, represent lower water table conditions. In general, downstream concentration patterns are the same in summer as fall, however, summer concentrations are higher for all species except O_2 and SO_4. Figures G.1, G.2, G.3, and G.4 contain conductivity, pH, dissolved oxygen, major ion chemistry, and trace metal chemistry of surface water samples collected (August and November, 1994) from the main course of the test stream.

4.1.3 Bioreceptors

Clams (*Mercenaria mercenaria*) were dredged from the upper 0.20 - 0.25 m of sediment at five locations (1 m^2) in the South River estuary (Figure 4.1.11). At each location, 5 - 30 individuals were combined to form one homogenized sample for PCB analysis and one for trace metal analysis. Based on clam size, and ICP-MS and sediment grain size analyses, a total of 38 parameters were available to describe the sediment and clam samples. The 38 parameters describing clam chemistry can be arranged into 3 groups according to their distribution patterns among the 5 sample locations in the South River estuary. Examples of these patterns are illustrated in Figure 4.1.12. Most of the elements (Fe, Mn, Cr, Co, Sb, Se, Cl, Ca, Sr, Sn, Ce, Li, La, Cs, Zn, V, Al, Ti, U and Ba) display peak concentrations in clams collected from the third site (E14). It should be noted that this sample contained the lightest mean individual weight and shortest mean shell length. The other two groups illustrated peak concentrations in clams collected from the

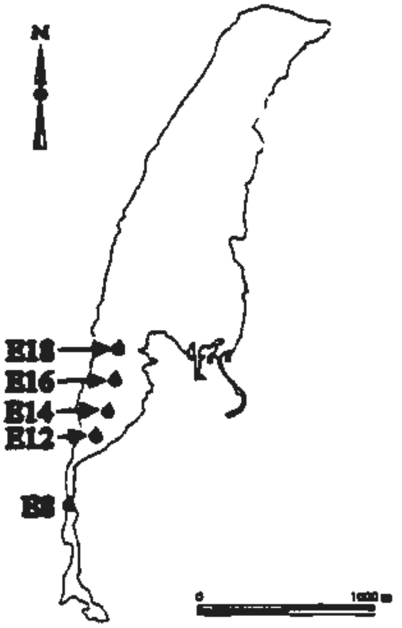

Figure 4.1.11 Locations (stars) of clam (*Mercenaria mercenaria*) samples collected from the South River estuary.

fourth site (E16) (Cd, I, Pb, Mo, As, B, Rb, and Si), or the fifth site (E18) (Cu, Ni, S, P, and Ag). Samples were collected for PCB analysis at the same five sites but PCBs were not present ≥ 0.05 ppm (wet weight). The entire clam chemistry data set is included in Table H.1.

4.1.4 Quality Control

Table I.1 contains the results of replicate sample analyses by X Ray Fluorescence. The replicate samples are a good measure of sample homogeneity and, except for Cl, the chemical constituents are all within 5 %. The precision of the XRF instrument is

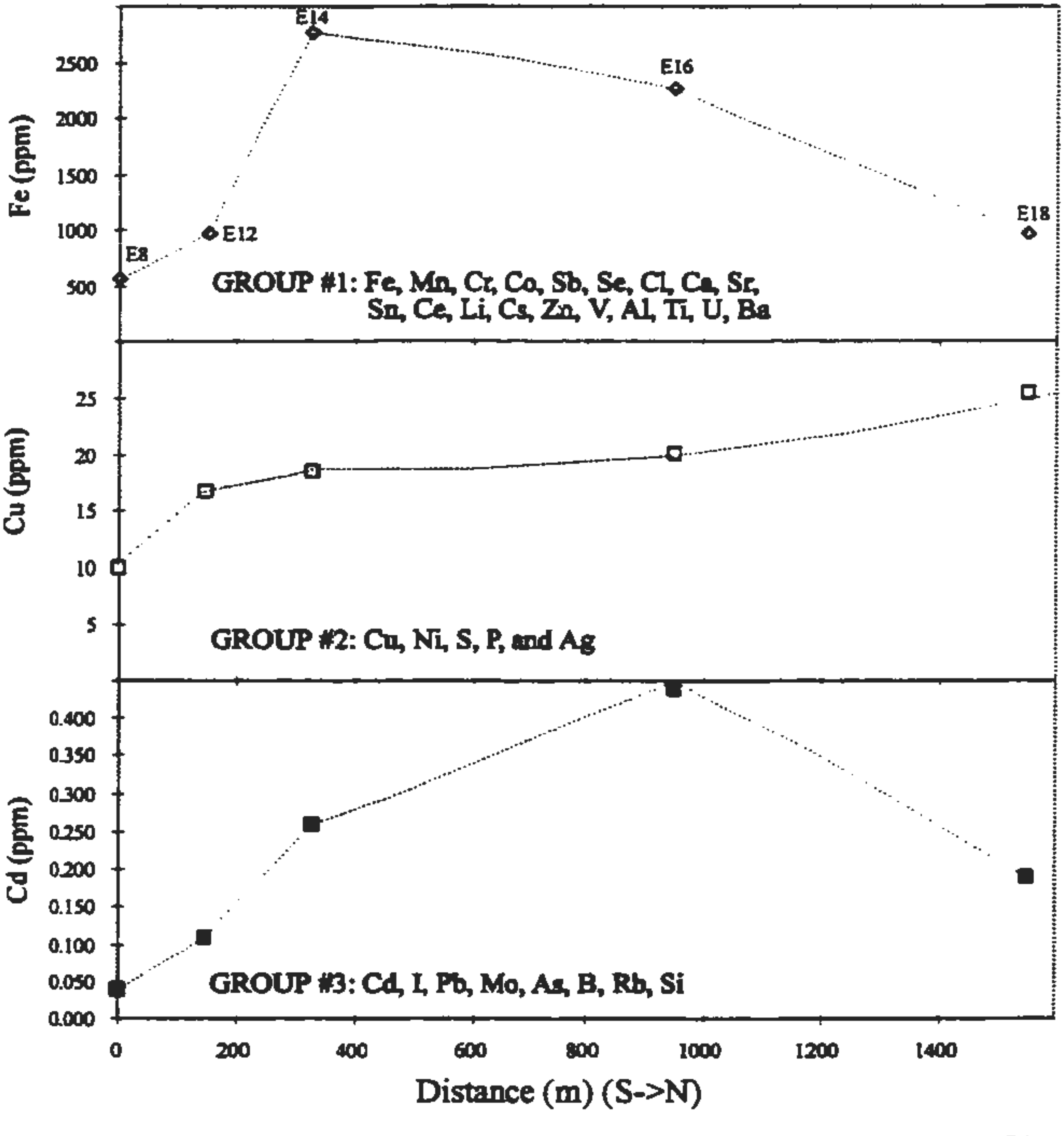

Figure 4.1.12 Fe, Cd, and Cu (ppm) in clam samples collected from the South River estuary plotted versus distance from south to north.

calculated to be within ±1.5 sd (Longerich, *pers. comm.*). Due to the excessive cost of PCB analyses, external replicate samples were not analysed. However, the analytical (instrument) precision at EPL, Zenon, and Fenwick is calculated to be within ±10 %, ±20 %, and ±10 % respectively.

Blank samples (DIW and distilled 8 N HNO_3) and several replicate samples were also analysed by IC and AA for quality assurance purposes. R^2 values from regression of standards were all $\geq$0.989 for the AA analyses, and $\geq$ 0.999 for the IC analyses. Table I.2 contains the results of replicate and blank sample analyses by IC and AA. In the case of replicate samples, the chemical constituents are all within 5 %. However, it should be noted that the blank samples contained up to 0.19 ppm Ca, therefore the acid may have contributed (<2 %) to the Ca concentration. The analytical precision of the IC and AA (waters) are both calculated to be within ±5 %.

Table I.3 also contains replicate and blank sample analyses by Inductively Coupled Spectrometry. One blank and one replicate clam sample were analysed. In the case of the replicate sample, the chemical constituents are all within 10 %. The analytical precision of the ICP (waters and biological) is calculated to be within ±5 - 10 %, depending on the element.

4.2 Contamination in the Makinsons Study Area

Describing the spatial distribution of PCBs and heavy metals in the Makinsons drainage basin was intended to document the extent of contamination. Therefore, it is important to determine whether concentrations are above background variation and thus indicative of contamination. The most significant natural inputs reflected in the geochemistry of the study area are believed to be: 1) erosion and chemical weathering of bedrock and glacial till, and 2) precipitation (wet and dry deposition). Additional natural influences affecting concentrations after input to the system include manganese coprecipitation, organic content, grain size, mineral precipitation, and redox conditions.

Discrepancies in concentrations of major elements expressed in percent between sediments / soils and unweathered bedrock are not reliable indicators of actual gains and losses caused by chemical weathering (Faure, 1991). A more appropriate means of estimating actual gains or losses of elements, as a result of chemical weathering, is based on the assumption that the concentration of one of the major-element oxides has remained constant (Faure, 1991). Al_2O_3 is the most often chosen oxide due to the limited solubility of $Al(OH)_3$ at pH values between 6 and 8 and the conservation of Al during incongruent solution of aluminosilicate minerals (Castaing *et al.*, 1986 and Faure, 1991). Therefore, sediment / soil samples with a similar metal to Al_2O_3 ratio as local bedrock will most likely be derived from the bedrock. However, samples with a greater metal to Al_2O_3 ratio than bedrock have been subject to either additional natural processes (i.e. soil formation) or anthropogenic influences. The metal to Al_2O_3 ratio is commonly (Helz *et al.*, 1983) expressed as an enrichment factor

(EF):

$$\mathbf{(X/Al)\ sediment\ /\ (X/Al)\ Earth's\ crust}$$

where X/Al is the ratio of the concentration of element X to Al. The dissolved load in both surface waters and ground waters of a drainage basin may also reflect the susceptibility of local bedrock / till to chemically weather. For example, waters flowing through shales often contain elevated concentrations of Cl and Na (Drever, 1988).

Precipitation is an additional source of solutes to the Makinsons drainage basin. It may be possible to differentiate between natural and anthropogenic sources of certain major ions and some metals by comparison with a reference species. For example, sodium and chloride are the dominant ions in the waters sampled in this study and are also the dominant ions in coastal area precipitation where they both originate from sea spray (Faure, 1991). If Cl is conservative, concentration ratios of major ions and Cl should indicate any excess of these ions relative to the natural marine input.

This enrichment rationale may also be applied to influences by manganese coprecipitation, organic content, grain size, mineral precipitation, and redox conditions. Direct correlations between MnO, LOI, and silt + clay %; and metals in sediments / soils may suggest that these natural influences are occurring, resulting in possible enrichment. Mineral saturation in ground waters and surface waters may also result in the enrichment of sediments / soils due to precipitation.

4.2.1 Sediments and Soils

The results of the analytical program include geochemistry of bulk sediments. Bulk sediments refer to the fact that the analytical instruments used in this study did not distinguish between natural aluminosilicate contributions and organically bound anthropogenic contributions. However, this was one of the goals of this study and an alternate approach was followed. When interpreting geochemical data, factor analysis is commonly used to distinguish between aluminosilicate input and other sources / processes. Unfortunately, as was previously mentioned, the data in this study were not suitable for multivariate statistical procedures that start with correlation matrices. Therefore, enrichment factors were used to distinguish between weathering of bedrock and anthropogenic input.

Weathering of bedrock was first considered and assessed as a natural process contributing to stream sediment / soil chemistry. Glacial till in the Makinsons drainage basin is assumed to be derived from the local bedrock (King, *pers. comm.*), therefore bedrock geochemistry is also assumed to represent till geochemistry. In the test stream (n=10) and control stream (n=2) sediments, the average X/Al ratio was calculated for each chemical constituent. There is no consensus in the literature regarding the X/Al ratio for the Earth's crust. Some workers (Fatima *et al.*, 1988 and Rule, 1986) use the average crustal abundance summarized by Taylor (1964), others (Helz et al., 1983) use the average crustal values for specific rock types (i.e. shales, granites, etc.) described by Turekian and Wedepohl (1961), and some workers compare both (Sinex and Helz, 1981). Therefore, the X/Al ratios in this study were compared with average crustal values (Taylor, 1964), average shale and sandstone values (Turekian and Wedepohl, 1961), and also the bottom of core E9. The bottom sample of core E9 (-0.21 m) was clean gray sand and was believed to be the best sample to represent background sediment chemistry in the area.

Table 4.1 lists concentrations for each of the estimates of background geochemistry. Of the 29 chemical constituents measured in test stream sediments, only 7 (Zn, Cr, Fe_2O_3, Pb, As, MnO, and P_2O_5) could not be explained by bedrock weathering. They had an EF >1 when compared to all four methods and may represent contamination in the Makinsons drainage basin. Only MnO was enriched in the control stream sediments. The EF for the 7 enriched constituents are listed in Table 4.2 and the remaining 22 are in included in Table J.1. Figure 4.2.1 individually presents the ratios of the 7 enriched elements / oxides along the test stream. Since MnO was also enriched in the control stream, it may represent manganese coatings on the sediments in both the control stream and test stream. It should be noted, however, that the EF (MnO) for the test stream are at least 10 times those of the control stream (Table 4.2). Since all 7 metals and oxides have similar distribution patterns (Figure 4.2.1), a similar source of enrichment is suspected.

Given that Zn, Cr, Fe_2O_3, Pb, As, MnO, and P_2O_5 are enriched in stream sediments collected from the Makinsons drainage basin, they may represent contamination. In similar investigations, the majority of these metals and oxides have been considered indicative of industrial input. For example, Zn and Pb have previously been considered as landfill / industrial associated contaminants (Mantei and Coonrod, 1989; Mantei and Foster, 1991; and Ntekim *et al.* 1993). Concentrations in this study (Zn= 80 - 1085 ppm; Pb= 20 - 84 ppm) far

Table 4.1 Chemical concentrations in four different "background" methods used to estimate enrichment in stream sediments in the study area.

Chemical Constituent	Backgound Sediment (1) (ppm)	Average Crust (2) (ppm)	Average Global Shale (3) (ppm)	Average Global Sandstone (4) (ppm)
Na2O	16500	31520	9600	3300
MgO	15000	36520	15000	7000
Al2O3	114800	157340	80000	25000
SiO2	606000	609760	73000	368000
P2O5	1600	1050	700	170
S	9752	260	2400	240
Cl	70	130	180	10
K20	21600	30280	26600	10700
CaO	7300	50040	22100	39100
Sc	16	22	13	1
TiO2	7300	9780	4600	1500
V	78	135	130	20
Cr	55	100	90	35
MnO	1100	950	850	90
Fe2O3T	58300	67960	47200	9800
Ni	13	75	68	2
Cu	6	55	45	9
Zn	90	70	95	16
Ga	19	15	19	12
As	< detection	1.8	13	1
Rb	85.5	90	140	60
Sr	124.3	375	300	20
Y	31.2	33	26	40
Zr	245.8	165	160	220
Nb	16.1	20	11	0.09
Ba	474	425	580	90
Ce	100	60	59	92
Pb	10	12.5	20	7
Th	9	9.6	12	1.7

(1)= Bottom sample of core E9 (- 0.21 m).
(2)= Average chemical composition of Earth crust (Taylor, 1964).
(3)= Average chemical composition of global shale (Turekian and Wedepohl, 1961).
(4)= Average chemical composition of global sandstone (Turekian and Wedepohl, 1961).

Table 4.2 Enrichment factors of stream sediments collected from the study area. The 7 enriched metals / oxides in the test stream are included.

Chemical Constituent	Enrichment Factor (1)	Enrichment Factor (2)	Enrichment Factor (3)	Enrichment Factor (4)
Zn				
test(n=10)	4.25	7.50	2.81	5.21
control(n=2)	0.66	1.16	0.43	0.81
Cr				
test(n=10)	3.20	2.41	1.36	1.09
control(n=2)	1.21	0.91	0.51	0.41
Fe2O3				
test(n=10)	2.34	2.76	2.02	3.04
control(n=2)	0.82	0.97	0.71	1.07
Pb				
test(n=10)	3.91	4.29	1.36	1.22
control(n=2)	0.73	0.80	0.25	0.23
As				
test(n=10)	N/A	75.26	5.30	21.53
control(n=2)	N/A	5.86	0.41	1.68
MnO				
test(n=10)	32.70	51.89	29.49	87.03
control(n=2)	1.26	2.00	1.14	3.36
P2O5				
test(n=10)	1.34	2.81	2.14	2.76
control(n=2)	0.43	0.91	0.69	0.89

(1)= Bottom sample of core E9 (- 0.21 m).
(2)= Average chemical composition of Earth crust (Taylor, 1964).
(3)= Average chemical composition of global shale (Turekian and Wedepohl, 1961).
(4)= Average chemical composition of global sandstone (Turekian and Wedepohl , 1961).

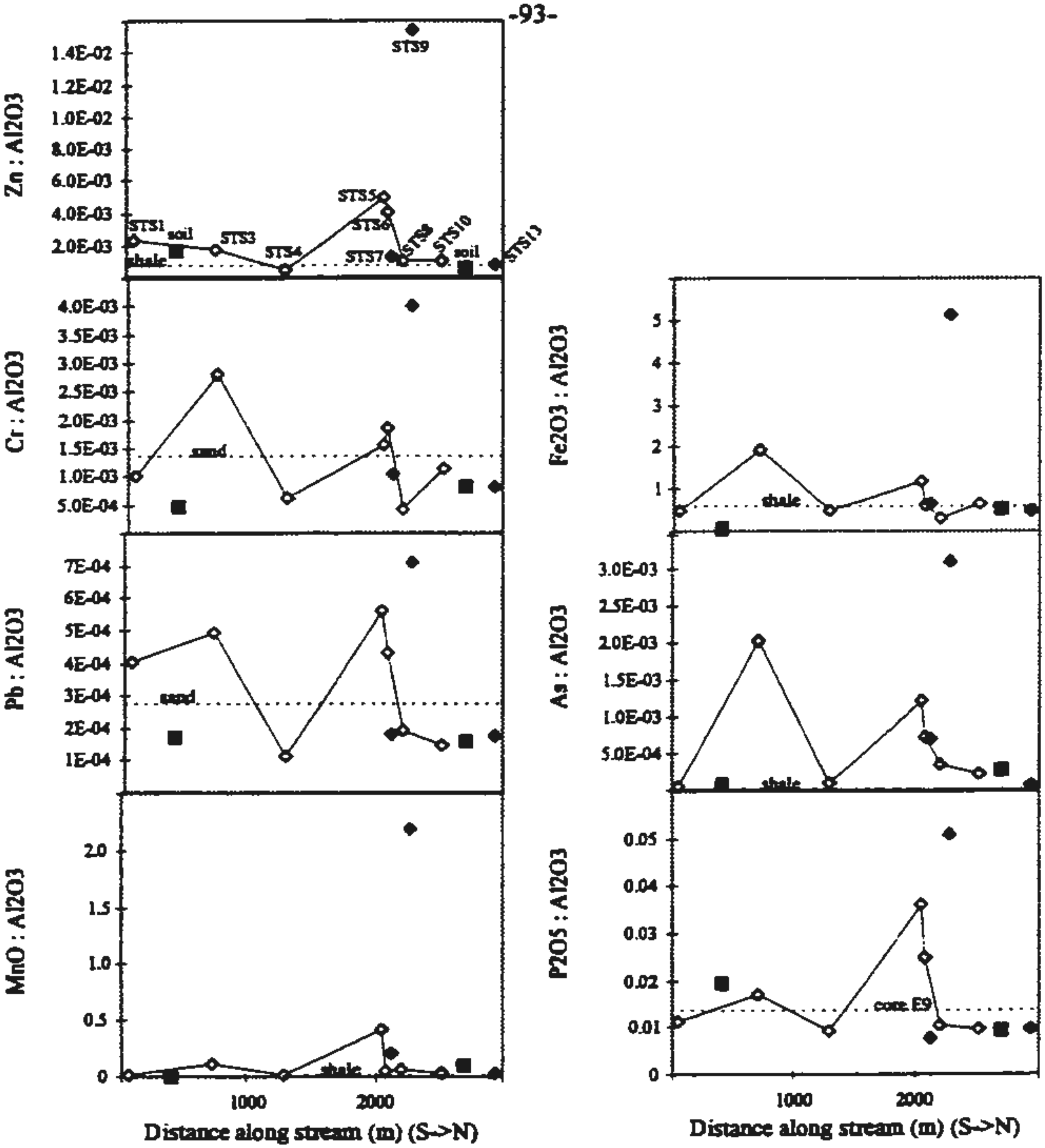

Figure 4.2.1 X/Al ratios in the sediment and soil samples. The sediments along the test stream are indicated by hollow diamonds joined by a line while samples from tributaries and ditches are indicated by solid diamonds. The average ratio in the soil samples at each of the two locations is also indicated by a solid square. The maximum natural X/Al ratio (i.e. shale, core E9, etc.) is included as a dotted line for comparison.

exceed those detected by Mantei and Coonrod (1989) (Zn= 11 - 51 ppm; Pb= 10 - 56 ppm). This does not appear to be the result of background variation in the study area since the Zn and Pb values in the test stream sediments are roughly 5 times the concentrations in the control stream (< 3 times in Mantei and Coonrod, 1989). Rule (1986) used X/Al ratios in river sediments to determine which trace metals were associated with industrial input. He too, found increased enrichment of Zn and Pb towards the industrialized section of the Elizabeth River, Virginia. An earlier study of river sediments in the same area (Rule, 1986 after Johnson and Villa, 1976) also suspected similar metals of being associated with industrial input: Cr, Pb, Zn, and Fe. Fatima *et al.* (1988) also used X/Al ratios from 17 sediment sample sites to determine which trace metals were associated with industrial input in a Belgian estuary. Suspected contaminants included Zn, As, and Pb. Using X/Al ratios, Biksham *et al.* (1991) detected enrichment of Fe, Mn, Cr, and Zn in suspended sediments from the Godvari River basin, India. Mantei and Sappington (1994) suspected Zn, Pb, and Cr contamination of stream sediments from a sanitary landfill in Missouri and Sinex and Helz (1981) considered enrichment of Mn, Fe, Zn, and Pb to be indicative of industrial input in Chesapeake Bay sediments.

Additional natural influences affecting concentrations in sediments and soils after input to drainage basins may include manganese coprecipitation, grain size, organic content, and mineral precipitation. Manganese is known to "scavenge" or coprecipitate metals (Hornbrook *et al.*, 1975 and Maynard, 1983). This phenomenon was investigated in the Makinsons drainage basin in order to distinguish between natural input (i.e. bedrock weathering) of metals into stream sediments and elevated concentrations of metals due to manganese coprecipitation. The distribution pattern of MnO in sediments along the test stream corresponds closest with Cr, Ni, As, Ba, Fe_2O_3, V, Cl, and PCBs (see group 4 in Figure 4.1.3). It should also be noted that stream sediments from the tributary STS9 are enriched, relative to adjacent stream sediments along the main course, in Ni, Cr, As, Fe_2O_3, MnO, Cl, CaO, Sr, and Cu. Site STS9 has the highest concentration of MnO (15.5 %) in the study, which may be responsible for coprecipitation of these elements. Sample STS9 is from a tributary draining a bog and the elevated concentrations of MnO and Fe_2O_3 may be due to secondary mineral formation of pyrolusite and bog iron, both associated with bog and swamp deposits (Maynard, 1983 and Whitten and Brooks, 1972).

Spearman rank correlations were calculated (SYSTAT, 1992) in order to provide statistical support for these observations. Spearman rank correlations were considered the most robust statistical method of confirming relationships in all 4 data sets (i.e. sediment, surface water, ground water, and clam), since some of the parameters were not normally distributed and contained outliers (Rollinson, 1993). Garrett (1993) recommends the use of Spearman rank correlations in applied geochemistry, since it does not require linear relationships between variables. Samples with missing values were omitted from the analyses. Sediment / soil variables significantly (n=12) correlated with MnO are: Fe_2O_3 (1), As (1), Ba (10), Cl (10), and Nb (10); based on a one-tailed test of correlation coefficient (r_S) significance (Rollinson, 1993) (the Spearman rank correlation matrix of the sediment and soil data is included in Table K.1). The numbers in brackets represent confidence limits (±C.L.

%). Table L.1 contains significance tables of the Spearman rank correlation coefficient.

Grain size of test stream sediments, measured as % silt and clay, is significantly correlated (directly) with LOI (10), P_2O_5 (10), Pb (10), S (10), Y (10), CaO (10), Cu (10), Ce (10), and Zn (10); based on a one-tailed test of correlation coefficient (r_S) significance. This means that smaller grain size of stream sediments, corresponds with increased organic content, P_2O_5, Pb, S, Y, CaO, Cu, Ce, and Zn. In addition, organic content (LOI) is significantly correlated (directly) with P_2O_5 (0.1), S (1), CaO (1), Y (1), Ce (1), Pb (1), As (10), Cr (10), Ni (10), Cu (10), Zn (10), and Th (10). Based on the Spearman rank correlations, LOI appears to be the parameter with the greatest influence on distribution of heavy metals in the sediments and soils of the drainage basin. Enrichment of heavy metals has been known to occur in sediments with high organic content and small grain size. For example, Subramanian *et al.* (1989) investigated 18 samples of bed sediments in the Cauvery Estuary, India, and discovered the greatest concentration of Fe, Mn, Zn, Cu, Cd, and Hg in sediments with the greatest organic content and smallest grain size.

Mineral saturation in waters may also enrich sediments / soils due to precipitation. This phenomenon was investigated in the Makinsons drainage basin using the MINTEQA2 geochemical speciation model (Allison *et al.*, 1991). Saturation indices (SI) (Allison *et al.*, 1991) for 106 minerals were calculated (Table M.1) but only six minerals were saturated in any of the ground water and surface water samples: $Al_4(OH)_{10}SO_4$, alunite ($KAl_3(SO_4)_2(OH)_6$), boehmite ($AlO(OH)$), diaspore ($AlO(OH)$), gibbsite ($AlO(OH)_3$), and hercynite ($FeAl_2O_4$). Therefore, precipitation of metals dissolved in surface waters and ground waters was eliminated as a significant influence on sediment and soil chemistry. Even though these calculations are theoretical, the composition of the minerals seems to suggest the importance of weathering reactions.

It was difficult to distinguish between background variation and anthropogenic input in the South River sediments. Even at high tide, the water depth was <0.50 m at both core locations. Based on personal observation, it is strongly suspected that ice activity during spring thaw disturbs and mixes the sediments, which may have obliterated any natural trends in sediment chemistry. Few parameters showed any distinct trends from top to bottom of the cores. In core E4, both LOI and Al display a peak approximately 160 mm of depth (Figure 4.1.6). This is unusual since increased aluminosilicate clastic input to sediments is traditionally correlated to reduced organic input. Natural environmental conditions may be a significant control on the sediment chemistry from core E9. The trend of LOI corresponds directly with: Cl, Cu, Pb, S, U, and Zn, and inversely with: Ba, Cr, K_2O, MnO, Rb, and Sc (Figure 4.1.7). The sharp decrease in LOI at the bottom of the core appears to be related to the lithology change from the dark yellowish brown sediment to olive gray. Nevertheless, the presence of PCBs in South River sediments (Figure 4.1.5), suggests that some transport has taken place, yet the extent is not known.

Various "hotspots" of suspected contamination were detected in the Makinsons drainage basin. Six metals, as well as PCBs, were detected in sediment / soil samples exceeding criteria set forth by the CCME (1991). This information is included in Table 4.3 and suggests that sites STS3, STS6, and STS9 deserve the most attention. With respect to

Table 4.3 Sediment and soil sample sites which exceed CCME (1991) criteria.

Element / Chemical	Sample Site	CCME criteria
PCB	STS3	5 ppm
Cr	SOS1, STS3, STS9, STS6	250 ppm
Ni	STS3, STS9, STS6	100 ppm
Cu	SOS1, SOS2	100 ppm
Zn	SOS2, STS5, STS9, STS6	500 ppm
As	SOS2, STS8, STS3, STS5, STS9, STS7, STS6	30 ppm
Ba	all sites except SOS2	500 ppm

PCBs, only the stream sediment sample STS3 (15.10 ppm) exceeds the criteria for Parkland / Residential areas (5 ppm) set forth by the CCME (1991). Another interesting observation was the extreme enrichment of metals in the tributary sediment sample STS9 that drains the bog (Figure 4.2.1). Either this area is anomalous compared to background conditions or there is an unidentified source of contamination in this area.

Zn, Cr, Fe_2O_3, Pb, As, MnO, and P_2O_5 are the only chemical constituents that could not be explained by bedrock weathering and are enriched in Makinsons drainage basin sediments (Figure 4.2.1). These elements and oxides may reflect contamination and possible sources / transport pathways will be discussed in section 4.3. The presence of PCBs throughout the basin (Figure 4.1.4) is direct evidence of contamination and possible sources and pathways will also be addressed in section 4.3.

4.2.2 Surface Waters and Ground Waters

Given that local bedrock accounts for most of the elements and oxides in the sediments, the composition of the dissolved load may also reflect chemical weathering of bedrock. The lithology change from the St. John's Group shales to the Conception Group sand and siltstones (see Figure 2.1.1) may contribute to the decrease in conductivity, Cl, Na, etc. along the test stream as it flows through the Makinsons drainage basin. The three surface water sample sites at the top of the basin are located on, or adjacent to, the St. John's Group and possess a significantly higher conductivity than the remaining samples on the Conception Group. Ground waters collected from the St. John's Group are much more concentrated in

Na and Cl than surface waters and lower basin ground waters (Figures E.2 and E.3), and may represent dissolution of the St. John's shale. Drever (1988) maintains that waters draining shales often contain elevated concentrations of Cl and Na. In addition, the Piper diagram (Figure 4.1.9) indicates that lower basin ground waters contain less Cl than both upper basin ground waters and surface waters.

Decomposition of organic material in soil typically consumes oxygen, and increases carbonic acid and natural organic acids (Gale *et al.*, 1984). However, in the Makinsons drainage basin, calcite and possibly dolomite most likely exist in sufficient quantity in the bedrock to consistently maintain the ground water pH above 6 and alkalinity typically above 15 ppm. Calcite may also react with the oxidation products of pyrite (FeS_2) (Drever, 1988 and Freeze and Cherry, 1979) which upon dissolution, could mimic the dissolution of gypsum. There are no known gypsum deposits in this area (King, *pers. comm.*), therefore the similarity of distribution patterns observed for dissolved Ca and SO_4 (see group 1, Figure 4.1.10) may be due to pyrite and calcite reactions.

Precipitation (wet and dry deposition) is a natural input to the geochemistry of the Makinsons drainage basin. Greater ion to chloride ratios in precipitation, relative to seawater, may be due to dissolution of mineral particles derived from soil or dust and / or anthropogenic contamination (Faure, 1991). In this study, ratios of Na and Cl in the drainage basin and control stream sample correspond to natural marine input (Figure 4.2.2). The slight excess of Na may be due to the dissolution of albite. Figure 4.2.2 also displays other major ions (Ca, K, and SO_4) versus Cl concentration relative to ratios in seawater (Ca= 0.021; K= 0.021;

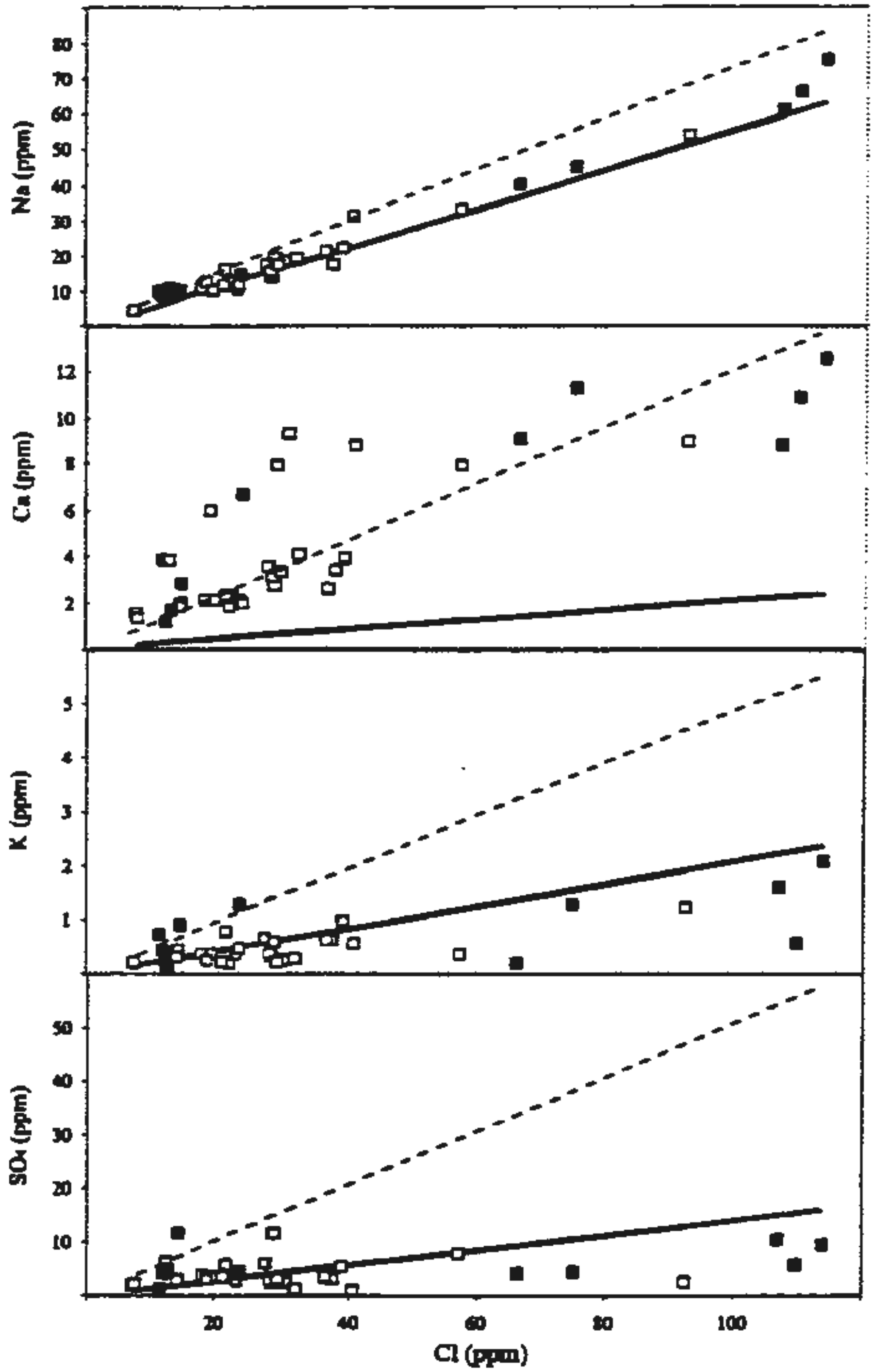

Figure 4.2.2 Ratio of sodium, calcium, potassium, and sulfate to chloride concentrations in the water samples collected. The solid lines represent the ratios in seawater and the dashed line is the average ratio in coastal rain water (Faure, 1991). Hollow squares are surface waters and solid squares are ground waters.

SO_4= 0.14) and the maximum enrichment factor (Ca= 5.7; K= 2.4; SO_4 = 3.6) that is commonly detected in rainwater over coastal areas (Faure, 1991). Many of the samples (including the control stream sample) are enriched in Ca relative to meteoric precipitation and dissolution of calcite, dolomite, anorthite, and apatite present in the basin (Hsu, 1972 and King, 1990), may be responsible. Potassium appears to be depleted with respect to Cl (Figure 4.2.2). Depletion of SO_4 in some of the ground water samples may be the result of reduction to sulfide (Siegel *et al.*, 1991). Some of these samples did not contain any measurable oxygen and were probably collected from a reducing environment. Previous workers (Ehlke, 1979 and Mather *et al.*, 1983) also detected lower concentrations of SO_4 in anoxic ground waters affected by landfill leachate. The abundance of Mg, NO_3 and HCO_3 in coastal rain varies irregularly (i.e. nonconservative behaviour) (Faure, 1991) and were excluded from this approach.

The assessment of precipitation as a source of trace elements is less exact. Jamieson (1993) measured trace element composition in wet deposition at the Salmonier Nature Park, 30 km south of Makinsons (see Figure 1.1). The average concentration of each element (n=24) estimated from Jamieson (1993), was assumed to represent precipitation over Makinsons. This value was divided by the average concentration measured in the surface waters collected in the summer (n=9) and fall (n=14), ground waters (n=12), and the control stream (n=1). The percent contribution of precipitation to the dissolved load in the surface and ground waters was estimated and listed in Table 4.4. This information was interpreted according to the criteria that if the concentration of trace metals in precipitation is

Table 4.4 Comparison of surface and ground water chemistry with precipitation chemistry (Jamieson, 1993). The estimated contribution of precipitation (%) to each of the dissolved constituents in the drainage basin is included. Contributions less than 100 % indicate additional processes to precipitation.

Chemical Constituent	Surface-Control (n=1)	Surface-Fall (n=14)	Surface-Summer (n=9)	Groundwater (n=12)
Pb	521.3	94.6	33.9	22.0
Cd	315.9	73.3	48.5	20.5
Cu	274.0	90.6	53.5	30.3
Sn	200.0	65.8	30.4	17.7
Ni	125.2	52.5	48.0	17.5
Sb	115.2	39.8	35.2	13.6
As	73.2	25.1	11.2	4.7
Ti	20.9	14.3	6.2	3.1
Rb	18.4	8.8	5.8	4.3
Co	18.1	7.4	0.9	0.6
I	15.0	7.1	3.3	2.2
Sr	14.7	8.7	4.4	3.2
Fe	11.5	5.4	0.5	1.0
La	8.1	2.1	0.9	0.4
Al	4.8	4.4	4.1	0.2
Ce	3.1	1.5	0.6	0.2
Mn	2.0	0.8	0.1	0.1
Ba	1.8	1.9	1.2	0.9
Zn	1.5	1.3	0.7	0.5
Si	0.4	0.4	0.4	0.2

approximately equal to (or greater than) the concentration in the water samples, there are no significant additional processes. In the control stream, precipitation appears to account for Pb, Cd, Cu, Sn, Ni, Sb, and As in the dissolved load. In the 14 surface water samples collected from the test stream in the fall, precipitation can account for Pb and Cu. Ground waters, and the suite of surface samples collected in the summer appear to be subject to additional influences, since precipitation does not contribute as significantly to their dissolved loads (Table 4.4).

Redox conditions were considered as an additional natural influence affecting geochemistry of the Makinsons drainage basin. Redox conditions in the surface waters and ground waters were not measured but dissolved oxygen concentrations may provide insight into possible reducing or oxidizing conditions since reducing environments tend to be relatively anoxic (Siegel *et al.*, 1991). The solubility of metals increases under reducing conditions and an increase in dissolution of precipitated species may occur (Siegel *et al.*, 1991). A one-tailed test of correlation coefficient (r_S) significance was performed to assess whether low dissolved oxygen concentrations in the ground water and surface water (fall) were correlated with increased dissolved load in the basin (the Spearman rank correlation matrices of the ground water and surface water chemistry data are included in Tables N.1 and O.1). In the ground water data set, dissolved oxygen (O2) is significantly (n=12) correlated (inversely) with 16 of the 34 water chemistry parameters: Fe (0.1), Sr (0.1), Ti (0.1), As (1), Ba (1), Ca (1), Ce (1), Conductivity (1), Mg (1), Na (1), Cl (10), Co (10), La (10), Alkalinity (10), Cs (10), and K (10). It should also be noted that only 6 parameters were directly correlated with dissolved oxygen. In the fall surface water set, dissolved oxygen (O2) is significantly (*n*=14) correlated (inversely) with 10 of the 33 water chemistry parameters: Fe (10), Ce (10), Cl (10), La (10), Alkalinity (10), Cs (10), Al, (10), Rb (10), NO_3, and K (10). In the surface water data set, only 4 variables were directly correlated with dissolved oxygen. Therefore, the Spearman rank correlations lend support to the theory that reducing conditions may be present and enhancing mineral dissolution in the basin. Also, the greater number of inverse correlations in the ground water data set (compared with the surface water data set), correspond to typical conditions where ground waters are less oxidized than surface waters and tend to be a more reducing environment.

Temporal variation in surface waters may also influence mineral dissolution. Except for O_2 and SO_4, concentrations are higher in surface water samples collected in August than those collected in November (see Figures G.1, G.2, G.3, and G.4). This pattern may be due to: 1) a decrease in solubility due to an increase in temperature, 2) less dilution of the stream water due to less precipitation (i.e. rain), 3) increased rock-water interaction, and 4) increased evaporation. Dissolved oxygen is expected to be lower in the summer due to increased biological demand (BOD) and the fact that gaseous solubility decreases with an increase in temperature.

It was not possible to distinguish between natural and anthropogenic input to the surface waters and ground waters of the Makinsons drainage basin. For example, enrichment of surface waters and ground waters, relative to seawater or precipitation, may be due to chemical weathering of bedrock, soil, or dust, as well as anthropogenic input. In fact, many of the ion concentrations could be explained by natural marine output (see Figure 4.2.2) or wet / dry deposition (see Table 4.4).

4.2.3 Bioreceptors

In order to determine the role that bioreceptors play in the attenuation and migration of PCBs and heavy metals, it was first necessary to establish whether contamination was present in *Mercenaria mercenaria* (clam) populations collected from the South River estuary. The rationale behind sampling these sedentary bivalves was that they are known to accumulate these contaminants even when ambient levels in water and sediments are below critical concentrations.

Trace element concentrations in the 5 homogenized samples from this study are compared with average concentrations in *M. mercenaria* along the Atlantic Coast of the US (Phillips, 1977 after Pringle *et al.*, 1968). Clams collected from the South River estuary are consistently enriched relative to the Atlantic coast of the US. Common metals in both studies are listed with the enrichment factor in brackets: Cr (2.2), Co (1.8), Ni (3.3), Mn (3.2), Fe (11.2), Zn (1.6), Cd (2.5), Pb (1.42), and Cu (1.5). Additional elements are compared to typical values reported for *M. mercenaria* in the literature (Eisler, 1981). These comparisons are less rigorous since contaminated or pristine sample locations were not distinguished. Elements and enrichment factors are as follows: Al (1.2), Sb (2), As (0.6), Ba (0.2), Bi (0.003), B (0.5), Cd (0.07), Ce (1.1), Cs (0.9), Hg (<0.07), Mo (0.5), Rb (1.2), Se (0.5), Ag (0.2), Sr (2.7), Sn (1.7), Ti (1.4), and V (0.2). However, factors that were not accounted for (i.e. age, sex, reproductive status), may be influencing the chemistry of the clam samples.

The chemical analyses may also be biassed by environmental influences and individual clam size. Clams are filter feeders and obtain trace elements from food, solution, and the ingestion of inorganic particulate matter (Moore, 1971). Therefore, the physical characteristics of sediments from which the clams were collected may influence their chemistry. Since there is not a consensus in the literature between bivalve size and accumulation of contaminants (Phillips, 1976*a*), the size of the clams collected in this study may influence the quantity of metals and PCBs accumulated. Concentrations of elements in clams that are significantly (n=5) correlated with sediment grain size are: P (10), S (10), Se (10), and I (10); based on a one-tailed test of correlation coefficient (r_S) significance (Rollinson, 1993) (the Spearman rank correlation matrix of the sediment and soil data is included in Table P.1). All correlations are inverse and suggest that concentrations decrease with increases in % silt +clay. Sediment LOI is significantly correlated (inversely) with only Cu (10), Mo (10), and Ag (10). Due to these limited correlations, the physical characteristics of the sediments appear to be independent of clam chemistry. Most elements display peak concentrations in sample E14 (Figure 4.1.12); the sample containing individuals with the least mean dry tissue weight. Average shell length and average dry tissue weight are expected to be highly correlated (r_S= 1.000). Average shell length is significantly correlated with Li, Al, Ti, V, Cr, Mn, Fe, Zn, Sr, Cd, Cs, Ba, Ce, Pb, U, Si, Co, Rb, and La. Average dry tissue weight is significantly correlated with Li, Al, Ti, V, Cr, Mn, Fe, Zn, Sr, Cd, Cs, Ba, Ce, Pb, U, Si, Co, Rb, La. Therefore, individuals of smaller weight and length appear to contain higher concentrations of the above elements. Based on these results, individual clam size appears to introduce the most bias into the data set and influence the concentrations of many of the heavy metals. In this study, the size of *M. mercenaria* is inversely related to metal concentrations and corresponds with Phillips (1976*a*, 1976*b*) who found that smaller and lighter individuals were found to contain significantly higher concentrations of heavy metals.

Clam samples (*Mercenaria mercenaria*) were collected for PCB analysis at the same five sites but PCBs were not present ≥ 0.05 ppm (wet weight). This is a significant discovery since bivalves are sedentary and known to bioaccumulate contaminants by extremely high factors (Farrington *et al.*, 1983). In a similar study, Shaw and Connell (1980), detected PCB concentrations in mussels (*Mytilus corscus*) that were up to 5 times the concentration found in estuary sediments.

4.3 Transport of PCBs and Heavy Metals in the Makinsons Study Area

Prior to this study, detailed work by FFC/BEAK (1992*d*) identified the salvage yard-bog area as a source of PCB contamination in the Makinsons drainage basin. In addition, the results of their reconnaisance work within the basin suggest that PCBs have been migrating from the salvage yard-bog area into the downstream ecosystem for a significant period of time. Therefore, the purpose of this study was to provide a more detailed investigation to determine how the PCBs, as well as heavy metals, are distributed in the downstream basin and whether they are available to bioreceptors in the South River estuary.

One of the main objectives of this study was to identify the roles that surface waters and ground waters, sediments within the stream and estuary, and other bioreceptors, play in the attenuation and migration of PCB and heavy metal releases. These roles are considered as major or minor pathways, and / or major / minor receptors. PCBs can migrate along atmospheric, ground water, and surface water pathways, yet surface waters with their greater load of negatively charged suspended and particulate matter, are assumed to be the main mode of PCB transport within aquatic environments (Dexter and Pavlou, 1978). One of the purposes of this study was to assess if this dominant mode of transport was operating in the Makinsons drainage basin, or whether there was evidence of the lesser suspected atmospheric / ground water pathways.

Given that PCBs are considered relatively insoluble in natural waters (Abarnou *et al.*, 1987), the salvage yard is considered to behave as a continuous source of contamination to the Makinsons drainage basin. Additional support is that the majority of PCBs released to the environment are proposed to be adsorbed on fine grain sediments near their point of release (Nisbet and Sarofim, 1972). If the salvage yard is behaving as a continuous source of contamination to the drainage basin, one should observe increases in contaminants in stream sediments sampled immediately downstream. Stream sediments enriched in metals would suggest adsorption on material carried into the stream by surface runoff from the salvage yard. Roberts *et al.* (1982), investigating a PCB spill in Saskatchewan, concluded that transport on particles in runoff was the most significant mechanism for migration.

The spatial distribution of PCBs in the stream sediments and soils implicate the salvage yard as a source to the downstream basin. Three patterns were observed to support this conclusion: *1*) an increase in concentration in the stream sediment sample (STS3) immediately downstream from the salvage yard, *2*) lower concentrations in the 2 upper basin soil samples, compared with the stream sediment sample STS3 (located 150 m further downstream from salvage yard, and *3*) concentration peaks at sites STS5 and / or STS6 (see Figure 4.1.4). These 3 patterns can be explained as surface runoff carrying contaminated sediments from a source into adjacent streams or ditches (Chou and Griffin, 1984 and Roberts *et al.*, 1982). Stream sediments immediately downstream from the salvage yard (site STS3) are expected to contain high concentrations of contaminants due to proximity to the source (i.e minimal dilution with uncontaminated sediments). The highest concentration of PCBs detected in this study (15.10 ppm at STS3), appears to be related to proximity and is not influenced by grain size or organic content (silt + clay= 8.7 % and LOI= 11.9 %). Lower concentrations in the 2 upper basin soil samples (compared with the stream sediment sample STS3), confirms the importance of stream suspended matter, versus ground water percolating through soils which contain little or no suspended material (Fetter, 1993). The influence of grain size and organic content on stream sediment chemistry, however, is evident at sites STS5 and STS6 which have very high silt + clay fractions (89.7 and 94.2 %), substantial LOI (67.1 and 42.0 %), and high PCB concentrations (1.89 and 3.54 ppm) (see Figure 4.1.4). The 3 relative distribution patterns of PCBs in this study, correspond to results from Law *et al.* (1990) who investigated the distribution of PCBs in 11 sediment samples downstream from a contaminated industrial site in the UK. They too, detected a progressive decrease of PCBs in sediments downstream from a source with a slight increase further downstream where fine sediments were accumulating.

The numerical simulation of surface water / ground water interaction in Chapter 2.3 was intended to determine the influence of physical hydrogeology on contaminant migration in the Makinsons drainage basin. Beneath the salvage yard, the equipotential surface of the aquifer is east-dipping, west of the stream and west-dipping, east of the stream. Therefore, ground water flow is channelled towards the valley where the stream runs and would appear to limit any significant lateral dispersion of contaminants from the salvage yard. In this study, PCBs were detected in 3 of the 4 shallow soils samples and this may be evidence that some transport of PCBs is occurring by subsurface processes. Nevertheless, the aquifer appears to be consistently discharging to the stream, and any quantity of PCBs reaching the aquifer should remain near the surface and not be transported deep into the ground water system. Therefore, the vertical dispersion of PCBs in the aquifer would also appear to be limited and any ground water migration of PCBs would be quickly directed towards the stream

The detection of PCBs in shallow soil samples suggest that ground waters may be playing a role in their migration. However, the results of the numerical simulation indicate that any contaminants reaching the aquifer would be channelled towards the test stream. Therefore, the numerical simulation supports the hypothesis that the test stream plays the dominant role in the transport of PCBs in the Makinsons drainage basin. The equipotential surface of the aquifer roughly reflects the surface topography which is considered to be the major factor controlling surface hydrology in the basin. During periods of increased precipitation, surface releases of PCBs in the salvage yard would be transported by surface runoff, also flowing towards the test stream. However, surface runoff is not expected to contain relatively large amounts of PCBs unless PCBs are transported on suspended particles (Roberts et al., 1982).

PCBs were unexpectedly detected in two tributaries of the test stream- STS9 (1.22 ppm) and STS13 (0.05 ppm) (see Figure 4.1.4). According to the numerical simulation in Chapter 2.3, these locations are upgradient from flow that would originate from the salvage yard and suggest an additional source of PCB contamination. The presence of PCBs in test stream sediment sample STS1 (1.82 ppm) and in the soil sample SOS3 (1.20 ppm) (both located upgradient from the stream), also suggest an additional source (see Figure 4.1.4). The most likely additional source of PCB contamination is the oiling of roads to control dust before they were paved. Several local residents of Makinsons have confirmed this and apparently the owners of the salvage yard did in fact use transformer oil for dust control in the 1950s and 60s. Trace levels of PCBs (0.06 ppm) were detected in tidal marsh samples (ESO1 and ESO2) from South River (see Figure 4.1.4), and in the top 50 mm of sediment cores (0.02 ppm-0.50 ppm) (see Figure 4.1.5). The source of PCBs to the South River estuary may be transport from the salvage yard, but is more likely the oil that was used on the nearby roadways. Based on the numerical simulation in Chapter 2.3, any PCB contamination resulting from the oiling of the roadways would also be channelled towards the stream.

Heavy metals are also relatively insoluble in natural waters (Sholkovitz, 1976) and their attenuation and migration in the environment is believed to correspond closely with that of PCBs. Their main mode of transport is believed to be surface waters with their greater load of negatively charged suspended and particulate matter. In the Makinsons drainage basin, a group of elements were found to display chemical behaviour that corresponded closely with PCBs: Cr, Ni, As, MnO, Ba, Fe_2O_3, V, and Cl (see group 4, in Figure 4.1.3). The chemical behaviour of these elements illustrates the three relative distribution patterns previously described with respect to PCBs. Given the fact that these elements display similar distribution patterns to PCBs, they may be transported by the same processes.

However, according to their EF (see Figure 4.2.1), only Cr, Fe_2O_3, As, and MnO are enriched relative to the Earth's crust. The Al_2O_3 ratios provide the best support of enrichment, therefore the salvage yard is strongly suspected as a source of Cr, Fe_2O_3, As, MnO, and probably Pb. Pb is added to this group since its EF pattern (see Figure 4.2.1) indicates a peak downstream from the salvage yard. This investigation appears to provide evidence that Cr, Fe_2O_3, As, MnO, and Pb, are originating from the same source (i.e. salvage yard). This group of metals display similar chemical behaviour as PCBs (synthetic contaminant) and also are detected above background variation in the Makinsons drainage basin.

One of the goals of this study was to describe relationships between PCBs and heavy metals in order to possibly predict PCB behaviour based on associated metal contamination. In order to achieve this objective, relationships and statistical correlations between PCBs and heavy metals were carefully documented. Sediment / soil variables significantly (n=12) correlated (directly) with PCB are: Ni (1), Cr (1), Pb (10), Cu (10), Zn (10), As (10), Y (10), CaO (10), Cl (10), S (10), and Ce (10); based on a one-tailed test of correlation coefficient (r_S) significance (Rollinson, 1993). The observed patterns, as well as the Spearman rank correlations, suggest that Cr is the heavy metal most indicative of PCB contamination in the Makinsons drainage basin.

Due to limited vertical and areal sampling in this study, it was not possible to define a plume of dissolved metals down gradient from the salvage yard-bog area since one could not be sure if the increase in dissolved metals was due to the leaching of scrap metal, septic influence, or dissolution of the metal-rich St. John's shale. It should also be noted that this study started ± 150 m (upstream/downstream) from the salvage yard. Even so, the relatively neutral pH conditions would seem to prevent significant dissolution of metals. Unless strong leaching agents are present in sufficient quantities, the solubility of heavy metals is low and they will tend to precipitate or adsorb on sediments for a considerable period of time (Ramamoorthy and Rust, 1978). Even if metals were leached within the salvage yard, most of them would be likely adsorbed or precipitated before they could be transported outside of the yard (Mantei and Coonrod, 1989; Mather *et al.*, 1983; and Spoljaric and Crawford, 1979). There is, however, a group of metals that display peak concentrations in the surface water sample (STW2) immediately downstream from the salvage yard-bog area: Cu, Ce, Co, Pb, Sn, Ni, Sb, Rb, and Al (see Cu in Figure 4.1.10). Several of these metals have been previously associated with similar industrial dumping practices. Mather *et al.* (1983), investigating landfill contamination in the UK, discovered slight increases in Pb, Cu, and Ni in landfill leachate. Based on a study that included 6 surface and 8 ground water samples, Ehlke (1979) suspected Pb as a contaminant originating from landfills. Borden and Yanoschak (1990) also associated Pb with contamination from industrial-related landfills. However, these metals (Cu, Ce, Co, Pb, Sn, Ni, Sb, Rb, and Al) are considered unlikely to represent a dissolved plume in the ground water, since their concentrations are greater in the ground water samples collected more than 2 km downstream from the salvage yard, than in the ground water samples collected immediately downstream from the salvage yard. Based on the above evidence, the contribution of the salvage yard to the dissolved metal load in the Makinsons drainage basin, is considered minimal.

Septic effluent is probably an additional source of contamination in the Makinsons drainage basin. Unfortunately, the exact locations of individual septic system releases in the Makinsons drainage basin was not able to be determined. However, the piezometers located near the top of the basin are suspected of having been placed in an area of septic effluent due to the characteristic odour detected during installation. This theory is further supported by the extremely low dissolved oxygen concentrations in the 6 ground water samples (SOW1 to SOW6) and the surface water sample (STW2) collected from this site (see Figure E.1). Since microbial activity associated with septic effluent consumes dissolved oxygen (Alhajjar *et al.*, 1990; Cantor and Knox, 1985; and Robertson *et al.*, 1991), the septic effluent may be creating a reducing environment and increasing ion solubility. Another factor to consider is that the effluent itself is contributing to the increased dissolved load in the upper basin ground waters.

Considering the time frame of activity in the salvage yard (approximately 25-30 years), it is clear that PCBs have been released to the downstream ecosystem for a significant period of time. This study intended to determine whether PCBs and heavy metals are available to bioreceptors (*Mercenaria mercenaria*) in the South River estuary. The salinity determinations in Figure C.1 were intended to address the issue that increases in salinity is known to reduce concentrations of dissolved and particulate phase PCBs in estuarine waters (Latimer, 1989). The bioreceptor sampling program in South River were intended to span the area where fresh and salt waters mix. This area of mixing displayed seasonal variation but generally occurred south of the sample sites. Fe, Mn, Cr, Cd, and Pb are all suspected contaminants in the Makinsons drainage basin and are believed to be migrating downstream adsorbed on suspended sediments in the stream. Except for Pb, all the metals are enriched, by a factor of at least 2, relative to average concentrations in *M. mercenaria* along the Atlantic coast of the US (Phillips, 1977 after Pringle *et al.*, 1968). Based on these results, it appears possible that these metals adsorbed on particulate matter may have been transported from the salvage yard and then deposited and subsequently made available to the bivalve bioreceptors. However, PCBs were not detected in these bioreceptors from the South River estuary. Therefore, PCBs originating from the salvage yard and adsorbed on suspended material, are either being deposited closer to the salvage yard or are being diluted in the South River estuary by uncontaminated suspended matter. Both theories may be possible, but the fact remains that significant quantities of PCBs are most likely not available to these relatively immobile bioreceptors in the South River estuary.

Chapter 5. CONCLUSIONS AND RECOMMENDATIONS

The first objective of this study was to determine how PCBs and heavy metals are distributed in the surface waters, ground waters, sediments within the stream and estuary, and other ecosystem receptors. Based on the these spatial distribution patterns, sources and pathways of contamination in the Makinsons drainage basin were identified. Within stream sediments in the Makinsons drainage basin, the relative distribution patterns of Cr, Ni, As, MnO, Ba, Fe_2O_3, V, Cl, and Pb correspond to PCBs. Based on enrichment factors however, only Cr, MnO, Fe_2O_3, As, and Pb (as well as PCB) are enriched, relative to background (i.e. natural input) levels, and are conclusive of contamination (i.e. anthropogenic input). These metals are suspected of originating from the same source as PCBs. The major pathway of contamination in this study, is believed to be surface runoff carrying contaminants adsorbed on sedimentary and particulate matter from the salvage yard to the stream. However, PCBs were unexpectedly detected in locations upgradient from the salvage yard suggesting an additional source of PCB contamination. This additional source may be related to the oiling of roads to control dust before they were paved.

The salvage yard does not appear to significantly influence the surface water and ground water chemistry of the Makinsons drainage basin. Due to limited vertical and areal sampling of ground waters in this study, it was not possible to define a plume of dissolved metals down gradient from the salvage yard-bog area since one could not be certain if the increase in dissolved metals was due to the leaching of scrap metal, septic effluent, or dissolution of the metal-rich St. John's shale. Even so, the relatively neutral pH levels detected in drainage basin ground waters, would limit the solubility and subsequent mobilization of heavy metals. Septic effluent is suspected as an additional source of contamination to surface waters and ground waters in the Makinsons drainage basin. Dissolved oxygen consumption associated with septic effluent may be creating a reducing environment and increasing ion solubility, or the effluent itself is contributing to the higher conductivity in the upper basin ground waters.

Fe, Ni, Mn, Cr, and Pb are included in the group of metals suspected of being adsorbed on stream suspended matter and migrating from the salvage yard. Except for Pb, their concentrations in *M. mercenaria* collected from South River, are enriched (by a factor of at least 2), relative to average concentrations in *M. mercenaria* collected along the Atlantic coast of the US. Therefore, these metals may have been transported from the salvage yard to the South River estuary, and subsequently made available to the bivalve bioreceptors. PCBs however, were not present ≥ 0.05 ppm (wet weight) in samples collected from these same locations in South River. Because these bivalves are sedentary and are known to bioaccumulate contaminants by extremely high factors, significant quantities of PCBs are most likely not migrating this far from the salvage yard.

There has been considerable public concern over the dumping of PCB oils at the salvage yard in Makinsons over the last 30-40 years. Since the salvage yard was opened, oily sheens, suspected of originating from transformers, have been observed by local residents throughout drainage basin surface waters. There have also been complaints of skin irritation during harvesting of hay at the exact location where the piezometers are installed near the top of the drainage basin. Residents suspected that PCB-contaminated dust derived from the salvage yard was being carried downwind. More recently, several drinking water wells had to be abandoned because of PCB contamination. Considering these public concerns, as well as PCB concentrations of up to 470 ppm in salvage yard soils, the results of this study do not indicate extensive migration of PCBs from the salvage yard, as one would have expected.

Due to incomplete records by the salvage yard owners, it is not possible to perform mass balance calculations on PCBs in the Makinsons drainage basin. However, PCBs have been detected in stream sediments and soils from the drainage basin, and traces have been detected in the upper reaches of the South River estuary. It is difficult to estimate the amount of PCBs that may have been transported by suspended material into Conception Bay, or volatilized from the salvage yard into the atmosphere. Due to low aqueous solubility of PCBs and their tendency to bind to negatively charged sediments / soils, a significant portion of the original mass of PCBs probably remained in the salvage yard and was recently removed under the National Contaminated Sites Remediation Program (NCSRP). Therefore, the input of PCBs to the marine environment (Conception Bay) is most likely negligible.

Upon conclusion of this study, there are two main recommendations for future efforts in the Makinsons drainage basin. First of all, additional remediation work should concentrate on removing fine grained sediments from areas of deposition along the test stream. The high correlations between PCB concentrations and the silt + clay fraction in the stream sediments, suggests that these areas are enriched in PCBs, and if disturbed in the future, may act as a source of contamination to the downstream environment. Since long term exposure to low levels of PCBs may be unsafe, future efforts should concentrate on removing these areas of contamination downstream from the salvage yard. Secondly, an array of multi-level piezometers down gradient from the salvage yard, would provide the vertical and areal sampling resolution necessary to delineate a possible plume of dissolved metals originating from the salvage yard. Unfortunately in this study, the exact sources (i.e. salvage yard, septic effluent, etc.) of metals in the drainage basin waters were not able to be distinguished. An array of multi level piezometers would definitely help alleviate the uncertainty.

Since anecdotal evidence (i.e. oiling of roads) from local residents assisted in arriving at conclusions in this study, extensive interviews, especially with the elder residents of Makinsons, would be important in discovering the extent of handling of PCB-contaminated oils throughout the community. This could help to determine if additional locations were used to dispose of PCB contaminated oils, especially during early salvage yard operations. Finally, I would recommend similar holistic studies into the distribution of PCBs and heavy metals in surface waters and ground waters, stream sediments, and ecosystem receptors, downstream from any uncontrolled landfill known to contain PCB-contaminated waste.

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APPENDIX A

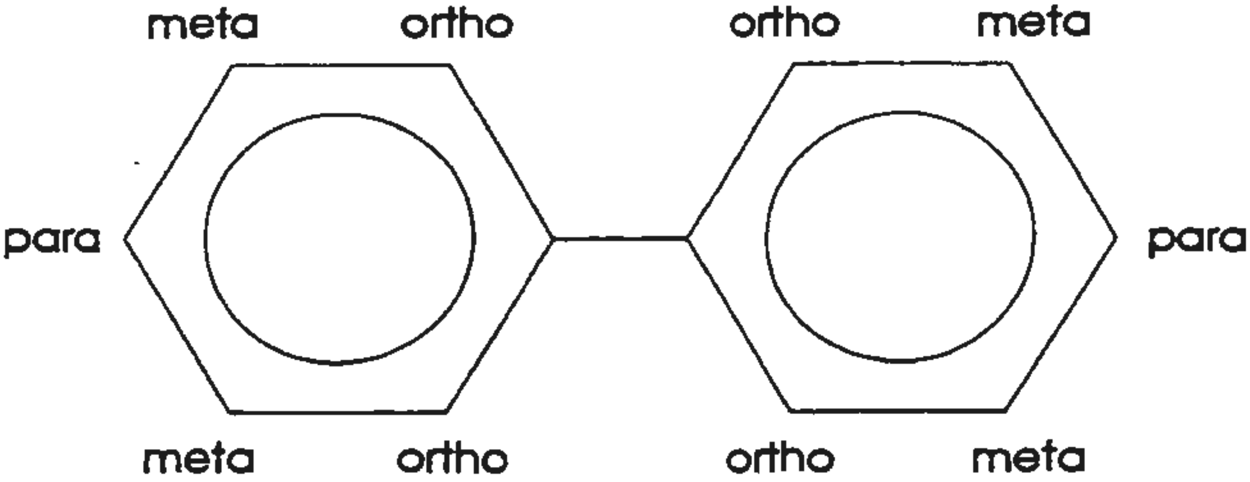


Figure A.1 Structure of a biphenyl molecule indicating the positions (i.e. *ortho*, *para*, and *meta*) where chlorine substitution is possible.

Table B.1 Sampling Matrix.

Sample Site ID	Sample Type	Date(s) Collected	Grain Size	LOI	XRF	PCB	AA	IC	ICP-MS	O2	ALK	Sample Site Description
Makinsons Basin												
STW1	surf. water	28-Aug					X	X	X	X	X	samples collected in ditch next to road
		16-Nov					X	X	X	X	X	upstream from salvage yard.
STS1	sediment	28-Aug	X	X	X	X						
STW2	surf. water	16-Nov					X	X	X	X	X	sample collected approx. 175 m downstream from salvage yard.
SOW1	g. water	16-Nov					X	X	X	X	X	sample collected from piezometer 1.
SOW2	g. water	16-Nov					X	X	X	X	X	sample collected from piezometer 2.
SOW3	g. water	16-Nov					X	X	X	X	X	sample collected from piezometer 3.
SOW4	g. water	16-Nov					X	X	X	X	X	sample collected from piezometer 4.
SOW5	g. water	16-Nov					X	X	X	X	X	sample collected from piezometer 5.
SOW6	g. water	16-Nov					X	X	X	X	X	sample collected from piezometer 6.
SOS1	soil	28-Aug		X	X	X						sample between piezometers 1 to 3 (approx. 30 cm. deep).
SOS2	soil	28-Aug		X	X	X						sample between piezometers 4 to 6 (approx. 30 cm. deep).
STW3	surf. water	28-Aug					X	X	X	X	X	samples collected in test stream; approx. 500 m
		17-Nov					X	X	X	X	X	downstream from salvage yard.
STS3	sediment	28-Aug	X	X	X	X						
SS1	bedrock	28-Aug		X	X							green siltstone bedrock (Conception Group).
STW4	surf. water	17-Nov					X	X	X	X	X	sample collected downstream of culverts (< 2 m).
STS4	sediment	28-Aug	X	X	X	X						sample collected at rink.
STW5	surf. water	28-Aug					X	X	X	X	X	samples collected 100m downstream from rink.
		17-Nov					X	X	X	X	X	
STS5	sediment	28-Aug	X	X	X	X						sample collected 50 m upstream from small gully.
STW6	surf. water	17-Nov					X	X	X	X	X	samples collected in small gully.

Table B.1 cont...

Sample Site ID	Sample Type	Date(s) Collected	Grain Size	LOI	XRF	PCB	AA	IC	ICP-MS	O2	ALK	Sample Site Description
STS6	sediment	28-Aug	X	X	X	X						samples collected in small gully.
STW7	surf. water	17-Nov					X	X	X	X	X	samples collected in small tributary draining an undeveloped portion of the drainage basin.
STS7	sediment	28-Aug	X	X	X							
STW8	surf. water	17-Nov					X	X	X	X	X	samples collected 100m downstream from small gully.
STS8	sediment	28-Aug		X	X							
STW9	surf. water	28-Aug					X	X	X	X	X	samples collected in small tributary draining a bog located next to a roadway.
		17-Nov					X	X	X	X	X	
STS9	sediment	28-Aug	X	X	X	X						
STW10	surf. water	28-Aug					X	X	X	X	X	samples collected in an area with four car wrecks nearby.
		17-Nov					X	X	X	X	X	
STS10	sediment	28-Aug	X	X	X	X						sample collected in stream (next to horse pasture).
STW11	surf. water	28-Aug					X	X	X	X	X	samples collected in stream approx. 200 m upstream from South River (also a horse pasture).
		16-Nov					X	X	X	X	X	
SOW7	g. water	16-Nov					X	X	X	X	X	sample collected from piezometer 7.
SOW8	g. water	16-Nov					X	X	X	X	X	sample collected from piezometer 8.
SOW9	g. water	16-Nov					X	X	X	X	X	sample collected from piezometer 9.
SOW10	g. water	16-Nov					X	X	X	X	X	sample collected from piezometer 10.
SOW11	g. water	16-Nov					X	X	X	X	X	sample collected from piezometer 11.
SOW12	g. water	16-Nov					X	X	X	X	X	sample collected from piezometer 12.
SOS3	soil	28-Aug	X	X	X	X						sample between piezometers 7 to 9 (approx. 30 cm deep).
SOS4	soil	28-Aug	X	X	X	X						sample between piezometers 10 to 12 (approx. 30 cm deep).
STW12	surf. water	28-Aug					X	X	X	X	X	sample collected just before main course joins a ditch near the bottom of the basin.
		16-Nov					X	X	X	X	X	
STW13	surf. water	28-Aug					X	X	X	X	X	samples collected in small ditch near bottom of basin.
		16-Nov					X	X	X	X	X	
STS13	sediment	28-Aug	X	X	X	X						

Table B.1 cont...

Sample Site ID	Sample Type	Date(s) Collected	Grain Size	LOI	XRF	PCB	AA	IC	ICP-MS	O2	ALK	Sample Site Description
STW14	surf. water	23-Mar					X	X	X	X	X	sample collected 10 m upstream from South River.
		28-Aug					X	X	X	X	X	
		16-Nov					X	X	X	X	X	
Control Basin												
CS1	surf. water	16-Nov					X	X	X	X	X	samples collected in control stream (approx. 10 m
SCS1	sediment	28-Aug	X	X	X	X						upstream from South River).
SCS2	sediment	28-Aug	X	X	X	X						sample collected in control stream.
SOC1	soil	28-Aug				X						control stream bog sample.
South River												
ESO1	sediment	28-Aug				X						tidal marsh sample collected in South River.
ESO2	sediment	28-Aug				X						tidal marsh sample collected in South River.
E2	core	April 94				X						sediment core collected from South River.
E4	core	April 94		X	X	X						sediment core collected from South River.
E8	core	April 94				X						top 100 mm of core analyzed for total PCB content,
	clam	17-Aug				X			X			and homogenized clam sample.
E9	core	April 94			X							sediment core collected from South River.
E12	clam	17-Aug				X			X			homogenized clam sample.
E13	core	April 94				X						top 100 mm of core analyzed for total PCB content.
E14	clam	17-Aug				X			X			homogenized clam sample.
E16	clam	17-Aug				X			X			homogenized clam sample.
E18	core	April 94				X						top 100 mm of core analyzed for total PCB content,
	clam	17-Aug				X			X			and homogenized clam sample.
SH1	bedrock	28-Aug		X	X							black shale (St. John's Group).
SS2	bedrock	28-Aug		X	X							red siltstone bedrock (Conception Group).
E22	core	April 94				X						top 100 mm of core analyzed for total PCB content.
E25	core	April 94				X						top 100 mm of core analyzed for total PCB content.
E27	core	April 94				X						top 100 mm of core analyzed for total PCB content.

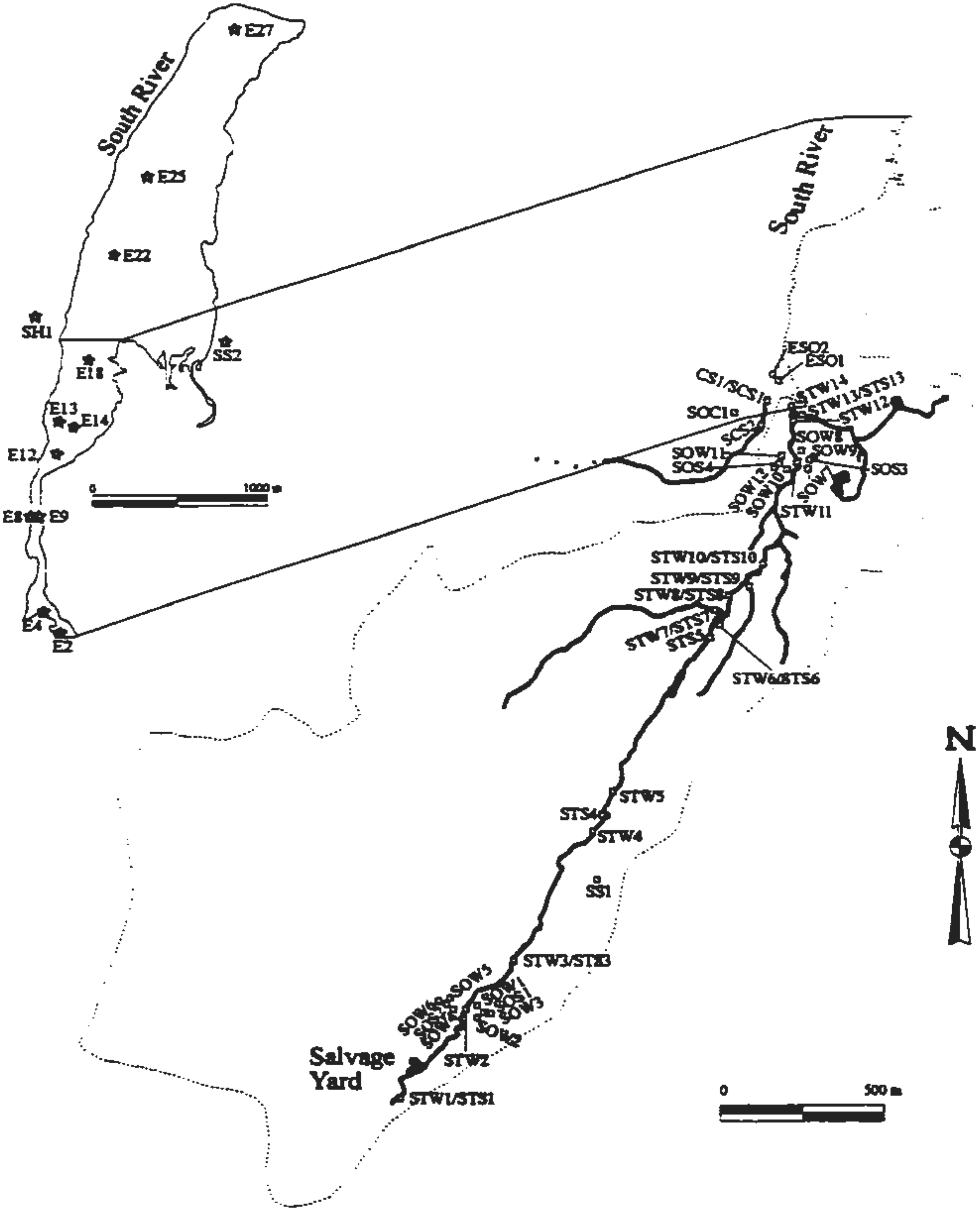


Figure B.1 Location map for sampling matrix.

APPENDIX C

Salinity Determination Equations.

The following procedure for determining salinity is outlined by Cox *et al.* (1967):

1. $R_t = C_{T,S} / C_{T,35}$

2. $C_{T,S}$ (mmho/cm) = measured conductivity at in situ temperature (T).

3. $C_{T,35} = 29.03916(1.0+0.029717T+0.00015551T^2+0.000000789T^3)$.

4. $R_{15} = C_{15,S} / C_{15,35}$

5. $C_{15,35} = 42.922$ mmho/cm at 15°C and 35 ‰ salinity.

6. $\Delta_{15} = 10^{-5}R_t(R_t-1.0)(T-15)[96.7-72.0R_t+37.3R_t^2-(0.63+0.21R_t^2)(T-15)]$.

7. $\Delta_{15} = R_{15} - R_t$

8. Salinity (‰) $= -0.08996+28.29720R_{15}+12.80832R_{15}^2 10.6789R_{15}^3+$
$0.98624R_{15}^4-1.32311R_{15}^5$.

APPENDIX C

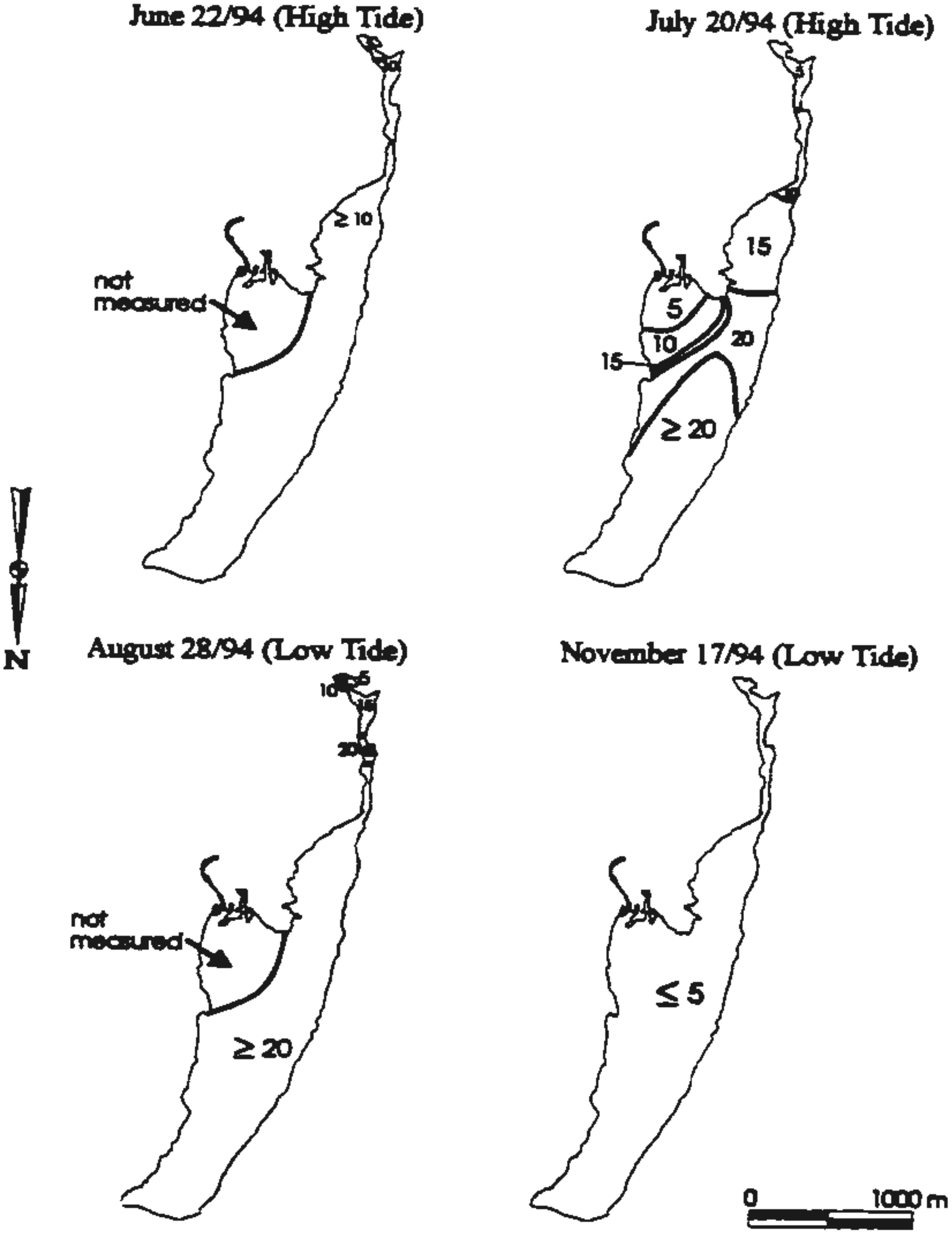


Figure C.1 Salinity Variation (‰) in the South River Estuary (1994).

APPENDIX D

Table D.1 Sediment and Soil Chemistry Data.

Sample	Description	Sample Type	Date sampled	Elevation (m)	Longitude (UTM)	Latitude (UTM)	Sheen	Grainsize (% < 63mm)	LOI (%)	Na2O (wt %)	MgO (wt %)	Al2O3 (wt %)
M08020I	SOS2	soil	28-Aug	55	281045	5261050	no	NA	78.59	0.38	0.74	87.90
M08021F	SCS2	sediment	28-Aug	0	281990	5263150	no	1.7	2.30	2.35	2.65	17.00
M08022B	STS8	sediment	28-Aug	15	281900	5262530	no	NA	61.83	0.86	0.94	39.65
M08023Y	SOS4	soil	28-Aug	5	282090	5262950	no	15.6	6.40	2.09	1.79	15.70
M08024V	STS13	sediment	28-Aug	0	282110	5263165	yes	15.1	6.70	2.51	1.83	15.17
M08025S	STS4	sediment	28-Aug	30	281485	5261765	yes	26.5	12.20	2.06	1.63	16.98
M08026P	SOS1	soil	28-Aug	55	281035	5261050	no	NA	50.85	1.74	1.63	22.40
M08027L	STS3	sediment	28-Aug	50	281245	5261280	no	8.7	11.92	1.98	1.53	12.37
M08028I	SCS1	sediment	28-Aug	0	282010	5263220	no	0.9	1.32	2.46	2.39	16.09
M08029F	SOS3	soil	28-Aug	5	282105	5262950	no	26.7	12.05	2.46	1.34	16.43
M08031O	STS5	sediment	28-Aug	15	281835	5262420	yes	89.7	67.06	1.16	0.87	14.87
M08032Y	STS9	sediment	28-Aug	15	281950	5262575	yes	85.9	44.17	0.75	0.71	7.05
M08033Q	STS1	sediment	28-Aug	70	280845	5260800	yes	97.7	11.28	2.25	1.92	16.00
M08034J	STS7	sediment	28-Aug	15	281865	5262470	no	2.5	10.94	2.40	1.54	14.20
M08035B	STS6	sediment	28-Aug	15	281855	5262430	yes	94.2	41.95	1.15	1.00	16.94
M08036T	STS19	sediment	28-Aug	10	282070	5262760	yes	11.9	11.05	2.26	1.75	14.50
M08037L	SS2	bedrock	28-Aug	10	283450	5263940	0	NA	0.73	2.38	3.64	16.90
M08038D	SS1	bedrock	28-Aug	20	282025	5262535	no	NA	0.68	2.86	2.03	14.78
M08039V	SH1	bedrock	28-Aug	45	282205	5263905	no	NA	1.35	2.33	3.20	16.87
PCB13SED	ESO1	sediment	28-Aug	0	282070	5263290	yes	NA	NA	NA	NA	NA
PCB14SED	ESO2	sediment	28-Aug	0	282045	5263280	yes	NA	NA	NA	NA	NA
PCB17SED	SOC1	soil	28-Aug	0	281980	5263180	yes	NA	NA	NA	NA	NA

APPENDIX D

Table D.1 cont...

Description	SiO2 (wt %)	P2O5 (wt %)	S (ppm)	Cl (ppm)	K20 (wt %)	CaO (wt %)	Sc (ppm)	TiO2 (wt %)	V (ppm)	Cr (ppm)	MnO (wt %)	Fe2O3T (wt %)	Ni (ppm)	Cu (ppm)
SOS2	17.30	1.00	5008	39	0.53	1.28	33	0.33	36	235	0.09	1.38	87	183
SCS2	62.72	0.09	390	54	2.84	0.35	17	0.82	102	113	0.14	7.04	36	8
STS8	42.01	0.41	5118	373	0.98	1.08	14	0.52	68	165	2.75	12.93	62	47
SOS4	59.65	0.13	553	95	2.53	0.31	14	0.72	86	115	2.24	9.22	39	13
STS13	65.01	0.15	906	174	2.47	0.60	18	0.71	76	124	0.37	7.44	36	18
STS4	63.47	0.16	677	146	2.34	0.40	12	0.88	96	108	0.20	8.05	32	11
SOS1	61.66	1.15	3292	85	2.62	0.88	47	0.96	103	257	0.15	4.39	72	133
STS3	53.26	0.21	992	347	2.20	0.67	13	0.68	97	346	1.34	23.73	116	42
SCS1	62.67	0.11	194	62	3.00	0.56	12	0.73	87	79	0.26	6.79	21	11
SOS3	64.30	0.18	689	127	1.94	0.59	16	0.73	84	144	1.06	7.01	45	17
STS5	51.11	0.54	4754	124	1.38	0.74	15	0.76	96	234	6.36	17.54	96	60
STS9	33.41	0.36	3128	672	0.86	2.39	< 9	0.44	67	283	15.42	36.07	115	47
STS1	61.94	0.18	1212	153	2.63	0.81	15	0.87	91	160	0.14	7.37	54	48
STS7	60.05	0.11	662	127	1.98	0.67	13	0.65	80	146	3.09	9.56	55	15
STS6	62.89	0.42	4334	181	1.38	0.82	21	0.78	98	318	0.78	10.49	111	40
STS19	61.42	0.14	1346	119	2.29	0.63	13	0.66	81	167	0.46	9.34	55	17
SS2	62.11	0.06	24	64	3.82	0.81	15	0.76	93	33	0.18	7.37	16	11
SS1	62.57	0.05	30	66	2.87	0.76	10	0.62	68	26	0.15	5.54	11	12
SH1	60.10	0.13	2921	73	2.92	0.64	16	0.73	121	68	0.12	7.87	23	30
ESO1	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
ESO2	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SOC1	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

APPENDIX D

Table D.1 cont...

Description	Zn (ppm)	Ga (ppm)	As (ppm)	Rb (ppm)	Sr (ppm)	Y (ppm)	Zr (ppm)	Nb (ppm)	Ba (ppm)	Ce (ppm)	Pb (ppm)	Th (ppm)	U (ppm)	PCB (ppm)
SOS2	1627	22	63	27.4	89.4	214.5	139.1	8.5	220	611	85	15	11	1.23
SCS2	88	21	14	94.2	105.2	28.6	247.9	16.6	532	73	12	10	<3	< 0.05
STS8	419	18	142	43.8	92.2	67.9	154.0	11.4	562	325	76	6	< 3	NA
SOS4	94	18	53	90.5	95.7	30.2	260.8	16.6	737	107	18	8	< 3	< 0.05
STS13	130	18	< 14	84.2	116.3	30.8	251.6	15.6	586	47	27	7	< 3	0.05
STS4	80	21	18	89.4	88.2	28.4	277.6	18.8	544	43	20	10	< 3	< 0.05
SOS1	178	24	28	96.0	120.4	119.4	342.7	24.7	631	550	105	22	11	0.09
STS3	213	18	252	74.7	89.4	34.7	199.1	15.1	766	187	61	7	< 3	15.10
SCS1	82	20	< 14	93.8	108.7	29.7	246.7	15.4	609	67	9	8	< 3	< 0.05
SOS3	93	20	34	77.0	107.3	30.9	256.9	18.0	544	209	34	9	< 3	1.20
STS5	744	18	181	59.5	96.4	65.5	215.0	15.6	988	390	84	8	5	1.89
STS9	1085	8	218	38.5	149.7	42.6	121.3	9.5	1785	203	50	< 3	< 3	1.22
STS1	379	21	< 14	94.8	110.0	38.5	279.9	19.1	606	98	64	9	< 3	1.82
STS7	184	18	100	72.7	122.3	25.7	228.9	14.4	748	99	26	6	< 3	NA
STS6	695	17	123	61.9	84.6	65.3	213.9	16.6	601	382	73	11	< 3	3.54
STS19	156	17	33	82.2	109.8	29.3	242.6	16.0	627	81	21	9	< 3	0.14
SS2	101	22	< 14	122.9	108.2	39.9	257.6	15.2	707	82	14	8	< 3	NA
SS1	71	21	< 14	95.1	103.3	26.2	209.6	13.0	694	66	5	9	4	NA
SH1	52	22	25	100.4	110.0	30.9	232.3	16.7	512	58	21	10	<3	NA
ESO1	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.06
ESO2	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.06
SOC1	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	1.76

APPENDIX E

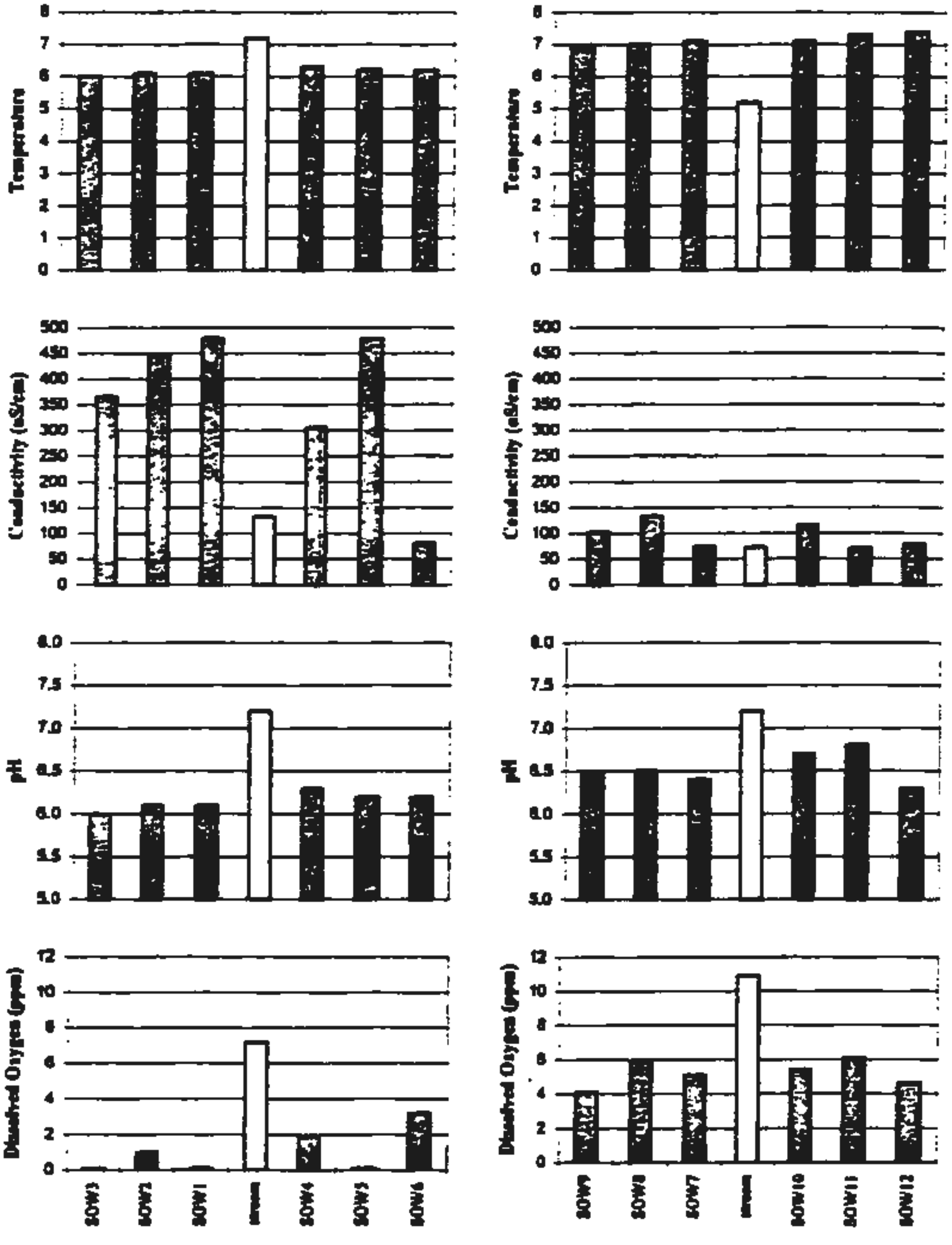


Figure E.1 Temperature, conductivity, pH, and dissolved oxygen measured at each of the 12 piezometers. Included is the appropriate surface water parameter between each set of piezometers.

APPENDIX E

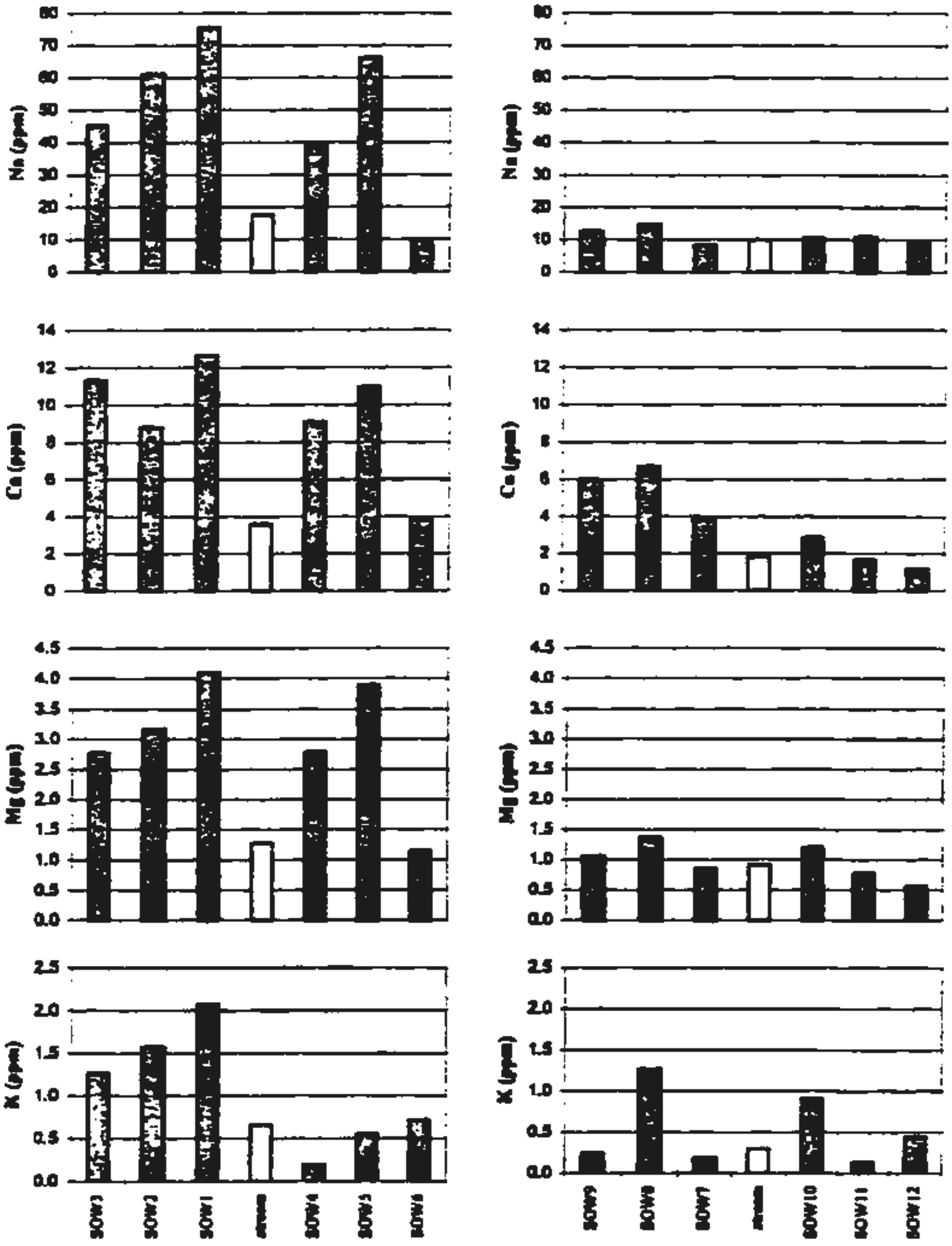


Figure E.2 Major cation chemistry measured at each of the 12 piezometers. Included is the appropriate surface water parameter between each set of piezometers.

APPENDIX E

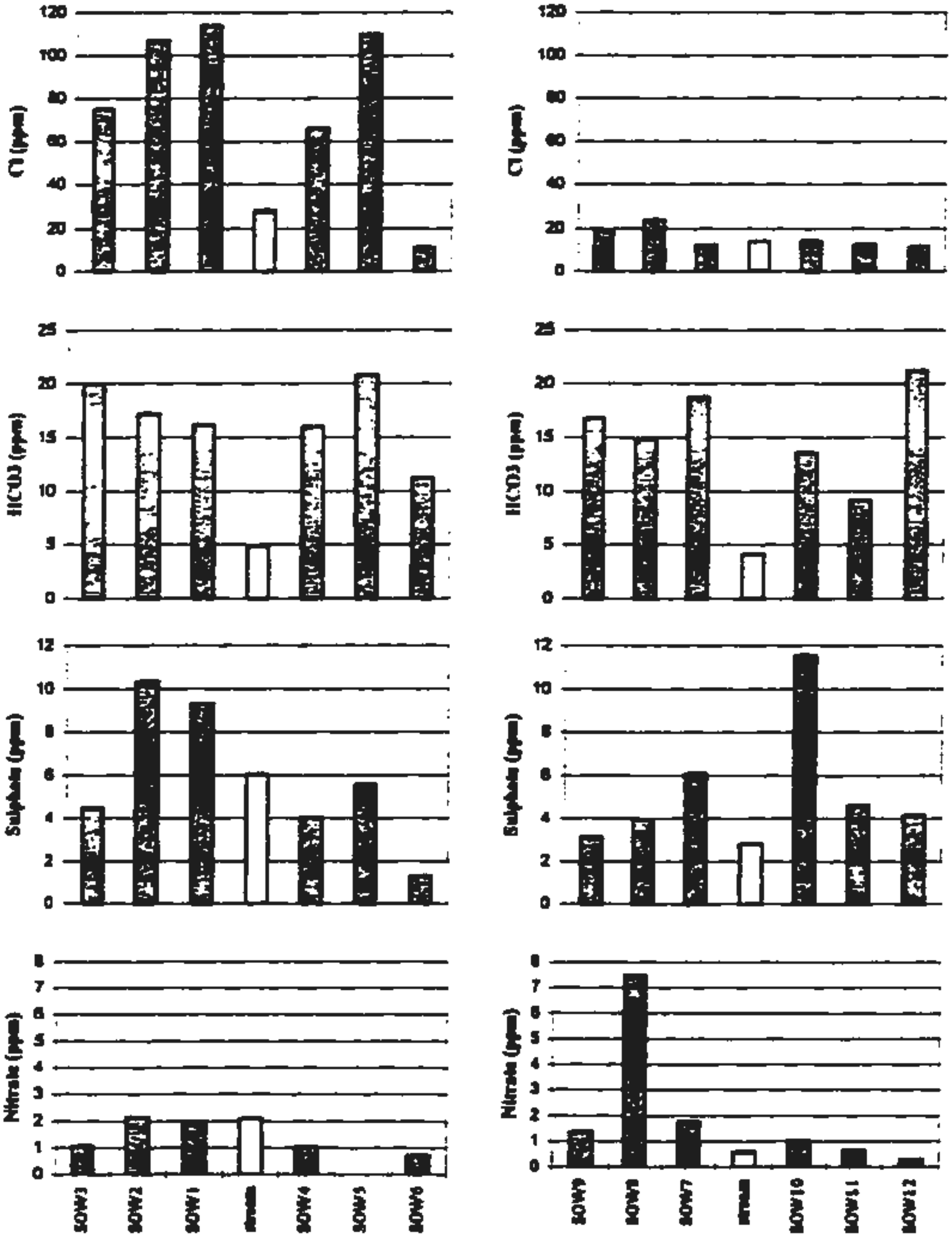


Figure E.3 Major anion chemistry measured at each of the 12 piezometers. Included is the appropriate surface water parameter between each set of piezometers.

APPENDIX F

Table F.1 Water Chemistry Data.

Sample#	Description	Sample Type	Date sampled	Elevation (m)	Longitude (UTM)	Latitude (UTM)	Temperature (Celsius)
S11611W	STW1	surface	16-Nov	70	280845	5260800	4.1
S21611W	STW2	surface	16-Nov	55	281040	5261050	5.6
S31711W	STW3	surface	17-Nov	50	281245	5261280	3.9
S41711W	STW4	surface	17-Nov	35	281475	5261735	3.0
S51711W	STW5	surface	17-Nov	30	281540	5261855	3.0
S61711W	STW6	surface	17-Nov	15	281855	5262430	3.4
S71711W	STW7	surface	17-Nov	15	281865	5262470	3.5
S81711W	STW8	surface	17-Nov	15	281900	5262530	3.0
S91711W	STW9	surface	17-Nov	15	281950	5262575	3.5
S101711W	STW10	surface	17-Nov	10	282015	5262670	2.9
S111611W	STW11	surface	16-Nov	5	282100	5262950	5.2
S121611W	STW12	surface	16-Nov	0	282095	5263160	5.2
S131611W	STW13	surface	16-Nov	0	282110	5263165	5.5
S141611W	STW14	surface	16-Nov	0	282100	5263195	5.4
C11611W	CS1	surface	16-Nov	0	282010	5263220	5.3
P11611W	SOW1	ground	16-Nov	55	281045	5261050	6.0
P21611W	SOW2	ground	16-Nov	55	281045	5261050	6.4
P31611W	SOW3	ground	16-Nov	55	281045	5261050	6.1
P41611W	SOW4	ground	16-Nov	55	281035	5261050	6.0
P51611W	SOW5	ground	16-Nov	55	281035	5261050	6.2
P61611W	SOW6	ground	16-Nov	55	281035	5261050	6.1
P71611W	SOW7	ground	16-Nov	5	282105	5262950	7.1
P81611W	SOW8	ground	16-Nov	5	282105	5262950	7.0
P91611W	SOW9	ground	16-Nov	5	282105	5262950	7.0
P101611W	SOW10	ground	16-Nov	5	282090	5262950	7.1
P111611W	SOW11	ground	16-Nov	5	282090	5262950	7.3
P121611W	SOW12	ground	16-Nov	5	282090	5262950	7.4
S12808W	STW1	ground	28-Aug	70	280845	5260800	21.7
S32808W	STW3	surface	28-Aug	50	281245	5261280	15.8
S52808W	STW5	surface	28-Aug	30	281540	5261855	19.5
S92808W	STW9	surface	28-Aug	15	281950	5262575	17.4
S102808W	STW10	surface	28-Aug	10	282015	5262670	19.1
S112808W	STW11	surface	28-Aug	5	282100	5262950	17.8
S122808W	STW12	surface	28-Aug	0	282095	5263160	16.9
S132808W	STW13	surface	28-Aug	0	282110	5263165	16.1
S142808W	STW14	surface	28-Aug	0	282100	5263195	17.1
S142303W	STW14	surface	23-Mar	0	282100	5263195	0.9

APPENDIX F

Table F.1 cont...

Description	Conductivity (mS/cm)	pH	O2 (ppm)	Alkalinity (ppm HCO3)	Na (ppm)	K (ppm)	Ca (ppm)	Mg (ppm)
STW1	165.6	7.2	13.4	4.1	19.524	0.580	7.944	1.323
STW2	133.0	7.2	7.2	4.8	17.508	0.663	3.588	1.280
STW3	162.3	7.1	8.9	7.8	22.032	0.967	3.958	1.476
STW4	90.6	7.4	10.6	4.7	12.590	0.193	2.363	1.077
STW5	87.0	7.4	10.4	4.7	11.901	0.221	2.307	1.059
STW6	81.7	7.2	11.7	4.5	11.095	0.359	2.136	1.009
STW7	39.1	7.4	10.9	3.5	4.721	0.193	1.566	0.863
STW8	73.4	7.5	11.6	4.5	9.934	0.415	1.908	0.984
STW9	105.1	7.1	8.8	5.5	15.885	0.774	1.823	0.674
STW10	74.4	7.3	10.4	4.3	9.934	0.442	1.936	0.973
STW11	72.4	7.2	10.9	4.1	9.934	0.304	1.823	0.923
STW12	77.8	7.2	9.0	4.3	10.721	0.387	2.107	0.959
STW13	86.2	7.7	6.8	4.2	11.606	0.470	1.936	1.102
STW14	79.0	7.5	10.6	4.0	10.475	0.387	2.107	0.991
CS1	40.1	7.6	10.1	3.9	4.574	0.221	1.310	0.977
SOW1	479.0	6.1	0.0	16.2	75.490	2.073	12.641	4.097
SOW2	445.0	6.1	1.0	17.2	61.228	1.575	8.798	3.170
SOW3	366.0	6.0	0.0	20.0	45.146	1.271	11.303	2.778
SOW4	306.0	6.3	1.9	16.0	40.032	0.193	9.082	2.792
SOW5	478.0	6.2	0.0	20.8	66.146	0.553	10.933	3.883
SOW6	80.8	6.2	3.2	11.2	9.787	0.719	3.844	1.155
SOW7	74.0	6.4	5.1	18.8	8.311	0.193	3.872	0.848
SOW8	134.1	6.5	5.9	14.8	14.754	1.271	6.691	1.376
SOW9	102.9	6.5	4.1	16.8	12.590	0.249	6.008	1.059
SOW10	115.6	6.7	5.4	13.6	10.573	0.912	2.876	1.205
SOW11	71.0	6.8	6.1	9.2	11.016	0.138	1.680	0.777
SOW12	78.1	6.3	4.6	21.2	8.852	0.442	1.196	0.567
STW1	254.0	7.2	9.3	9.1	33.049	0.359	7.944	1.922
STW3	371.0	7.2	8.9	15.5	53.999	1.216	8.940	3.277
STW5	136.0	7.6	9.8	9.9	18.590	0.249	9.367	2.179
STW9	223.0	7.2	5.2	62.8	31.377	0.553	8.855	2.350
STW10	106.6	7.4	9.7	8.4	14.213	0.332	2.762	1.237
STW11	114.2	8.6	9.9	10.0	15.787	0.359	3.104	1.319
STW12	131.5	6.3	12.7	11.1	17.754	0.608	3.445	1.433
STW13	196.8	6.9	0.0	32.9	19.574	0.276	4.100	1.558
STW14	133.4	7.0	8.4	12.8	17.361	0.221	3.388	1.455
STW14	145.6	7.1	13.8	6.2	21.295	0.608	2.648	1.169

APPENDIX F

Table F.1 cont...

Description	Cl (ppm)	Nitrate (ppm)	Phosphate (ppm)	Sulfate (ppm)	Li (ppb)	Be (ppb)	B (ppb)	Al (ppb)
STW1	29.210	1.130	0.00	11.410	0.88	<1.87	<205.81	77.0
STW2	27.790	2.110	0.00	6.040	3.29	<1.87	<205.81	99.2
STW3	39.065	2.720	0.00	5.380	3.30	<1.87	<205.81	92.8
STW4	22.295	1.340	0.00	3.395	<0.63	<1.87	<205.81	87.9
STW5	21.335	1.385	0.00	3.405	5.03	<1.87	<205.81	75.4
STW6	17.895	1.450	0.00	3.740	7.01	<1.87	<205.81	67.5
STW7	7.219	0.214	0.00	1.945	<0.63	<1.87	<205.81	88.5
STW8	13.856	0.572	0.00	2.690	0.96	<1.87	<205.81	73.3
STW9	21.805	1.110	0.00	5.520	2.75	<1.87	<205.81	21.4
STW10	14.127	0.601	0.00	2.825	1.58	<1.87	<205.81	72.4
STW11	13.917	0.592	0.00	2.836	6.92	<1.87	<205.81	74.9
STW12	23.508	1.662	0.00	2.922	<0.63	<1.87	<205.81	75.4
STW13	23.905	1.510	0.00	4.520	1.20	<1.87	<205.81	117.2
STW14	19.696	1.618	0.00	3.402	0.78	<1.87	<205.81	78.0
CS1	7.246	0.308	0.00	2.235	<0.63	<1.87	<205.81	71.9
SOW1	113.840	1.970	0.00	9.320	6.67	<1.87	<205.81	296.3
SOW2	106.890	2.140	0.00	10.340	5.52	<1.87	<205.81	422.8
SOW3	74.900	1.070	0.00	4.480	9.25	<1.87	<205.81	608.6
SOW4	66.255	1.045	0.00	4.020	1.89	<1.87	<205.81	303.1
SOW5	109.760	0.000	0.00	5.580	3.76	<1.87	<205.81	356.6
SOW6	11.088	0.713	0.00	1.312	7.29	<1.87	<205.81	601.0
SOW7	12.220	1.780	0.00	6.101	28.31	<1.87	<205.81	308.2
SOW8	24.045	7.485	0.00	3.955	2.23	<1.87	<205.81	42.2
SOW9	18.770	1.375	0.00	3.130	3.07	<1.87	2369.07	11736.1
SOW10	14.292	1.038	0.00	11.538	11.13	<1.87	<205.81	43.9
SOW11	12.596	0.652	0.00	4.610	2.89	<1.87	2148.37	3259.9
SOW12	11.595	0.285	0.00	4.154	4.18	<1.87	<205.81	44.6
STW1	57.320	1.115	0.00	7.670	7.30	<1.87	<205.81	100.0
STW3	92.530	2.970	0.00	2.630	1.28	<1.87	<205.81	55.9
STW5	30.880	1.690	0.00	2.355	1.45	<1.87	<205.81	43.0
STW9	40.765	0.970	0.00	1.060	1.69	<1.87	<205.81	42.5
STW10	28.775	1.185	0.00	2.405	0.76	<1.87	<205.81	56.6
STW11	28.640	1.265	0.00	2.800	21.02	<1.87	<205.81	28.0
STW12	37.565	2.395	0.00	3.040	0.87	<1.87	<205.81	28.5
STW13	32.135	1.655	0.00	1.250	0.97	<1.87	<205.81	377.4
STW14	29.740	1.855	0.00	3.000	2.22	<1.87	<205.81	35.8
STW14	36.675	1.905	0.00	3.585	<0.63	<1.87	<205.81	67.6

APPENDIX F

Table F.1 cont...

Description	Si (ppb)	P (ppb)	S (ppb)	Ti (ppb)	V (ppb)	Cr52 (ppb)	Mn (ppb)	Fe57 (ppb)	Co (ppb)	Ni (ppb)
STW1	3056	<346	<7682	2.25	<0.83	<0.47	133.68	281	0.94	1.13
STW2	2498	<346	<7682	1.75	1.02	1.02	148.25	429	0.63	1.21
STW3	2420	<346	<7682	2.08	1.16	<0.47	289.74	456	1.09	1.06
STW4	1852	<346	<7682	1.12	0.75	<0.47	148.48	181	0.26	1.19
STW5	1784	<346	<7682	1.01	<0.72	<0.47	122.26	146	0.22	1.01
STW6	2004	<346	<7682	0.63	<0.73	<0.47	136.49	146	0.26	7.12
STW7	1910	<346	<7682	0.52	<0.62	<0.47	24.46	91	0.08	2.25
STW8	1837	<346	<7682	0.67	<0.69	<0.47	62.22	104	0.10	1.22
STW9	1655	<346	<7682	0.80	<0.75	<0.47	117.48	126	0.19	1.12
STW10	1830	<346	<7682	1.14	<0.70	<0.47	81.64	215	0.22	1.01
STW11	1806	<346	<7682	1.14	<0.69	<0.47	43.64	104	0.10	1.55
STW12	1833	<346	<7682	0.95	<0.71	<0.47	46.53	113	0.10	1.10
STW13	2205	<346	<7682	1.80	0.78	<0.47	15.78	321	0.14	1.39
STW14	1761	<346	<7682	1.00	<0.71	<0.47	46.94	123	0.10	3.37
CS1	2082	<346	<7682	0.82	<0.61	<0.47	39.58	96	0.13	0.77
SOW1	3043	348	<7682	7.94	2.59	0.76	993.92	1087	3.55	2.96
SOW2	2852	375	<7682	6.40	3.75	0.91	595.17	677	2.65	6.65
SOW3	3634	<346	<7682	11.69	2.85	0.91	762.72	4420	6.27	4.95
SOW4	2762	<346	<7682	6.91	2.06	0.63	634.10	2019	3.92	2.33
SOW5	3309	<346	<7682	11.30	<1.78	<1.78	710.30	3597	6.30	3.03
SOW6	2853	<346	<7682	6.00	1.15	0.94	343.92	1488	3.71	4.81
SOW7	1089	<346	<7682	5.63	1.97	1.97	180.73	175	0.70	14.35
SOW8	1345	<346	<7682	0.62	1.00	<0.47	879.36	<29	2.33	4.96
SOW9	7377	<346	<7682	5.43	2.91	0.57	978.98	76	1.94	7.98
SOW10	1881	<346	<7682	1.40	<0.70	<0.70	6811.23	157	3.56	8.18
SOW11	7179	<346	<7682	3.08	1.06	<0.47	1409.48	42	1.22	3.71
SOW12	1926	<346	<7682	0.68	<0.67	<0.67	2801.21	29	7.22	2.10
STW1	3059	<346	<7682	4.47	1.44	1.44	261.34	699	1.58	3.33
STW3	2663	<346	<7682	3.85	2.05	<0.47	675.64	552	2.29	1.91
STW5	1606	<346	<7682	1.40	<0.83	<0.47	326.36	190	0.34	1.09
STW9	1836	<346	<7682	1.75	1.28	<0.47	2533.74	697	2.19	4.31
STW10	1663	<346	<7682	0.99	1.09	<0.47	47.48	143	0.14	2.22
STW11	1660	<346	<7682	1.16	<0.79	<0.47	49.62	65	0.09	1.07
STW12	1786	<346	<7682	1.35	<0.81	<0.47	56.21	69	0.09	0.97
STW13	2762	<346	<7682	8.68	1.59	<0.47	2803.08	18123	16.18	1.98
STW14	2239	<346	<7682	1.26	1.08	1.08	196.02	531	0.67	1.19
STW14	1628	<346	<7682	1.41	0.93	<0.47	74.42	70	0.13	2.75

APPENDIX F

Table F.1 cont...

Description	Cu (ppb)	Zn (ppb)	As (ppb)	Br (ppb)	Se (ppb)	Rb (ppb)	Sr (ppb)	Mo (ppb)	Ag (ppb)	Cd (ppb)
STW1	4.84	139.74	0.33	73.00	<1.52	0.79	35.37	0.14	<0.25	0.07
STW2	8.57	96.90	0.54	119.84	<1.56	0.91	15.93	0.04	<0.25	0.07
STW3	5.49	48.26	0.63	97.63	<1.54	0.90	19.86	0.03	<0.25	0.14
STW4	5.10	503.18	0.39	50.36	<1.51	0.55	12.09	<0.03	<0.25	0.27
STW5	3.29	52.19	0.23	<44.27	<1.49	0.69	12.87	0.04	<0.25	0.17
STW6	5.37	85.91	0.41	50.31	<1.51	0.69	12.52	0.05	<0.25	0.15
STW7	9.73	362.49	0.50	<44.27	<1.49	0.50	9.61	<0.03	<0.25	0.21
STW8	5.79	190.94	0.29	<44.27	<1.49	0.58	11.28	<0.03	<0.25	0.07
STW9	3.46	61.78	0.28	<44.27	<1.50	0.80	9.73	<0.03	<0.25	0.09
STW10	5.33	90.56	0.30	<44.27	<1.50	0.61	11.06	<0.03	<0.25	0.09
STW11	7.69	161.40	0.26	<44.27	<1.50	0.77	11.44	0.03	<0.25	0.07
STW12	2.87	43.91	0.44	<44.27	<1.50	0.68	11.87	<0.03	<0.25	0.09
STW13	5.77	77.80	0.29	<44.27	<1.49	1.05	12.04	0.11	<0.25	0.14
STW14	8.41	222.41	0.43	<44.27	<1.50	0.75	12.82	0.05	<0.25	0.18
CS1	1.93	137.57	<0.14	<44.27	<1.49	0.35	8.35	<0.03	<0.25	<0.04
SOW1	5.11	182.32	3.03	83.45	<1.53	1.30	76.26	0.50	<0.25	0.22
SOW2	19.20	182.01	2.93	69.62	<1.52	1.67	73.76	0.24	<0.25	1.08
SOW3	9.74	228.70	6.01	118.36	<1.56	1.93	78.17	0.24	<0.25	0.28
SOW4	9.59	104.48	2.98	62.03	<1.51	0.67	43.50	0.09	<0.25	0.22
SOW5	5.29	228.19	2.54	84.15	<1.53	1.38	62.76	0.04	<0.25	0.11
SOW6	16.54	329.84	4.47	63.05	<1.52	1.23	25.77	0.14	<0.25	0.39
SOW7	72.62	2021.01	0.62	65.38	<1.52	2.64	17.85	0.20	<0.25	1.10
SOW8	10.02	84.51	0.29	60.57	<1.51	1.67	24.76	0.04	<0.25	0.41
SOW9	17.04	163.11	0.44	60.02	<1.51	1.08	23.45	0.21	<0.25	0.42
SOW10	26.84	514.33	0.34	86.10	<1.53	2.20	13.36	0.07	<0.25	0.65
SOW11	12.28	241.10	0.32	56.82	<1.51	1.07	10.78	0.20	<0.25	0.46
SOW12	4.89	128.31	<0.17	<44.27	<1.50	0.99	7.24	<0.03	<0.25	0.21
STW1	17.86	886.61	0.89	111.54	<1.55	1.62	36.14	0.09	<0.25	0.37
STW3	5.91	171.58	1.29	90.34	<1.54	1.58	45.87	0.05	<0.25	0.13
STW5	4.70	79.53	0.43	74.33	<1.52	0.85	20.80	<0.03	<0.25	0.08
STW9	21.01	228.94	1.18	96.34	<1.54	1.30	37.78	0.07	<0.25	0.32
STW10	15.94	607.80	0.59	76.37	<1.53	0.89	18.51	0.07	<0.25	0.33
STW11	5.19	35.40	0.42	70.83	<1.52	0.80	19.70	0.05	<0.25	0.13
STW12	4.92	169.33	<0.24	60.60	<1.51	1.19	21.97	0.05	<0.25	0.07
STW13	8.11	160.45	2.08	75.08	<1.53	0.66	23.38	0.14	<0.25	0.25
STW14	5.36	185.51	0.56	78.13	<1.53	1.17	25.45	0.35	<0.25	0.08
STW14	10.79	206.33	<0.29	<44.27	<1.50	0.76	14.59	0.04	<0.25	0.18

APPENDIX F

Table F.1 cont...

Description	Sn (ppb)	Sb (ppb)	I (ppb)	Cs (ppb)	Ba (ppb)	La (ppb)	Ce (ppb)	Hg (ppb)	Tl (ppb)
STW1	0.19	0.06	4.44	0.01	59.48	0.38	0.61	<0.19	0.02
STW2	0.24	0.22	4.16	0.02	28.70	0.70	0.88	<0.19	<0.02
STW3	0.14	0.11	6.34	0.02	50.84	0.76	0.78	<0.19	<0.02
STW4	0.27	0.04	2.98	0.01	22.93	0.68	0.37	<0.19	<0.02
STW5	0.16	0.06	9.79	0.01	39.70	0.33	0.34	<0.19	<0.02
STW6	0.21	0.04	8.13	0.01	49.01	0.30	0.25	<0.19	0.02
STW7	0.31	0.02	2.15	0.01	30.77	0.22	0.23	<0.19	<0.02
STW8	0.21	0.05	3.42	0.01	45.98	0.26	0.27	<0.19	<0.02
STW9	0.16	0.02	5.19	<0.01	51.44	0.10	0.16	<0.19	<0.02
STW10	0.22	0.03	3.05	0.01	46.47	0.23	0.35	<0.19	<0.02
STW11	0.28	0.04	5.67	0.01	56.62	0.25	0.28	<0.19	<0.02
STW12	0.16	0.03	2.43	0.01	22.68	0.42	0.33	<0.19	<0.02
STW13	0.17	0.05	2.72	0.01	56.38	2.32	0.94	<0.19	<0.02
STW14	0.26	0.04	2.86	0.01	49.60	0.45	0.42	<0.19	<0.02
CS1	0.07	<0.02	2.13	0.01	46.62	0.14	0.21	<0.19	<0.02
SOW1	0.25	0.22	9.00	0.03	129.37	2.60	3.81	<0.19	0.02
SOW2	0.22	0.12	7.63	0.05	182.39	2.37	4.60	<0.19	0.03
SOW3	0.28	0.23	32.84	0.04	185.24	5.28	12.71	<0.19	0.03
SOW4	0.41	0.07	10.63	0.01	40.43	1.50	3.20	<0.19	0.02
SOW5	0.23	0.06	16.30	0.03	236.43	2.31	5.34	<0.19	0.03
SOW6	0.46	0.23	19.19	0.03	86.22	3.29	7.06	<0.19	0.02
SOW7	2.39	0.39	38.16	0.04	142.04	2.13	4.78	<0.19	0.04
SOW8	0.28	0.10	8.23	0.01	23.47	7.41	0.98	<0.19	0.02
SOW9	2.55	0.20	7.92	0.01	22.46	2.27	2.95	<0.19	0.06
SOW10	1.14	<0.19	20.66	0.02	67.35	0.27	0.44	<0.19	<0.02
SOW11	0.99	0.13	3.17	0.01	13.54	0.96	0.33	<0.19	0.02
SOW12	0.27	0.09	3.85	0.01	14.76	0.25	0.60	<0.19	0.02
STW1	0.84	0.07	9.74	0.03	95.17	0.81	1.09	<0.19	0.06
STW3	0.37	0.19	8.59	0.05	124.08	1.48	0.63	<0.19	0.03
STW5	0.17	0.05	7.70	0.02	34.17	1.88	0.29	<0.19	<0.02
STW9	0.90	0.04	18.70	0.01	39.35	0.50	0.59	<0.19	0.03
STW10	0.52	0.03	5.94	0.01	80.95	0.55	0.38	<0.19	0.02
STW11	0.21	0.04	14.35	0.01	74.26	0.62	0.14	<0.19	<0.02
STW12	0.34	0.04	4.66	0.04	29.33	1.35	0.26	<0.19	<0.02
STW13	0.39	0.06	10.56	0.01	64.53	3.19	6.36	<0.19	<0.02
STW14	0.40	0.07	5.70	0.03	90.69	0.48	0.44	<0.19	0.04
STW14	0.50	0.03	1.71	0.02	11.93	0.36	0.34	<0.19	<0.02

APPENDIX F

Table F.1 cont...

Description	Pb (ppb)	Bi (ppb)	U (ppb)	Charge Balance (%)
STW1	0.72	<0.01	0.02	6.943
STW2	2.26	<0.01	<0.02	0.266
STW3	1.03	<0.01	0.05	6.164
STW4	1.05	<0.01	<0.02	4.866
STW5	0.55	<0.01	<0.02	6.581
STW6	0.73	<0.01	<0.02	3.590
STW7	1.71	<0.01	0.03	2.782
STW8	0.87	<0.01	<0.02	2.681
STW9	0.46	<0.01	<0.02	3.323
STW10	1.04	<0.01	<0.02	2.651
STW11	1.06	<0.01	<0.02	2.388
STW12	0.49	<0.01	<0.02	13.880
STW13	2.06	<0.01	<0.02	12.010
STW14	1.40	<0.01	0.03	2.884
CS1	0.20	<0.01	<0.02	2.378
SOW1	1.37	0.01	0.04	5.311
SOW2	2.15	0.02	0.17	4.509
SOW3	2.09	<0.01	0.08	2.764
SOW4	2.23	0.01	0.02	1.189
SOW5	1.26	<0.01	0.05	0.712
SOW6	8.36	0.01	0.07	9.449
SOW7	15.31	0.03	0.22	20.270
SOW8	4.86	<0.01	<0.02	8.360
SOW9	7.09	<0.01	0.05	32.110
SOW10	6.01	<0.01	0.02	5.218
SOW11	5.41	<0.01	<0.02	15.650
SOW12	0.62	<0.01	<0.02	29.270
STW1	12.14	0.02	0.14	0.505
STW3	1.18	0.01	<0.02	1.184
STW5	1.29	<0.01	0.04	7.614
STW9	3.69	0.01	0.05	21.340
STW10	3.51	<0.01	0.03	12.680
STW11	1.21	<0.01	<0.02	11.320
STW12	0.78	<0.01	<0.02	16.800
STW13	3.07	<0.01	0.03	1.622
STW14	0.81	<0.01	0.18	10.080
STW14	1.62	<0.01	<0.02	6.168

APPENDIX G

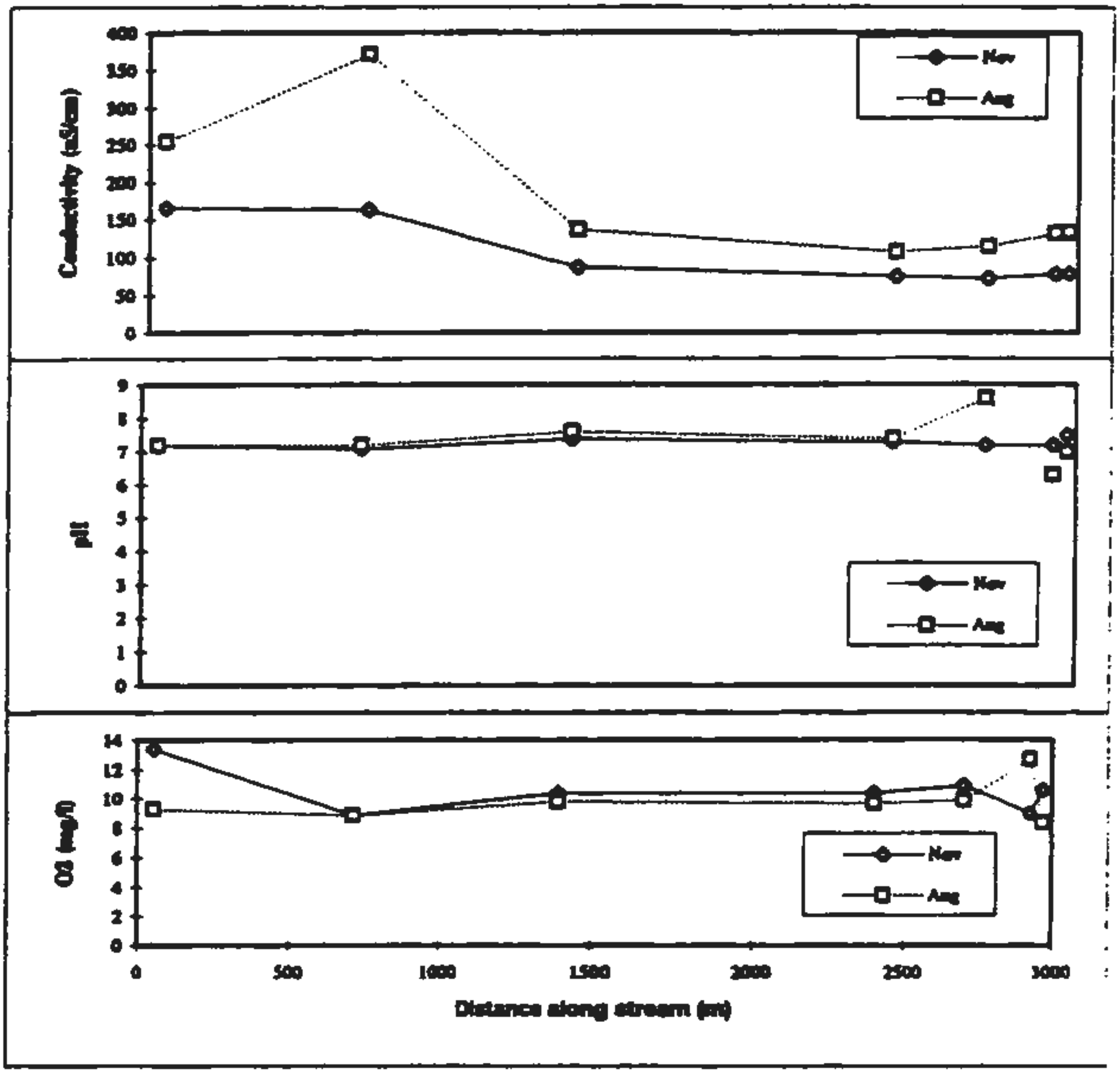


Figure G.1 Conductivity, pH, and dissolved oxygen measurements of the surface water samples collected (August and November, 1994) from the main course of the test stream.

APPENDIX G

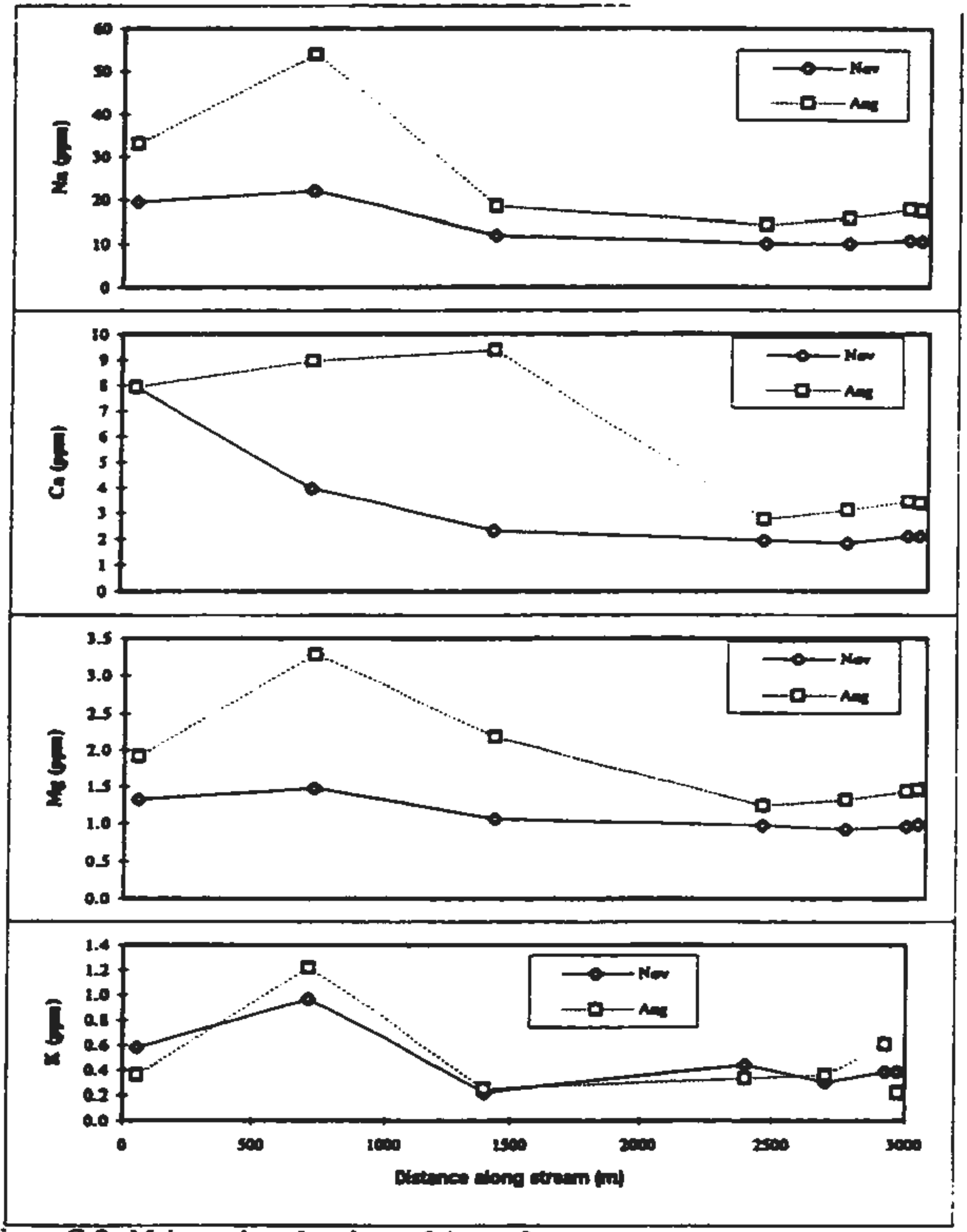


Figure G.2 Major cation chemistry of the surface water samples collected (August and November, 1994) from the main course of the test stream.

APPENDIX G

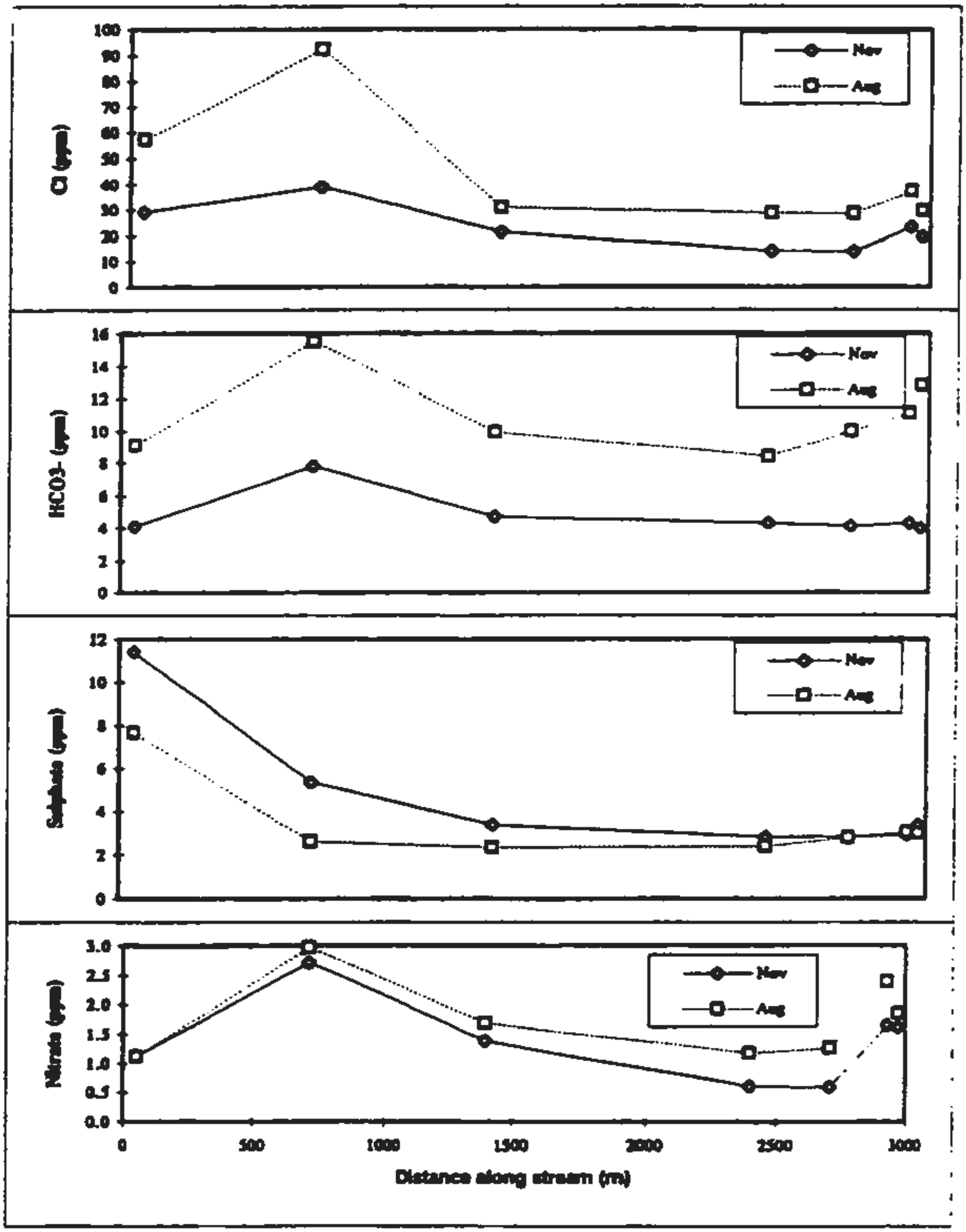


Figure G.3 Major anion chemistry of the surface water samples collected (August and November, 1994) from the main course of the test stream.

APPENDIX G

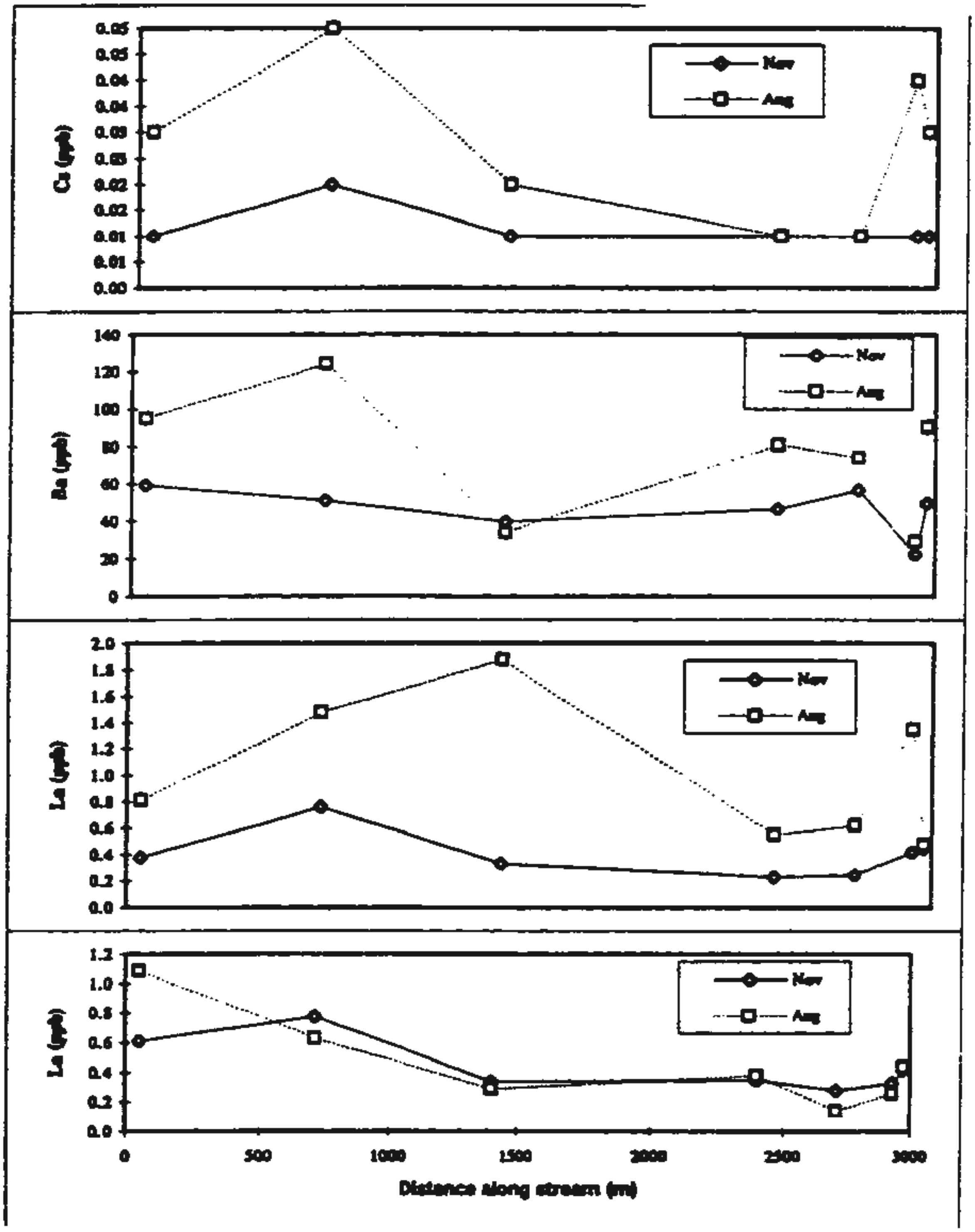


Figure G.4 Trace element chemistry of the surface water samples collected (August and November, 1994) from the main course of the test stream.

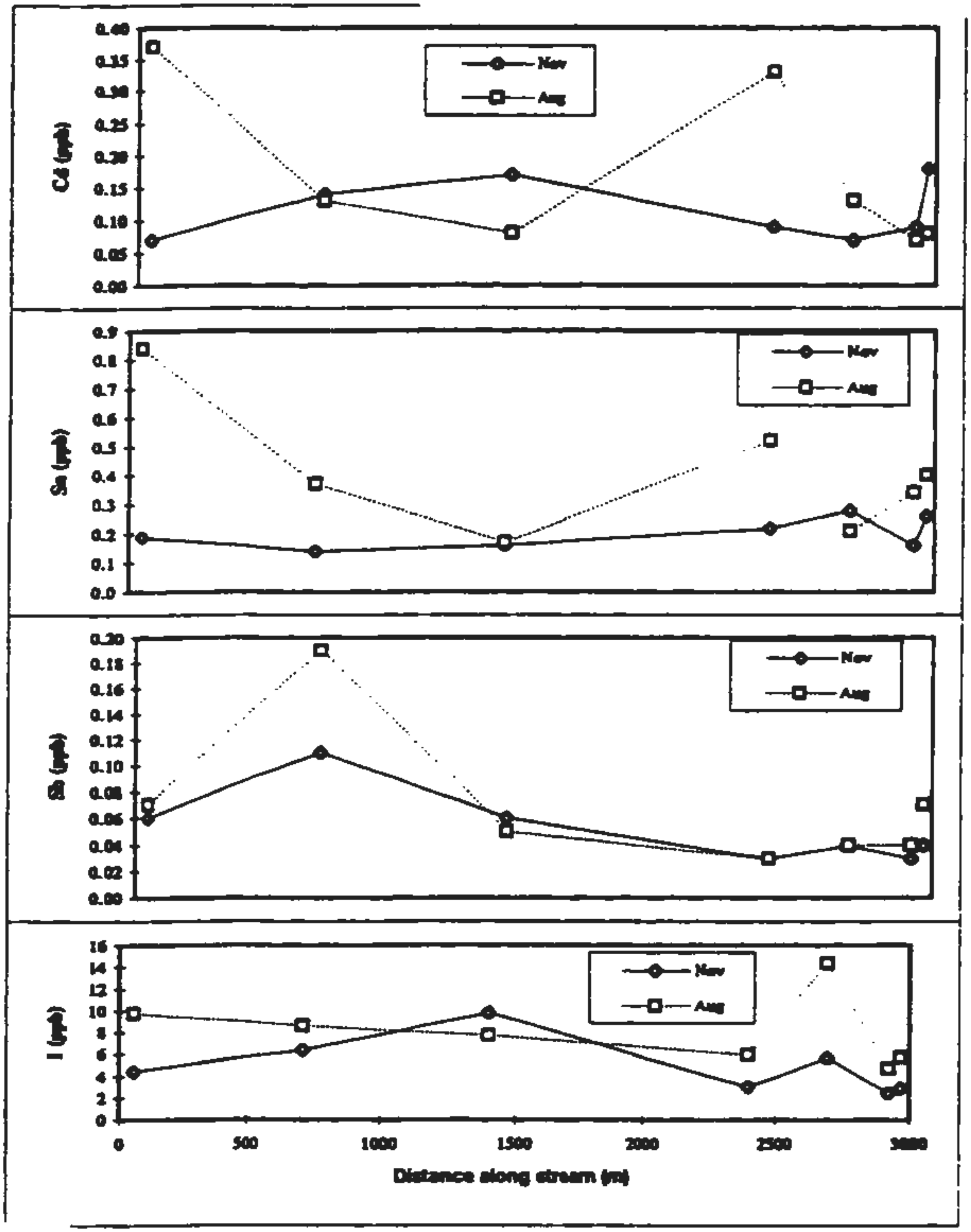


Figure G.4 cont...

APPENDIX G

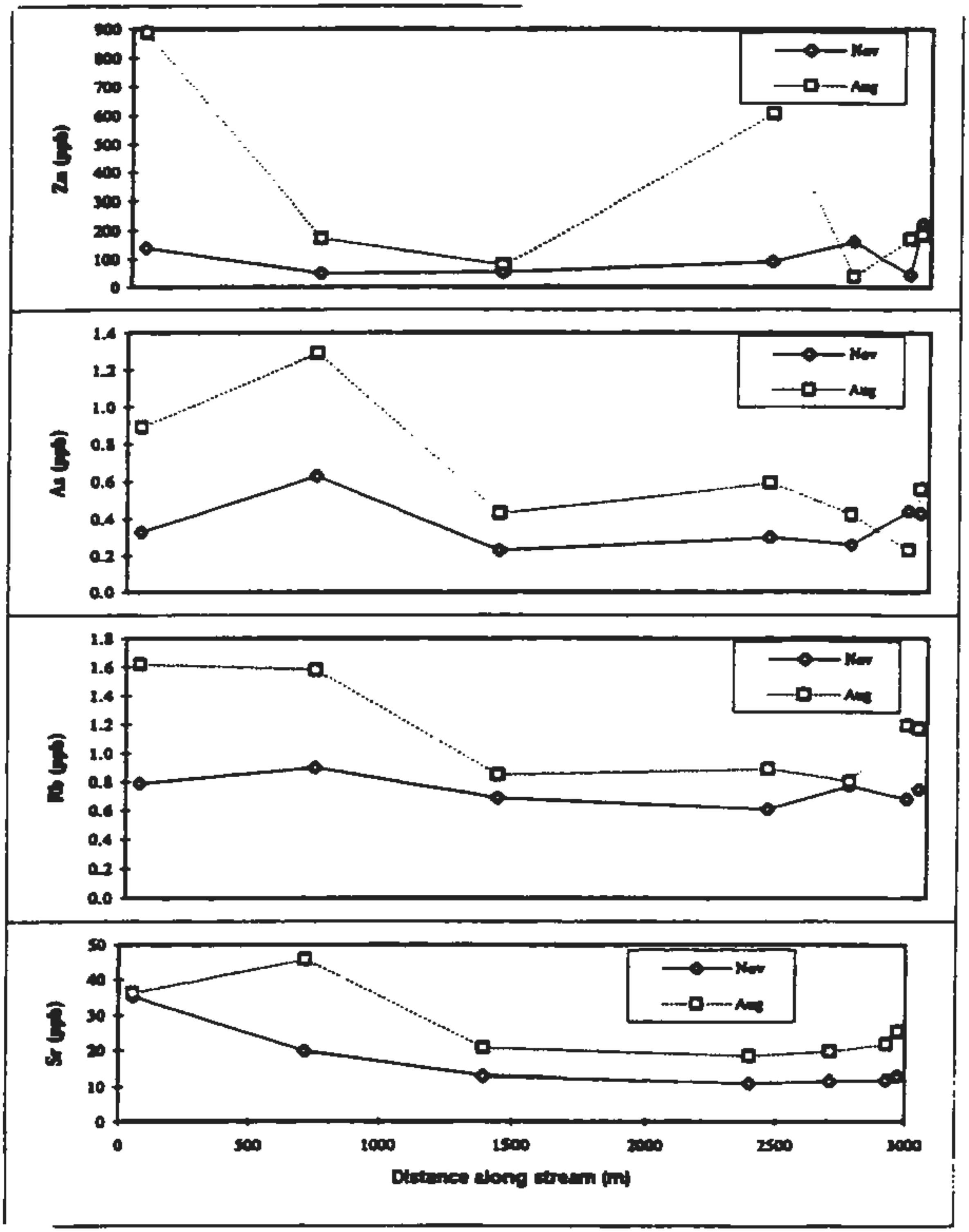


Figure G.4 cont...

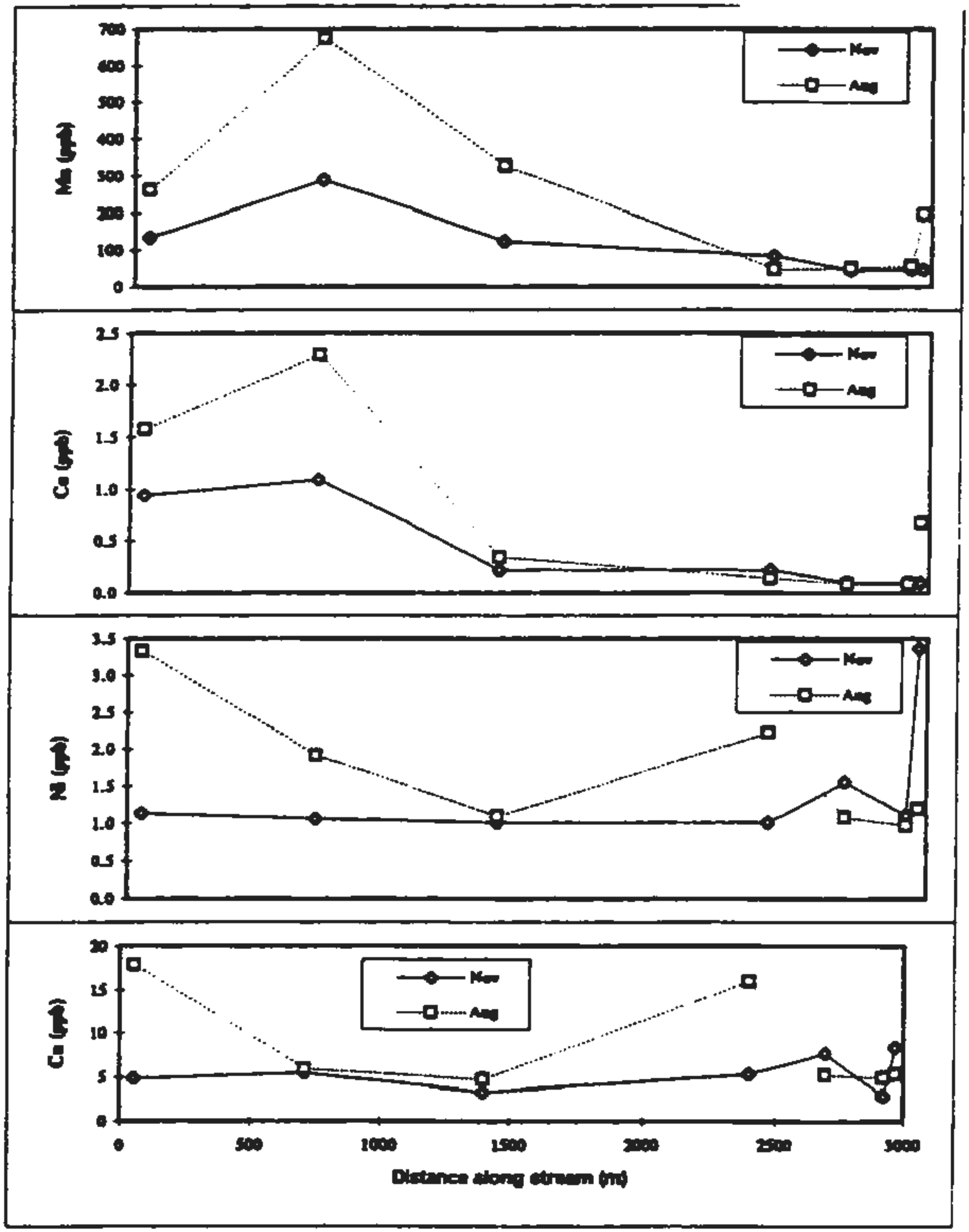


Figure G.4 cont...

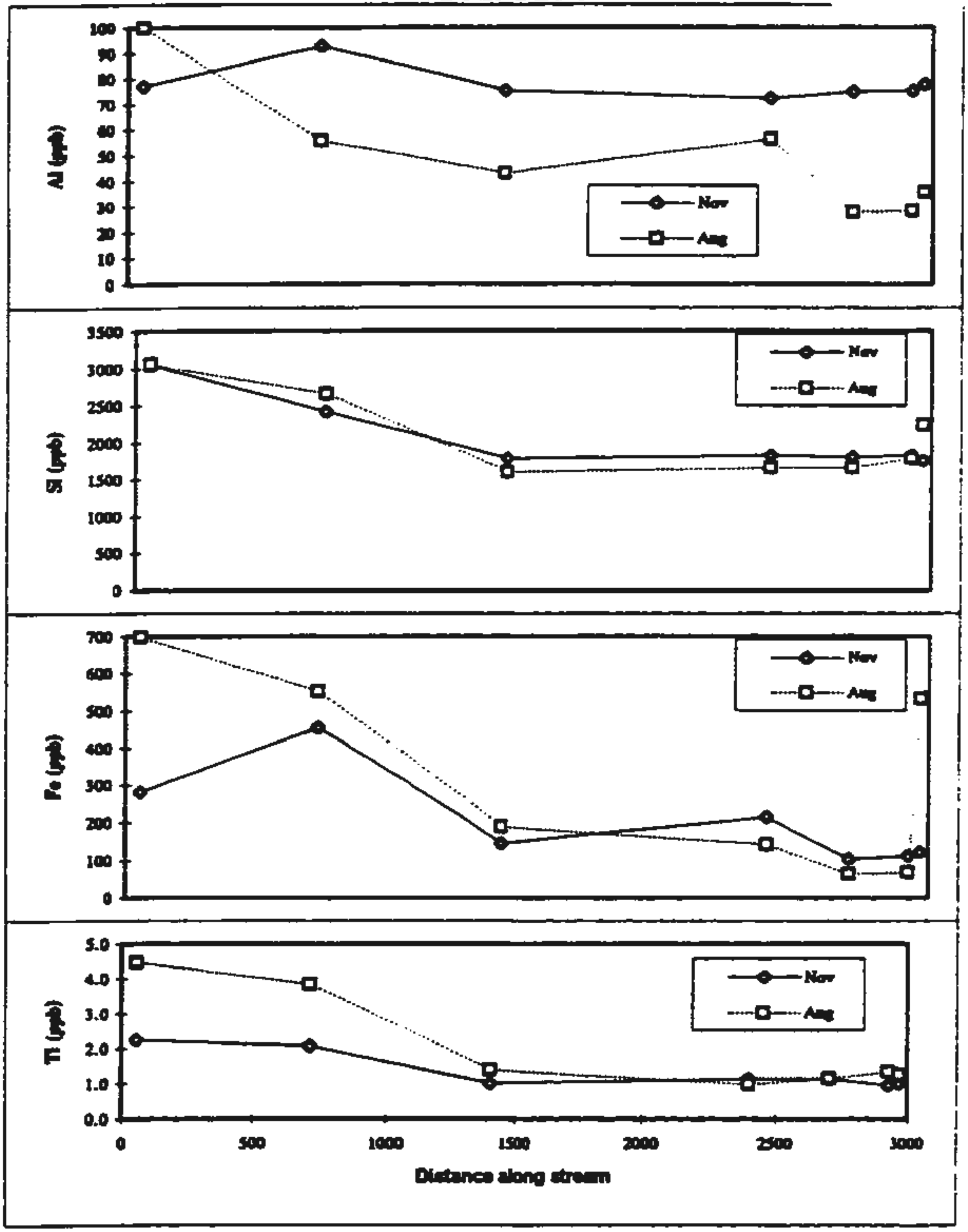


Figure G.4 cont…

APPENDIX G

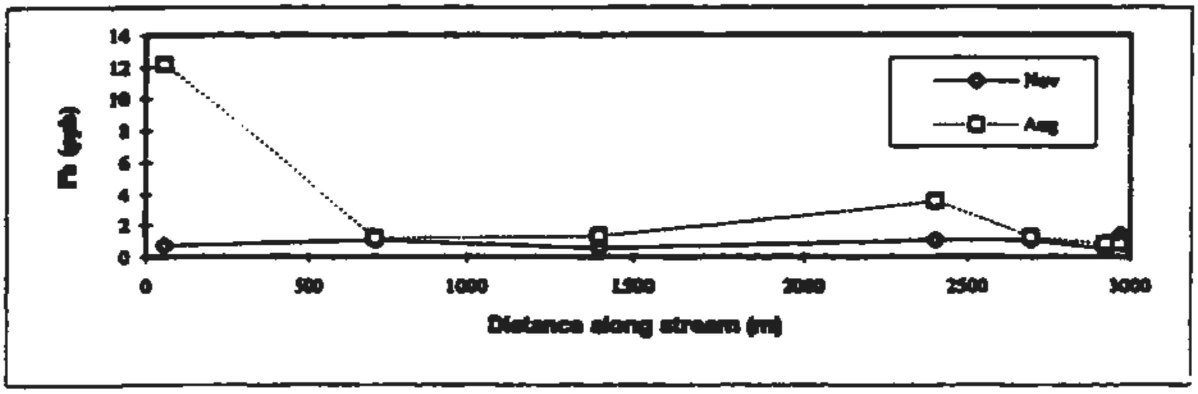


Figure G.4 cont…

APPENDIX H

Table H.1 Clam (*Mercenaria mercenaria*) Chemistry Data. Dry weight concentrations have been converted to wet weight (division by 4.5), traditionally reported in the literature (Greig and Sennefelder, 1985).

Sample Site	Date Sampled	Sample Size	Dry Weight (g)	Mean Dry Weight (g)	Mean Shell Length (cm)	sd Shell Length (cm)	Longitude (UTM)	Latitude (UTM)	Grainsize % < 63 mm	LOI (%)
E08	17-Aug	5	0.3272	0.06544	2.29	0.12	282070	5263640	92.9	26.7
E12	17-Aug	5	0.2338	0.04676	1.99	0.12	282200	5263870	85.8	28.2
E14	17-Aug	10	0.2022	0.02022	1.62	0.05	282290	5264005	97.7	18.9
E16	17-Aug	10	0.2191	0.02191	1.64	0.09	282345	5264160	72.9	17.6
E18	17-Aug	10	0.2567	0.02567	1.67	0.05	282400	5264315	37.4	13.9

Sample Site	Li (ppm)	Be (ppm)	B (ppm)	Al (ppm)	Si (ppm)	P (ppm)	S (ppm)	Cl (ppm)	Ca (ppm)	Ti (ppm)
E08	0.11	< 0.01	0.70	56.76	7.78	553.78	521.33	< 12.7	244.67	2.35
E12	0.30	0.02	3.08	132.38	15.11	1634.44	1751.33	30.22	787.11	7.08
E14	0.71	0.02	2.78	296.67	23.11	1600.67	1710.00	34.89	1030.22	14.17
E16	0.48	0.02	3.70	223.24	24.22	1863.56	1898.89	30.67	602.00	12.37
E18	0.22	0.02	1.92	121.49	15.33	1872.89	1932.67	29.56	611.78	5.92

Sample Site	V (ppm)	Cr (ppm)	Mn (ppm)	Fe (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	As (ppm)	Br (ppm)
E08	0.11	0.28	13.15	126.00	0.33	0.31	2.22	12.00	0.51	< 0.32
E12	0.26	0.46	8.65	216.67	0.31	0.61	3.74	26.25	1.42	1.82
E14	0.60	1.17	28.30	616.00	0.40	1.27	4.12	54.49	1.07	2.18
E16	0.53	0.65	18.94	502.44	0.41	0.44	4.49	45.64	1.49	2.62
E18	0.29	0.84	22.60	214.67	0.34	1.29	5.68	30.42	1.26	2.79

APPENDIX H

Table H.1 cont...

Sample Site	Se (ppm)	Rb (ppm)	Sr (ppm)	Mo (ppm)	Ag (ppm)	Cd (ppm)	Sn (ppm)	Sb (ppm)	I (ppm)	Cs (ppm)
E08	0.21	0.43	2.79	0.17	0.03	0.01	1.09	0.00	0.02	0.01
E12	0.61	1.18	8.02	0.35	0.04	0.02	4.14	0.00	0.04	0.02
E14	0.58	1.32	12.46	0.51	0.07	0.06	4.57	0.01	0.03	0.05
E16	0.70	1.35	8.24	0.63	0.07	0.10	3.80	0.01	0.08	0.03
E18	0.62	1.13	7.05	0.54	0.09	0.04	3.15	0.01	0.06	0.02

Sample Site	Ba (ppm)	La (ppm)	Ce (ppm)	Hg (ppm)	Pb (ppm)	Bi (ppm)	U (ppm)
E08	0.40	0.21	0.40	< 0.01	0.19	0.00	0.22
E12	1.07	0.36	0.70	< 0.01	0.35	0.01	0.46
E14	2.54	0.57	1.19	< 0.01	0.47	0.00	0.75
E16	1.81	0.47	0.97	< 0.01	2.18	0.00	0.69
E18	1.06	0.28	0.55	< 0.01	0.35	0.00	0.42

PCB SAMPLES	Sample Size	Wet Weight (g)	Mean Wet Weight (g)	Mean Shell Length (cm)	sd Shell Length (cm)	Total PCB
	10	8.9	0.89	2.60	0.59	< 0.05 ppm
	15	8.2	0.55	2.15	0.15	< 0.05 ppm
	30	7.2	0.24	1.70	0.07	< 0.05 ppm
	30	10.0	0.33	1.84	0.53	< 0.05 ppm
	30	9.5	0.32	1.77	0.12	< 0.05 ppm

APPENDIX I

Table I.1 Replicate sample results (XRF).

	SCS1	replicate	SH1	replicate
Na2O	2.46	2.44	2.33	2.36
MgO	2.39	2.38	3.20	3.25
Al2O3	16.09	15.87	16.87	17.12
SiO2	62.67	62.00	60.10	60.96
P2O5	0.11	0.11	0.13	0.13
S	194	197	2921	2987
Cl	62	78	73	47
K20	3.00	2.94	2.92	2.96
CaO	0.56	0.55	0.64	0.67
Sc	12	12	16	17
TiO2	0.73	0.72	0.73	0.74
V	87	88	121	117
Cr	79	78	68	68
MnO	0.26	0.25	0.12	0.13
Fe2O3	6.79	6.76	7.87	8.01
Ni	21	23	23	23
Cu	11	10	30	30
Zn	82	83	52	55
Ga	20	19	22	21
As	8	9	25	30
Rb	93.8	93.5	100.4	100.1
Sr	108.7	110.4	110.0	110.6
Y	29.7	29.0	30.9	31.6
Zr	246.7	246.2	232.3	233.5
Nb	15.4	15.7	16.7	16.9
Ba	609	593	512	532
Ce	67	73	58	72
Pb	9	11	21	20
Th	8	9	10	10
U	1	2	3	2

Table I.2 Replicate and blank sample results (IC and AA).

	STW5	replicate	SOW1	replicate	Blank1	Blank2
Cl	30.88	30.86	113.84	109.35	0.00	0.00
NO3	1.69	1.445	1.97	1.76	0.00	0.00
SO4	2.36	2.28	9.32	8.74	0.00	0.00
K	0.25	0.19	2.07	1.99	0.00	0.00
Na	18.59	18.58	75.49	75.24	0.00	0.10
Ca	9.37	9.66	12.64	12.78	0.14	0.19
Mg	2.18	2.21	4.10	4.03	0.01	0.01

APPENDIX I

Table I.3 Replicate and blank sample results (ICP, clam analyses).

	E18	replicate	Blank		E18	replicate	Blank
Li	1.07	1.00	<0.09	Br	10.99	12.56	<1.83
Be	<0.05	0.07	<0.05	Se	2.93	2.77	<0.10
B	10.79	8.65	<2.37	Rb	5.14	5.08	0.01
Al	512.1	546.7	4.7	Sr	32.45	31.72	0.01
Si	65	69	<11	Mo	2.46	2.44	0.01
P	8053	8428	<12	Ag	0.42	0.42	<0.00
S	8273	8697	<556	Cd	0.20	0.19	<0.01
Cl	99	133	<72	Sn	14.51	14.17	2.89
Ca	2663	2785	<107	Sb	0.03	0.03	<0.00
Ti	27.23	26.63	0.14	I	0.29	0.29	<0.01
V	1.34	1.32	<0.01	Cs	0.08	0.08	<0.00
Cr	3.0	3.8	0.15	Ba	4.75	4.78	0.08
Mn	3.78	3.69	0.02	La	1.26	1.28	<0.00
Fe	902	916	<6	Ce	2.5	2.48	0.00
Co	1.49	1.52	0.00	Hg	<0.04	<0.04	<0.04
Ni	5.77	5.81	0.12	Pb	1.54	1.56	0.13
Cu	25.54	25.55	0.22	Bi	0.02	0.02	<0.00
Zn	135.73	136.87	12.50	U	1.94	1.91	<0.01
As	5.66	5.69	<0.01				

APPENDIX J

Table J.1 Enrichment factors (EF) of the metals / oxides not enriched in the study area.

Chemical Constituent	Enrichment Factor (1)	Enrichment Factor (2)	Enrichment Factor (3)	Enrichment Factor (4)
Na2O				
test(n=10)	0.83	0.59	0.99	0.90
control(n=2)	1.01	0.73	1.21	1.10
MgO				
test(n=10)	0.71	0.40	0.50	0.33
control(n=2)	1.17	0.66	0.81	0.54
SiO2				
test(n=10)	0.71	0.97	4.12	0.26
control(n=2)	0.72	0.98	4.15	0.26
S				
test(n=10)	0.18	9.34	0.51	1.61
control(n=2)	0.02	1.07	0.06	0.18
Cl				
test(n=10)	3.26	2.40	0.88	4.97
control(n=2)	0.58	0.43	0.16	0.88
K2O				
test(n=10)	0.67	0.66	0.38	0.29
control(n=2)	0.94	0.92	0.53	0.41
CaO				
test(n=10)	1.14	0.23	0.26	0.05
control(n=2)	0.43	0.09	0.10	0.02
Sc				
test(n=10)	0.61	0.61	0.52	2.13
control(n=2)	0.63	0.63	0.54	2.19
TiO2				
test(n=10)	0.74	0.76	0.82	0.79
control(n=2)	0.73	0.75	0.81	0.78
V				
test(n=10)	0.87	0.69	0.36	0.74
control(n=2)	0.84	0.67	0.35	0.72
Ni				
test(n=10)	4.90	1.16	0.65	6.94
control(n=2)	1.55	0.37	0.21	2.19
Cu				
test(n=10)	4.75	0.71	0.44	0.69
control(n=2)	1.09	0.16	0.10	0.16
Ga				
test(n=10)	0.69	1.20	0.48	0.24
control(n=2)	0.75	1.30	0.52	0.26
Rb				
test(n=10)	0.64	0.84	0.27	0.20
control(n=2)	0.76	0.99	0.33	0.24
Sr				
test(n=10)	0.72	0.33	0.21	0.98
control(n=2)	0.60	0.27	0.17	0.81
Y				
test(n=10)	1.06	1.37	0.89	0.18
control(n=2)	0.65	0.84	0.54	0.11
Zr				
test(n=10)	0.69	1.41	0.74	0.17
control(n=2)	0.70	1.43	0.75	0.17
Nb				
test(n=10)	0.73	0.81	0.75	28.61
control(n=2)	0.69	0.76	0.70	26.89
Ba				
test(n=10)	1.54	2.35	0.88	1.77
control(n=2)	0.84	1.28	0.48	0.96
Ce				
test(n=10)	1.44	3.29	1.70	0.34
control(n=2)	0.48	1.11	0.57	0.11
Th				
test(n=10)	0.63	0.81	0.33	0.73
control(n=2)	0.70	0.89	0.36	0.80

(1)= Bottom sample of core E9 (~0.21 m).
(2)= Average chemical composition of Earth crust (Taylor, 1964).
(3)= Average chemical composition of global shale (Turekian and Wedepohl, 1961).
(4)= Average chemical composition of global sandstone (Turekian and Wedepohl, 1961).

APPENDIX K

Table K.1 Sediment Chemistry Spearman Rank Correlation Matrix

	GSIZE	LOI	NA2O	MGO	AL2O3
GSIZE	1.000				
LOI	0.539	1.000			
NA2O	-0.427	-0.789	1.000		
MGO	-0.315	-0.813	0.770	1.000	
AL2O3	0.298	0.371	-0.113	-0.042	1.000
P2O5	0.615	0.952	-0.778	-0.697	0.420
S	0.543	0.776	-0.732	-0.597	0.147
CL	0.060	-0.189	0.056	-0.092	-0.559
K2O	-0.203	-0.606	0.644	0.915	0.095
CAO	0.591	0.693	-0.692	-0.557	0.085
SC	0.312	0.280	-0.053	-0.028	0.685
CR	0.221	0.497	-0.644	-0.551	-0.203
MNO	-0.099	-0.077	-0.167	-0.370	-0.725
FE2O3	-0.049	-0.084	-0.261	-0.223	-0.799
NI	0.249	0.510	-0.704	-0.633	-0.350
CU	0.508	0.678	-0.620	-0.410	0.140
ZN	0.560	0.629	-0.789	-0.608	-0.112
AS	0.032	0.406	-0.674	-0.743	-0.406
Y	0.627	0.790	-0.722	-0.608	0.294
BA	0.032	-0.007	-0.306	-0.071	-0.720
CE	0.466	0.776	-0.683	-0.696	0.343
PB	0.585	0.769	-0.599	-0.477	0.343
TH	0.270	0.476	-0.194	-0.117	0.874
PCB	0.391	0.341	-0.343	-0.436	-0.242
SIO2	-0.112	-0.469	0.768	0.530	0.259
ZR	0.021	-0.343	0.585	0.731	0.420
RB	-0.151	-0.538	0.613	0.862	0.231
NB	0.214	-0.211	0.466	0.574	0.456
GA	0.056	0.193	0.134	0.219	0.781
TIO2	0.332	0.036	0.191	0.417	0.349
V	0.172	0.126	-0.074	0.124	0.182
SR	0.072	-0.102	0.215	0.211	-0.343

APPENDIX K

Table K.1 cont...

	P2O5	S	CL	K2O	CAO
P2O5	1.000				
S	0.776	1.000			
CL	-0.194	-0.168	1.000		
K2O	-0.421	-0.514	-0.155	1.000	
CAO	0.775	0.792	0.127	-0.393	1.000
SC	0.411	0.427	-0.469	0.116	0.297
CR	0.578	0.678	0.308	-0.444	0.751
MNO	-0.152	-0.120	0.408	-0.429	-0.146
FE2O3	-0.142	0.021	0.648	-0.321	0.002
NI	0.550	0.671	0.322	-0.567	0.707
CU	0.776	0.839	-0.182	-0.225	0.855
ZN	0.647	0.867	0.098	-0.577	0.855
AS	0.358	0.378	0.256	-0.737	0.342
Y	0.891	0.853	-0.175	-0.391	0.848
BA	0.072	0.112	0.287	0.025	0.177
CE	0.844	0.741	-0.357	-0.489	0.654
PB	0.880	0.846	-0.168	-0.250	0.806
TH	0.506	0.350	-0.594	0.004	0.170
PCB	0.381	0.515	0.462	-0.447	0.513
SIO2	-0.438	-0.538	0.196	0.514	-0.502
ZR	-0.205	-0.476	-0.357	0.866	-0.428
RB	-0.363	-0.559	-0.217	0.972	-0.428
NB	-0.063	-0.358	-0.200	0.717	-0.287
GA	0.259	-0.088	-0.637	0.402	-0.039
TIO2	0.170	-0.062	-0.058	0.605	-0.123
V	0.284	0.049	0.070	0.331	-0.039
SR	-0.013	0.025	0.042	0.342	0.292

	SC	CR	MNO	FE2O3	NI
SC	1.000				
CR	0.119	1.000			
MNO	-0.570	0.183	1.000		
FE2O3	-0.715	0.392	0.794	1.000	
NI	-0.056	0.958	0.380	0.543	1.000
CU	0.462	0.622	-0.246	-0.154	0.601
ZN	0.168	0.720	0.092	0.238	0.783
AS	-0.287	0.694	0.709	0.649	0.830
Y	0.580	0.664	-0.127	-0.158	0.636
BA	-0.483	0.406	0.655	0.750	0.531
CE	0.566	0.601	0.028	-0.182	0.594
PB	0.615	0.671	-0.289	-0.210	0.601
TH	0.615	0.049	-0.655	-0.623	-0.098
PCB	0.089	0.735	0.236	0.384	0.775
SIO2	0.217	-0.503	-0.317	-0.329	-0.657
ZR	0.224	-0.601	-0.493	-0.518	-0.706
RB	0.112	-0.503	-0.444	-0.375	-0.629
NB	0.225	-0.389	-0.428	-0.388	-0.512
GA	0.497	-0.410	-0.751	-0.875	-0.515
TIO2	0.186	-0.146	-0.374	-0.137	-0.244
V	0.154	0.287	-0.042	0.161	0.203
SR	0.014	-0.014	0.004	-0.088	-0.042

APPENDIX K

Table K.1 cont...

	CU	ZN	AS	Y	BA
CU	1.000				
ZN	0.832	1.000			
AS	0.245	0.546	1.000		
Y	0.916	0.811	0.382	1.000	
BA	0.196	0.301	0.518	0.112	1.000
CE	0.720	0.629	0.511	0.902	0.063
PB	0.916	0.720	0.252	0.951	0.049
TH	0.203	-0.021	-0.238	0.336	-0.566
PCB	0.494	0.632	0.580	0.540	0.220
SIO2	-0.566	-0.720	-0.694	-0.497	-0.510
ZR	-0.266	-0.657	-0.785	-0.315	-0.203
RB	-0.308	-0.657	-0.746	-0.413	-0.049
NB	-0.270	-0.568	-0.638	-0.225	-0.193
GA	0.193	-0.263	-0.577	0.151	-0.543
TIO2	-0.007	-0.291	-0.458	-0.011	0.033
V	0.056	-0.126	0.077	0.154	0.266
SR	0.270	0.067	-0.284	0.091	0.347

	CE	PB	TH	PCB	SIO2
CE	1.000				
PB	0.825	1.000			
TH	0.448	0.448	1.000		
PCB	0.441	0.586	-0.096	1.000	
SIO2	-0.503	-0.357	0.133	-0.266	1.000
ZR	-0.315	-0.175	0.322	-0.515	0.594
RB	-0.455	-0.280	0.140	-0.529	0.552
NB	-0.196	-0.070	0.460	-0.316	0.628
GA	0.144	0.235	0.588	-0.393	0.193
TIO2	-0.109	0.193	0.400	-0.050	0.459
V	0.168	0.322	0.329	0.284	0.203
SR	-0.049	0.063	-0.350	-0.206	0.004

	ZR	RB	NB	GA	TIO2
ZR	1.000				
RB	0.937	1.000			
NB	0.916	0.832	1.000		
GA	0.630	0.476	0.467	1.000	
TIO2	0.750	0.666	0.836	0.357	1.000
V	0.392	0.378	0.558	0.074	0.797
SR	0.186	0.259	0.070	-0.000	-0.036

	V	SR
V	1.000	
SR	-0.291	1.000

APPENDIX L

Table L.1 Significance tables for the Spearman rank correlation coefficient for sample size *n*, at the 10 %, 1 %, and 0.1 % significant levels (one-tailed test) and the 20 %, 2 %, and 0.2 % significance levels (two-tailed test).

	One-sided test		
n	**10%**	**1%**	**0.1%**
4	1.000		
5	0.800	1.000	
6	0.657	0.943	
7	0.571	0.893	1.000
8	0.524	0.833	0.952
9	0.483	0.783	0.917
10	0.455	0.745	0.879
12	0.406	0.687	0.818
14	0.367	0.626	0.771
16	0.341	0.582	0.729
18	0.317	0.550	0.695
20	0.299	0.520	0.662
25	0.265	0.466	0.598
30	0.240	0.425	0.549
35	0.222	0.394	0.510
40	0.207	0.368	0.479
45	0.194	0.347	0.453
50	0.184	0.329	0.430
60	0.168	0.300	0.394
70	0.155	0.278	0.365
80	0.145	0.260	0.342
90	0.136	0.245	0.323
100	0.129	0.233	0.307
	20%	**2%**	**0.2%**
	Two-sided test		

APPENDIX M

Table M.1 **Minerals for which saturation indices were calculated using MINTEQA2 (Allison *et al.*, 1991).**

1 ALOH3(A)
2 ALOHSO4
3 AL4(OH)10SO4
4 ALUNITE
5 ANHYDRITE
6 ARAGONITE
7 ARTINITE
8 BARITE
9 BOEHMITE
10 BRUCITE
11 CALCITE
12 CELESTITE
13 DIASPORE
14 DOLOMITE
15 EPSOMITE
16 GIBBSITE
17 Al2O3
18 GYPSUM
19 HALITE
20 HUNTITE
21 HYDRMAGNESITE
22 MAGNESITE
23 MELANTERITE
24 MIRABILITE
25 NATRON
26 NESQUEHONITE
27 SIDERITE
28 STRONTIANITE
29 THENARDITE
30 THERMONATRITE
31 WITHERITE
32 RHODOCHROSITE
33 MNCL2, 4H2O
34 MNSO4
35 MELANOTHALLITE
36 CUCO3
37 CU(OH)2
38 ATACAMITE
39 CU2(OH)3NO3
40 ANTLERITE
41 LANGITE
42 TENORITE
43 CUOCUSO4
44 CUSO4
45 CHALCANTHITE
46 ZNCL2
47 SMITHSONITE
48 ZNCO3, 1H2O
49 ZN(OH)2
50 ZN5(OH)8CL2
51 ZN2(OH)2SO4
52 ZN4(OH)6SO4
53 ZNNO3)2,6H2O
54 ZNO
55 ZINCITE
56 ZN3O(SO4)2
57 ZINCOSITE
58 ZNSO4, 1H2O
59 BIANCHITE
60 GOSLARITE
61 ZNBR2, 2H2O
62 ZNI2
63 OTAVITE
64 CDCL2
65 CDCL2, 1H2O
66 CDCL2,2.5H2O
67 CD(OH)2 (A)
68 CDOHCL
69 CD3(OH)4SO4
70 CD3OH2(SO4)2
71 CD4(OH)6SO4
72 MONTEPONITE
73 CDSO4
74 CDSO4, 1H2O
75 COTUNNITE
76 PHOSGENITE
77 CERRUSITE
78 MASSICOT
79 LITHARGE
80 PBO, .3H2O
81 PB2OCO3
82 LARNAKITE
83 PB3O2SO4
84 PB4O3SO4
85 PB3O2CO3
86 ANGLESITE

APPENDIX M

Table M.1 cont...

87 PB(OH)2
88 LAURIONITE
89 PB2(OH)3CL
90 HYDCERRUSITE
91 PB2O(OH)2
92 PBI2
93 PB4(OH)6SO4
94 NICO3
95 NI(OH)2
96 NI4(OH)6SO4
97 BUNSENITE
98 RETGERSITE
99 MORENOSITE
100 MALACHITE
101 AZURITE
102 LIME
103 PORTLANDITE
104 WUSTITE
105 PERICLASE
106 HERCYNITE

APPENDIX N

Table N.1 Ground Water Chemistry Spearman Rank Correlation Matrix

	COND	O2	NA	K	CA
COND	1.000				
O2	-0.796	1.000			
NA	0.916	-0.711	1.000		
K	0.716	-0.470	0.558	1.000	
CA	0.881	-0.803	0.867	0.519	1.000
MG	0.965	-0.746	0.902	0.642	0.888
CL	0.923	-0.683	0.965	0.544	0.868
NITRATE	0.294	-0.014	0.259	0.498	0.406
SULFATE	0.308	-0.120	0.245	0.302	0.140
LI	-0.049	-0.155	-0.280	0.298	-0.049
AL	-0.175	-0.204	0.063	-0.309	0.042
SI	0.161	-0.373	0.427	-0.070	0.252
TI	0.657	-0.901	0.657	0.246	0.797
MN	-0.098	0.331	-0.028	0.049	-0.322
FE	0.573	-0.831	0.497	0.193	0.678
CO	0.385	-0.535	0.217	0.211	0.182
NI	-0.210	0.331	-0.287	0.067	-0.140
CU	-0.378	0.423	-0.420	-0.130	-0.322
ZN	-0.315	0.099	-0.364	-0.137	-0.228
AS	0.524	-0.782	0.462	0.354	0.678
SR	0.853	-0.859	0.818	0.632	0.930
CD	-0.413	0.526	-0.385	-0.086	-0.347
SN	-0.701	0.596	-0.666	-0.601	-0.490
SB	-0.256	0.007	-0.308	0.121	-0.011
I	0.140	-0.261	-0.105	0.109	0.254
CS	0.384	-0.549	0.249	0.477	0.425
BA	0.643	-0.732	0.483	0.481	0.671
LA	0.497	-0.408	0.483	0.632	0.629
CE	0.420	-0.739	0.294	0.305	0.594
PB	-0.580	0.535	-0.580	-0.368	-0.392
TEMP	-0.729	0.773	-0.676	-0.420	-0.827
PH	-0.676	0.904	-0.560	-0.597	-0.687
ALK	0.280	-0.507	0.154	0.098	0.280
RB	0.165	-0.004	-0.011	0.427	0.186

	MG	CL	NITRATE	SULFATE	LI
MG	1.000				
CL	0.902	1.000			
NITRATE	0.315	0.343	1.000		
SULFATE	0.329	0.392	0.112	1.000	
LI	-0.056	-0.182	0.049	0.476	1.000
AL	-0.154	-0.042	-0.175	-0.259	-0.021
SI	0.119	0.287	-0.273	-0.210	-0.238
TI	0.692	0.636	-0.035	0.175	0.189
MN	-0.231	-0.028	-0.252	0.175	-0.147
FE	0.629	0.469	-0.161	0.105	0.266
CO	0.266	0.154	-0.552	-0.105	-0.007
NI	-0.168	-0.161	0.469	0.238	0.476
CU	-0.273	-0.336	0.329	0.217	0.420
ZN	-0.210	-0.322	-0.259	0.413	0.776
AS	0.594	0.399	0.133	-0.000	0.329
SR	0.867	0.783	0.371	0.105	0.084
CD	-0.319	-0.294	0.469	0.315	0.347
SN	-0.634	-0.616	-0.039	-0.270	0.140
SB	-0.214	-0.280	0.319	0.032	0.725
I	0.210	0.000	0.042	0.147	0.664
CS	0.421	0.307	0.264	0.509	0.717
BA	0.671	0.545	0.140	0.420	0.517
LA	0.517	0.406	0.538	-0.266	0.035
CE	0.448	0.273	0.091	-0.091	0.413
PB	-0.434	-0.559	0.217	-0.203	0.238
TEMP	-0.796	-0.602	-0.236	0.130	0.060
PH	-0.623	-0.518	-0.141	-0.099	-0.289
ALK	0.112	0.266	-0.091	0.147	0.189
RB	0.186	0.144	0.417	0.532	0.704

APPENDIX N

Table N.1 cont...

	AL	SI	TI	MN	FE
AL	1.000				
SI	0.804	1.000			
TI	0.385	0.441	1.000		
MN	-0.266	0.161	-0.455	1.000	
FE	0.301	0.301	0.944	-0.503	1.000
CO	-0.217	0.049	0.343	0.126	0.462
NI	0.133	-0.217	-0.224	-0.210	-0.182
CU	0.224	-0.224	-0.252	-0.301	-0.168
ZN	0.259	-0.000	0.154	-0.147	0.252
AS	0.364	0.315	0.874	-0.552	0.895
SR	0.168	0.294	0.846	-0.434	0.769
CD	0.165	-0.249	-0.354	-0.172	-0.350
SN	0.249	-0.014	-0.396	0.067	-0.291
SB	0.326	0.053	0.130	-0.231	0.130
I	-0.105	-0.294	0.406	-0.427	0.580
CS	0.183	-0.255	0.608	-0.567	0.586
BA	0.070	-0.007	0.769	-0.559	0.776
LA	0.112	0.140	0.378	-0.441	0.329
CE	0.322	0.140	0.776	-0.755	0.804
PB	0.252	-0.161	-0.322	-0.315	-0.203
TEMP	-0.095	-0.246	-0.779	0.433	-0.778
PH	-0.123	-0.180	-0.795	0.426	-0.725
ALK	-0.028	-0.028	0.329	-0.133	0.238
RB	-0.186	-0.378	0.061	-0.217	0.115

	CO	NI	CU	ZN	AS
CO	1.000				
NI	-0.636	1.000			
CU	-0.671	0.916	1.000		
ZN	-0.224	0.455	0.538	1.000	
AS	0.238	-0.077	-0.049	0.238	1.000
SR	0.252	-0.112	-0.231	-0.126	0.832
CD	-0.802	0.851	0.932	0.441	-0.172
SN	-0.525	0.522	0.592	0.396	-0.210
SB	-0.427	0.529	0.494	0.644	0.410
I	0.119	0.392	0.301	0.573	0.517
CS	0.004	0.355	0.311	0.512	0.630
BA	0.252	0.189	0.070	0.336	0.678
LA	-0.049	0.133	-0.049	-0.140	0.531
CE	0.273	0.056	-0.014	0.245	0.818
PB	-0.692	0.706	0.832	0.483	-0.021
TEMP	-0.296	0.285	0.299	0.169	-0.863
PH	-0.507	0.299	0.377	0.070	-0.771
ALK	0.448	-0.147	-0.343	-0.182	0.035
RB	-0.263	0.753	0.560	0.525	0.126

	SR	CD	SN	SB	I
SR	1.000				
CD	-0.277	1.000			
SN	-0.553	0.505	1.000		
SB	0.102	0.484	0.482	1.000	
I	0.308	0.088	0.252	0.504	1.000
CS	0.593	0.264	-0.332	0.471	0.523
BA	0.748	-0.067	-0.445	0.196	0.636
LA	0.727	-0.074	-0.319	0.284	0.245
CE	0.734	-0.186	-0.280	0.368	0.608
PB	-0.343	0.732	0.837	0.578	0.322
TEMP	-0.873	0.406	0.346	-0.067	-0.338
PH	-0.835	0.409	0.686	-0.129	-0.246
ALK	0.210	-0.368	-0.427	-0.161	0.105
RB	0.210	0.523	0.051	0.470	0.644

APPENDIX N

Table N.1 cont...

	CS	BA	LA	CE	PB
CS	1.000				
BA	0.878	1.000			
LA	0.403	0.476	1.000		
CE	0.750	0.832	0.622	1.000	
PB	-0.007	-0.196	-0.007	-0.042	1.000
TEMP	-0.317	-0.525	-0.595	-0.634	0.183
PH	-0.682	-0.729	-0.532	-0.796	0.518
ALK	0.333	0.441	-0.042	0.392	-0.573
RB	0.671	0.609	0.329	0.329	0.259

	TEMP	PH	ALK	RB
TEMP	1.000			
PH	0.683	1.000		
ALK	0.042	-0.504	1.000	
RB	0.079	-0.109	0.133	1.000

APPENDIX O

Table O.1 Surface Water Chemistry Spearman Rank Correlation Matrix

	COND	NA	K	CA	CL
COND	1.000				
NA	0.987	1.000			
K	0.588	0.582	1.000		
CA	0.787	0.773	0.274	1.000	
CL	0.877	0.898	0.610	0.765	1.000
NITRATE	0.569	0.607	0.396	0.666	0.758
SULFATE	0.916	0.903	0.656	0.639	0.820
TI	0.592	0.586	0.512	0.587	0.717
MN	0.732	0.731	0.275	0.774	0.499
FE	0.793	0.772	0.605	0.737	0.802
CO	0.853	0.839	0.472	0.845	0.706
NI	-0.383	-0.396	-0.333	-0.317	-0.400
CU	-0.363	-0.373	-0.064	-0.284	-0.341
ZN	-0.332	-0.400	-0.474	-0.203	-0.473
SR	0.732	0.722	0.278	0.926	0.719
CD	-0.078	-0.094	-0.553	0.004	-0.134
SB	0.583	0.592	0.362	0.723	0.571
I	0.411	0.439	0.196	0.346	0.134
CS	0.570	0.613	0.710	0.154	0.463
LA	0.516	0.541	0.249	0.675	0.741
CE	0.534	0.510	0.401	0.655	0.719
PB	-0.209	-0.227	-0.108	-0.097	-0.086
TEMP	0.190	0.222	0.335	0.112	0.454
PH	-0.430	-0.496	-0.459	-0.248	-0.378
O2	-0.311	-0.354	-0.474	-0.023	-0.487
ALK	0.589	0.645	0.429	0.389	0.437
MG	0.723	0.709	0.352	0.878	0.741
AL	0.279	0.296	0.080	0.359	0.497
SI	0.424	0.430	0.295	0.556	0.516
AS	0.167	0.186	0.168	0.376	0.326
RB	0.609	0.630	0.734	0.307	0.671
SN	-0.524	-0.566	-0.571	-0.333	-0.575
BA	0.209	0.183	0.430	-0.062	0.134

APPENDIX O

Table O.1 cont…

	NITRATE	SULFATE	TI	MN	FE
NITRATE	1.000				
SULFATE	0.582	1.000			
TI	0.400	0.550	1.000		
MN	0.398	0.525	0.284	1.000	
FE	0.619	0.722	0.777	0.604	1.000
CO	0.474	0.728	0.611	0.880	0.864
NI	-0.147	-0.163	-0.380	-0.345	-0.389
CU	-0.125	-0.240	-0.062	-0.262	-0.148
ZN	-0.521	-0.398	-0.185	-0.116	-0.350
SR	0.692	0.688	0.614	0.613	0.661
CD	0.105	-0.212	-0.341	0.038	-0.078
SB	0.498	0.540	0.641	0.487	0.638
I	0.099	0.433	0.176	0.574	0.269
CS	0.356	0.579	0.187	0.463	0.405
LA	0.811	0.455	0.594	0.288	0.659
CE	0.640	0.486	0.845	0.240	0.789
PB	0.064	-0.143	0.235	-0.221	0.152
TEMP	0.527	0.431	0.367	-0.365	0.176
PH	-0.224	-0.459	-0.172	-0.484	-0.230
O2	-0.540	-0.331	-0.309	0.009	-0.462
ALK	0.393	0.437	0.124	0.733	0.487
MG	0.613	0.618	0.711	0.596	0.830
AL	0.464	0.224	0.487	0.009	0.440
SI	0.297	0.402	0.466	0.341	0.579
AS	0.517	0.103	0.031	0.299	0.246
RB	0.559	0.810	0.637	0.130	0.617
SN	-0.469	-0.499	-0.221	-0.252	-0.401
BA	-0.130	0.398	0.429	-0.138	0.183

	CO	NI	CU	ZN	SR
CO	1.000				
NI	-0.397	1.000			
CU	-0.292	0.675	1.000		
ZN	-0.274	0.565	0.582	1.000	
SR	0.724	-0.125	-0.108	-0.191	1.000
CD	-0.104	0.168	-0.000	0.183	-0.036
SB	0.615	-0.145	0.114	-0.147	0.828
I	0.559	-0.222	-0.262	-0.358	0.424
CS	0.419	-0.282	0.018	-0.371	0.129
LA	0.432	-0.020	0.059	-0.165	0.710
CE	0.506	-0.176	0.121	-0.086	0.692
PB	-0.136	0.497	0.846	0.530	0.011
TEMP	-0.074	0.357	0.372	-0.100	0.325
PH	-0.477	0.324	0.308	0.475	-0.172
O2	-0.115	0.400	0.086	0.538	-0.002
ALK	0.607	-0.515	-0.360	-0.477	0.245
MG	0.777	-0.156	-0.011	-0.121	0.881
AL	0.156	0.105	0.427	0.134	0.422
SI	0.552	0.108	0.226	0.024	0.503
AS	0.222	0.148	0.343	0.042	0.290
RB	0.421	-0.043	0.057	-0.458	0.486
SN	-0.372	0.606	0.663	0.884	-0.305
BA	0.143	0.156	0.064	-0.073	0.147

APPENDIX O

Table O.1 cont...

	CD	SB	I	CS	LA
CD	1.000				
SB	-0.279	1.000			
I	-0.221	0.442	1.000		
CS	-0.237	0.187	0.322	1.000	
LA	0.132	0.672	-0.103	0.080	1.000
CE	-0.067	0.703	-0.095	0.080	0.868
PB	0.136	0.190	-0.415	-0.080	0.363
TEMP	-0.253	0.272	-0.241	0.231	0.515
PH	0.368	0.001	-0.507	-0.652	0.163
O2	-0.012	-0.110	0.117	-0.581	-0.410
ALK	-0.075	0.348	0.539	0.711	0.203
MG	-0.004	0.871	0.262	0.120	0.815
AL	0.242	0.485	-0.385	0.080	0.759
SI	-0.174	0.565	-0.029	0.080	0.521
AS	0.201	0.110	-0.328	0.258	0.409
RB	-0.383	0.523	0.330	0.571	0.475
SN	0.156	-0.278	-0.169	-0.382	-0.239
BA	-0.329	0.145	0.358	0.092	-0.068

	CE	PB	TEMP	PH	O2
CE	1.000				
PB	0.468	1.000			
TEMP	0.485	0.438	1.000		
PH	0.167	0.444	-0.083	1.000	
O2	-0.410	-0.176	-0.371	0.103	1.000
ALK	0.071	-0.336	-0.238	-0.472	-0.467
MG	0.829	0.204	0.219	0.007	-0.121
AL	0.739	0.682	0.557	0.281	-0.383
SI	0.525	0.323	0.277	-0.120	0.062
AS	0.284	0.321	0.326	-0.225	-0.099
RB	0.557	0.139	0.684	-0.340	-0.542
SN	-0.141	0.654	0.018	0.361	0.417
BA	0.134	-0.037	0.243	-0.179	0.135

	ALK	MG	AL	SI	AS
ALK	1.000				
MG	0.307	1.000			
AL	-0.088	0.594	1.000		
SI	0.053	0.714	0.576	1.000	
AS	0.041	0.308	0.509	0.530	1.000
RB	0.272	0.462	0.318	0.277	-0.004
SN	-0.550	-0.285	0.108	-0.015	0.094
BA	-0.210	0.121	-0.121	0.046	-0.381

	RB	SN	BA
RB	1.000		
SN	-0.433	1.000	
BA	0.585	-0.161	1.000

APPENDIX P

Table P.1 Clam Chemistry Spearman Rank Correlation Matrix

	WEIGHT	LI	B	AL	CA
WEIGHT	1.000				
LI	-0.900	1.000			
B	-0.500	0.700	1.000		
AL	-0.900	1.000	0.700	1.000	
CA	-0.600	0.700	0.300	0.700	1.000
TI	-0.900	1.000	0.700	1.000	0.700
V	-1.000	0.900	0.500	0.900	0.600
CR	-0.900	0.700	0.200	0.700	0.700
MN	-0.800	0.500	-0.100	0.500	0.400
FE	-0.900	1.000	0.700	1.000	0.700
NI	-0.500	0.300	-0.000	0.300	0.700
ZN	-1.000	0.900	0.500	0.900	0.600
MO	-0.700	0.500	0.600	0.500	0.100
SR	-0.900	1.000	0.700	1.000	0.700
CD	-0.900	0.800	0.700	0.800	0.300
SN	-0.700	0.900	0.600	0.900	0.900
I	-0.400	0.300	0.700	0.300	-0.000
CS	-0.975	0.975	0.616	0.975	0.667
BA	-0.900	1.000	0.700	1.000	0.700
CE	-0.900	1.000	0.700	1.000	0.700
PB	-0.872	0.872	0.821	0.872	0.359
U	-0.900	1.000	0.700	1.000	0.700
LENGTH	1.000	-0.900	-0.500	-0.900	-0.600
GSIZE	-0.100	0.300	-0.200	0.300	0.300
LOI	0.500	-0.100	0.000	-0.100	0.100
SI	-0.900	0.800	0.700	0.800	0.300
P	-0.300	0.100	0.400	0.100	0.100
S	-0.300	0.100	0.400	0.100	0.100
CO	-0.800	0.600	0.400	0.600	-0.000
CU	-0.600	0.300	0.300	0.300	0.200
AS	-0.300	0.400	0.900	0.400	0.100
SE	-0.400	0.300	0.700	0.300	-0.000
RB	-0.800	0.900	0.900	0.900	0.400
AG	-0.667	0.359	0.205	0.359	0.359
LA	-0.900	1.000	0.700	1.000	0.700

APPENDIX P

Table P.1 cont...

	TI	V	CR	MN	FE
TI	1.000				
V	0.900	1.000			
CR	0.700	0.900	1.000		
MN	0.500	0.800	0.900	1.000	
FE	1.000	0.900	0.700	0.500	1.000
NI	0.300	0.500	0.800	0.600	0.300
ZN	0.900	1.000	0.900	0.800	0.900
MO	0.500	0.700	0.600	0.500	0.500
SR	1.000	0.900	0.700	0.500	1.000
CD	0.800	0.900	0.700	0.600	0.800
SN	0.900	0.700	0.600	0.300	0.900
I	0.300	0.400	0.300	0.100	0.300
CS	0.975	0.975	0.821	0.667	0.975
BA	1.000	0.900	0.700	0.500	1.000
CE	1.000	0.900	0.700	0.500	1.000
PB	0.872	0.872	0.616	0.462	0.872
U	1.000	0.900	0.700	0.500	1.000
LENGTH	-0.900	-1.000	-0.900	-0.800	-0.900
GSIZE	0.300	0.100	-0.000	0.100	0.300
LOI	-0.100	-0.500	-0.600	-0.700	-0.100
SI	0.800	0.900	0.700	0.600	0.800
P	0.100	0.300	0.400	0.200	0.100
S	0.100	0.300	0.400	0.200	0.100
CO	0.600	0.800	0.600	0.700	0.600
CU	0.300	0.600	0.700	0.600	0.300
AS	0.400	0.300	0.100	-0.200	0.400
SE	0.300	0.400	0.300	0.100	0.300
RB	0.900	0.800	0.500	0.300	0.900
AG	0.359	0.667	0.821	0.718	0.359
LA	1.000	0.900	0.700	0.500	1.000

APPENDIX P

Table P.1 cont…

	NI	ZN	MO	SR	CD
NI	1.000				
ZN	0.500	1.000			
MO	0.400	0.700	1.000		
SR	0.300	0.900	0.500	1.000	
CD	0.300	0.900	0.900	0.800	1.000
SN	0.400	0.700	0.200	0.900	0.500
I	0.300	0.400	0.900	0.300	0.700
CS	0.410	0.975	0.616	0.975	0.872
BA	0.300	0.900	0.500	1.000	0.800
CE	0.300	0.900	0.500	1.000	0.800
PB	0.205	0.872	0.821	0.872	0.975
U	0.300	0.900	0.500	1.000	0.800
LENGTH	-0.500	-1.000	-0.700	-0.900	-0.900
GSIZE	-0.300	0.100	-0.600	0.300	-0.200
LOI	-0.500	-0.500	-0.800	-0.100	-0.600
SI	0.300	0.900	0.900	0.800	1.000
P	0.600	0.300	0.800	0.100	0.500
S	0.600	0.300	0.800	0.100	0.500
CO	0.100	0.800	0.800	0.600	0.900
CU	0.700	0.600	0.900	0.300	0.700
AS	0.100	0.300	0.700	0.400	0.600
SE	0.300	0.400	0.900	0.300	0.700
RB	0.100	0.800	0.700	0.900	0.900
AG	0.821	0.667	0.821	0.359	0.667
LA	0.300	0.900	0.500	1.000	0.800

	SN	I	CS	BA	CE
SN	1.000				
I	0.100	1.000			
CS	0.821	0.359	1.000		
BA	0.900	0.300	0.975	1.000	
CE	0.900	0.300	0.975	1.000	1.000
PB	0.616	0.667	0.895	0.872	0.872
U	0.900	0.300	0.975	1.000	1.000
LENGTH	-0.700	-0.400	-0.975	-0.900	-0.900
GSIZE	0.400	-0.800	0.205	0.300	0.300
LOI	0.200	-0.600	-0.308	-0.100	-0.100
SI	0.500	0.700	0.872	0.800	0.800
P	-0.000	0.900	0.205	0.100	0.100
S	-0.000	0.900	0.205	0.100	0.100
CO	0.200	0.500	0.718	0.600	0.600
CU	0.100	0.800	0.462	0.300	0.300
AS	0.300	0.900	0.359	0.400	0.400
SE	0.100	1.000	0.359	0.300	0.300
RB	0.700	0.600	0.872	0.900	0.900
AG	0.205	0.667	0.526	0.359	0.359
LA	0.900	0.300	0.975	1.000	1.000

APPENDIX P

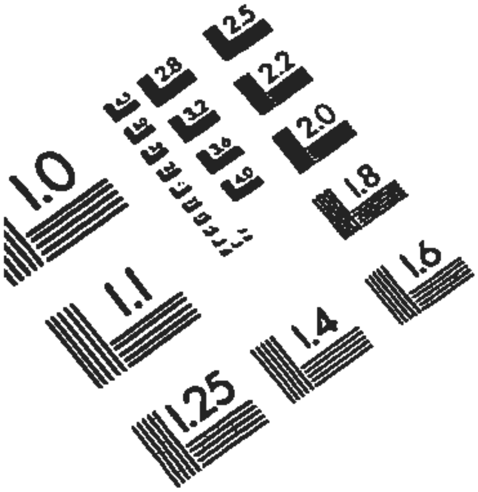
Table P.1 cont...

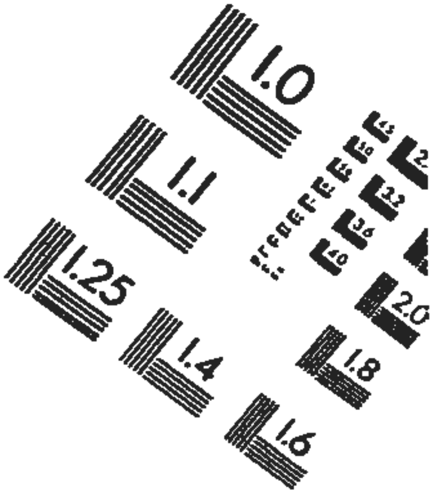
	PB	U	LENGTH	GSIZE	LOI
PB	1.000				
U	0.872	1.000			
LENGTH	-0.872	-0.900	1.000		
GSIZE	-0.103	0.300	-0.100	1.000	
LOI	-0.410	-0.100	0.500	0.600	1.000
SI	0.975	0.800	-0.900	-0.200	-0.600
P	0.410	0.100	-0.300	-0.900	-0.700
S	0.410	0.100	-0.300	-0.900	-0.700
CO	0.821	0.600	-0.800	-0.100	-0.700
CU	0.564	0.300	-0.600	-0.700	-0.900
AS	0.667	0.400	-0.300	-0.600	-0.200
SE	0.667	0.300	-0.400	-0.800	-0.600
RB	0.975	0.900	-0.800	-0.000	-0.200
AG	0.526	0.359	-0.667	-0.564	-0.872
LA	0.872	1.000	-0.900	0.300	-0.100

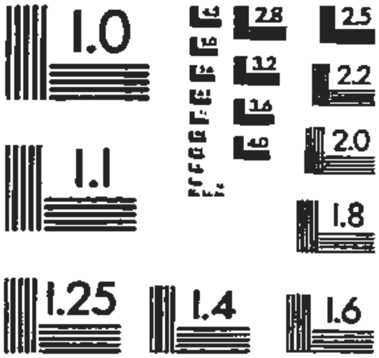
	SI	P	S	CO	CU
SI	1.000				
P	0.500	1.000			
S	0.500	1.000	1.000		
CO	0.900	0.100	0.300	1.000	
CU	0.700	0.900	0.900	0.600	1.000
AS	0.600	0.700	0.700	0.300	0.500
SE	0.700	0.900	0.900	0.500	0.800
RB	0.900	0.300	0.300	0.700	0.400
AG	0.667	0.821	0.821	0.564	0.975
LA	0.800	0.100	0.100	0.600	0.300

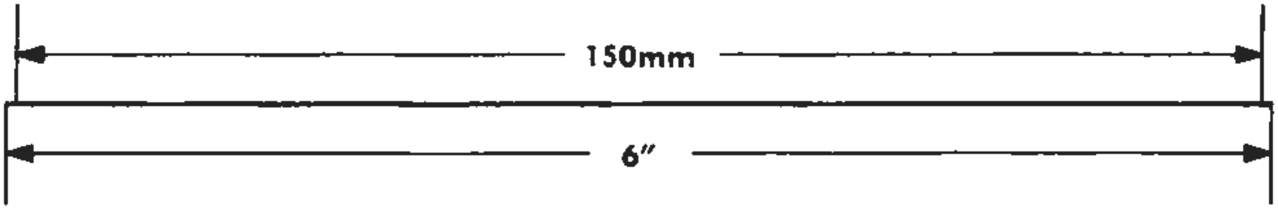
	AS	SE	RB	AG	LA
AS	1.000				
SE	0.900	1.000			
RB	0.700	0.600	1.000		
AG	0.359	0.667	0.359	1.000	
LA	0.400	0.300	0.900	0.359	1.000

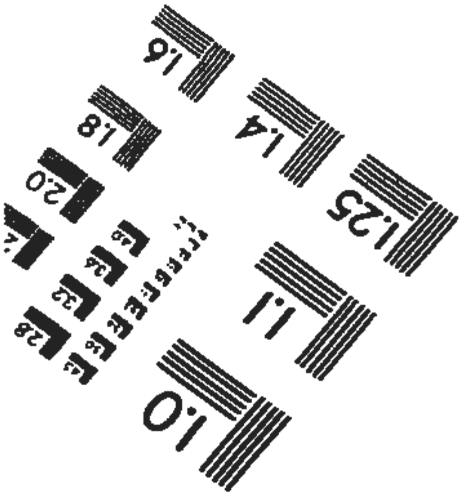
IMAGE EVALUATION
TEST TARGET (QA-3)











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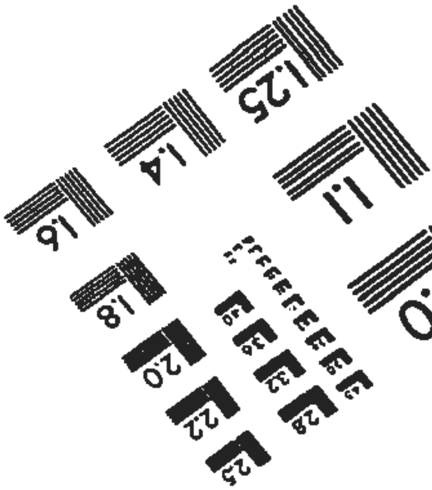

mobilization of dissolved metals from the salvage yard-bog area was found to be negligible. Relatively neutral pH (> 6) conditions detected in drainage basin ground waters most likely limited the aqueous solubility of metals and resulted in the predominant species being adsorbed to the soil framework. An additional source of contamination to the drainage basin is suspected to include domestic septic effluent. *M. mercenaria* collected from the South River estuary were enriched in Fe, Ni, Mn, Cd, Cr, and Pb, relative to average concentrations of *M. mercenaria* collected along the Atlantic coast of the US. However, PCBs were not present ≥ 0.05 ppm (wet weight) in *M. mercenaria* from the estuary. Therefore, PCBs adsorbed on suspended material are either being deposited closer to the salvage yard or are being diluted by uncontaminated suspended matter. Regardless, PCBs are not available to these relatively immobile bioreceptors in the estuary.

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