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Inorganic Geochemistry of the
Groundwater at the Smithville Site-
Phase I Investigation

by

L. Zanini, K. Novakowski and P. Lapcevic

NWRI contribution No: 97-128

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MANAGEMENT PERSPECTIVE

Title: Inorganic geochemistry of the groundwater at the Smithville Site - Phase I investigations

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EC Priority/Issue:

This report presents the results of an extensive groundwater sampling program undertaken in February/March 1997 as part of ongoing GWRP studies at Smithville ON. Samples were obtained from 46 different zones in seven boreholes. The primary purpose of this study was to aid in the development of a detailed conceptual model of groundwater flow and contaminant transport in the fractured bedrock underlying the CWML waste site. The work is unique in developing techniques for effectively characterizing the geochemistry of fractured rock systems and in the detailed nature of the investigation.

The results indicate that Fe reducing zones exist closest to the ground surface where the groundwater is considered to be in a post-oxic state. The transition from post-oxic conditions to more anaerobic conditions occurs with increasing depth where SO_4 reducing conditions prevail.

This work supports EC priorities under COA Stream 1.6 (groundwater) and Stream 1.4 (contaminated sites). Additionally, it supports GWRP deliverables under Toxics Result #3.

Current Status:

The report is intended to be released as a NWRI contribution and will be incorporated into a journal manuscript later in the year after the completion of further field sampling and interpretation.

Next Steps:

The results presented in the report are currently being used to plan a second and third sampling survey this summer and fall. The results of all three surveys will be used to support other studies at the Smithville site and will lead to a journal manuscript.

EXECUTIVE SUMMARY

During February and March of 1997, a study was undertaken to characterize the inorganic constituents of the groundwater at the CWML site in Smithville, Ontario. Samples were collected from four boreholes: 60, 62, 53 and 61 which are completed with Westbay sampling devices and from three monitoring wells: 11, 21 and 12 which are completed as multilevel piezometers.

By measuring relative concentrations of redox reactive species, such as iron (Fe), ammonia (NH_3)/nitrate (NO_3), sulfate (SO_4)/dissolved sulfide (HS^-) and dissolved oxygen (DO), specific reduction-oxidation (redox) zones within the aquifer may be defined. The primary purpose of this study is to aid in the development of a detailed conceptual model of groundwater flow, transport and chemical properties of the Smithville groundwater system. This study is also conducted to develop and implement accurate sampling techniques for inorganic geochemistry in fractured media.

Samples for inorganic geochemistry analyses were collected using the Westbay sampling device for boreholes 60, 62, 53 and 61. The device consists of two stainless steel sampling chambers. Sample chambers were electronically located at depth specific sampling ports designed to draw groundwater directly from the formation. This eliminates the need to purge the borehole of standing water. Boreholes 11, 21 and 12 are installed with 1.25 inch diameter PVC multilevel piezometers with varying screen lengths. Wells were purged three times their volume using a Waterra hand held pump prior to procuring measurements and samples.

Dissolved Oxygen (DO), pH, oxidation-reduction potential (Eh), alkalinity and electrical conductance were measured in the field. Collected samples were analyzed for trace metals by inductively coupled plasma spectroscopy and anions by ion chromatography. Samples were also analyzed for NH_3 and DOC using colourimetric techniques.

Analyses for both electron acceptor availability (such as NO_3^- , SO_4^{2-} and Fe^{3+}) and the products of microbial metabolism (NH_3 , HS^- , Fe^{2+} and CH_4^+) in the groundwater provide further insight into groundwater redox characterization. Analytical results at the Smithville site suggest that although few decreases in SO_4 concentrations are observed, HS concentrations generally increase with depth suggesting that SO_4 reduction processes are occurring. Sulfate concentrations in solution likely remain high due to the presence of gypsum that is abundant in the Lockport group formations. The dissolution of gypsum compensates for decreases in SO_4 concentrations occurring during SO_4 reduction. Moreover, dissolved sulfide may either precipitate from solution with soluble metals or be released as

sulfide gas. Black precipitate was observed in many samples collected and all boreholes contain high concentrations of Fe at shallow depths but tend to decrease to low levels ($\sim <0.2$ mg/L) as the sulfate reducing zone is encountered. This suggests that FeS precipitation is occurring. Thus, the observed lack of significant HS increase in the groundwater at some of the boreholes does not rule out the presence of SO_4 reduction processes.

The distribution of Eh and the byproducts of degradation are contoured in the direction of groundwater flow in order to provide a two dimensional (2D) representation of the redox zones in the groundwater system. Highly reducing horizons are observed in zones at lower elevations in boreholes 11 and 21 (approximately 145 to 170 m.a.s.l.). Dissolved HS concentrations are elevated in areas of low Eh values. In contrast, Fe concentrations are highest (>1 mg/L) in areas where Eh values are also high and HS concentrations are low. The 2D cross sections of the distribution of redox processes demonstrate that Fe reducing zones exist closest to the ground surface where the groundwater is considered to be in a post-oxic state. The transition from post-oxic conditions to more anaerobic conditions occurs with increasing depth where SO_4 reducing conditions prevail.

The elevated values of Eh generally observed in the shallowest intervals implies that freshly recharged groundwater is migrating along the contact between the overburden and the bedrock at the Smithville site. Although a highly permeable basal gravel is present in the overburden, continuity and the degree of groundwater flow in this unit is unknown. In areas where higher Eh conditions persist with depth, there is likely considerable vertical interaction between the groundwater in the basal gravel unit and the fracture system.

A sampling session is planned for the summer/fall of 1997. In this session samples will be analyzed for stable isotope content to determine the possible influx of meteoric water. In addition, geochemical speciation modelling will also be undertaken to determine what mineral phases may be in equilibrium with the groundwater at various elevations and along the groundwater flow path.

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INTRODUCTION

During the late 1970's and early 1980's a PCB waste management site (Chemical Waste Management Ltd.) was operated on the outskirts of the town of Smithville, Ontario. In 1985, groundwater contamination was discovered in monitoring wells located in the vicinity of the waste site. Subsequently, it was discovered that PCB oils and associated solvents had penetrated the overburden and pervaded the upper bedrock. During 1994, a detailed study of the groundwater flow system in the bedrock was initiated in order to establish a conceptual model for groundwater flow and transport. In the winter of 1997, a preliminary study was undertaken to characterize the inorganic constituents in the groundwater at Smithville. The purpose of this study was to augment the work done from previous and current studies at the site and aid in the development of the conceptual model. To date, there has been no previous study of inorganic groundwater components at the site.

Characterization of the inorganic constituents of the groundwater at the CWML site will determine the presence of chemical oxidants/reductants which may address the potential for intrinsic bioremediation. The relative concentrations of redox reactive species, such as iron (Fe), ammonia (NH_3)/nitrate (NO_3), sulfate (SO_4)/dissolved sulfide (HS) and dissolved oxygen (DO), can be used to define redox zones within the flow system. The determination of more oxic zones, as indicated by oxidized species in solution or high redox potential values determined from an Eh probe, can lead to the location of possible recharge zones which will assist in defining active groundwater flow systems.

The presence and concentration of specific compounds such as NaCl and SO_4 are also an indication of groundwater travel time. For example, in carbonate sequences, groundwater will evolve from HCO_3 to Cl and SO_4 enriched, with travel distance. High concentrations of total dissolved solids (TDS) suggest that the groundwater has been in contact with the geological material for a lengthy amount of time and are thus strong indicators of sluggish groundwater flow. Alternatively, the presence of low TDS and abundant DO in the fractures within the carbonate sequences suggest local fresh water recharge.

In this study, the inorganic geochemical analyses of samples collected from four boreholes completed with Westbay sampling devices and three monitoring wells completed with multilevel piezometers, are presented. Redox characterization of the groundwater at the Smithville site is

represented in two dimensional (2D) cross sections in the direction of groundwater flow. A discussion is presented in which the dissolved inorganic constituents are related to groundwater flow.

SITE DESCRIPTION

The CWML site (Figure 1) is located just east of the town of Smithville, Ontario. The source of groundwater contamination at the site was an industrial waste storage facility located at the northwest corner of Spring Creek Rd and Thompson Ave. (Figure 1). Approximately 5 to 10 m of clay till overburden underlies the site. The clay till is of minimal permeability ($K \sim 10^{-9}$ to 10^{-11} m/s) although pervaded by frequent vertical fractures (Golders Associates, 1995). Although it is unclear as to whether the fractures penetrate the entire thickness of the till, PCB oil and solvents were observed in the upper rock units during site investigations conducted in 1987 and 1988 (Golders Associates, 1995). The bedrock underlying the site consists of four geological members in the Lockport formation that dip to the south. These are fine to medium grained dolostones containing minor gypsum and shale (Golders Associates, 1989, Lapcevic et al., 1995). The upper member (Eramosa) of the Lockport formation is fractured in a relatively uniform manner. Transmissivity of the of the fractures can be as high as 10^{-2} m²/s (Lapcevic et al., 1995). The Vinemount member, which underlies the Eramosa, is characterized by a weathered vuggy zone and a zone of unfractured rock of relatively low transmissivity (10^{-10} m²/s). Fracture frequency in the lower units (Goat Island and Gasport members) is more sparse, although transmissivity is no less than that observed in the Eramosa member. The Lockport formation is underlain by an impermeable shale which is considered a regional aquitard.

Based on measurements of hydraulic head obtained from regional boreholes, groundwater flow in the fracture system is to the southeast, following stratigraphic dip of the geological units. Local directions of flow can vary depending on the nature of the connections within the fracture system.

METHODOLOGY

Samples for analyses of inorganic geochemistry were collected using the Westbay sampling tool for boreholes 60, 62, 53 and 61 (Figure 1). The tool consists of two stainless steel sampling chambers connected to an actuating device (Appendix I). These chambers were evacuated with a hand held air pump prior to lowering into the borehole casing. Sample chambers were electronically located at depth

specific sampling ports designed to draw groundwater directly from the formation located outside the borehole casing. This eliminates the need to purge the borehole of standing water. Once the valve on the sample chamber was opened, water was drawn into the chamber by pressure differences between the formation and the chamber. The chamber was full usually within 3 to 5 minutes. In a few sampling zones, groundwater influx was observed to be sluggish (e.g. borehole 61 at 46 m depth and borehole 60 at 20 m depth) and collection of samples was difficult. Only small volumes of sample were obtained from these intervals and inorganic ion analyses was not possible.

Boreholes 11, 21 and 12 (Figure 1) are completed with 1.25 inch diameter PVC multilevel piezometers having varying screen lengths (Appendix II). The volume in each piezometer was purged three times using a Waterra hand held pump prior to procuring measurements and samples.

Dissolved Oxygen (DO), pH, oxidation-reduction potential (Eh), alkalinity and electrical conductance were measured in the field. For the Westbay boreholes, DO was the first parameter measured once the sampling chambers were opened. Dissolved oxygen was measured by colourimetric techniques using Chemets ampoules. This procedure is an effective way to obtain rapid DO analyses in the field by eliminating messy titration techniques used in other methods. However, should the sample be turbid or contain too much particulate matter, colourimetric techniques may over-predict the actual amount of DO.

Eh and pH were measured by immersing probes (Orion 96-78-00 platinum electrode and Corning 3 in 1 combination electrode calibrated with pH buffers 4 and 7 respectively) in a small volume (30 ml). Values were recorded when the reading stabilized, usually within 2-5 minutes. Alkalinity was measured by titrating a known volume of sample with 1.6 N sulfuric acid using a HACH digital titrator. Electrical conductance was measured by immersing an Orion conductivity probe in a small volume of sample. For the multilevel piezometers, pH, Eh, electrical conductance and DO were measured using a flow through cell. Dissolved oxygen was measured using an Orion DO meter and probe (model # 830). Probes were allowed to equilibrate with continuously pumped groundwater from the monitoring wells, and values were recorded once readings were steady, usually within 15 to 20 minutes.

Samples were filtered in the field using a 0.45 μm filters and preserved using trace metal grade HCl for metal analyses and zinc acetate for dissolved sulfide analyses. Samples collected from the Westbay boreholes were sent to the Water Technology International Corporation for analyses of major metals (Ca, Fe, Al, Mg, Mn, Na, K) using inductively coupled plasma spectroscopy, anions (NO_3 , SO_4 , PO_4 , Cl, and Br) using ion chromatography and, for NH_3 and dissolved organic content (DOC).

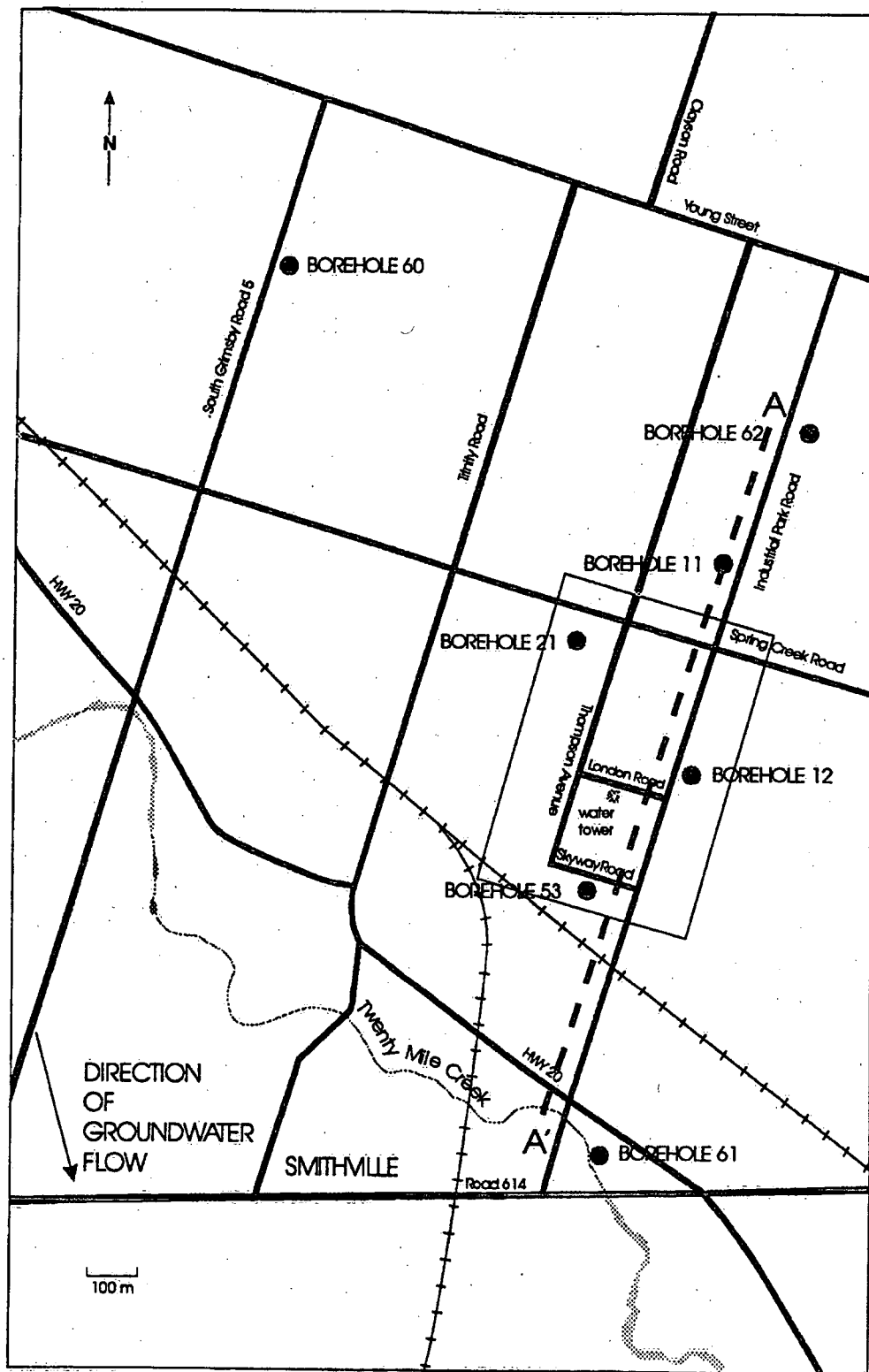


Figure 1: Locations of boreholes and cross section A to A' at the Smithville site .

Samples collected from the multilevel piezometers were sent to the National Laboratory for Environmental Testing for analyses of trace metals using inductively coupled plasma spectroscopy, anions using ion chromatography, and nutrients for PO_4 , NH_3 and DOC. Tabulated results are given in Appendix II.

Quality assurance and control procedures were performed by submitting for analyses several duplicates, equipment blanks and laboratory blanks (Appendix III).

RESULTS AND DISCUSSION

Inorganic Ion Analyses

The results of the analyses are plotted for each borehole with respect to depth (Figures 2-8). Each point on the diagrams represents either the middle of the isolated Westbay interval or the middle of an approximately five foot screen interval for the case of the multi-level piezometer completions.

Values of pH were observed to range between neutral and 7.7 with the lowest pH values (~6.9) located in borehole 61 near the Twenty Mile Creek (Figure 10). Redox potentials vary from values of -143 mV to 220 mV. Common to all boreholes, Eh values are highest (>0 mV) near the ground surface and generally decrease (<100 mV) at approximately 130 - 170 m.a.s.l. (Figures 2-8). This is indicative of conditions typical of transition zones from aerobic to anaerobic environments (Apello and Postma, 1993). However, the amount of DO in the Westbay boreholes does not reflect this. Dissolved oxygen concentrations range from a low of 1 mg/L to a high of ~5.5 mg/L, suggesting a more aerobic environment. Few consistent DO trends with depth are observed, and in one case DO concentrations increase as Eh values decrease. Such contradictory data suggests that colourimetric methods for determination of DO concentrations in the Smithville groundwater may not be appropriate and other techniques such as the Winkler titration method should be utilized. In contrast, DO measurements obtained by meter and probe (boreholes 11,12 and 21; Appendix I and II) indicate that in most cases DO is generally lower than 0.5 mg/L.

Alkalinity is slightly higher (~400 mg/L as CaCO_3) in the upper zones of the Westbay boreholes (10 to 15 m below the ground surface) and gradually decreases (~250-300 mg/L as CaCO_3) with depth. Measured alkalinity values in the piezometers are relatively stable with values ranging from ~300 to ~200 mg/L (CaCO_3). Large increases in dissolved ion concentrations are observed at lower depths. For example, in boreholes 60, 62, 61 and 11, Ca increases from approximately 250-350 mg/L to values

between 500 and 600 mg/L at elevations between 140 and 160 m.a.s.l. (Figures 2, 3, 5 and 6). However, in boreholes 12, 21 and 53, Ca concentrations increase from between 200 - 500 mg/L to values ranging from 1200 to 5000 mg/L with depth (130 to 150 m.a.s.l.). Chloride and Na concentrations also increase with depth in most boreholes, approaching brine conditions (Cl ~2000-30000 mg/L, Na ~2000-7500 mg/L) at 130 - 140 m.a.s.l. in boreholes 12, 21 and 53.

In borehole 60 and 53, SO_4 concentrations are high (>2000 mg/L) at 15 m below the ground surface, decrease to values of <1000 mg/L at 160 - 180 m.a.s.l. and then increase to concentrations around 1500 mg/L between 140 and 160 m.a.s.l. In borehole 62 values generally decrease from approximately 2500 mg/L at 185 m.a.s.l. to concentrations of approximately 1000 mg/L with increasing depth. Sulfate concentrations in borehole 61 follow a similar trend to that of borehole 60 and 53, yet concentrations never increase above 2000 mg/L. In the multilevel piezometers, SO_4 concentrations are generally low (~400 mg/L) near the ground surface (170 - 180 m.a.s.l.) and increase (~1700 mg/L) with depth.

The trends in alkalinity and dissolved ion concentrations suggest that the groundwater is evolving chemically toward the composition of sea water and follows the Chebotarev Sequence (Freeze and Cherry, 1979). The three distinct zones defined in the Chebotarev sequence are: The upper zone which is characterized by HCO_3 as the dominant anion, the intermediate zone which is characterized by less active groundwater, high total dissolved solids and SO_4 as the dominant anion, and the lower zone, characterized by sluggish groundwater flow, high in total dissolved solids and Cl concentrations. Based on this scheme, the groundwater in all boreholes is approaching the intermediate zone of evolution with depth. However, at elevations <140 m.a.s.l. in boreholes 53, 21 and 12, high Ca, Mg, Na, K and Cl concentrations suggest sluggish groundwater flow and a trend towards the lower zone of groundwater composition.

Charge balance calculations were performed (Appendix IV) on all samples submitted for analyses. In most cases, charge imbalances calculated for the samples from the Westbay boreholes are <5%. However; in three samples submitted for analyses from borehole 21, charge imbalances range from 11 to 30%. Large charge imbalances (>5 %) may be a result of a field/laboratory analytical error, precipitation of solids from collected samples or the omission of analyses of an ion that contributes significantly to electroneutrality. At this point, the cause of these charge imbalances is not evident. Most likely, either a sampling or analyses error has occurred since only borehole 21 displays the large charge differences. Future sampling sessions will evaluate this problem.

BH60

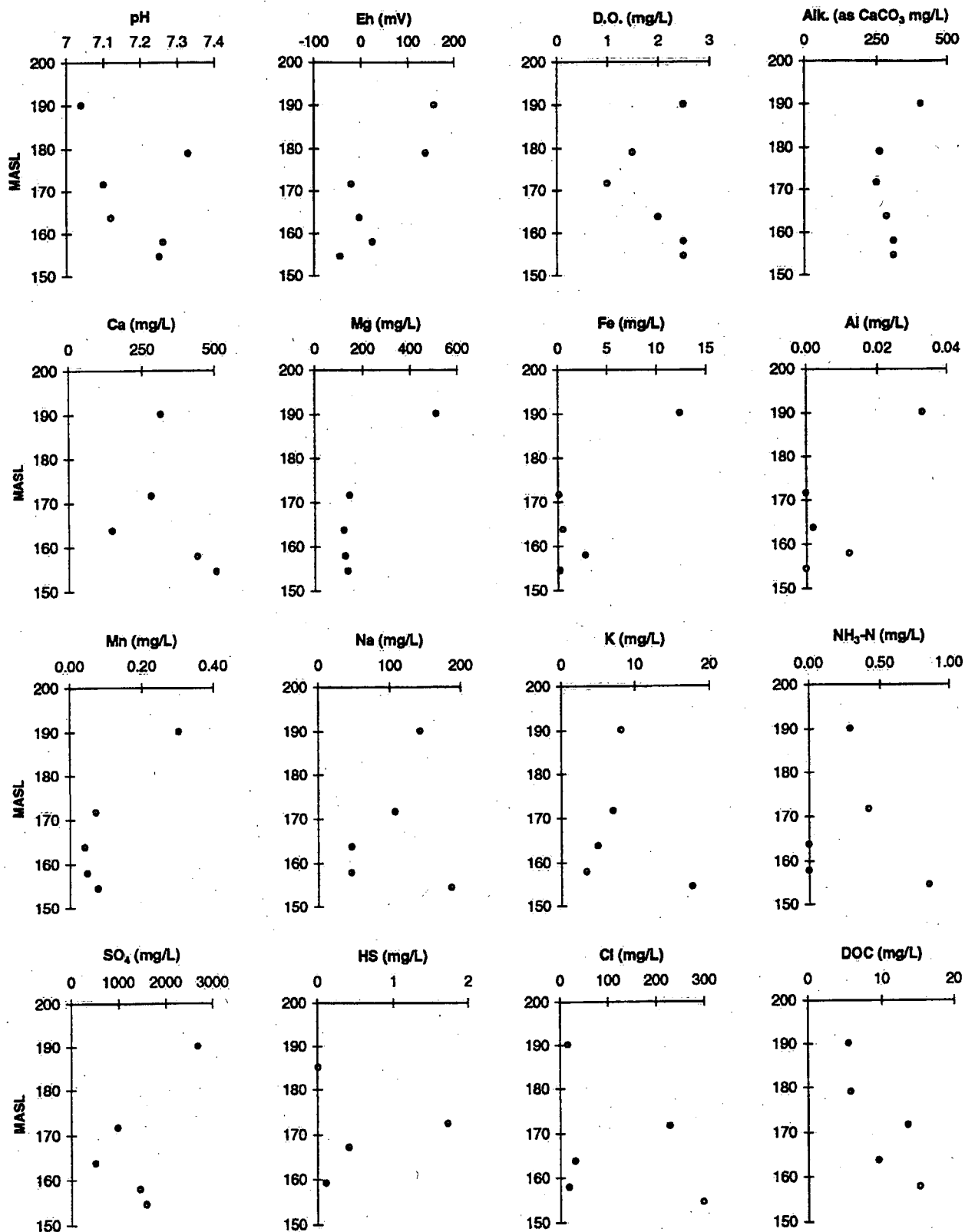


Figure 2: Summary of groundwater inorganic geochemistry in borehole 60.

BH62

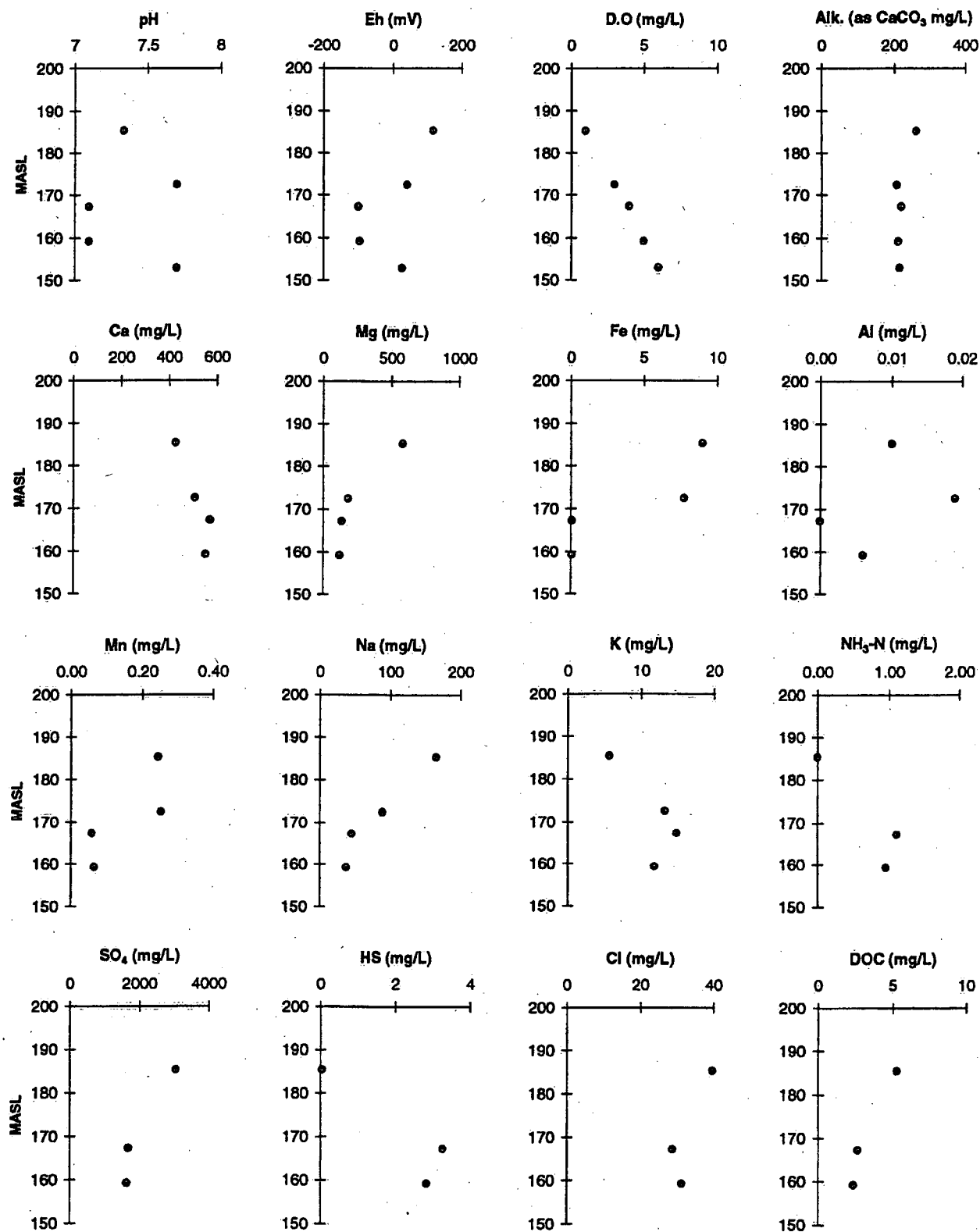


Figure 3: Summary of groundwater inorganic geochemistry in borehole 62

BH53

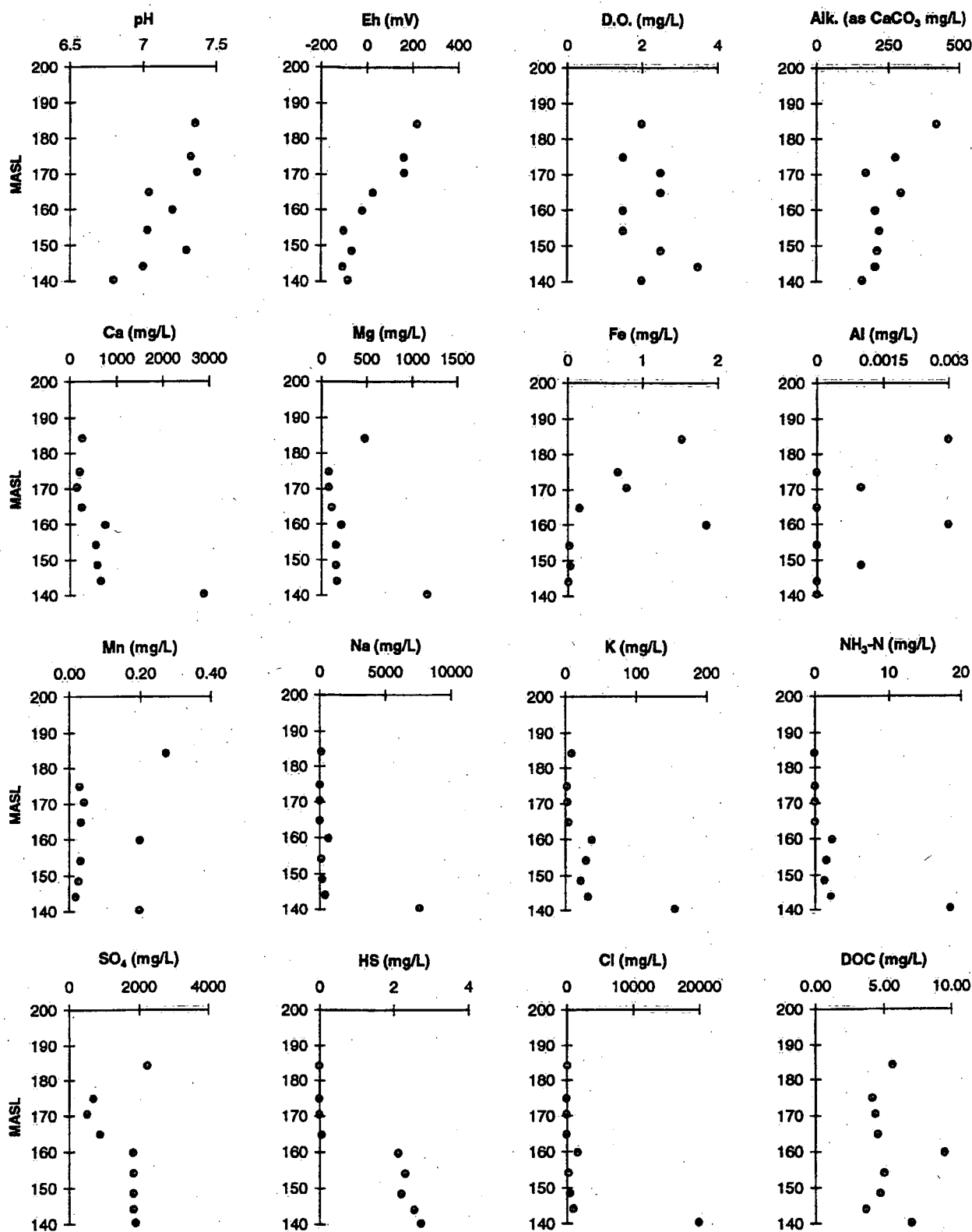


Figure 4: Summary of groundwater inorganic geochemistry in borehole 53.

BH61

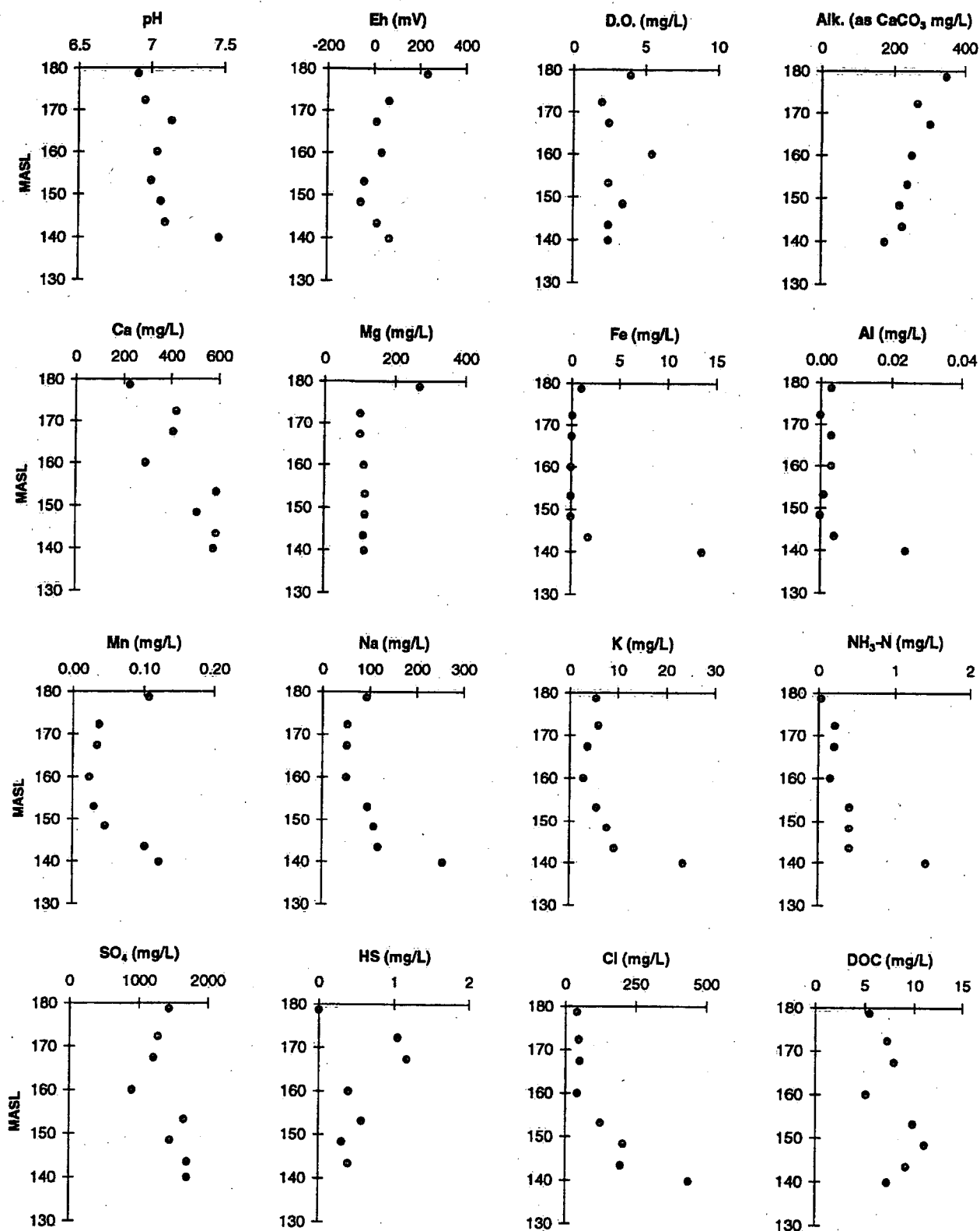


Figure 5: Summary of groundwater inorganic geochemistry in borehole 61.

BH11

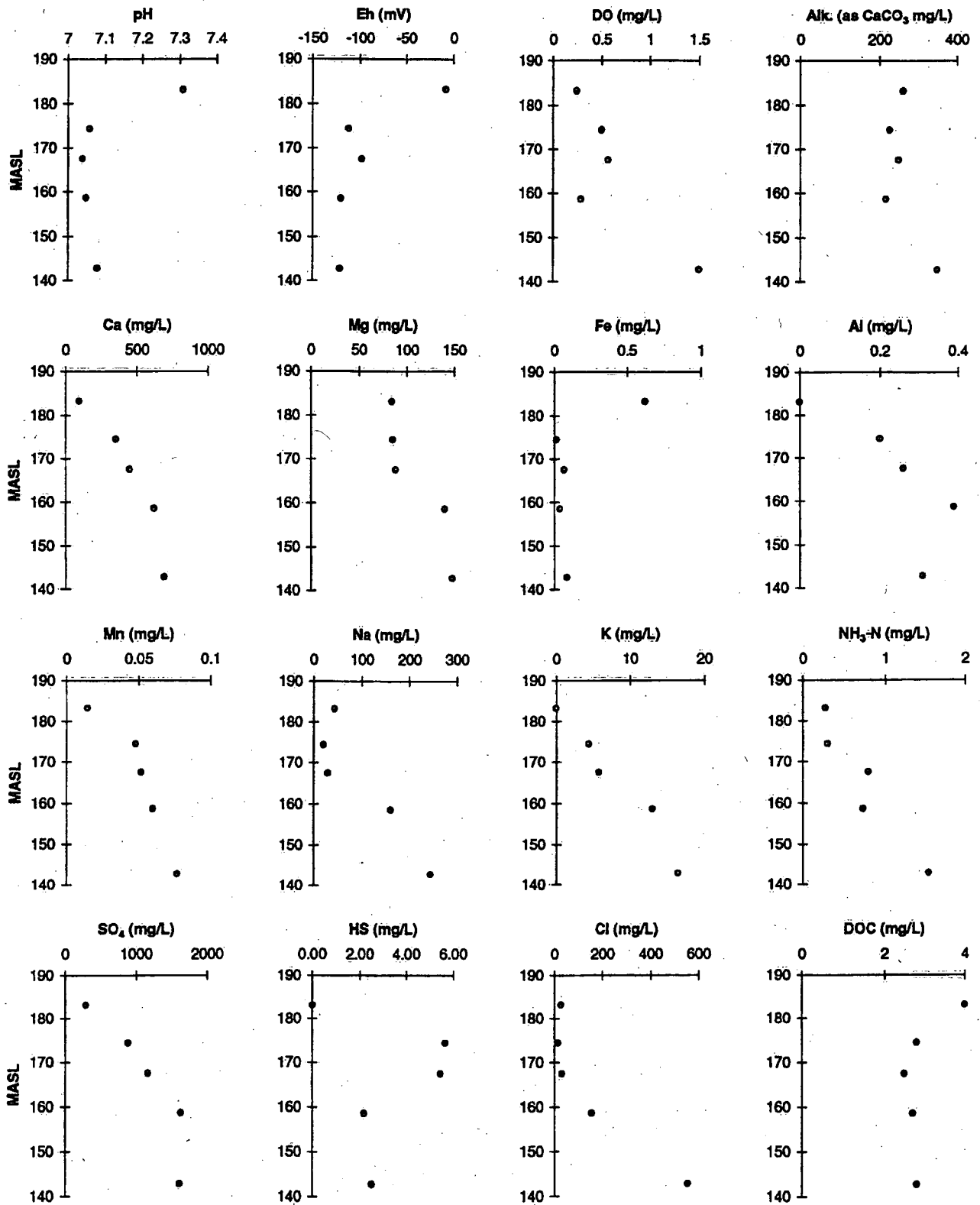


Figure 6: Summary of groundwater inorganic geochemistry in borehole 11.

BH21

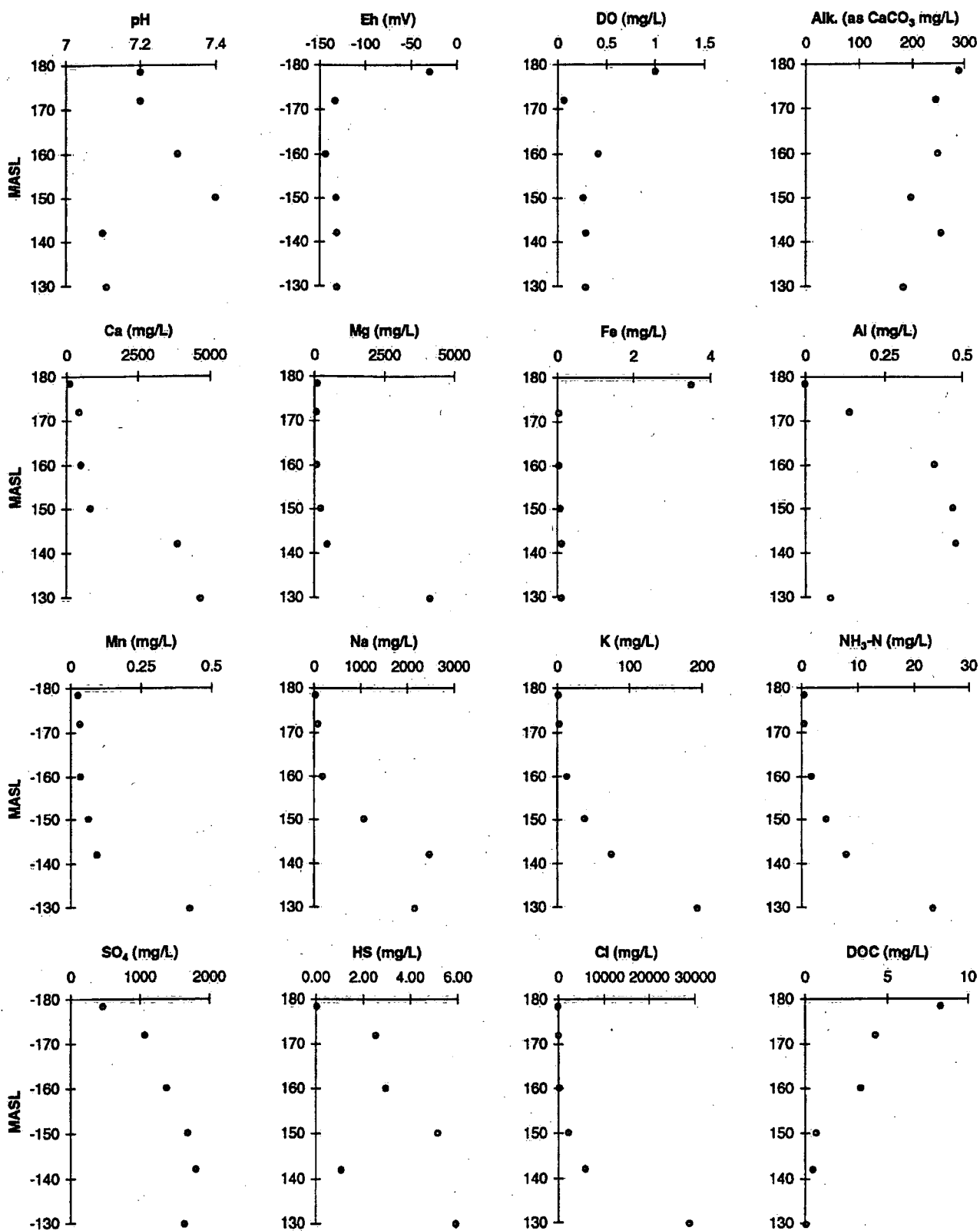


Figure 7: Summary of groundwater inorganic geochemistry in borehole 21.

BH12

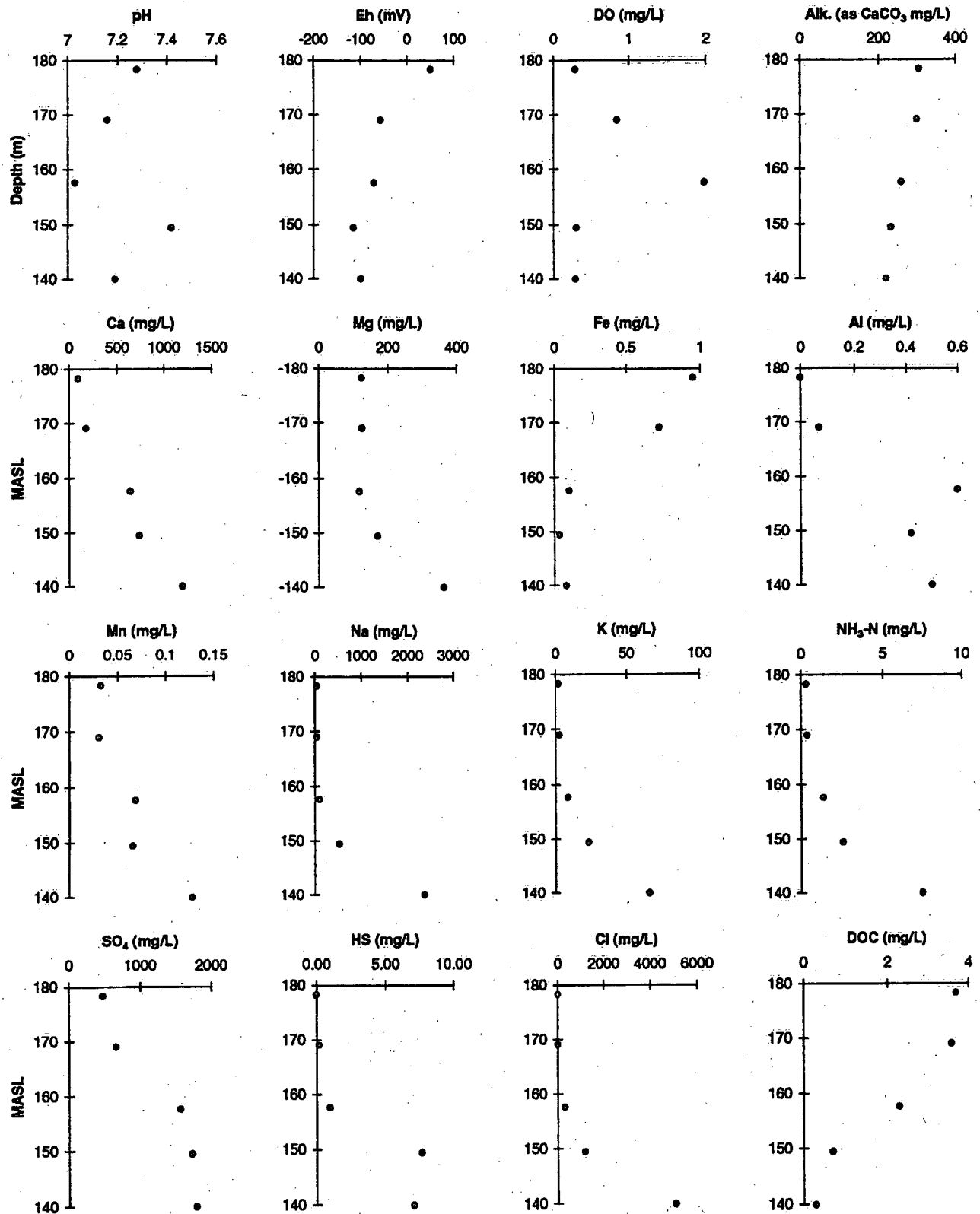


Figure 8: Summary of groundwater inorganic geochemistry in borehole 12.

Redox conditions

One objective in the analyses of Smithville groundwater for inorganic constituents is to provide more information on the redox environment of the flow system. Redox zones may be classified as either oxic ($\text{DO} > 10^{-6}$ moles), post-oxic ($\text{DO} < 10^{-6}$ moles and $\text{Fe} > 10^{-6}$ moles) or reducing where DO is non-detectable, and Fe and S_2 are detectable (Barcelona and Holm, 1991, Appelo and Postma, 1993). Several methods may be used to evaluate the oxidation-reduction processes in groundwater systems. Redox potentials are commonly measured using Eh platinum electrodes despite much uncertainty in the accuracy of measurement (Appelo and Postma, 1993; Chapelle et al., 1996). Many natural waters do not contain redox species whose potentials can be measured accurately and platinum electrodes are subject to a variety of interferences (Chapelle et al., 1996). Despite this, attempts are often made to characterize an aquifer based solely on Eh values.

Eh versus pH stability diagrams (Figure 9) are one of the many tools used to help define groundwater redox characteristics. These diagrams are constructed by plotting measured Eh and pH values and comparing them to equilibrium lines for redox couples measured in the groundwater (e.g. $\text{SO}_4/\text{H}_2\text{S}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$). Eh values observed in several zones for boreholes 11, 21 and 53 are sufficiently negative (i.e. plot close to $\text{SO}_4/\text{H}_2\text{S}$ equilibrium stability line) so as to be characterized as SO_4 reducing (Figure 9). However, most Eh values lie closer to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ equilibrium stability line. Chapelle et al. (1996), observed a similar trend in a shallow water table aquifer and suggested that since the reduction of Fe^{3+} is highly electroactive on the platinum electrode, this may bias electrode measured Eh values. Even so, quite a few Eh values reported here are more positive than $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox stability which may indicate NO_3 reducing conditions.

Analyses for both electron acceptor availability (such as DO, NO_3 , SO_4 and Fe^{3+}) and the products of microbial metabolism (NH_3 , HS, Fe^{2+} and CH_4) in the groundwater provide further insight into groundwater redox characterization. For example, depleted SO_4 concentrations and elevated HS concentrations are indicators that SO_4 reduction processes are occurring. The presence of dissolved Fe in the groundwater may indicate the reduction of Fe^{3+} from iron (oxy)hydroxides. Analytical results from the Smithville groundwater suggest that although few decreases in SO_4 concentrations are observed, HS concentrations generally increase with depth suggesting that SO_4 reduction processes are occurring. Sulfate concentrations in solution likely remain high due to the presence of gypsum which is abundant in the Lockport group formations. Thus, the dissolution of gypsum could provide for an

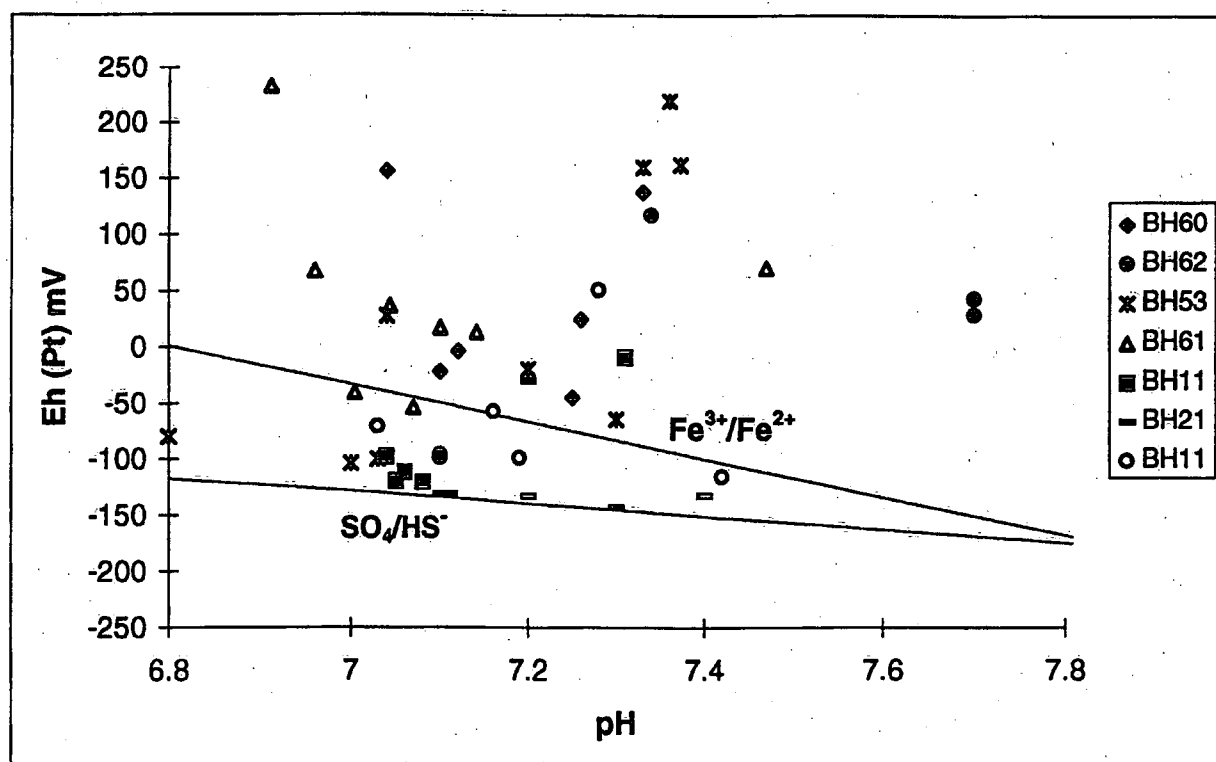


Figure 9: Eh-pH diagram for borehole samples showing equilibrium lines for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{SO}_4^{2-}/\text{HS}^-$ redox couples. Redox equilibria determined by $\text{Eh} = 0.056 (16 - \log(\text{Fe}^{2+}) - 3\text{pH})$ and $\text{Eh} = 0.056 (4.25 + 1/8 \log (\alpha_{2,\text{S(IV)}} * \text{S(VI)} / \alpha_{1,\text{S(-II)}} * \text{S(-II)}) - 9/8\text{pH})$ where S(VI) and S(II) represent total sulfur of valence VI and II calculated using observed concentrations in Westbay boreholes; $\alpha_{2,\text{S(IV)}}$ and $\alpha_{1,\text{S(-II)}}$ are pH dependent dissociation constants (Chapelle et al., 1996).

independent source of SO_4 , compensating for decreases in SO_4 concentrations which occur during SO_4 reduction. Also, dissolved sulfide will readily precipitate from solution with soluble metals (Chapelle et al., 1995, Yager et al., 1997) and the lack of significant HS concentrations in the groundwater does not rule out the presence of SO_4 reduction processes. This latter reaction may occur through the formation of a black precipitate which was observed in the groundwater during pumping and sample collection at many locations. Similar precipitate was analyzed in a previous study conducted in the same rock formation at Niagara Falls, New York, and was found to contain both Fe and S (Noll, 1989). In addition, all boreholes contain high concentrations of Fe at more shallow depths but tend to decrease to low concentrations ($\sim < 0.2 \text{ mg/L}$) as the SO_4 reducing zones are encountered, suggesting that FeS precipitation is occurring.

The distribution of Eh and the byproducts of degradation are contoured along cross section AA' (Figures 10 to 12) to provide a two dimensional representation of the redox zones in the groundwater system. Contours are shaped to represent possible zones of fracture network connections although specific correlation to zones of high transmissivity has not yet been conducted. However, transmissivity is found to be closely linked to the location of the geological units (Lapcevic et al., 1995). For example, the lower Vinemount unit (Vinemount 1; Figures 10 - 12) is reported to contain very few fractures and hydraulic testing suggests that a low zone of permeability exists. In contrast, 77% of the fractures measured are located within the Eramosa unit and the remainder in the Gasport and Goat Island members (Lapcevic et al., 1995). The Rochester formation, which immediately underlies the Lockport formation, is considered to be intact and impermeable with hydraulic conductivities ranging between 10^{-8} m/s and 10^{-6} m/s (Golders Associates, 1995).

Highly reducing areas ($\text{Eh} < -100 \text{ mV}$) are observed at lower depth zones in most boreholes (11, 12, 21 and 53) at approximately 145 to 170 m.a.s.l. in the Goat Island and Gasport members (Figure 10). Reducing conditions are also observed at the lowest depths of the Eramosa member (170 to 177 m.a.s.l.). More aerobic conditions (-8 to 233 mV) are observed just below the ground surface and in the upper elevations of the Eramosa units at elevations between 177 - 195 m.a.s.l. (Figure 10). Slightly higher Eh values (-44 to 71 mV) are observed in the Rochester formation at approximately 154 m.a.s.l. in borehole 62 and at approximately 137 - 155 m.a.s.l. in borehole 61 (Figure 10).

The elevated values of Eh generally observed in the shallowest intervals implies that freshly recharged groundwater is migrating along the contact between the overburden and the bedrock.

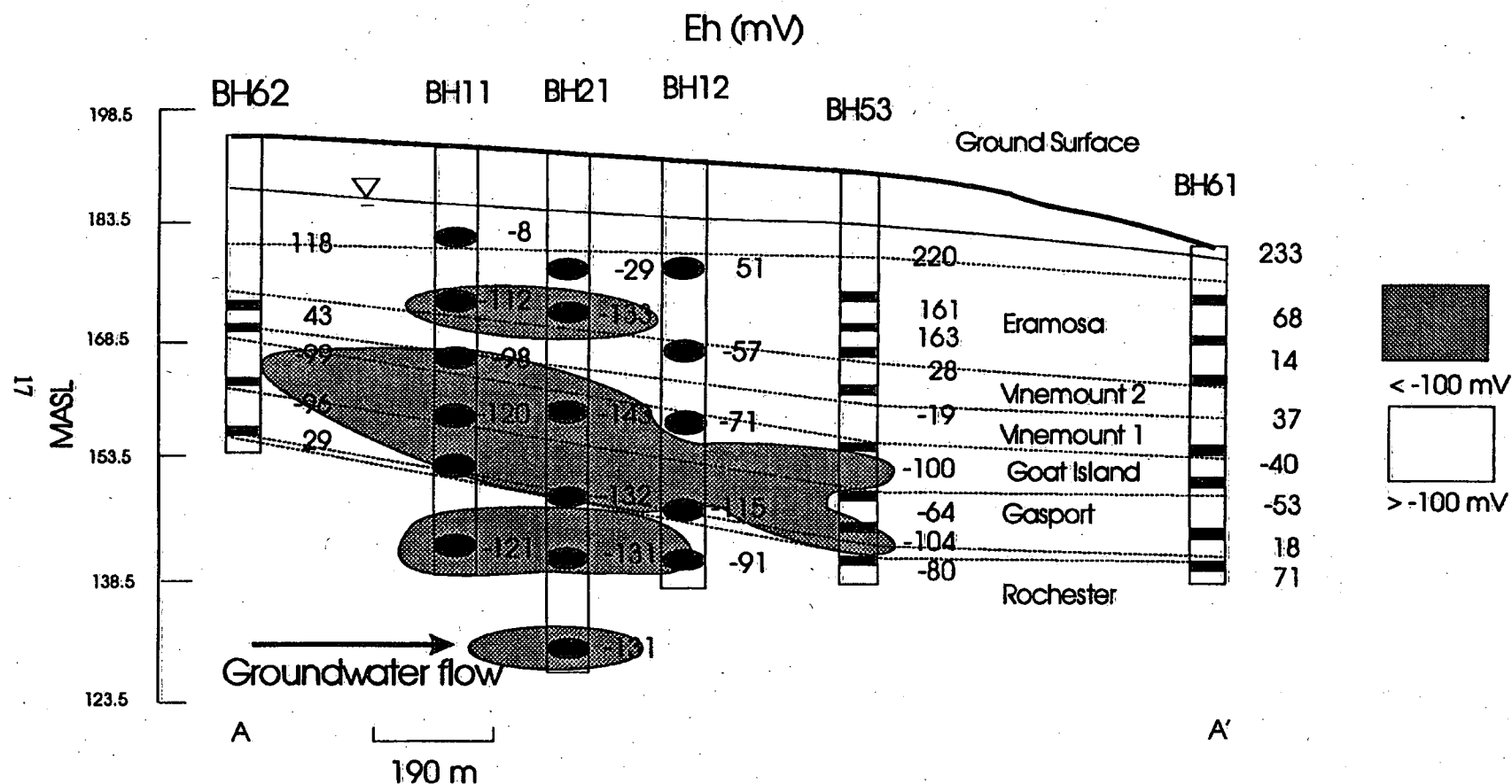


Figure 10: Cross section (AA') showing distribution of Eh values in the direction of groundwater flow. Dark shaded rectangles indicate location of zones sample in boreholes 62, 53 and 61. Shaded ovals indicate center of well screens for boreholes 11, 21 and 12.

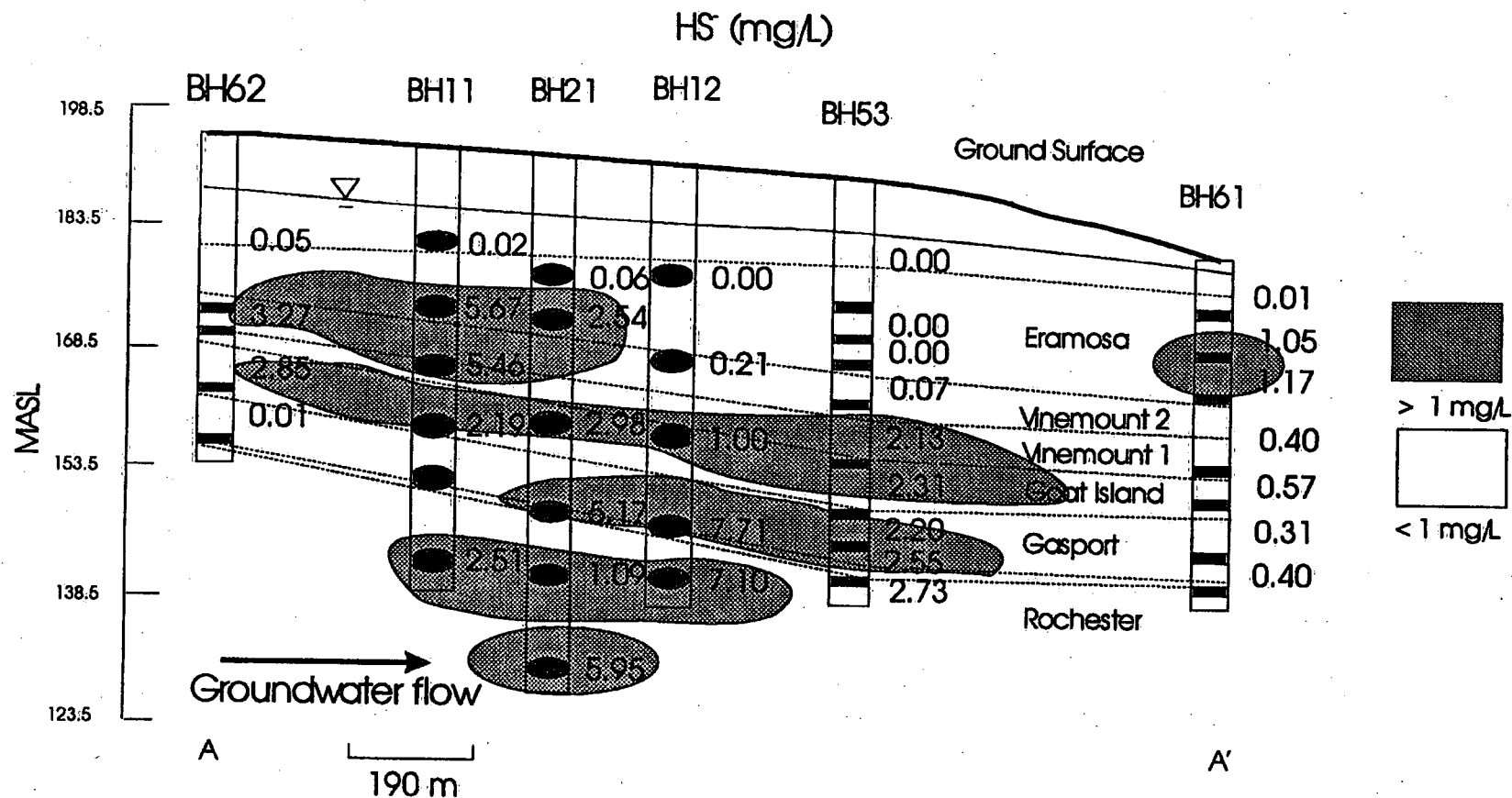


Figure 11: Cross section (AA') showing distribution of HS concentrations in the direction of groundwater flow. Dark shaded rectangles indicate location of zones sampled in boreholes 62, 53 and 61. Shaded ovals indicate center of well screens for boreholes 11, 21 and 12.

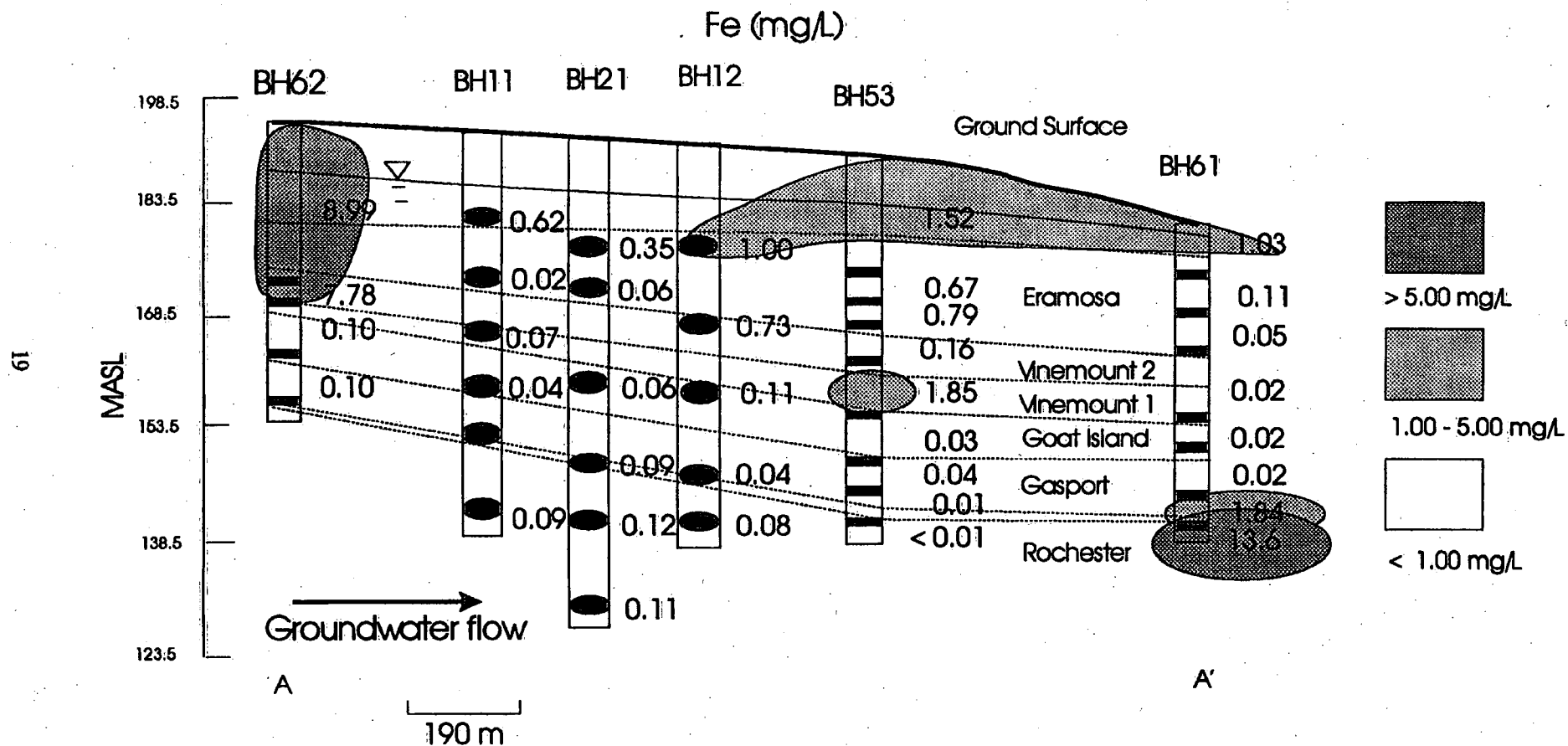


Figure 12: Cross section (AA') showing distribution of Fe concentrations in the direction of groundwater flow. Dark shaded rectangles indicate location of zones sampled in boreholes 62, 53 and 61. Shaded ovals indicate center of well screens for boreholes 11, 21 and 12.

Although a highly permeable basal gravel is present in the overburden, continuity and the degree of groundwater flow in this unit is unknown. In areas where higher Eh conditions persist with depth (boreholes 53, 61 and 62), there is likely considerable vertical interaction between the groundwater in the basal gravel unit and the fracture system in the Eramosa.

The strongly reducing conditions observed in those boreholes closer to the contaminant source (12, 21 and 53) cannot be directly attributed to the contamination, as the location of the boreholes is such that considerable lateral migration of the observed contaminant plume would be required. Thus, the observed low Eh values in these boreholes suggests that there are local groundwater flow conditions in which little interaction between the basal gravel in the overburden and the upper Eramosa takes place.

Dissolved HS concentrations are elevated in areas of low Eh values (Figure 11). Zones where HS concentrations are greater than 1 mg/L (~160 to 170 m.a.s.l. and ~130 to 155 m.a.s.l. in boreholes 11 and 12, 21 respectively) are roughly observed in the same locations (formation members) of lowest Eh values. In contrast, Fe concentrations are highest (>1 mg/L) near the surface (~175 m.a.s.l. and above) and in the Rochester formation (~135 to 145 m.a.s.l.) at borehole 61 (Figure 12). The high Fe concentrations in the Rochester formation correspond to relatively high Eh values and low HS concentrations. This may be attributed to remnant drill water which has yet to flush from the interval.

Should water used during drilling in the summer of 1996 still exist within the formation, it could impose a more aerobic nature in localized areas. Generally, when oxygen is introduced into a reducing environment, it is consumed by reactions with reduced substances within the system. However, oxygen must first diffuse into the surrounding environment. Equilibrium time calculations, based on the free water diffusion coefficient for dissolved oxygen ($2.1 \times 10^{-9} \text{ m}^2/\text{s}$ at 25°C), can be made using a two dimensional radial diffusion model, RADIF2 (Novakowski and van der Kamp, 1996). Assuming diffusion occurs in the x, y plane only, hydraulic conductivity is negligible, and the porosity of the shale is approximately 5%, a conservative estimate of 2.5 to 3 years is required for the dissolved oxygen in a volume (~18 L) of drill water to diffuse into the shaley formation. This time frame may be somewhat lengthy as it does not include the diffusion of reducing substances into the borehole which will further decrease oxygen concentrations. Further stable isotope analyses (^{18}O , ^3H and ^2H) of the groundwater in these zones will aid in the determination of the existence of drill water.

In contrast, borehole 53, constructed one year earlier than the other Westbay boreholes, exhibits relatively low Eh values (-80 mV) and Ca, Na, K and Cl concentrations are one to two orders of

magnitude higher than that of the other Westbay boreholes. This suggests that the drill water in this zone is already in equilibrium with the surrounding formation waters, likely due to higher localized permeability. Transmissivities measured at these elevations were $10^{-6.5}$ m²/s in borehole 53 in comparison to 10^{-8} m²/s measured in boreholes 61 and 62.

SUMMARY

The inorganic geochemistry observed at the Smithville site implies that at approximately 10 to 20 meters below the ground surface, redox conditions are post-oxic and iron reducing (low DO and high Fe concentrations in solution). The elevated values of Eh generally observed in the shallowest intervals implies that freshly recharged groundwater is migrating along the contact between the overburden and the bedrock. Increases in HS concentrations from microbial metabolism corresponding to observed reductions in Eh values and Fe concentrations suggests that geochemical conditions change from Fe to SO₄ reducing at elevations of approximately 130 to 170 m.a.s.l. The low Eh values observed in boreholes 11, 12 and 21 (~175 m.a.s.l) suggest that there are local groundwater flow conditions in which little interaction between the basal gravel in the overburden and the upper Eramosa takes place. In boreholes 60, 61 and 62, conditions in the Rochester formation gradually become more anaerobic. This may be a reflection of the existence drill water at depth.

FUTURE WORK

A sampling session is planned for the summer/fall of 1997. In this session improved techniques will be utilized to obtain representative samples:

1. Pumped samples will be obtained in Westbay boreholes to offer a comparison with samples collected using the Westbay sampling device.
2. Attempts will be made to analyze samples for NO₃ using lower detection limits so that the NO₃/NH₃ redox couple is represented
3. The Winkler titration method (or similar) will be used to obtain representative DO measurements in the field.

4. Analyses will be completed for stable isotopes (especially ^{18}O , ^3H and ^2H) to determine the possible presence of meteoric water within the fracture network.
5. Geochemical speciation modelling will be performed to determine what mineral phases may be in equilibrium with the groundwater and how this varies with depth and along the groundwater flow path.

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APPENDIX I

The Westbay Sampling Device

A schematic representation of the Westbay sampling device is presented in figure A1. Sampling containers are connected in sequence to the sampling probe. The sampling probe contains a transducer which can measure the pressure and temperature of the formation waters.

The sampling containers are rinsed with DI water and air is evacuated with a hand held pump or a peristaltic pump prior to lowering into the borehole. The device locates sampling ports by a magnetic collar which sends a signal to the CPU signaling the user of its location. Once the device is positioned on the sampling port, the mechanical arm is released to properly position the sampling valve against the borehole casing. The sampling valve is positioned such that it samples formation waters located outside of the borehole casing, thereby eliminating the need to purge the borehole of standing water. Once the sampling valve is opened, the difference in the sampling chamber pressures and the surrounding formation pressures causes water to flow into the sampling chambers via the sampling valve. The sample chamber is full when the pressures inside the chamber is equal to the formation pressures. The valve is then closed, the mechanical arm retracted and the sample brought to surface for analyses.

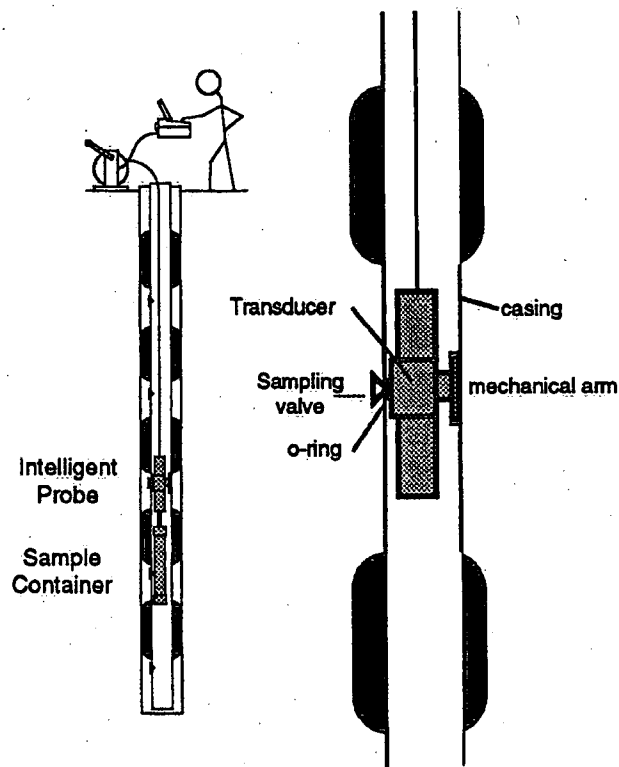


Figure IA: Schematic of the Westbay sampling device.

APPENDIX II

Table IIA: Field measured parameters for geochemical analyses of Westbay boreholes.

Date	Sample	depth bct* (m)	Bottom zone MASL	Top zone MASL	pH	Temp (°C)	Corrected Eh (mV)	Alkalinity (as mg/L CaCO ₃)	D.O. (mg/L)	Conductivity (uS)
2/7/97	BH60-15	15	183.11	197.04	7.04		157	405	2.5	2200??
2/17/97	BH60-18		175.65	182.37	7.33	8.00	139	262	1.5	1223
2/18/97	BH60-27	27	168.19	174.91	7.10	10.00	-21	250	1	4610
2/18/97	BH60-36	36	159.90	167.44	7.12	9.13	-3	285	2	1521
2/18/97	BH60-46	46	156.58	159.15	7.26	9.62	25	310	2.5	2570
2/18/97	BH60-50	50	153.02	155.84	7.25	9.55	-44	310	2.5	3460
2/19/97	BH62-23	23	175.01	195.45	7.34	9.16	118	263	>1	4880
2/19/97	BH62-26	26	171.30	173.44	7.70	8.89	43	208	1	3090
2/19/97	BH62-30.5	30.5	163.88	170.56	7.10	9.37	-99	221	1	2910
2/19/97	BH62-39.5	39.5	155.23	163.14	7.10	9.40	-96	212	1	2930
2/19/97	BH62-50	50	151.36	154.49	7.70	8.71	29	216	>1	
2/7/97	BH53-16.5	16.5	176.45	191.75	7.36		220	420	2	3140??
2/12/97	BH53-19.5	19.5	173.93	175.69	7.33	8.87	161	275	1.5	1408
2/12/97	BH53-22.5	22.5	167.64	173.18	7.37	9.70	163	173	2.5	1512
2/12/97	BH53-30	30	162.61	166.89	7.04	8.44	28	295	2.5	1830
2/12/97	BH53-36	36	157.58	161.85	7.20	9.27	-19	206	1.5	7380
2/12/97	BH53-42	42	151.29	156.82	7.03	9.30	-100	220	1.5	3810
2/12/97	BH53-49.5	49.5	146.26	150.53	7.30	10.00	-64	213	2.5	4230
2/12/97	BH53-55.5	55.5	142.48	145.50	7.00	10.00	-104	205	3.5	5190
2/12/97	BH53-60	60	138.96	141.73	6.80	10.00	-80	161	2	Over Range
2/8/97	BH61-7	7	175.03	182.24	6.91		233	348	4	2480??
2/8/97	BH61-10	10	170.12	174.29	6.96	10.38	68	268	2	2160??
2/8/97	BH61-16	16	165.20	169.38	7.14		14	303	2.5	870??
2/8/97	BH61-22	22	155.37	164.46	7.04	10.60	37	253	5.5	1912??
2/12/97	BH61-34	34	151.68	154.63	7.00		-40	240	2.5	3250
2/12/97	BH61-37.5	37.5	145.54	150.95	7.07	9.51	-53	218	3.5	3330
2/12/27	BH61-46	46	141.85	144.80	7.10		18	226	2.5	3350
2/12/27	BH61-51	51	138.41	141.12	7.47		71	177	2.5	4600

*refers to below casing top

Table IIB: Inorganic geochemical analyses for Westbay boreholes: Cations, Ammonium and Dissolved Organic Content

Sample	depth bct* (m)	Bottom Zone MASL	Top Zone MASL	Al (mg/L)	Fe (mg/L)	Ca (mg/L)	Mg (mg/L)	Mn (mg/L)	Na (mg/L)	K (mg/L)	NH ₃ -N (mg/L)	DOC (mg/L)
BH60-15	15	183.11	197.04	0.03	12.40	318.00	511.00	0.30	143.00	8.21	0.29	5.52
BH60-27	27	168.19	174.91	0.00	0.17	282.00	148.00	0.07	108.00	7.09	0.42	5.77
BH60-36	36	159.90	167.44	0.00	0.54	148.00	121.00	0.04	47.10	5.03	0.00	13.60
BH60-46	46	156.58	159.15	0.01	2.84	443.00	128.00	0.05	46.90	3.43	0.00	9.53
BH60-50	50	153.02	155.84	0.00	0.24	506.00	137.00	0.08	187.00	17.70	0.85	15.20
BH62-23	23	175.01	195.45	0.01	8.99	428.00	586.00	0.25	166.00	5.70	0.00	5.30
BH62-26	26	171.30	173.44	0.02	7.78	510.00	185.00	0.26	89.30	13.30		
BH62-30.5	31	163.88	170.56	0.00	0.10	573.00	138.00	0.06	45.50	14.90	1.12	2.68
BH62-39.5	40	155.23	163.14	0.01	0.10	554.00	123.00	0.07	37.40	11.90	0.96	2.39
BH62-50	50	151.36	154.49									
BH53-16.5	17	176.45	191.75	0.00	1.52	278.00	482.00	0.27	150.00	9.81	0.00	5.68
BH53-19.5	20	173.93	175.69	0.00	0.67	219.00	84.00	0.03	36.00	2.90	0.04	4.18
BH53-22.5	23	167.64	173.18	0.00	0.79	159.00	87.40	0.04	42.90	3.28	0.05	4.42
BH53-30	30	162.61	166.89	0.00	0.16	263.00	114.00	0.03	49.90	4.63	0.08	4.59
BH53-36	36	157.58	161.85	0.00	1.85	774.00	224.00	0.20	686.00	37.60	2.40	9.50
BH53-42	42	151.29	156.82	0.00	0.03	573.00	163.00	0.03	151.00	29.30	1.61	5.04
BH53-49.5	50	146.26	150.53	0.00	0.04	605.00	162.00	0.03	223.00	22.00	1.32	4.75
BH53-55.5	56	142.48	145.50	0.00	0.01	676.00	174.00	0.02	449.00	31.90	2.17	3.73
BH53-60	60	138.96	141.73	0.00	0.00	2890.00	1170.00	0.20	7630.00	155.00	18.50	7.06
BH61-7	7	175.03	182.24	0.00	1.03	228.00	270.00	0.11	93.70	5.53	0.04	5.50
BH61-10	10	170.12	174.29	0.00	0.11	421.00	102.00	0.04	53.70	5.98	0.22	7.30
BH61-16	16	165.20	169.38	0.00	0.05	410.00	102.00	0.04	52.70	3.82	0.21	7.95
BH61-22	22	155.37	164.46	0.00	0.02	295.00	113.00	0.02	51.40	2.98	0.16	5.14
BH61-34	34	151.68	154.63	0.00	0.02	591.00	116.00	0.03	96.10	5.64	0.41	9.90
BH61-37.5	38	145.54	150.95	0.00	0.02	511.00	116.00	0.05	110.00	7.85	0.41	11.10
BH61-46	46	141.85	144.80	0.00	1.84	592.00	112.00	0.10	119.00	9.40	0.41	9.24
BH61-51	51	138.41	141.12	0.02	13.60	582.00	115.00	0.12	257.00	23.60	1.42	7.26

* below casing top

Table IIC: Inorganic geochemical analyses for Westbay boreholes: Anions.

Sample	depth bct* (m)	Bottom Zone MASL	Top Zone MASL	Sulfide (mg/L)	HS (mg/L)	Cl (mg/L)	Br (mg/L)	NO ₃ (mg/L)	PO ₄ -P (mg/L)	SO ₄ (mg/L)
BH60-15	15	183.11	197.04	0.012	0.01	16.5	<DL	<DL	<DL	2690
BH60-27	27	168.19	174.91	1.68	1.73	229	<DL	<DL	<DL	979
BH60-36	36	159.90	167.44	0.403	0.42	32.1	<DL	<DL	<DL	519
BH60-46	46	156.58	159.15	0.109	0.11	18.5	<DL	<DL	<DL	1450
BH60-50	50	153.02	155.84	0.115	0.12	298	<DL	<DL	<DL	1580
BH62-23	23	175.01	195.45	0.048	0.05	39.8	<DL	<DL	<DL	3050
BH62-26	26	171.30	173.44							
BH62-30.5	30.5	163.88	170.56	3.18	3.28	28.9	<DL	<DL	<DL	1690
BH62-39.5	39.5	155.23	163.14	2.77	2.85	31.3	<DL	<DL	<DL	1650
BH62-50	50	151.36	154.49					<DL	<DL	
BH53-16.5	16.5	176.45	191.75	0.004	0.00	122	<DL	<DL	<DL	2240
BH53-19.5	19.5	173.93	175.69	0.004	0.00	8.8	<DL	<DL	<DL	701
BH53-22.5	22.5	167.64	173.18	0.002	0.00	23.5	<DL	<DL	<DL	520
BH53-30	30	162.61	166.89	0.065	0.07	35.4	<DL	<DL	<DL	899
BH53-36	36	157.58	161.85	2.07	2.13	1710	17	<DL	<DL	1830
BH53-42	42	151.29	156.82	2.24	2.31	281	<DL	<DL	<DL	1850
BH53-49.5	49.5	146.26	150.53	2.14	2.20	475	<DL	<DL	<DL	1840
BH53-55.5	55.5	142.48	145.50	2.48	2.55	1050	10.7	<DL	<DL	1840
BH53-60	60	138.96	141.73	2.65	2.73	19900	218	<DL	<DL	1900
BH61-7	7	175.03	182.24	0.005	0.01	42.4	<DL	<DL	<DL	1440
BH61-10	10	170.12	174.29	1.02	1.05	50.3	<DL	<DL	<DL	1280
BH61-16	16	165.20	169.38	1.14	1.17	52.4	<DL	<DL	<DL	1220
BH61-22	22	155.37	164.46	0.389	0.40	45.1	<DL	<DL	<DL	909
BH61-34	34	151.68	154.63	0.556	0.57	127	<DL	<DL	<DL	1660
BH61-37.5	37.5	145.54	150.95	0.304	0.31	208	<DL	<DL	<DL	1460
BH61-46	46	141.85	144.80	0.386	0.40	198	<DL	<DL	<DL	1710
BH61-51	51	138.41	141.12			440	<DL	<DL	<DL	1710

* below casing top

Table IID: Field measured parameters for geochemical analyses of multilevel piezometers.

Date	Sample	depth bct* (m)	Bt. of Screen MASL	Top of Screen MASL	pH	Temp (°C)	Corrected Eh (mV)	Alkalinity (as mg/L CaCO ₃)	D.O. (mg/L)	Conductivity (uS)
2/26/97	BH11a	53.8	139.8	145.6	7.08	9.2	-121	350	1.5	3590
2/26/97	BH11c	36.6	157	160.1	7.05	9	-120	217	0.29	3030
2/26/97	BH11d	27.1	166.5	168.4	7.04	8.8	-98	250	0.57	2050
2/26/97	BH11e	21.6	172	176.8	7.06	9.3	-112	227	0.5	1234
2/26/97	BH11f	12	181.6	184.7	7.31	8.7	-8	261	0.25	766
3/5/97	BH21a	66	128.2	131.2	7.11	7.9	-131	185	0.29	1790
3/4/97	BH21b	54.1	140.4	143.5	7.1	8	-131	256	0.29	9360
3/4/97	BH21c	46	148.5	151.6	7.4	7.6	-132	198	0.27	7380
3/5/97	BH21d	36.2	158.3	161.6	7.3	7.6	-143	250	0.42	1743
3/4/97	BH21e	24.4	170.1	173.6	7.2	5.5	-133	246	0.07	2730
3/4/97	BH21f	18	180.2	176.5	7.2	6.3	-29	291	1.01	901
2/24/97	BH12a	54	137.3	142.6	7.19	9	-99	220	0.3	18610
2/24/97	BH12b	45.4	145.9	152.8	7.42	7.6	-115	233	0.31	5220
2/25/97	BH12c	36.4	154.9	160.2	7.03	9.5	-71	259	1.98	3260
2/25/97	BH12d	24.8	166.5	171.4	7.16	10.1	-57	300	0.85	1004
2/25/97	BH12e	15.1	176.2	180.3	7.28	9.5	51	306	0.3	1184

* below casing top

Table III: Inorganic geochemical analyses for multilevel piezometers: Cations, ammonium and dissolved organic carbon

Sample	depth bct* (m)	Bt. of Screen MASL	Top of Screen MASL	Al (mg/L)	Fe (mg/L)	Ca (mg/L)	Mg (mg/L)	Mn (mg/L)	Na (mg/L)	K (mg/L)	Sr (mg/L)	NH ₃ -N (mg/L)	DOC (mg/L)
BH11a	53.8	139.8	145.6	0.31	0.089	692	148	0.077	245	16.5	10.4	1.55	2.8
BH11c	36.6	157	160.1	0.39	0.04	622	140	0.06	161	13	9.2	0.733	2.7
BH11d	27.1	166.5	168.4	0.26	0.068	449	88.5	0.052	29.5	5.8	6.47	0.795	2.5
BH11e	21.6	172	176.8	0.2	0.016	354	85.4	0.048	20.3	4.4	6.05	0.305	2.8
BH11f	12	181.6	184.7	0	0.622	96.5	84.5	0.015	43.2	0	2.76	0.273	4
BH21a	66	128.2	131.2	0.08	0.11	4700	4180	0.425	2170	194	83.5	23.5	0.1
BH21b	54.1	140.4	143.5	0.48	0.122	3910	474	0.095	2480	74.8	23.4	8.01	0.5
BH21c	46	148.5	151.6	0.47	0.086	863	231	0.066	1080	38.2	13.5	4.46	0.7
BH21d	36.2	158.3	161.6	0.41	0.056	528	106	0.036	196	13.5	7.72	1.78	3.4
BH21e	24.4	170.1	173.6	0.14	0.056	463	88.9	0.035	93.2	3.5	7.1	0.485	4.3
BH21f	18	180.2	176.5	0	3.51	123	116	0.028	43	2.3	2.59	0.485	8.3
BH12a	54	137.3	142.6	0.5	0.083	1190	363	0.128	2370	65.9	19.3	7.5	0.3
BH12b	45.4	145.9	152.8	0.42	0.04	741	171	0.066	526	23.5	11.2	2.55	0.7
BH12c	36.4	154.9	160.2	0.6	0.107	651	118	0.069	103	8.9	8.77	1.39	2.3
BH12d	24.8	166.5	171.4	0.07	0.728	180	126	0.031	52.9	2.9	3.83	0.394	3.6
BH12e	15.1	176.2	180.3	0	0.955	97.5	125	0.033	52.8	2.2	2.79	0.323	3.7

* below casing top

Table IIF: Inorganic geochemical analyses for multilevel piezometers: Anions.

Date	Sample	depth bct (m)	Bt. of Screen MASL	Top of Screen MASL	HS (mg/L)	Cl (mg/L)	Br (mg/L)	NO ₃ (mg/L)	PO ₄ -P (mg/L)	SO ₄ (mg/L)
2/26/97	BH11a	53.8	139.8	145.6	2.51	555	6	0.014	0.0105	1610
2/26/97	BH11c	36.6	157.0	160.1	2.19	156	1.71	<0.005	0.0132	1630
2/26/97	BH11d	27.1	166.5	168.4	5.46	32.1	0.47	<0.005	0.0114	1160
2/26/97	BH11e	21.6	172.0	176.8	5.67	15.6	<D.L.	<0.005	0.0126	883
2/26/97	BH11f	12	181.6	184.7	0.02	28.6	<D.L.	<0.005	0.012	299
3/5/97	BH21a	66	128.2	131.2	5.94	28890	>21.5	N/A	0.3942	1650
3/4/97	BH21b	54.1	140.4	143.5	1.09	6010	>21.5	N/A	0.0152	1820
3/4/97	BH21c	46	148.5	151.6	5.17	2350	>21.5	N/A	0.0074	1700
3/5/97	BH21d	36.2	158.3	161.6	2.98	333	4.21	N/A	0.0037	1390
3/4/97	BH21e	24.4	170.1	173.6	2.54	140	1.58	N/A	0.0104	1080
3/4/97	BH21f	18	180.2	176.5	0.06	9.53	<D.L.	N/A	0.0232	470
2/24/97	BH12a	54	137.3	142.6	7.10	5110	>21.5	<0.005	0.02	1790
2/24/97	BH12b	45.4	145.9	152.8	7.70	1190	<D.L.	<0.005	0.0098	1730
2/25/97	BH12c	36.4	154.9	160.2	1.00	334	<D.L.	<0.005	0.0113	1570
2/25/97	BH12d	24.8	166.5	171.4	0.21	24.5	0.27	<0.005	0.0199	665
2/25/97	BH12e	15.1	176.2	180.3	0.00	19.7	<D.L.	<0.005	0.0232	478

* below casing top

APPENDIX III

Table III: Analyses for duplicates and equipment blanks A) Westbay boreholes and B) multilevels.

A)

	BH60-15 (mg/L)	BH60-15(2) (mg/L)	BH60-36 (mg/L)	BH60-36(2) (mg/L)	BH62-39.5 (mg/L)	BH62-39.5(2) (mg/L)	BH61-34 (mg/L)	BH61-34(2) (mg/L)	Equipment Blank (mg/L)
Cations									
Al	0.033	0.027	0.002	0.004	0.006	<D.L.	0.001	<D.L.	0.001
Fe	12.4	14.2	0.535	1.81	0.098	0.122	0.022	0.029	0.01
Ca	316	319	148	151	554	557	591	592	0.112
Mg	511	516	121	122	123	123	116	116	0.04
Mn	0.304	0.318	0.042	0.041	0.068	0.063	0.031	0.048	0.001
Na	143	143	47.1	46.2	37.4	37.9	96.7	96.7	<D.L.
K	8.21	7.38	5.03	4.74	11.9	12.4	5.64	11.2	0.046
NH ₃	0.29	0.28	<D.L.	<D.L.	0.96	0.94	0.41	0.4	<D.L.
DOC	5.52	5.9	13.6	8.66	2.39	2.12	9.9	9.36	0.96
Anions									
HS ⁻	0.01	0.01	0.42	0.30	2.85	0.02	0.57	0.31	
Cl ⁻	16.5	7.48	32.1	29.1	31.3	31.2	127	130	0.28
Br ⁻	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.
NO ₃ ⁻	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.
PO ₄ ³⁻	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.
SO ₄ ²⁻	2690	2740	979	541	1650	1630	1660	1600	1.97

B)

	BH11D (mg/L)	BH11D(2) (mg/L)	BH21E (mg/L)	BH21E(2) (mg/L)	BH12D (mg/L)	BH12D(2) (mg/L)	Acid Blank (mg/L)
Cations							
Al	0.26	0.33	0.14	0.41	0.07	0.05	<0.05
Fe	0.068	0.08	0.056	0.058	0.728	0.74	0.005
Ca	449	473	463	470	180	182	<1.0
Mg	88.5	92.1	88.9	91.5	126	125	<1.0
Mn	0.052	0.056	0.035	0.038	0.031	0.031	<0.002
Na	29.5	30.9	93.2	101	52.9	51.6	<2.0
K	5.8	6	3.5	4.4	2.9	2.5	<2.0
Sr	6.47	6.7	7.1	7.07	3.83	3.81	0.008
NH ₃	0.495	0.485	0.485	0.45	<D.L.	<D.L.	
DOC	2.5	2.8	3.6	3.6	4.3	4.4	
Anions							
HS ⁻	5.18	5.53	0.00	0.00	0.21	0.40	
Cl ⁻	32.1	30.7	140	35.3	24.5	25.1	
Br ⁻	0.47	0.44	1.58	1.61	0.27	<D.L.	
NO ₃ ⁻	<D.L.	<D.L.	N/A	N/A	<D.L.	<D.L.	
PO ₄ ³⁻	0.0114	0.0101	0.0104	0.0101	0.0199	0.0195	
SO ₄ ²⁻	1160	1200	1080	1120	665	1540	

APPENDIX IV

Table IV: Charge balance calculations

Cations	Molecular Mass (g)	Charge	Sample (meq)				
			BH60-15	BH60-27	BH60-36	BH60-46	BH60-50
Al	26.98154	3	3.67E-06	0	2.22E-07	1.33E-06	0
Fe	55.847	2	0.000444	6.09E-06	1.92E-05	0.000102	8.74E-06
Ca	40.08	2	0.015768	0.014072	0.007385	0.022106	0.02525
Mg	24.305	2	0.042049	0.012014	0.009957	0.010533	0.011273
Mn	54.938	2	1.11E-05	2.66E-06	1.53E-06	1.75E-06	2.88E-06
Na	22.98977	1	0.00622	0.004698	0.002049	0.00204	0.008134
K	39.0983	1	0.00021	0.000181	0.000129	8.77E-05	0.000453
Sum of Cations			0.064706	0.030974	0.01954	0.034871	0.045121
Anions							
HS ⁻	33.0679	-1	-3.7E-07	-5.2E-05	-1.3E-05	-3.4E-06	-3.6E-06
Cl ⁻	35.453	-1	-0.00047	-0.00646	-0.00091	-0.00052	-0.00841
Br ⁻	79.904	-1					
NO ₃ ⁻	62.0049	-1					
PO ₄ ³⁻	94.97136	-3					
SO ₄ ²⁻	96.0576	-2	-0.05601	-0.02038	-0.01081	-0.03019	-0.0329
CO ₃ ⁻	100.0882	-2	-0.00809	-0.005	-0.00569	-0.00619	-0.00619
Sum of Anions			-0.06457	-0.03189	-0.01742	-0.03691	-0.0475
Charge Imbalance			0.11	-1.46	5.74	-2.84	-2.57

Cations	Molecular Mass (g)	Charge	Sample (meq)			
			BH62-23	BH62-26	BH62-30.5	BH62-39.5
Al	26.98154	3	1.11E-06	2.11E-06	0	6.67E-07
Fe	55.847	2	0.000322	0.000279	3.65E-06	3.51E-06
Ca	40.08	2	0.021357	0.025449	0.028593	0.027645
Mg	24.305	2	0.048221	0.015223	0.011356	0.010121
Mn	54.938	2	8.99E-06	9.28E-06	2.22E-06	2.48E-06
Na	22.98977	1	0.007221	0.003884	0.001979	0.001627
K	39.0983	1	0.000146	0.00034	0.000381	0.000304
Sum of Cations			0.077276	0.045187	0.042315	0.039704
Anions						
HS ⁻	33.0679	-1	-1.5E-06		-9.9E-05	-8.6E-05
Cl ⁻	35.453	-1	-0.00112		-0.00082	-0.00088
Br ⁻	79.904	-1				
NO ₃ ⁻	62.0049	-1				
PO ₄ ³⁻	94.97136	-3				
SO ₄ ²⁻	96.0576	-2	-0.0635		-0.03519	-0.03435
CO ₃ ⁻	100.0882	-2	-0.00526	-0.00416	-0.00442	-0.00424
Sum of Anions			-0.06988		-0.04052	-0.03956
Charge Imbalance			5.02		2.17	0.18

Table IV: (con't)

Cations	Molecular Mass (g)	Charge	Sample (meq)									
			BH53-16.5	BH53-19.5	BH53-22.5	BH53-30	BH53-38	BH53-42	BH53-49.5	BH53-55.5	BH53-60	
Al	26.98154	3	3.34E-07	0	1.11E-07	0	3.34E-07	0	1.11E-07	0	0	
Fe	55.847	2	5.44E-05	2.4E-05	2.62E-05	5.73E-06	6.63E-05	9.31E-07	1.29E-06	5.01E-07	0	
Ca	40.08	2	0.013872	0.010928	0.007934	0.013124	0.038623	0.028593	0.03019	0.033733	0.144212	
Mg	24.305	2	0.039663	0.006912	0.007192	0.009381	0.018432	0.013413	0.013331	0.014318	0.096276	
Mn	54.938	2	9.97E-06	1.13E-06	1.57E-06	1.24E-06	7.24E-06	1.2E-06	1.02E-06	6.92E-07	7.21E-06	
Na	22.98977	1	3.12E-05	0.001566	0.001866	0.002171	0.029839	0.006568	0.0097	0.01953	0.331887	
K	39.0983	1	0.000251	7.42E-05	8.39E-05	0.000118	0.000962	0.000749	0.000563	0.000816	0.003964	
Sum of Cations			0.053882	0.019506	0.017106	0.0248	0.08793	0.049325	0.053785	0.068398	0.576346	
Anions												
HS ⁻	33.0679	-1	-1.2E-07	-1.2E-07	-6.2E-08	-2E-08	-6.4E-05	-7E-05	-6.7E-05	-7.7E-05	-8.3E-05	
Cl ⁻	35.453	-1	-0.00344	-0.00025	-0.00066	-0.001	-0.04823	-0.00793	-0.0134	-0.02962	-0.56131	
Br ⁻	79.904	-1					-0.00021			-0.00013	-0.00273	
NO ₃ ⁻	62.0049	-1										
PO ₄ ³⁻	94.97136	-3										
SO ₄ ²⁻	96.0576	-2	-0.04664	-0.0146	-0.01083	-0.01872	-0.0381	-0.03852	-0.03831	-0.03831	-0.03956	
CO ₃ ²⁻	100.0882	-2	-0.00839	-0.0055	-0.00346	-0.00589	-0.00412	-0.0044	-0.00426	-0.0041	-0.03319	
Sum of Anions			-0.05847	-0.02034	-0.01495	-0.02561	-0.09073	-0.05091	-0.05603	-0.07223	-0.63687	
Charge Imbalance			4.09	-2.09	6.74	-1.61	-1.57	-1.58	-2.05	-2.73	4.99	
Cations	Molecular Mass (g)	Charge	Sample (meq)									
			BH61-7	BH61-10	BH61-16	BH61-22	BH61-34	BH61-37.5	BH61-46	BH61-51		
Al	26.98154	3	3.34E-07	0	3.34E-07	3.34E-07	1.11E-07	0	4.45E-07	2.67E-06		
Fe	55.847	2	3.69E-05	4.01E-06	1.86E-06	8.59E-07	7.88E-07	6.8E-07	6.59E-05	0.000487		
Ca	40.08	2	0.011377	0.021008	0.020459	0.014721	0.029491	0.025499	0.029541	0.029042		
Mg	24.305	2	0.022218	0.008393	0.008393	0.009298	0.009545	0.009545	0.009216	0.009463		
Mn	54.938	2	3.93E-06	1.38E-06	1.27E-06	8.74E-07	1.13E-06	1.71E-06	3.75E-06	4.48E-06		
Na	22.98977	1	0.004076	0.002336	0.002292	0.002236	0.00418	0.004785	0.005176	0.011179		
K	39.0983	1	0.000141	0.000153	9.77E-05	7.62E-05	0.000144	0.000201	0.00024	0.000604		
Sum of Cations			0.037853	0.031895	0.031246	0.026333	0.043363	0.040032	0.044244	0.050782		
Anions												
HS ⁻	33.0679	-1	-1.6E-07	-3.2E-05	-3.6E-05	-1.2E-05	-1.7E-05	-9.5E-06	-1.2E-05	0		
Cl ⁻	35.453	-1	-0.0012	-0.00142	-0.00148	-0.00127	-0.00358	-0.00587	-0.00558	-0.01241		
Br ⁻	79.904	-1										
NO ₃ ⁻	62.0049	-1										
PO ₄ ³⁻	94.97136	-3										
SO ₄ ²⁻	96.0576	-2	-0.02998	-0.02665	-0.0254	-0.01893	-0.03456	-0.0304	-0.0356	-0.0356		
CO ₃ ²⁻	100.0882	-2	-0.00695	-0.00536	-0.00605	-0.00506	-0.0048	-0.00436	-0.00452	-0.00354		
Sum of Anions			-0.03813	-0.03346	-0.03297	-0.02527	-0.04296	-0.04063	-0.04572	-0.05155		
Charge Imbalance			-0.37	-2.39	-2.68	2.07	0.47	-0.74	-1.64	-0.75		

Table IV: (con't)

Cations	Molecular		Sample (meq)				
	Mass (g)	Charge	BH11a	BH11c	BH11d	BH11e	BH11f
Al	26.98154	3	3.45E-05	4.34E-05	2.89E-05	2.22E-05	0
Fe	55.847	2	3.19E-06	1.43E-06	2.44E-06	5.73E-07	2.23E-05
Ca	40.08	2	0.034531	0.031038	0.022405	0.017665	0.004815
Mg	24.305	2	0.012179	0.01152	0.007282	0.007027	0.006953
Mn	54.938	2	2.8E-06	2.18E-06	1.89E-06	1.75E-06	5.46E-07
Na	22.98977	1	0.010657	0.007003	0.001283	0.000883	0.001879
K	39.0983	1	0.000422	0.000332	0.000148	0.000113	0
Sr	87.62	2	0.000237	0.00021	0.000148	0.000138	6.3E-05
Sum of Cations			0.058066	0.050151	0.0313	0.02585	0.013734
Anions							
HS ⁻	33.0679	-1	-7.59E-05	-6.6E-05	-0.00017	-0.00017	-6E-07
Cl ⁻	35.453	-1	-0.015655	-0.0044	-0.00091	-0.00044	-0.00081
Br ⁻	79.904	-1	-7.51E-05	-0.00214	-5.9E-06	0	0
NO ₃ ⁻	62.0049	-1	-2.26E-07	0	0	0	0
PO ₄ ³⁻	94.97136	-3	-3.32E-07	-4.2E-07	-3.6E-07	-4E-07	-3.8E-07
SO ₄ ²⁻	96.0576	-2	-0.033522	-0.03394	-0.02415	-0.01838	-0.00623
CO ₃ ²⁻	100.0882	-2	-0.006994	-0.00434	-0.005	-0.00454	-0.00522
Sum of Anions			-0.056321	-0.04488	-0.03022	-0.02353	-0.01225
Charge Imbalance			1.53	5.55	1.75	4.69	5.72

Cations	Molecular		Sample (meq)					
	Mass (g)	Charge	BH21a	BH21b	BH21c	BH21d	BH21e	BH21f
Al	26.98154	3	8.89E-06	5.34E-05	5.23E-05	4.56E-05	1.56E-05	0
Fe	55.847	2	3.94E-06	4.37E-06	3.08E-06	2.01E-06	2.01E-06	0.000126
Ca	40.08	2	0.234531	0.19511	0.043064	0.026347	0.023104	0.006138
Mg	24.305	2	0.342316	0.039004	0.019008	0.008722	0.007315	0.009545
Mn	54.938	2	1.55E-05	3.46E-06	2.4E-06	1.31E-06	1.27E-06	1.02E-06
Na	22.98977	1	0.09439	0.107874	0.046977	0.008526	0.004054	0.00187
K	39.0983	1	0.004962	0.001913	0.000977	0.000345	8.95E-05	5.88E-05
Sr	87.62	2	0.001906	0.000534	0.000308	0.000162	0.000162	5.91E-05
Sum of Cations			0.678133	0.344497	0.110393	0.044152	0.034744	0.017798
Anions								
HS ⁻	33.0679	-1	-0.00018	-3.3E-05	-0.00016	-9E-05	-7.7E-05	-1.8E-06
Cl ⁻	35.453	-1	-0.814882	-0.16952	-0.06628	-0.00939	-0.00395	-0.00027
Br ⁻	79.904	-1	-0.000269	0	0	-5.3E-05	-2E-05	0
NO ₃ ⁻	62.0049	-1	0	0	0	0	0	0
PO ₄ ³⁻	94.97136	-3	-1.25E-05	-4.8E-07	-2.3E-07	-1.2E-07	-7.3E-07	-7.3E-07
SO ₄ ²⁻	96.0576	-2	-0.034354	-0.03789	-0.0354	-0.02894	-0.00979	-0.00979
CO ₃ ²⁻	100.0882	-2	-0.003697	-0.00512	-0.00396	-0.005	-0.00492	-0.00581
Sum of Anions			-0.853394	-0.21256	-0.10579	-0.04347	-0.01875	-0.01587
Charge Imbalance			-11.44	23.68	2.13	0.78	29.90	5.72

Table IV: (con't)

Cations	Molecular Mass (g)	Charge	Sample (meq)				
			BH12a	BH12b	BH12c	BH12d	BH21e
Al	26.98154	3	5.56E-05	4.67E-05	6.67E-05	7.78E-06	0
Fe	55.847	2	2.97E-06	1.43E-06	3.83E-06	2.61E-05	3.42E-05
Ca	40.08	2	0.059381	0.036976	0.032485	0.008982	0.004865
Mg	24.305	2	0.02987	0.014071	0.00971	0.010368	0.010286
Mn	54.938	2	4.66E-06	2.4E-06	2.51E-06	1.13E-06	1.2E-06
Na	22.98977	1	0.103089	0.02288	0.00448	0.002301	0.002297
K	39.0983	1	0.001685	0.000601	0.000228	7.42E-05	5.63E-05
Sr	87.62	2	0.000441	0.000256	0.000199	8.74E-05	6.37E-05
Sum of Cations			0.19453	0.074834	0.047174	0.021848	0.017603
Anions							
HS ⁻	33.0679	-1	-0.000215	-0.00023	-3E-05	-6.4E-06	0
Cl ⁻	35.453	-1	-0.144134	-0.03357	-0.00942	-0.00069	-0.00056
Br ⁻	79.904	-1	0	0	0	0	0
NO ₃ ⁻	62.0049	-1	0	0	0	0	0
PO ₄ ³⁻	94.97136	-3	-6.32E-07	-3.1E-07	-3.6E-07	-6.3E-07	-7.3E-07
SO ₄ ²⁻	96.0576	-2	-0.037269	-0.03602	-0.03269	-0.01385	-0.00995
CO ₃ ²⁻	100.0882	-2	-0.004396	-0.00466	-0.00518	-0.00599	-0.00611
Sum of Anions			-0.186015	-0.07447	-0.04732	-0.02054	-0.01662
Charge Imbalance			2.24	0.24	-0.15	3.09	2.86

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