Mobilization and Transport of Arsenic by Landfill Leachates and Contamination of Groundwater at Winthrop, Maine

by

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Field Work Advisors: Profs. M. Stute and J. Simpson

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EXECUTIVE SUMMARY

Groundwater contamination beneath the Winthrop landfill has shown concentrations of arsenic ranging from 19 to 308 parts per billion (ppb) while the Maximum Contaminant Level (MCL) is set at 50 ppb. Although a "pump and treat" system is continuously in operation for the purpose of arsenic decontamination, a plume of arsenic has been detected over a distance of about 200m (see Figure 2) from the landfill to the lake.

The Winthrop Landfill, a Superfund site located in southwest Maine (latitude 44.275, longitude 69.988), is analysed by the Lamont-Doherty Earth Observatory (LDEO) as well as other agencies (including United Technologies Research Center and MacTec Corporation). For monitoring groundwater quality at this site, a number of multi-level wells were installed.

This thesis is based on a research project led by Professors Martin Stute and James Simpson, amongst other scientists from Lamont-Doherty Earth Observatory (LDEO). In January 2001, sulfur hexafluoride (SF_6) and bromide (NaBr) tracers were injected in the wells on the landfill in order to obtain a better understanding of the leachate and groundwater flows; the measurements of SF_6 were performed by LDEO. Also, 300 samples were collected for the analysis of bromide and other anions.

In the summer of 2001, the author, supervised by Prof. Stute, carried out a series of experiments on the collected water samples. The experiment consisted of measuring the bromide (as the tracer), chloride, and sulfate concentrations of the 300 samples obtained from a number of wells and at different depths, by using the ion chromatograph technique.

The objectives of this thesis are to use the experimental results to a) describe the landfill leachate and groundwater flows that are responsible for the mobilization of arsenic in the environment and b) discuss the advantages and disadvantages of the remediation techniques proposed by LDEO and other agencies, as well as some other possibilities for remediation.

The thesis consists of three sections:

1) Groundwater transport and use of tracers.
2) Redox chemistry and microbiology involved in the mobilization of arsenic.
3) A discussion of the advantages and disadvantages of the various remediation techniques

The tracers injected in the wells on the landfill provided a better understanding of the groundwater flow and transport of the leachate solutions responsible for the mobilization of arsenic. The similar patterns of bromide and SF_6 suggest bromide is a conservative tracer. However, adsorption (desorption) mechanisms may occur at deep (shallow) levels based on the tracers ratios. On the basis of the bromide measurements and interpretation of the data, it was possible to determine the direction and rate of the groundwater flows and, therefore, the distribution of the contaminants. The bromide concentrations obtained also indicate the wells where the leachate solution is most influential. The information derived from the tracers was also useful in evaluating the performance of past remediation, and the design and implementation of alternatives.

The reduction/oxidation and microbiological reactions are important processes that determine the release of arsenic; the groundwater transport of the leachate, as a carbon source and electron donor, contributes to these mechanisms. The sulfate measurements obtained from the ion chromatograph suggest sulfate concentrations increase with depth and sulfate reduction is an important mechanism at shallow levels close to the landfill.

Finally, a number of remediation techniques have been proposed in lieu of the current "pump and treat" which has proved to be inefficient. The proposed and potential remediation methods, including physical barriers, oxidation by chemical additives and bioremediation, are evaluated by delineating the advantages and disadvantages of each of them. The appropriate remediation technique to be implemented on the site remains uncertain and more research is required regarding the arsenic cycling rate, the microbiology and the remedial options.

Although the focus of the thesis is on the Winthrop landfill, on a broader perspective, this study shows the substantial effort and the economic consequences involved in cleaning up the environmental impact of old landfills, and demonstrates the long-term environmental effects of landfilling.

From an educational point of view, the thesis highlights an environmental problem that links several disciplines: hydrology, transport, aquatic chemistry, and microbiology, which are all closely interconnected in this project. These are disciplines in which the author was introduced during her master's program (isotope hydrology, aquatic chemistry, mineralogy, environmental microbiology, transport and chemical rate phenomena) and which have been applied in this thesis.

ACKNOWLEDGEMENTS

The author gratefully thanks the Lamont-Doherty Earth Observatory, The Earth Engineering Center, and the Department of Earth and Environmental Engineering, especially Professors M. Stute, P. Schlosser and J. Simpson for offering the opportunity to work on this project and Professors N. J. Themelis and T. Yegulalp whose contributions were most valuable in the completion of this thesis. The author also acknowledges Professor Anid of Manhattan College for her input.

Elisabeth Law-wai
New York City, December 2001

CONTENTS

INTRODUCTION

Arsenic contamination is a worldwide problem that can occur naturally in bedrocks and sediments such as iron and sulfide-based geology or as a result of various anthropogenic activities such as industrial effluent of arsenic-containing products, and leaching of tailings and sulfide minerals. Known as a carcinogen, arsenic ingested poses risks of lung and skin cancer, which currently affects millions of people in countries like Bangladesh who have been drinking water contaminated with elevated concentrations of arsenic over the standard limit of 50 parts per billion (ppb). A number of mechanisms, physical and biochemical, such as leaching, adsorption/desorption and reduction/oxidation processes promote the release of arsenic into the environment-soil, surface water and groundwater-depending on the specification of the area such as the geology, type of sediments, proximity to mining activities or landfills. In naturally occurring arsenic environments, microorganisms play an important role in the catalysis of reduction/oxidation reactions responsible for the mobilization of arsenic. In microbe-arsenic interactions, microorganisms can act in a detrimental or beneficial way, either in favoring groundwater contamination or used as the means for bioremediation of contaminated water resources.

Beneath the Winthrop landfill, in southern Maine (Figure 1), groundwater is contaminated with arsenic, having a concentration of approximately 300 ppb while the maximum concentration level (MCL) set by EPA (Environmental Protection Agency) is 50 ppb. The contaminated area occurs beneath an old landfill and leaks as a plume toward a lake located approximately 200 meters from the landfill. Arsenic is released naturally from bedrock and soil by sorption mechanisms and microbial reduction/oxidation but the process is enhanced by an anthropogenic source, the leachate solution originating from the landfill and transported by the groundwater flow. In order to determine the groundwater transport, a bromide tracer has been injected in the landfill by Lamont-Doherty researchers and monitored by sampling water from multilevel wells placed on the landfill for a duration of seven months.

In this paper, the groundwater transport, as reflected by the bromide tracer, the geochemistry, and the microbiology at this location were combined to analyse the mobilization of arsenic beneath the Winthrop landfill. A background on contaminant transport, redox chemistry and microbiology is provided to give an overview of the mechanisms responsible for the release of arsenic at this location. It is also given to support the bromide experiment and the following results and discussion. The experiment consisted of groundwater sampling at different depths for the measurement of bromide, as the tracer, and other anions such as chloride and sulfate, by means of the ion chromatograph technique. The discussion is about the analysis of the bromide tracer data and compares them with another tracer, sulfur hexafluoride (SF_6), which was used as a benchmark. The bromide, which retraces the groundwater flow and distribution of the leachate, is then related to the geochemistry and microbial activity of arsenic. Finally, the remediation methods which are currently being used, and those under study as well as potential ones, are being evaluated. The purpose of this case study is not only to explain how arsenic can be mobilized, but also to elucidate the detrimental environmental impact and inefficiency of old landfills.

SITE DESCRIPTION & INFORMATION

The site is a landfill located in Winthrop, in southwest Maine, at latitude 44.27583° and longitude 69.988331° (EPA Superfund). The landfill, approximately 22 acres in size, is located at about 200 meters from the Annabessacook lake (see Figures 1-2-3, LDEO). Originally a sand and gravel pit, the Winthrop landfill served as a waste disposal site starting in the 1930s, by first receiving commercial, municipal and industrial waste, and then hazardous waste from the early 1950s to the mid 1970s (EPA Superfund). According to EPA, at least 3 million gallons of chemicals were disposed at this site which contained complex organic compounds. The site was then used as a municipal landfill between 1972 an 1982 and was finally covered with clay.

Since 1989, an on-site pump and treat facility extracts groundwater at about 65 gallons/minute from EW2 well (see Figures 2-3, LDEO) and treats the contaminated water before it is discharged into a reinjection well (UTC, 2000). Despite the pump and treat remediation, leaks of groundwater containing arsenic from the landfill leachate persist and end up in the lake, as observed on Figure 2. Monitoring of groundwater beneath the landfill and in the southern flow, from the landfill to the lake, is made possible through a number of multi-level wells, the disposition of which is shown in Figure 3.

The strata from the surface consists of the landfill with a depth of approximately 30 feet, then sand and gravel, followed by a bedrock of quartz-biotite muscovite schist starting at a depth of 47 to 64 feet (UTC, 2000). The water table is at approximately 30 feet and, hence, can be in contact with the bottom of the landfill depending on seasonal variations. According to United Technologies Corporation (UTC), arsenic concentration in bedrock and soil is approximately 20 mg/kg and in groundwater beneath the landfill, varies from 19 to 308 µg/l, as measured from wells closest to the extraction well for treatment.

Although not a populated area, there are a few residences in the vicinity of the landfill, some of which are located between the landfill and the lake. However, their drinking water supply does not come from the surface or groundwater of the area, but from another source, and therefore does not constitute a threat to the population; there are no land uses or agricultural practices in the nearby area.

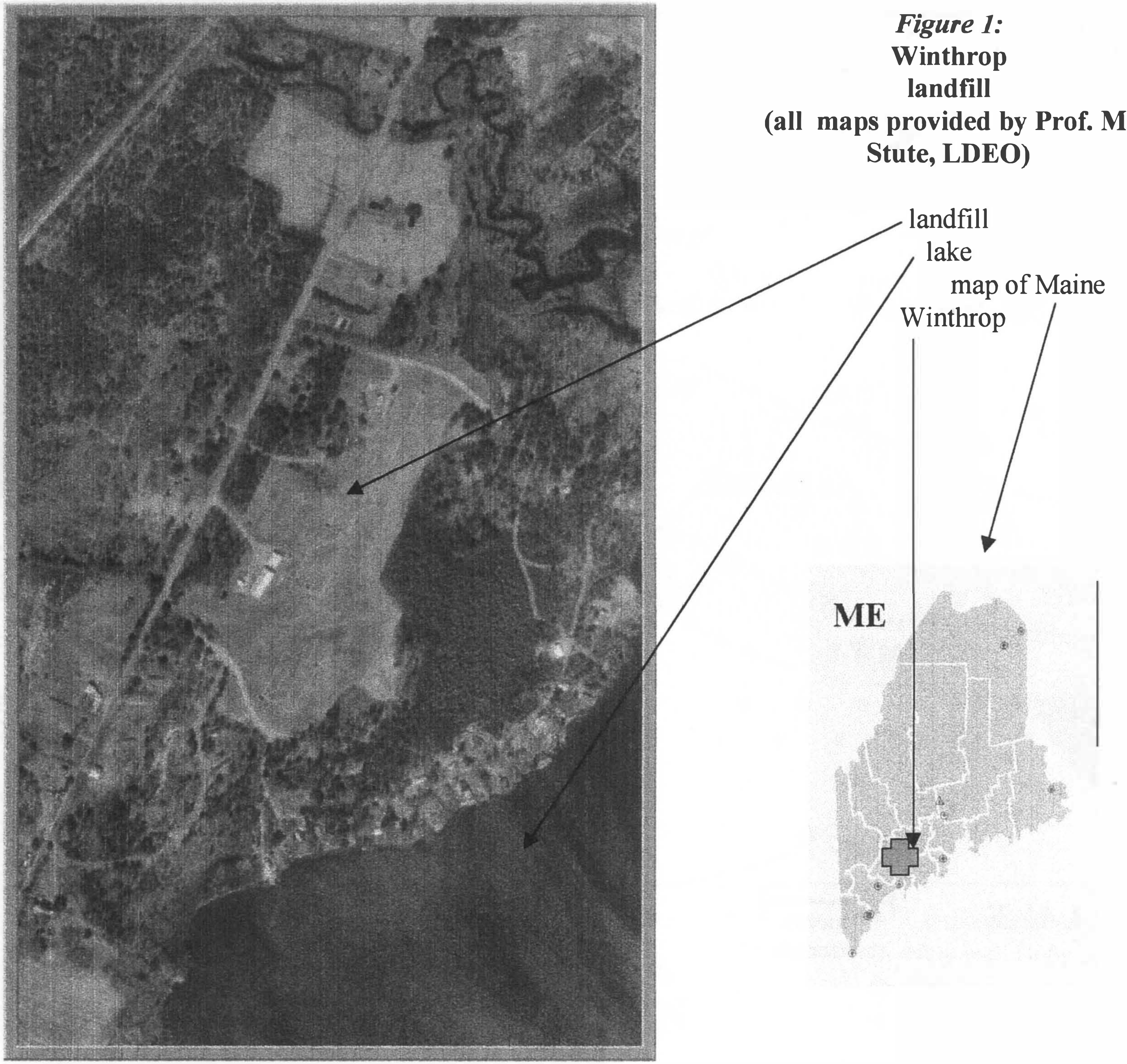


***Figure 1:* Winthrop landfill (all maps provided by Prof. M. Stute, LDEO)**

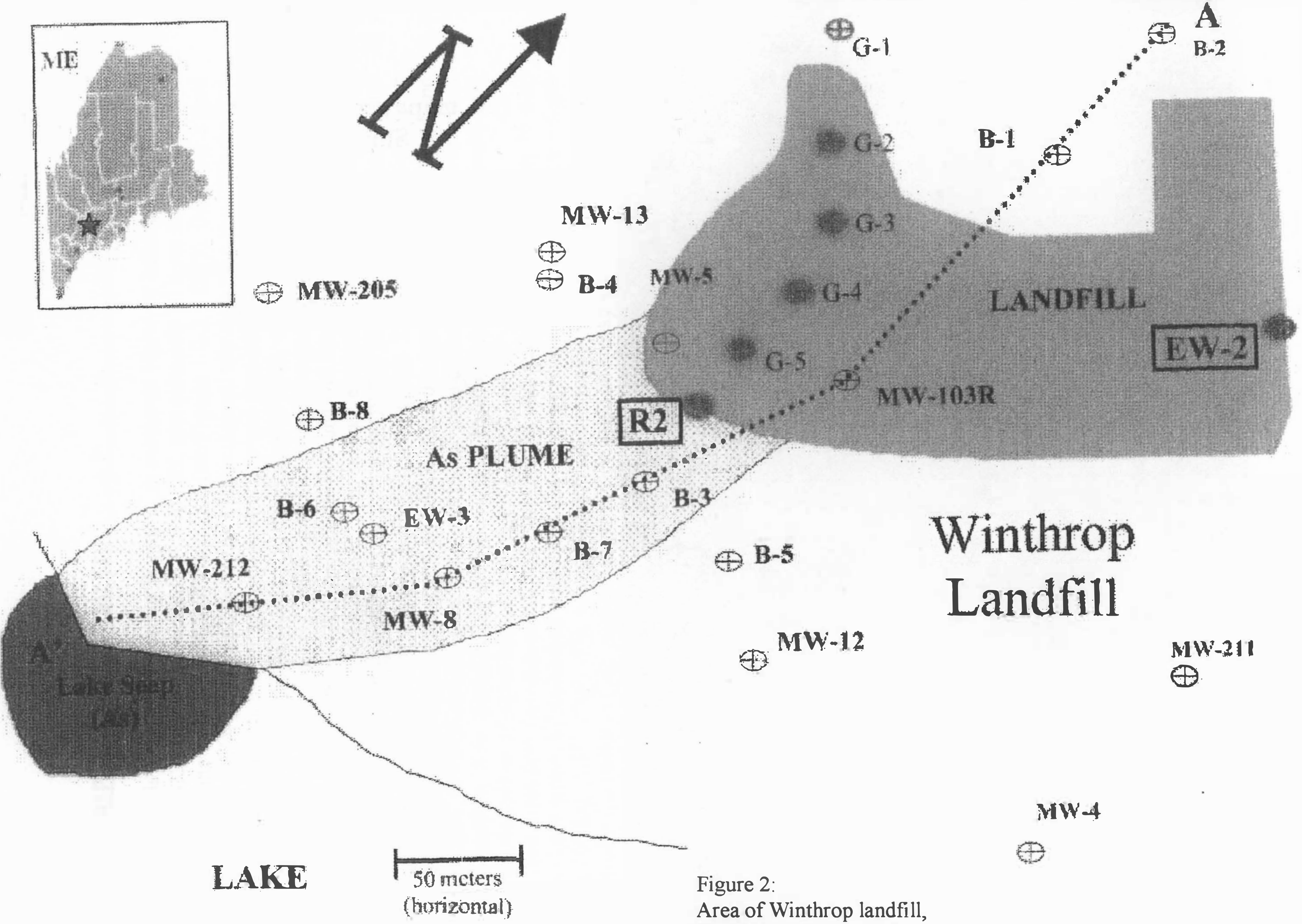


Figure 2:
Area of Winthrop landfill,
estimated plume,
and location of wells
(by Prof. M. Stute, LDEO)

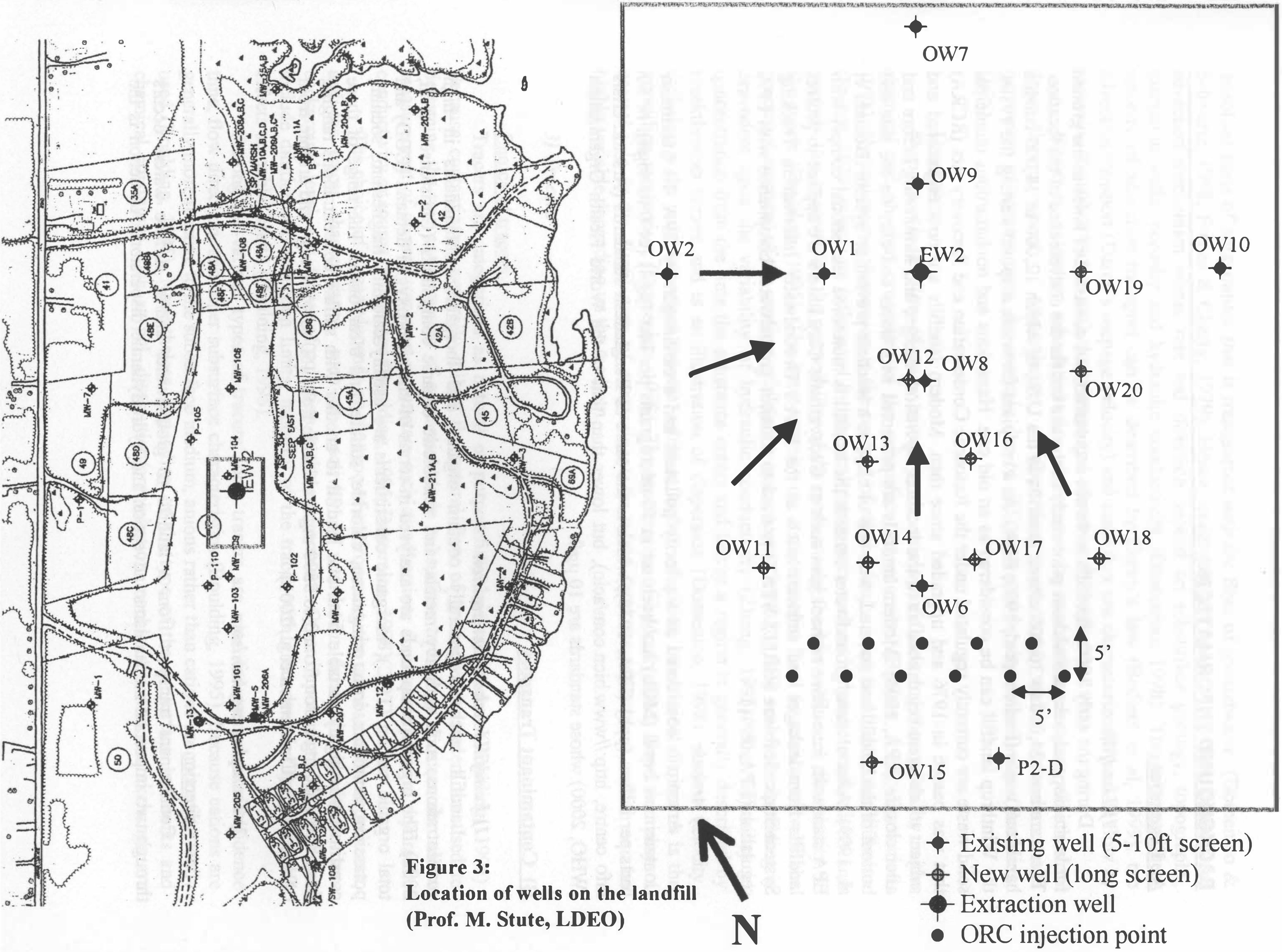


Figure 3:
Location of wells on the landfill
(Prof. M. Stute, LDEO)

BACKGROUND INFORMATION

A) Regulations

1) Landfills

During the early 1900s landfills were not engineered, but consisted of holes in the ground for waste disposal, selected without prior study of the site but for the convenience of the location. There are now 24,000 to 36,000 closed landfills in the U.S., of which 12,000 to 18,000 contain hazardous waste (Bedient et al, 1999; EPA). As a recipient for waste disposal starting the 1930s, the Winthrop landfill can be considered as an old one. Hazardous and nonhazardous municipal solid waste are currently regulated under the Resource Conservation and Recovery Act (RCRA) that was passed in 1976 and upgraded since then. Modern landfills are now engineered and subject to stringent regulations as to the location, operation, design, and monitoring before and after closure (EPA, 1991). Modern landfills are protected with liners and clay on the side and bottom of the landfill and covered, with soil or clay, as a leachate prevention system (Bedient et al, 1999). After closure, groundwater beneath the landfill is monitored and should comply with EPA standards; innovative technologies such as Geosynthetic Clay Liners are applied to protect landfills from leakages and software such as the EPA's Groundwater Information Tracking System/Static Software (GRITS/STAT) is used to monitor groundwater compliance with EPA regulation (EPA, 1991).

2) Arsenic

Arsenic is considered as a priority pollutant and a carcinogen by EPA. Its Maximum Contaminant Level (MCL) has been set at 50 micrograms per liter (μg/l) (or 0.05 mg/l), or 50 parts per billion (ppb) (EPA, 1975), which is the same as Bangladesh standards (Arsenic crisis info centre, http://www.bicn.com/acic), but lower than that of the World Health Organization (WHO, 2000) whose standards are 10 μg/l.

B) Contaminant Transport

1) Landfill leachate composition

Landfill leachates generally contain organic and inorganic contaminants in high concentrations, such as heavy metals, and xenobiotic organic compounds (Christensen et al, 2001). The organic compounds are analysed in terms of chemical oxygen demand (COD) and total organic carbon (TOC); inorganic constituents are usually calcium, magnesium, sodium, potassium, ammonia, iron, manganese, chloride, sulfate, and bicarbonate. The range of these constituents is highly variable from one landfill to another with sulfate concentrations ranging from 8 to 7750 mg/l, iron from 3 to 5500 mg/l, chloride from 150 to 4500 mg/l and arsenic from 0.01 to1 mg/l (Christensen et al, 2001).

2) Transport mechanisms

Advection

Contaminant transport from a landfill to groundwater and/or surface waters occurs through two important mechanisms: advection and hydrodynamic dispersion. Advection is the dissolved mass of contaminant that is transported with the flow of groundwater (Domenico & Schwartz, 1998; Freeze & Cherry, 1979). Hence, understanding groundwater flow dictates the advection mechanism whose rate and direction depend on subsurface geology, topography, extraction wells, porosity and hydraulic conductivity (Domenico, 1998). The average linear velocity of advective transport can be described by Darcy's law (Bedient et al, 1999): the advective transport (Darcy's seepage velocity) and mass flux are characterized by a 3-D flow by assuming the solute moves with the average and advective flow (Zheng, 1995).

However, advection calculations are undermined by retardation processes, which slow down the movement of contaminants, or dispersion mechanisms, which can enhance the movement of contaminants, for example due to differences in density or viscosity (Boulding, 1995).

Dispersion

Dispersion is the flow of water caused by the mixing of fluids and the variability in the chemical and physical properties of the subsurface environment (Bedient, 1999; Domenico, 1998). Hydrodynamic dispersion is the process of mechanical mixing and molecular diffusion (Freeze, 1979) which are influenced by physical parameters such as hydraulic conductivity and porosity that characterize the permeability of the medium and therefore influence the velocity of the solute (Boulding, 1995). The heterogeneity on a microscopic level is associated with the porosity (structure) of the medium while on a macroscopic level (or field scale) the spreading is dependent upon the variability of hydraulic conductivity (Zheng, 1995). The variability in concentration from the time the substance enters and leaves a region is generally described by breakthrough curves and is an illustration of dispersion (Domenico, 1998). At low velocity, diffusion is the most important process, while at higher velocities, mechanical dispersion is the prevailing mechanism (Domenico, 1998). The mechanism of hydrodynamic dispersion plays a central role in the distribution of contaminants in micro (and macro) regions, which can be highly variable depending on the medium.

3) Tracers

Choice of tracers:

Tracers are categorized as natural or purposefully injected tracers (Boulding, 1995). Because contaminants generally follow the natural flow of groundwater, tracers are used to determine the rate and direction of contaminants in subsurface hydrology. Tracers also allow measurement of diverse transport parameters such as advection, dispersion, porosity, hydraulic conductivity or source of recharge (Boulding, 1995; Domenico, 1998).

The choice of tracers depends on the type of environment, the purpose of the experiment, and the tracer characteristics, such as reactivity or retardation from biodegradation, low background level, and degree of pollution to the environment. Other important tracer properties include dilution and detection limits, mobility of the tracer with groundwater flow, cost, and effects on public health (Boulding, 1995).

Among the various types of tracers, ionic tracers are used for groundwater residence time, flow direction, and other subsurface characteristics (Boulding, 1995). Because cations are generally more reactive to the subsurface medium, anions rather than cations are more frequently used (Boulding, 1995). Nevertheless, depending on the type of the subsurface sediments and chemical conditions such as pH, dissolution/precipitation mechanisms and ion exchange are possible; for example, anion exchange between anions and certain minerals and some organic compounds occur under a low pH environment (Boulding, 1995).

Bromide tracer:

Bromide tracers are an example of purposefully injected ionic tracers and have been widely used in diverse types of environments. Although bromide is generally considered non-reactive, background levels exist at various concentrations and field experiments have demonstrated bromide to be a reactive tracer under specific conditions (Boulding, 1995; Brooks et al, 1998). Retardation of bromide has been assumed to depend on the chemical balance and ionic strength of the medium or solution (Brooks et al, 1998). In a number of studies, bromide has been demonstrated to be non-reactive with limestone and fractured granite, but evidenced to be reactive with ferrihydrite, in unsaturated fine-grained soil, and in dolomite with which retardation has compromised transport parameters (Brooks et al, 1998).

Sulfur hexafluoride (SF_6):

SF_6 is a purposefully injected tracer, which is inert, requires a small quantity for injection and is easily measured with the gas chromatograph (Stute et al, 2001).

4) Origin and fate of contaminants

Groundwater is not only subject to transport mechanisms but also to chemical reactions during the flow path. With the use of tracers, contaminant transport in groundwater has made possible the understanding of groundwater transport mechanisms such as advection and dispersion. Landfill leachates can be one of the various sources of contaminants that can cause irregularities in groundwater transport mechanisms and modification of the physico-chemical properties of the groundwater environment such as redox reactions and mobilization of trace metals, processes through which microbial activity plays an important role. The fate of contaminants being transported does not end in groundwater but ultimately impacts lakes, surface and drinking water.

Sorption (absorbtion/adsorption or desorption) of contaminants onto or out of solid particles, such as sediments, is one of the fate mechanisms that causes retardation in the case of sorbtion or enhanced contaminant transport in the case of desorption in groundwater flows. In water treatment systems, contaminants may not be captured because of sorption processes, the rate of which needs to be determined to evaluate the treatment efficiency or the actual mass of contaminant present (Bedient, 1999). Sorption may occur through ion exchange; however, organic contaminants, being nonionic, are adsorbed not by ion exchange, but by Van der Waals and hydrophobic bonding (Boulding, 1995).

Sorption also influences redox reactions, another important fate transport mechanism. Redox reactions, that is the transfer of electrons from the contaminant to another substance, involve two half reactions: oxidation and reduction, or the removal and addition respectively of one or several electrons from the contaminant (Brock, 2000). Redox reactions can be abiotic, for which reactions are mostly irreversible, or biotic which are mostly reversible reactions; these reactions are very important in the solubility of trace metals (Boulding, 1995).

C) Subsurface Chemistry

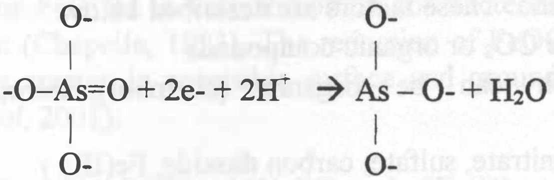
1) Landfill leachates and redox chemistry

The thermodynamic properties are important in determining the prevalence or "zonation" of a reduction/oxidation reaction (see the free energy (ΔG) of major redox reactions in landfill leachates, Appendix A). The higher the Gibbs free energy, meaning the more negatively large, the more favorable is the reaction to proceed. From the electron acceptors, O_2 is the first to be used (negatively large ΔG) then NO^{3-}, Mn, Fe, SO_4^{2-}, and finally methanogenesis and fermentation (negatively small ΔG). With depth, the zonation generally occurs in this order. However, these zones may vary or occur simultaneously depending on the geochemistry of the subsurface (Christensen et al, 2001).

Landfill leachates generally modify the geochemistry of the subsurface. In areas close to the landfill, methanogenesis and sulfate reduction prevail, followed by iron reduction, manganese reduction, denitrification, and aerobic degradation (Christensen et al, 2001). This description of zones is with distance (horizontal) away from the landfill and is subject to modification or occurrence of more than one redox reaction in the same zone (Christensen et al, 2001).

2) Arsenic chemistry

Reduction/oxidation and adsorption/desorption reactions are the major mechanisms that dictate the mobilization of arsenic into the environment (Deutsch, 1997). Arsenic can be in gaseous, organic, as well as inorganic forms and can be found in four oxidation states: +V, +III, 0, and –III (see table in Appendix B for physical properties and arsenic compounds). Gaseous arsenic, that is arsine, is the most toxic form of arsenic (Vallee, 1977) while methylated (organic) arsenic is the least toxic (Deutsch, 1997; Thompson et al, 1999). The inorganic forms of arsenic, and of focus in this study, are arsenate [As(V)] and arsenite [As(III)], which are the most important redox states of arsenic in nature and the most common toxic forms in groundwater (Freeze, 1979; Deutsch, 1997). The reduction of arsenate to arsenite is as follows where arsenate is the acceptor and arsenite the product (Brock, 2000):



$$\text{-O}-\overset{\text{O-}}{\underset{\text{O-}}{\text{As}}}=\text{O} + 2e\text{-} + 2H^+ \rightarrow \overset{\text{O-}}{\underset{\text{O-}}{\text{As}}} - \text{O-} + H_2O$$

The release of arsenic in groundwater depends upon the pH/Eh state of the aquifer, the subsurface medium, the interfacial adsorptive capacity and the groundwater composition (Deutsch, 1997). Arsenate is anionic ($[H_2AsO_4^-]$, $[H_2AsO_4^{2-}]$) and prevails in oxidizing (to slightly reducing) environments in the pH range of 4 to 9 while arsenite is most stable in reducing environments under the neutral form ($[H_3AsO_3^0]$) and anionic form ($[H_3AsO_3^-]$) (Allen, 1993; Deutsch, 1997) (also see pe/pH diagram of arsenic in Appendix B, Deutsch, 1997). In water, arsenic can be almost insoluble (arsenate) to very soluble (arsenite). In soil, arsenate and arsenite are converted through microorganisms to dimethylarsine, which is very toxic and can be assimilated by other living organisms such as fish. In the process, arsenate is reduced to arsenite, which is methylated to methyl arsonic acid, which in turn is reduced to dimethylarsine (Vallee, 1977). Because the most toxic form of inorganic arsenic (arsenite) exists in reducing environments, anaerobic bacteria play a major role in the redox reactions; therefore, anaerobic soil and groundwater environments are of major concern regarding arsenic mobilization.

Arsenic is generally associated with iron ($FeAsO_4$), lead ($Pb_3[AsO_4]_2$), manganese ($Mn_3[AsO_4]_2$), and sulfur (As_3S_3) compounds (Deutsch, 1997). Arsenate, more than arsenite, sorbs strongly on iron, manganese and aluminum oxyhydroxide (USGS, 2000), and therefore is less toxic to the environment. However, the sorption capacity of arsenate will be limited by the number of sites available on the interface (Deutch, 1997). Arsenite, which binds less strongly to sediments, is more mobile in groundwater, and because of this mobility, poses a more important threat to the environment. In aerobic environments, arsenate is the most stable and will be strongly sorbed by ferrihydrite while in anoxic and reducing conditions, arsenate will be reduced to arsenite which binds less strongly to ferrihydrite; the latter will dissolve as the redox potential declines (<100mV) (Deutsch, 1997).

C) Microbiology[1]

1) Classification of microorganisms

Microorganisms can be classified based on the concept of electron donors and electron acceptors. Our concern in the unsaturated environment is on those bacteria that do not use oxygen as electron acceptors; they are anaerobic respirers as well as fermenters. Fermenters are those microorganisms whose electron acceptors proceed without added terminal electron acceptor (Brock, 2000); they breakdown complex organic compounds into simple organics. In aerobic environments, respirers utilize oxygen as electron acceptor and organic compounds as electron donors and carbon source.

2) Microbial growth

A favorable environment with the right nutrients and conditions is necessary for the survival and reproduction of bacteria. These factors are described below:

- A carbon source, which can be CO_2 or organic compounds
- An electron donor, which can be organic (chemoorganotrophs) or inorganic (chemolithotrophs)
- An electron acceptor (such as nitrate, sulfate, carbon dioxide, Fe(III))
- Macronutrients (Nitrogen, Phosphate) and micronutrients (Ca^{2+}, Mg, trace metals)
- Temperature
- pH
- Moisture, which can vary with seasonal fluctuations

These conditions form a niche which allows microorganisms to thrive and can be extremely diverse depending on the nature of the minerals or presence of organic compounds within which they grow (Chapelle, 1993). These factors are therefore fundamental in understanding the

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[1] Based on notes from Environmental Microbiology course (Prof. Anid), class texbooks (Chapelle, 1993; Brooks, 2000), and paper on microbial role in arsenic contamination for the course.

microbial growth of those organisms, which influence the mobilization of metalloids and from an engineering point of view in implementing remediation.

3) Population interactions

Microbial populations can interact positively or negatively either by influencing other populations to thrive or by discouraging them to grow based on competition, for example for the same nutrients (Chapelle, 1993). These interactions are important in the discussion of iron and sulfate reducing microorganisms which compete for the same nutrients. Others microorganisms can live in consortium or in synergy whereby the presence of one category of bacteria would encourage or favor the growth of other microorganisms (Chapelle, 1993).

4) Groundwater microorganisms relevant to the mobilization of arsenic

Soil and groundwater are environments where microorganisms proliferate either in aerobic or anaerobic conditions (Chapelle, 1993). The most important microorganisms that catalyze the redox reactions resulting in the release of arsenic are the iron reducers and sulfide oxidizers. In the process of arsenate reduction, facultative chemoorganotrophs use Fe(III), Mn(IV) and organic compounds as electron acceptors (Brock, 2000). Because they catalyze redox reactions, the role of bacteria is important as to the mobility and toxicity of arsenic in the environment.

Bacteria use energy from the catalysis of redox reactions and arsenate reduction to arsenite yields energy that sustains growth. Ahmann et al. (1995) discovered the first arsenic respirer, *Sulfurospirillum arsen-ophilum*, or previously known MIT13 which uses arsenate as terminal electron acceptor, reducing it to arsenite. This microbe is important in the removal of arsenic from soil; it acts as a mediator for the conversion of insoluble-soil-embedded arsenate to soluble-highly-mobile arsenite in water (Ahmann, 1995, Thompson, 1999).

Iron reducing microorganisms:

The Fe(III) reducing bacteria are obligate chemoorganotrophic and chemolithotrophic anaerobes that utilize fermented organic compounds (acetate, formate) and hydrogen as electron donors and Fe(III) oxyhydroxides (FeOOH) as electron acceptor (Chapelle, 1993). A geological formation that contains FeOOH is very important for bacterial growth of Fe(III) reducers in anaerobic environment (Chapelle, 1993). The reduction of FeOOH is one of the most common processes that releases arsenic in anaerobic surface and groundwater. The stoichiometry is as follows (McArthur *et al*, 2001):

$$8FeOOH + CH3COO^- + 15H_2CO_3 \rightarrow 8Fe(II) + 17HCO_3 + 12H_2O$$

whereby CH_3COO^- represents organic compounds. Other organic compounds could be CH_2O; in the process, the sorbed arsenic from FeOOH is released into solution (Nickson et al, 1999).

Sulfate-reducing microorganisms:

The major chemoorganotrophs, gram-negative rods, obligate anaerobes, and reducers of sulfate to hydrogen sulfide (H_2S) in terrestrial and aquatic environment include *Desulfovibrio* (Brock, 2000). These microorganisms use fermented organic compounds (acetate, lactate, pyruvate) or H_2 as electron donor, sulfate as electron acceptor, and carbon dioxide or organic compounds as carbon source; other genera reduce sulfur, instead of sulfate, to sulfide (Brock, 2000). Since sulfate reducers utilize fermented products, they are heavily dependent on fermenters which partially oxidize carbohydrates, the complex organic compounds, to simple organic acids and H_2 (Chapelle, 1993). Leachates in methanogenic phase will tend to have low concentration of sulfate due to sulfate reduction by sulfate reducing bacteria (SRB) (Christensen et al). Although sulfate-reducing bacteria are anaerobic, living in oxygen-free environments, they can be found in microhabitats of aerobic environments (Chapelle, 1993).

Sulfide and iron oxidizing bacteria:

Chemolithotrophic bacteria include the genus *Thiobacillus,* a gram-negative bacteria whose electron donors are hydrogen sulfide (H_2S), sulfur and S_2O_3 in aerobic neutral or acidic environment (Brock, 2000). The electron acceptor for the sulfide oxidizing bacteria is oxygen and the carbon source is organic compounds. Sulfide oxidizers are important in catalyzing the reactions that favor the mobilization of arsenic in aerobic environments. Other chemolithotrophs such as *Thiobacillus ferrooxidans* utilize ferrous iron Fe(II) as electron donors from iron pyrite (FeS_2) and sulfides in aerobic, acidic environment (Brock, 2000). These Fe(II) oxidizers utilize oxygen as electron donor and CO_2 as carbon source.

EXPERIMENTAL PROCEDURE[2]

A) Field

SF_6 and bromide tracers were injected on January 9, 2001 in OW14 well (see injection calculations in Appendix C by Prof. M. Stute, LDEO) on the landfill. Until August 2001, samples for SF_6 measurement were collected on a regular basis and the results have been provided by LDEO for comparison with the bromide tracer.

For the bromide tracer, approximately 300 samples were collected from the time of injection in January 2001 to August 2001. The wells from which these samples were derived are located on the landfill and were collected from the extraction well (EW2) and the other wells at depth increments of 5 feet from approximately 65 feet (level 1) to 40 feet (level 6). These wells are the following: OW6, OW11, OW12, OW13, OW14, OW15, OW16, OW17, and OW18. In July 2001, samples were taken from wells of the southern flow line, that is the area from the landfill to the lake, and include MW8, MW12, MW13, MW204, MW211, and MW212. The water table is at a depth of approximately 30 feet and is subject to seasonal variation.

B) Laboratory/Data Tabulation

The 300 samples were measured by the Dionex ion chromatograph DX-100 for the analysis of bromide, and other anions such as chloride and sulfate. The laboratory activities consisted of preparing standard solutions at different concentrations (0.05, 0.1, 0.2, 0.4, 0.6, 1, 2,and 5 mg/l) (see standard anion solution, Appendix D), filtering and diluting the samples when necessary, and following the required procedure to operate the ion chromatograph. All samples were contained in 5ml-vials and diluted with DI water by a factor of 5 except for EW2 (extraction well) and MW (southern flow) samples because of the low concentrations. Each run contained the standard samples, DI water, and the samples from the wells, all in duplicates (triplicates for standards, and at least one DI sample per rack) to verify the replicability of the samples.

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[2] Experimental procedure (field, laboratory, data tabulation and charts) advised by Stute M., LDEO.

The peak areas obtained from the chromatograms were fitted to the calibration curves (see Appendix D) obtained from the standards. During the data analysis (see data section, Appendix E), the bromide background level was subtracted from all other bromide measurements. The background concentration was chosen as the first or last measurement at each level of each well, or as the lowest concentration. All standard measurements were fitted for each run and then on one chart (containing all standards from all runs) for variability check. The data were plotted by well and by level for bromide, chloride and sulfate separately. The SF_6 data provided by LDEO were combined with the bromide measurements for comparison and verification of bromide as a non-reactive tracer; the SF_6/bromide charts were plotted by well and level (or depth). All concentration values for OW wells measured on the ion chromatograph, including bromide, chloride, sulfate, and phosphate have been corrected (meaning adjusted from the dilution factor) and are presented in mg/l on the spreadsheet and time series in detail in the appendixes.

RESULTS & DISCUSSION

A) Groundwater Transport

1) Evaluation of bromide as a conservative tracer

A "conservative" tracer is non-reactive with its environment, meaning the tracer is subject to the minimum possible addition of natural source or minimum retardation from adsorption reactions and ion exchange (or biodegradation and radioactivity depending on the choice of tracer). In other words, the tracer is to reflect as much as possible the groundwater flow patterns. The properties of bromide as a conservative tracer can be observed for a number of wells in this study. Bromide has been detected at a low background level, on average at concentrations below 0.5mg/l, which indicates the measurements obtained for bromide are derived mostly from the tracer since the natural source is very low. In addition, the identical patterns of bromide versus SF_6 can be observed in most of the charts with large bromide concentrations, the highest recorded concentrations being 17.2 mg/l (at well OW14, level 2) (see Figures 4-9, next page). Time series of bromide versus SF_6, for example OW11 level 2, OW12 level 4, OW14 levels 2&3 and OW17 levels 1&2 indicate a similarity in the behavior of the tracers (see Figures 4-9). Assuming SF_6 is an inert tracer and a benchmark, the parallelism with bromide suggests bromide is a conservative tracer. However, discrepancies between bromide and SF_6 exist.

For the time series at small bromide concentrations (<<0.5mg/l), the parallelism of the tracers is less apparent compared to those of higher concentrations (see Appendix F). This variability can be explained by the compilation of all bromide standards (Appendix D) where the area, obtained from the ion chromatograph, is plotted against the corresponding mg/l/area; the chart shows a higher variability at small concentrations than at high concentrations (or areas). In other words, the detection of bromide concentration when the latter is very small is subject to a wide variability probably due to the small amount of sample used (1ml) for ion chromatography reading. However, when the replicability of random samples at very small and very large concentration was verified, the results show a very small standard deviation in both cases, 0.039 and 0.15 respectively. This verification test suggests no large deviation exists when the same sample is measured several times whether the sample contains very small or high concentrations

Figures 4-9

SF_6 versus bromide concentrations at different depths (levels) and wells as a function of time
(depth of levels are from level 1 to level 6 in a 5-ft increment from 65 to 40 ft, respectively)
(x-axis for all figures are the dates the sample was collected)

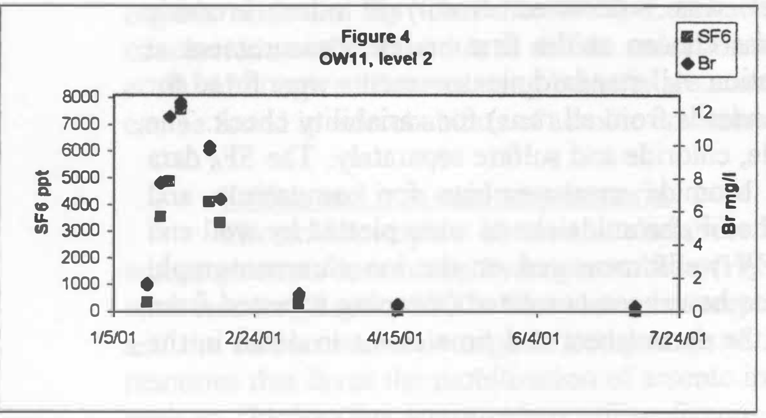


Figure 4
OW11, level 2

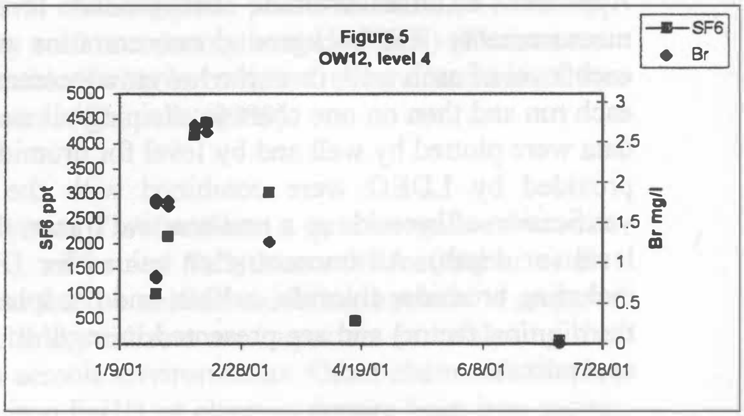


Figure 5
OW12, level 4

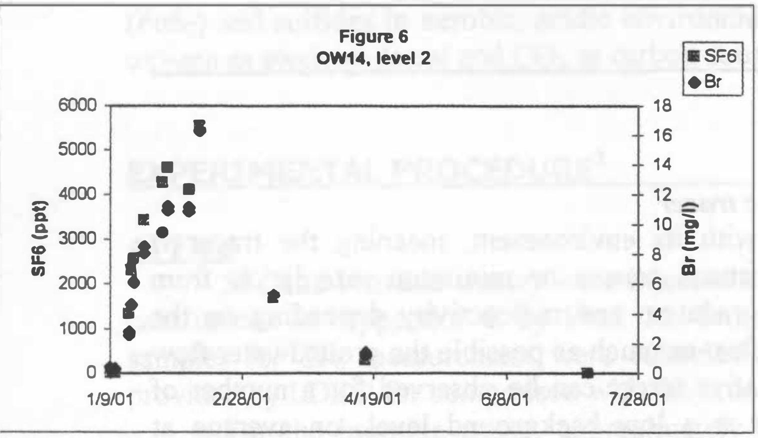


Figure 6
OW14, level 2

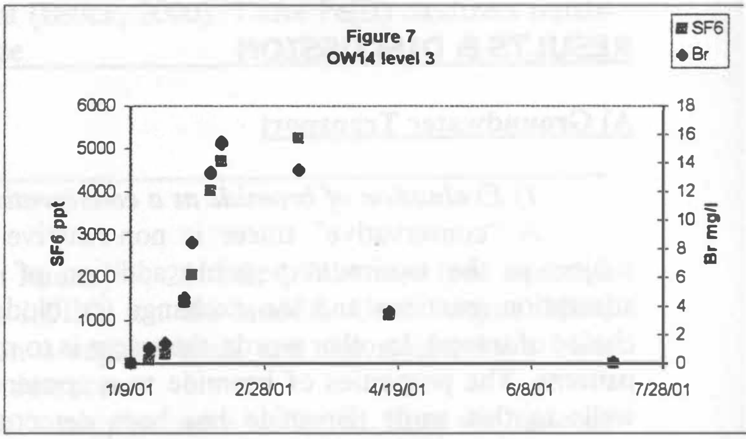


Figure 7
OW14 level 3

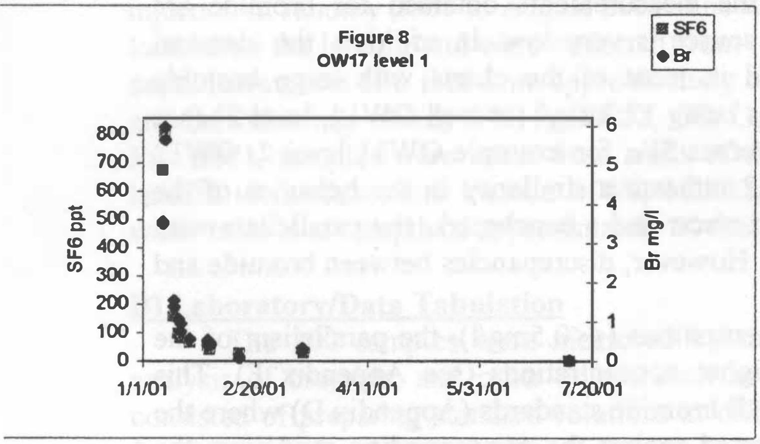


Figure 8
OW17 level 1

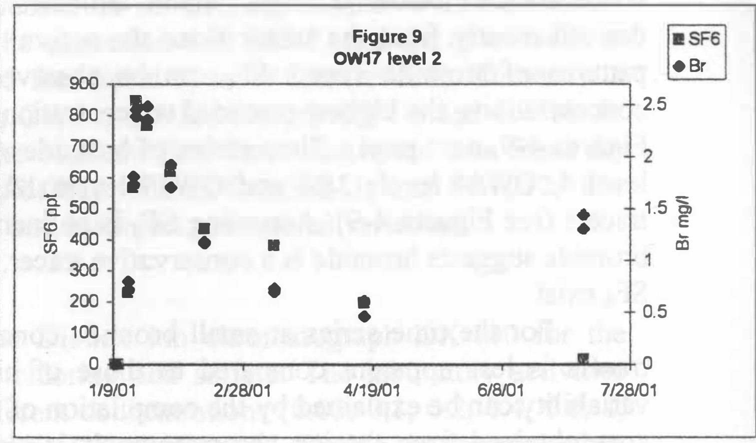


Figure 9
OW17 level 2

of bromide. The good replicability can also be observed from the standard deviation of duplicates for all samples. For example, OW 14, which is the well having the largest number of samples and offering a large variation of concentrations, shows the standard deviation for 83% of the samples is below 11%. In addition to verifying the variability in the measurement, these statistics as well as the regularity in the measurement from the standard solutions (see appendix D) also indicate a good functioning of the instrument.

Another discrepancy observed in the SF_6-bromide comparison is their ratio, which is subject to large fluctuations ranging from a ratio of approximately 1800 to below 1, or on average in a range from 500 to below 1 (Appendix F). However, the ratio SF_6/Br for the extraction well (EW2) samples is in general constant, at an average of approximately 200 (see data section, Appendix E). These irregularities can be explained by the large fluctuations obtained from the bromide standards at low concentrations, as explained earlier or by adsorption/desorption or other physical mechanisms.

If the ratio of SF_6/Br, being constant for EW2, is used as a benchmark to analyse the discrepancy in the ratios for the OW wells, then a high ratio (superior to 200) could indicate retardation caused by adsorption while a small ratio (below 200) would refer to desorption or competitive anion exchange mechanisms. At deep levels in OW wells, ratios tend to be high, which indicate the bromide concentration is lowered in groundwater due to adsorption of bromide enhanced by generally decreasing pH with depth. In contrast, at shallow levels, decreasing ratios, meaning the bromide concentration is high in solution, could be attributed to higher pH in areas near the landfill which discourage sorption onto sediments, alkalinity being generally higher close to the landfill. In addition, the low ratio and high bromide in solution can be due to anionic competitive interfacial exchange with sulfate whose concentrations are generally low at shallow levels because of preferential sulfate adsorption rather than bromide. In areas near landfills, or at shallow levels, sulfate reduction is generally an important mechanism induced by the concentrated landfill leachate (Christensen et al, 2001).

Since the bromide is negatively charged, ion exchange with the subsurface media can occur at different rates depending on the substrate properties, the ionic strength of the solution, the chemical balance, and competitive interactions at the interface with other anions. Retardation of bromide can be observed when compared with the SF_6 data (see all SF_6 vs. Br time series in Appendix F); the discrepancies between SF_6 and Br could be interpreted as the existence of retardation. However, because of seasonal variations, which affect the local environment, as well as fluctuations in pH, temperature, and properties of the solute, sorption reaction rates can vary widely. In addition, these mechanisms occur in local regions on a microscopic level, and therefore can be highly variable from one site to another making the retardation factor difficult to estimate.

If bromide is assumed to be a conservative tracer, the information obtained can be used to describe the major transport mechanisms that take place. The locations where the mass flux is most important should give an idea of the porosity and hydraulic conductivity at different depths in different wells. The mass transport can then be linked to the transport of landfill leachates and hence, of organic compounds.

2) Transport mechanisms

Advective/groundwater flow

Once the first arrival time of the tracer can be estimated, a flow pattern actually exists between two points from the injection to the extraction well and maximum velocity can be calculated (Boulding, 1995). The peaks for the extraction well (EW2) occur at different arrival times for Br and SF_6, although this is not always the case for the remaining wells. Another discrepancy in the peak arrival time of bromide versus SF_6 can be observed for OW14 at level 3, but most of the time series with large concentrations show Br and SF_6 peaks at approximately the same arrival time (OW12: levels 2,3,4,5; OW13: level 3; OW14: levels 2,4; OW16: level 2; OW17: levels 1,2; see Appendix F). If the injection took place on January 9, 2001 at OW14, and the first peak for EW2 occurs on February 8, 2001, the average maximum velocity is estimated at about 2 ft/day assuming the distance between OW14 and EW2 is about 60 feet. This velocity is a broad estimate and subject to variations; it is also influenced by the extraction well that pumps water at a rate of 65 gallons per minute and therefore modifies the natural flow of groundwater. The seepage (or Darcy's) velocity can be measured if the hydraulic gradient, porosity, and hydraulic conductivity are known. Estimates of advective transport at the Winthrop landfill (UTC, 2000) suggest a range of seepage velocity between 0.5 and 1.25 ft/day and an average groundwater flow of 1 ft/day. The same study by UTC shows a wide variability in hydraulic conductivity at selective wells varying between 1.60 to 290.3 ft/day and a groundwater seepage velocity from OW5/OW1 to EW2 from 0.27 ft/day to 12.1 ft/day. This large diversity of hydraulic conductivity illustrates the complexity of the subsurface beneath the Winthrop landfill.

If the tracer is a reflection of the groundwater flow, the latter is in 3-dimensional. The longitudinal (horizontal) flow is in the direction of the extraction well (EW2), or in sequence: OW14 to OW13, to OW12 as expected, considering the groundwater flow is influenced by the force of the pumping well at EW2. This sequence can be observed in Figure 13 (next page) at level 4. If the 3 peaks observed for each well at the same level are a reflection of the groundwater flow at level 4, it takes approximately 15 days for the solute to travel from OW14 to OW13 (20 feet) and 9 days from OW13 to OW12 (18 feet), which gives a velocity of about 1.3 ft/day and 2ft/day respectively. The larger velocity closer to EW2 could be influenced by the extraction well and/or high permeability/hydraulic conductivity of the medium.

The descending flux is less important closer to the extraction well where the flow pattern is upward because of the force exerted by the pumping well. This mechanism can be observed for measurements from OW12 which is closest to the pumping well and where concentrations of bromide in shallow wells are the highest observed. This elevation of solute concentration can be observed starting OW13 (level 5) and increases further by OW12 at shallow levels (levels 5 and 6)(see Figure 14, next page).

The longitudinal flow (horizontal) is more important than the vertical transport, and therefore limits the transport of oxygen vertically, assuming groundwater flow travels parallel to the bedding structure of the subsurface. Based on the peaks at similar concentrations, the vertical velocity in OW14 from level 4 to level 2 (27days) is approximately 0.37 ft/day compared to the horizontal velocity calculated above from OW14 to OW13 (level 4) which is 1.3 ft/day (see Figures 10-15). Although the advective transport offers an estimate of the average groundwater flow, the dispersive transport offers a more accurate distribution of the solute. This dispersion effect can be observed from the wide differences in concentrations from one peak to another in

Figures 10-15

Bromide concentrations at different levels (depths) in different wells
(from level 1= 65 feet to level 6= 40 feet with a 5-foot increment between levels)
(x-axis for all figures are dates the samples were collected)

Figure 10
Br Level 1

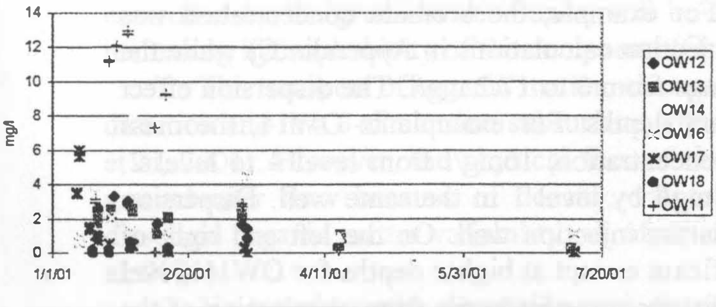


Figure 11
Br Level 2

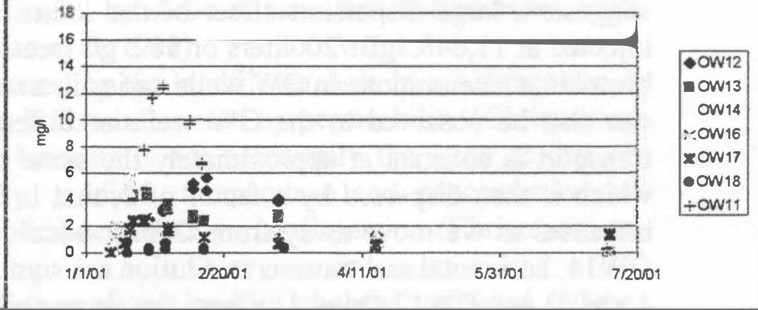


Figure 12
Br Level 3

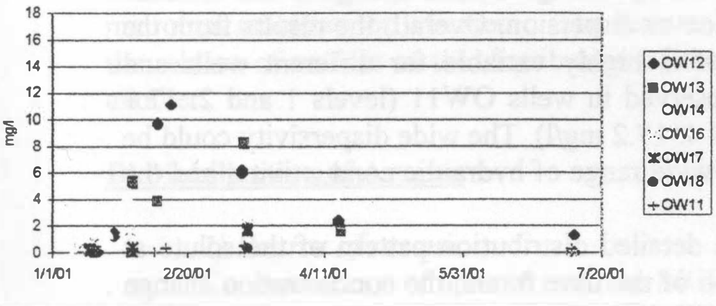


Figure 13
Br Level 4

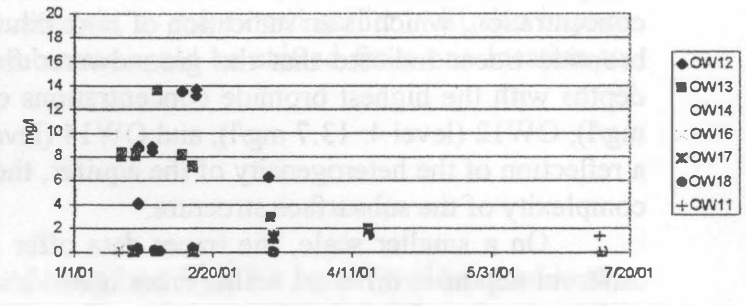


Figure 14
Br Level 5

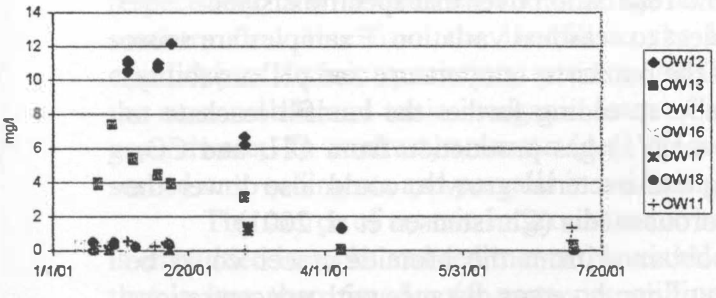
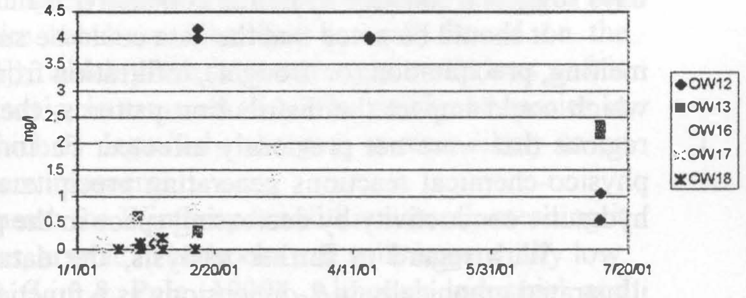


Figure 15
Br level 6



the same well from one level to the next, or at the same level but from one well to the adjacent one.

Dispersion

Hydrodynamic dispersion is an important transport mechanism in this complex environment. The wide range of bromide concentrations in different wells at different depths suggests a large dispersion effect of the solute. For example, the bromide concentration was injected at 11,648.3gBr/200liters or 58.2 g/l (see injection calculations in Appendix C) while the bromide concentrations in OW wells varies in a range from 0 to 17.2 mg/l. The dispersion effect can also be observed in the OW wells at different depths. For example in OW14, the mass transport is constant at approximately the same concentration, 16mg/l from level 4 to level 2, which is then dispersed by a factor of 2, that is 8mg/l by level 1 in the same well. Dispersion increases as we move away from OW14, which is the injection well. On the left and right of OW14, horizontal and transverse dilution are significant except at higher depths for OW11 (level 1 and 2) and OW17 (level 1) where the permeability seems to be larger from observation of the concentrations. Similarly, OW16 shows more permeability at higher distances below the surface compared to shallow levels. These observations are based on the drastic change in the bromide concentration, which is an indication of high dilution or dispersion. Overall, the results from the bromide tracer indicate that the groundwater flow is highly variable for different wells and depths with the highest bromide concentrations observed in wells OW11 (levels 1 and 2: 12.9 mg/l), OW12 (level 4: 13.7 mg/l), and OW14 (level 4: 17.2 mg/l). The wide dispersivity could be a reflection of the heterogeneity of the aquifer, the wide range of hydraulic conductivity, and the complexity of the subsurface structure.

On a smaller scale, the tracer data offer a detailed distribution pattern of the solute at different depths in different wells. From observation of the time frame, the concentration change and the distance, it is possible to obtain an idea of the permeability in local regions. For instance, the identical peak concentrations obtained at OW13 and OW12 on level 4 in an elapsed time of 9 days suggest a constant hydraulic conductivity and no retardation over that specific distance.

It should be noted that the data could be subject to seasonal variation. Examples are snow melting, precipitation (or drought), infiltration from the outskirts, temperature and pH variability, which could impact the distribution patterns, thereby spreading further the landfill leachate to regions that were not previously affected. Factors such as gas production from CH_4 and CO_2, physico-chemical reactions generating precipitates, and bacterial growth, could also lower the hydraulic conductivity by decreasing space in the porous media (Christensen et al, 2001).

With regard to further analysis, the data obtained from the bromide tracer could be illustrated graphically in 2-dimensions as a function of depth versus distance with concentrations contours (gradients) that reflect the dispersivity and advective flow (Christensen et al, 2001). Modeling based on the advection-dispersion equation, i.e. the addition of dispersive transport terms to the advective equation, could be used to simulate the variation of velocity and concentration in 3-dimensional space (Zheng, 1995). The advection-dispersion equation would include chemical reactions such as the equilibrium-controlled sorption between the liquid and solid phases, whose rate is generally difficult to obtain and is generally represented by a sink/source term (Zheng, 1995). The graphical illustration in 2-D and the modeling would be useful tools in the implementation and evaluation of remediation.

Transport of organic matter

The advective transport and resulting dispersion of the solute (the bromide tracer) is used to retrace the landfill leachate and the groundwater flow patterns. As the landfill leachate with its load of dissolved organic and inorganic compounds enters and moves with the natural flow of groundwater, their distribution occurs on a microscopic level and a variability of niches are formed depending on the medium. On a micro level, the distribution of organic particles, controlled by the groundwater fluxes, will be affected by sorbtion rates that will increase with increasing hydrophobicity of the compound (Oman et al, 1999).

The transport of organic matter, characterized by the landfill leachate in a 3-dimensional direction and in a 3-dimension subsurface strata, is also influenced by permeability (Christensen et al, 2001). However, the physical flux of the leachate is not necessarily the same as that of groundwater flow because of density, viscosity, gradient, temperature and concentration of dissolved organic matter variability, all of which impact velocity and dispersion (Christensen et al, 2001).

Nevertheless, the dispersion and distribution of the landfill leachate, provided by the tracer tests, provide useful information as to the vulnerable locations where organic matter, nutrients and moisture are being transported to provide the adequate environment for the microbial mobilization of arsenic. The seasonal variation, as mentioned earlier, will also impact the release of arsenic as the distribution of the substrate could be shifted from one location to another.

B) Mobilization of Arsenic

1) Source of arsenic

Concentrations of arsenic over the MCL of 50µg/l set by EPA have been detected in the Winthrop groundwater beneath the landfill. These concentrations, recorded in the influent water to the extraction well (EW2, Figure 3) are 300 µg/l; in wells OW1 and OW2, 308 and 19 µg/l, respectively, and in bedrock and soil, up to 20mg/kg (UTC, 2000). An arsenic plume in the southern flow line from the landfill to the lake has been identified as well. Based on the chemistry of arsenic speciation, arsenite (As[III]), which prevails in reducing conditions and is the most mobile and toxic inorganic form of arsenic, is assumed to be the dominant species in groundwater. In contrast, arsenate (As[IV]), which is negatively charged, is most likely to be sorbed onto sediments and prevails in oxidizing environments.

The source of arsenic in groundwater beneath the Winthrop landfill is natural, meaning it is embedded in rocks and sediments. Nevertheless, arsenic in bedrocks and soils is generally low, that is less than 6mg/kg (6 parts per million) (Lin & Puls, 1999). Although industrial and commercial waste from the landfill could provide a source of anthropogenic arsenic, no evidence so far has been provided (UTC, 2000). Assuming arsenic is natural and originates from iron-based structures and sulfide deposits, the organic compounds derived from the landfill leachate presumably provide the substrate that feeds microorganisms and influences the redox reactions that contribute to the mobilization of arsenic in the subsurface hydrogeology.

2) Organic compounds as substrate for respirers and fermenters

The landfill leachate, composed of organic compounds, serves as the substrate for the growth of microorganisms and is distributed through the advective and dispersive flows of groundwater. Studies have shown that landfill leachates are composed of generally high organic matter measured as Chemical Oxygen Demand (COD) ranging from 7750 to 60000 mg/l (Kennedy, 2000) for typical leachate. Therefore, landfill leachates provide more carbon than in the case of uncontaminated aquifers; this explains the abundance of microbially driven reactions whose electron donors and carbon source are provided by the leachate. The groundwater transport thus acts as a carrier for carbon source and moisture, both of which are essential for the survival and growth of microorganisms.

In addition to being rich in organic compounds, typical landfill leachates are generally very reducing (high NH_4 concentrations), and represent a source of electron donors (Christensen et al, 2001). Landfill leachates in general are also rich in microorganisms in the vicinity of the landfill, but tend to decrease at distances away from the landfill based on studies of the microbiology of landfill leachates (Christensen et al, 2001). Based on the tracer data from the Winthrop landfill, locations where the mass flux is the most important provide information on the distribution of organic compounds and the locations where they are most influential.

At distances closer to the surface, aerobic respirers, which use organic compounds as electron donor and carbon source and oxygen as electron acceptor, deplete the oxygen pool. The chemistry data (see Appendix H for subsurface characteristics) show no dissolved oxygen in groundwater starting at level 6, which is below the water table for most wells; exceptions occur at some of the levels in OW18 well. Where molecular oxygen is no longer available, the environment becomes anaerobic and respirers utilize organic compounds as electron donor and carbon source and inorganic molecules as electron acceptors, for example in the reduction of nitrate, sulfate and iron.

The landfill leachates then provide organic matter as substrate to fermenters and anaerobic bacteria in anoxic environments. A synergistic relationship, whereby the populations benefit from each other, exist between the fermenters and the respirers. In anaerobic groundwater, fermenters break down complex organic compounds such as carbohydrates, and lignins and fermentation products still contain some energy since fermentative bacteria cannot oxidize organic constituents (Chapelle, 1993). Products of fermentation (hydrogen and acetate) can then be utilized as substrate by anaerobic respirers (Fe[III] reducers, sulfate reducers, methanogens) that cannot metabolize complex organic compounds or carbohydrates but can break down fermentation products which are more simple organic compounds (Chapelle, 1993). Hence, the presence of complex organic constituents and the resulting fermentation influence the growth of anaerobic respirative microorganisms. The synergistic relationship between fermenters and iron reducers suggests both processes occur in the same redox zone.

3) Iron reduction

Iron reduction is one of the most important mechanisms responsible for the release of arsenic. The adequate anaerobic environment with iron oxide geology, available simple organic compounds, and moisture, are necessary for iron reducers to thrive and release arsenic into solution. In the subsurface, iron-embedded geology is very common. In a study of arsenic by USGS on the natural occurrence of arsenic in groundwater in 145 wells located in New England (Maine, New Hampshire, and Rhode Island) concentrations of arsenic above 0.05mg/l in a number of wells were detected (USGS). This occurrence supports the presence of arsenic in Winthrop as a natural phenomenon.

A study of the biogeochemistry of landfill leachates (Christensen et al, 2001) has shown the importance of organic compounds in catalyzing the reduction of iron in close proximity of the landfill where the source of organic compound is abundant and Fe(III) present, the reduction of iron was significant and all Fe(III) were reduced. At distances away from the landfill, not enough organic compounds was available to drive the reduction of iron, but when acetate was added, iron reduction was enhanced. The conclusion is that knowledge of the distribution and dispersion of organic constituents, or landfill leachate, is important since organics are determinant in the reduction of iron even at distances far from the landfill if the subsurface contains Fe(III). In addition to the availability of organic compounds, in particular acetate (electron donors), the presence of Fe(III) oxides (electron acceptors) is also a controlling factor in enhancing the kinetics of iron reduction (Brock et al, 2000; Ludvigsen et al, 1998).

Evidence of arsenic in solution can be identified based on a number of parameters. Indicators such as pH, dissolved oxygen (DO), and dissolved inorganic carbon are associated with arsenic in solution. The reduction of FeOOH is the typical mechanism responsible for the release of arsenic in anoxic waters, and is often associated with a pH of 6.5 to 7.5, no dissolved oxygen or nitrate (which are removed by reduction) and high concentrations of Fe and bicarbonate (Mc Arthur et al, 2001). The presence of bicarbonate is illustrated by the chemical balance shown above in the background section on iron reducing microorganisms whereby the reduction (or dissolution of FeOOH) produces HCO_3^-, Fe(II), and FeOOH that contains arsenic. However, other sources such as the natural removal from solution or the weathering of other iron-based structure may result in overestimates of the concentration of dissolved iron (McArthur et al, 2001). Similarly, other sources of bicarbonate may be present in the system. In landfill leachates, the alkalinity tends to be elevated due to decomposition and dissolution; iron reduction; or calcite dissolution by CO_2 (Christensen et al, 2001).

4) Arsenic mobilization from sulfide oxidation

Besides the mechanism of iron reduction, another process, sulfide oxidation, can be responsible for the release of arsenic in groundwater. However, contrary to iron reduction which takes place in anaerobic conditions, the oxidation of sulfide occurs in aerobic environments or aerobic micropockets in unsaturated conditions. Like iron oxides, sulfide deposits are common in the subsurface.

Arsenic can be mobilized by sulfide oxidation when the environment is in close proximity to the surface or near the water table in areas of sulfide deposits and where carbon source is also available. The reaction is catalyzed by sulfide oxidizers whose electron donors and carbon source are the organic compounds derived from the landfill leachate distribution and whose electron acceptor is molecular oxygen. At locations where sulfide oxidation takes place, one would expect large concentrations of sulfate depending on the microbial rate of reaction.

Based on the Winthrop data, large concentrations of sulfate are detected at deeper levels (meaning sulfate increases with depth) where oxygen is depleted. This undermines the hypothesis of arsenic mobilization from sulfide oxidation at these locations. However, the large number of wells placed on the landfill and used on a regular basis for monitoring may provide a source of oxygen at these locations. At shallow levels, closer to the water table (close proximity to oxygen source) and where organic constituents are abundant, sulfide oxidation can be a mechanism that releases arsenic. Although the concentration of sulfate recorded is low (see data section, Appendix E) at shallow levels, sulfide oxidation, beside the mechanism of iron reduction, could be responsible for the release of arsenic. However, most of the shallow levels indicate no dissolved oxygen with some exceptions for OW18.

5) Phosphate analysis

Studies have shown that the sorption capacity of arsenic onto soils is strongly limited by the presence of phosphate (Deutsch, 1997). Competitive anionic exchange at interfaces can be an explanation. If phosphate is present, arsenic mobility is enhanced in groundwater. However, the absence or low phosphate concentrations recorded from the ion chromatograph indicate that ionic competitive exchange of phosphate with arsenic is not a major mechanism in this system.

6) A common phenomenon

The presence and distribution of organic matter drive the redox reaction catalysed by microbial activity and therefore control the mobility of arsenic. This suggests that wherever a source of organic compounds is in the proximity of FeOOH or sulfide deposits, with the corresponding anaerobic/aerobic environment, the mobility of arsenic can be considered as a threat. In Winthrop, the microbial release of arsenic is driven by the source of carbon from the landfill leachates, which is a common phenomenon at various locations where iron (or sulfide deposit) and carbon sources are available.

Several cases in the U.S and in other parts of the world have shown elevated concentrations of arsenic in the vicinity of organic sources. In Bangladesh, in a similar mechanism as in Winthrop, the reaction is driven by the microbial fermentation of organic compounds which serve as the electron donors for the reduction of arseniferous Fe(III) oxyhydroxide under anaerobic conditions (Nickson et al, 1999). High concentrations of arsenic pollution have been determined in areas of large buried peat deposits, or organic matter in aquifer sediments, both necessary to complete the redox reaction (McArthur et al, 2001). Bangladesh arsenic studies have also shown fermentative products such as short chain carboxylic acids and methylated amines and a correlation of arsenic with the presence of ammonium and phosphorus whose source originates from buried peat.

7) Recommendations

Redox zones in the vicinity of the landfill could be identified whereby the oxygen respirers would be closer to the surface and below the landfill, methanogenesis, iron and sulfate reduction, as well as fermentation would prevail in anoxic environments. A graphical presentation, or mapping of potential iron reduction (or sulfate and chloride concentration) as a function of depth versus distance from the landfill showing concentration gradients (or contours) could be implemented to distinguish the different redox zones (Christensen et al, 2001). This information, could then provide useful information for remedial investigation.

Studies of microbial identification in landfill leachate, which are few, could confirm the redox zones in groundwater from observation of the species (Christensen et al, 2001). Similarly, studies on fermentation in the landfill leachate concept have been poorly available (Christensen et al, 2001). Fermentation is highly associated with iron reduction and the rate at which both are metabolically driven could provide useful information as to the mobilization of arsenic.

A number of methods could be used to identify microbial diversity, among which are the culture enrichment and isolation technique, whose concept is to recreate the niche of the microorganisms in order to identify the type of microbial activity (Brock et al, 2000; Haack & Bekins, 1999). Other techniques include fluorescence staining for quantification and viability of microbes; the use of nucleic acid probe from fluorescent in situ hybridization for counting and identifying microorganisms; and radioisotopes and microelectrodes for microbial activity measurement (Brock et al, 2000). Laboratory microcosms are also used to recreate in-situ environments to analyse the dominant microbial mechanisms (Haack, 1999).

Also with regard to the mobility of arsenic, studies of sediments and sorption rates could be implemented. Furthermore, studies have shown great uncertainty as to the rate at which microorganisms influence the cycling of arsenate and arsenite (Jones C.A, 2000).

D) Zonation in the vicinity of the landfill

Knowledge of the different redox zones could be useful for the implementation of bioremediation. Typical zones of redox mechanisms have been suggested with distance from the landfill and in unsaturated aquifer (Chapelle, 1993; Christensen et al, 2001). The different zones, however, could differ depending on the water table fluctuations, the variability in groundwater direction, and the sediment distribution (Christensen et al, 2001).

1) Sulfate reduction

The environment beneath the landfill at Winthrop, which is anaerobic in most of the wells starting at shallow levels, suggests that sulfate reduction must be an important mechanism. Assuming the bromide tracer represents the groundwater flux responsible for the dispersion of the organic compounds from the landfill leachate, a link may exist between the bromide and sulfate data. If sulfate reduction is enhanced with increased flux of organic compounds, the expectation is a decreasing concentration of sulfate, as observed in the Figures 16-17 below for OW14 at level 4.

Figure 16
Bromide concentrations in OW wells
at level 4 as a function of time

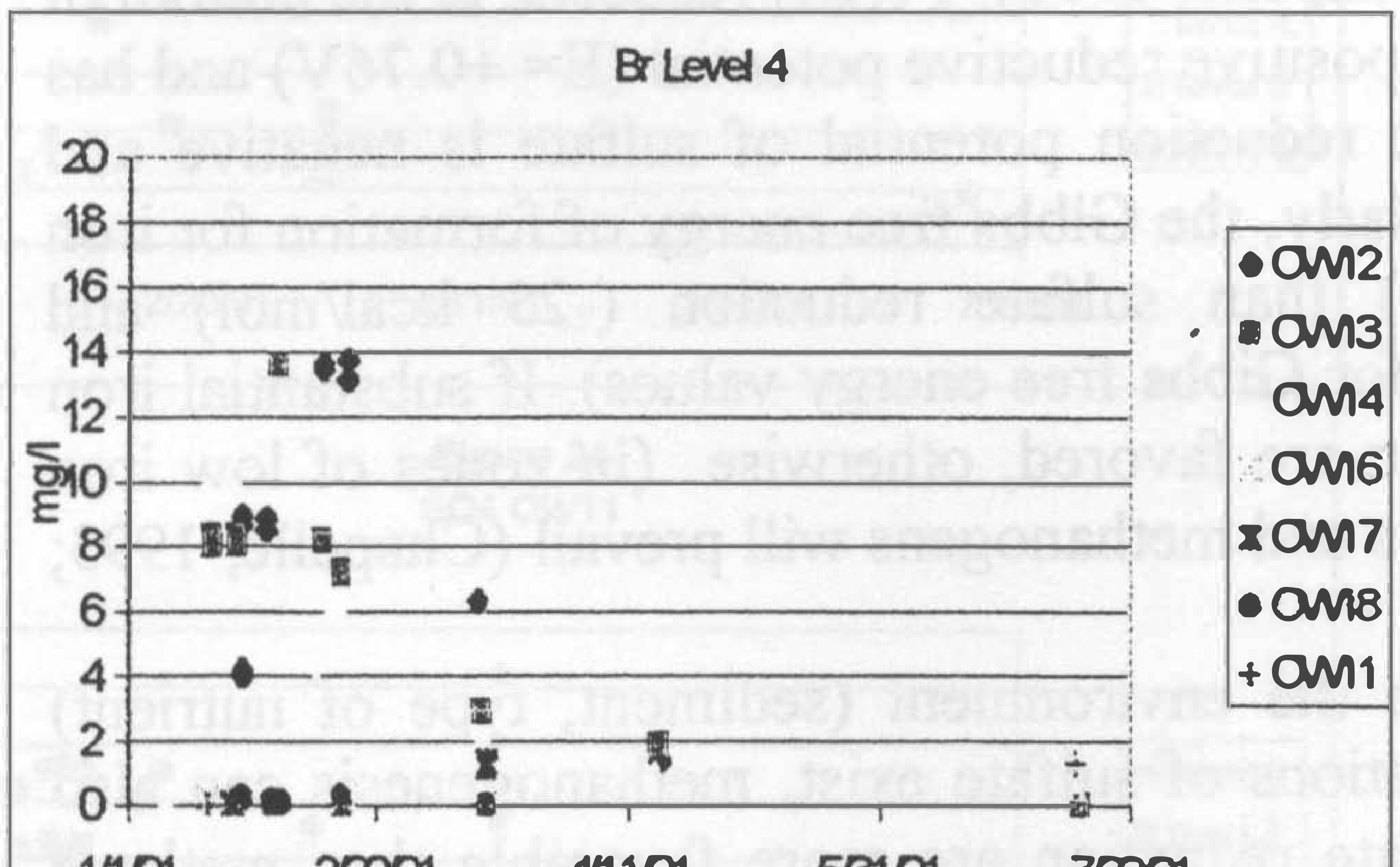
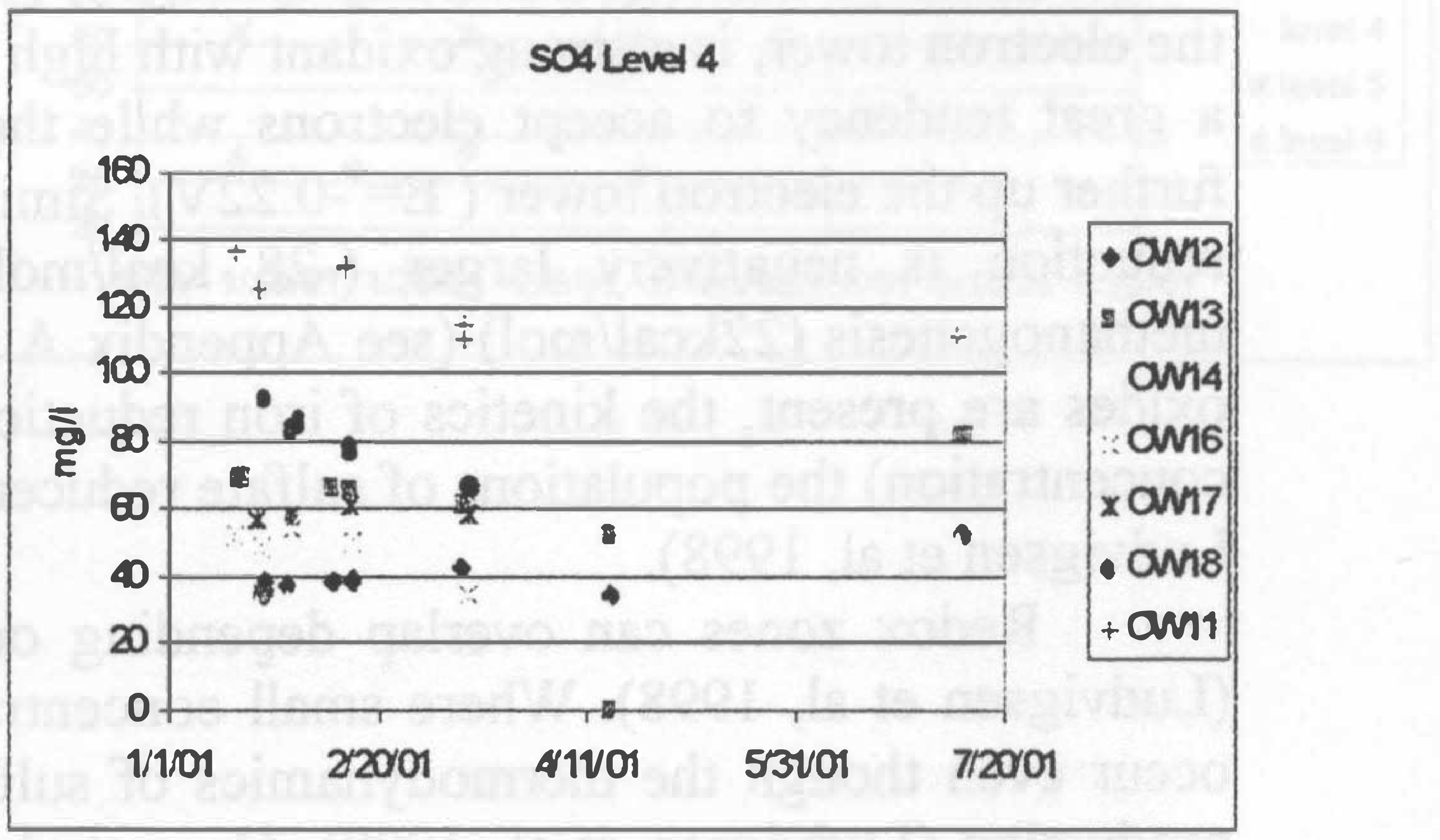


Figure 17
Sulfate concentrations in OW wells
at level 4 as a function of time



At this location, where the highest bromide concentration is recorded (17.2 mg/l), the sulfate concentration is very small (the average sulfate concentration for all wells is between 20 and 350 mg/l). At locations where the concentration of sulfate remains elevated and the concentration of bromide decreases significantly indicate that sulfate reduction is not enhanced in the system when the mass flux of organics (or groundwater flux) is not significant.

Studies on biogeochemistry have identified redox zonations in unsaturated aquifer (Chapelle, 1993) and in landfill leachates with distance from the landfill (Christensen et al, 2001). The typical zonation would be a depletion of oxygen, nitrate, sulfate and increase in S^{2-} and Fe(II) close to the landfill and an oxidizing environment (aerobic degradation) at distances far from the landfill and close to the surface; in other words, methanogens and sulfate reducers are generally abundant in close proximity to the landfill, and their number tends to decrease with distance away from the landfill (Christensen et al, 2001; Ludvigsen, 1998; Haack, 1999); this may explain the observed pattern of sulfate from the data. In the Winthrop landfill, small concentrations of sulfate have been recorded at shallow levels, which are closer to the landfill.

The sulfate data also show a constant concentration at the same level in most of the wells, then a decrease by the mid-period (see Figures 18-25, next page). This decrease is most pronounced at deep levels (levels 1 and 2), which suggests an increase in sulfate reduction. This declining sulfate concentration (sulfate reduction) could be the result of increased distribution of carbon source and moisture caused by the seasonal change due to infiltration from snow melting since the decrease can be observed starting the spring season. Because an upper level redox zone travels downstream and the measurements obtained are based on the composition of groundwater (Ludvigsen, 1998), the data may not reflect the actual redox condition of the sampling.

2) *Other redox processes*

Other redox processes compete with sulfate reduction, and the dominant mechanism will be favored based on the thermodynamics of the reaction. The hydrogeology or groundwater flow will also affect the redox processes with the variable fluxes of nutrients and electron acceptors. With regard to iron and sulfate, Fe(III) reducers compete with and exclude sulfate reducers (and methanogens) for fermentative products such as acetate, formate, and hydrogen; sulfate reducers competitively exclude methanogens as both compete for the same substrate, which are fermentation products (acetate and hydrogen) (Chapelle, 1993). Fe(III) reducers, at the bottom of the electron tower, is a strong oxidant with high positive reductive potential (E= +0.76V) and has a great tendency to accept electrons while the reduction potential of sulfate is negative and further up the electron tower (E= -0.22V). Similarly, the Gibbs free energy of formation for iron reduction is negatively larger (-28 kcal/mol) than sulfate reduction (-25 kcal/mol) and methanogenesis (22kcal/mol) (see Appendix A for Gibbs free energy values). If substantial iron oxides are present, the kinetics of iron reduction are favored, otherwise (in zones of low iron concentration) the populations of sulfate reducers and methanogens will prevail (Chapelle, 1993; Ludvigsen et al, 1998).

Redox zones can overlap depending on the environment (sediment, type of nutrient) (Ludvigsen et al, 1998). Where small concentrations of sulfate exist, methanogenesis can also occur even though the thermodynamics of sulfate reduction are more favorable than methane production (Ludvigsen et al, 1998). On a study on biogeochemistry of a landfill leachate, low sulfate concentration near the landfill was explained by the prevalence of methanogenesis when high concentration of organic compounds was present (Christensen et al, 2001). Because organic compounds that are used by methanogens may not be used by sulfate reducers, microorganisms at different locations require different nutrients (Haack, 1999). Knowledge of the geology (or

Figures 18-23

Sulfate concentrations per well at different levels (depth)

(x-axis for all figures is the date the samples were collected)

Figure 18

SO4 OW12

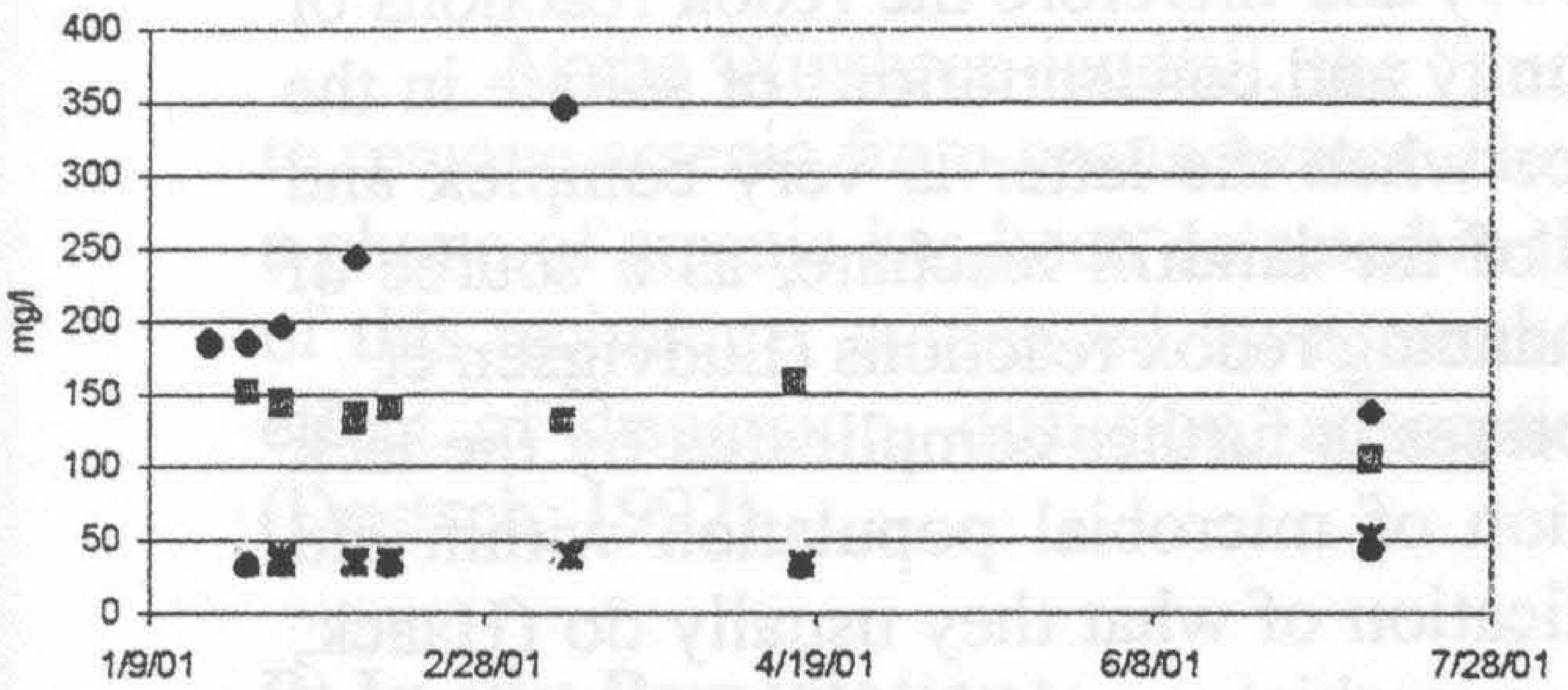


Figure 19

SO4 OW13

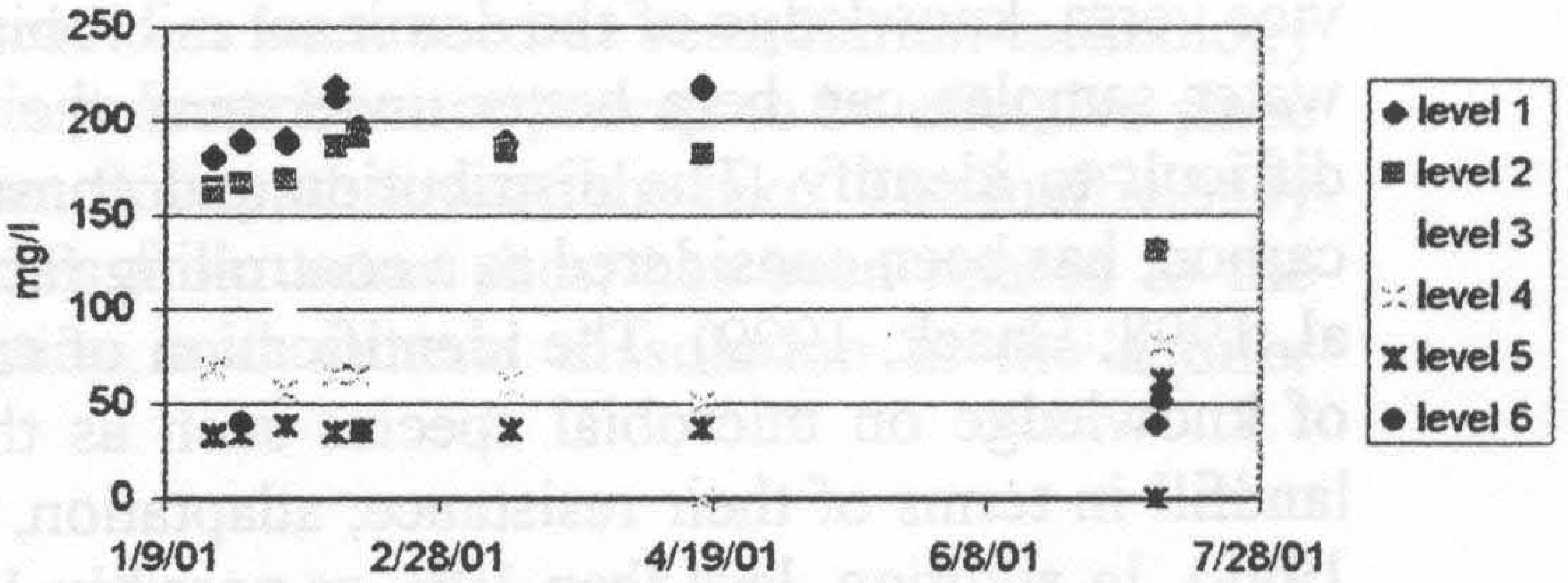


Figure 20

SO4 OW14

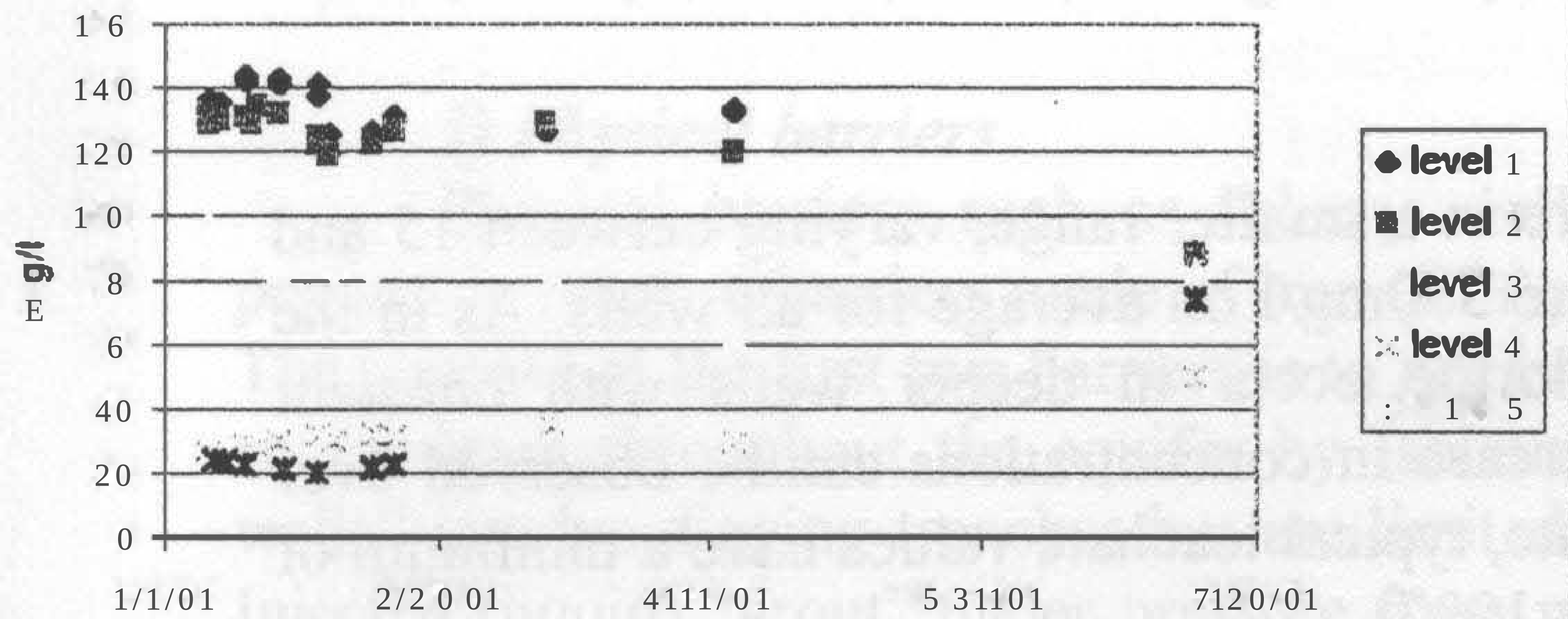


Figure 21

SO4 OW16

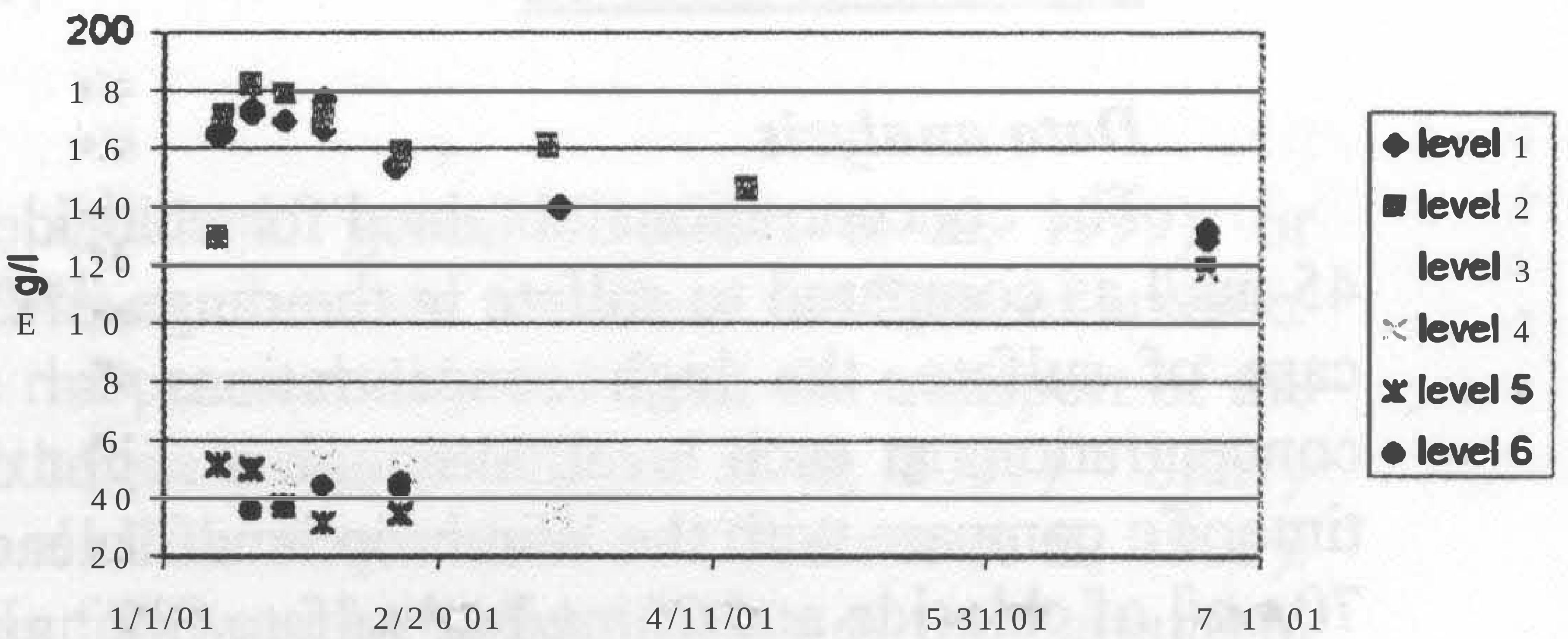


Figure 22

SO4 OW17

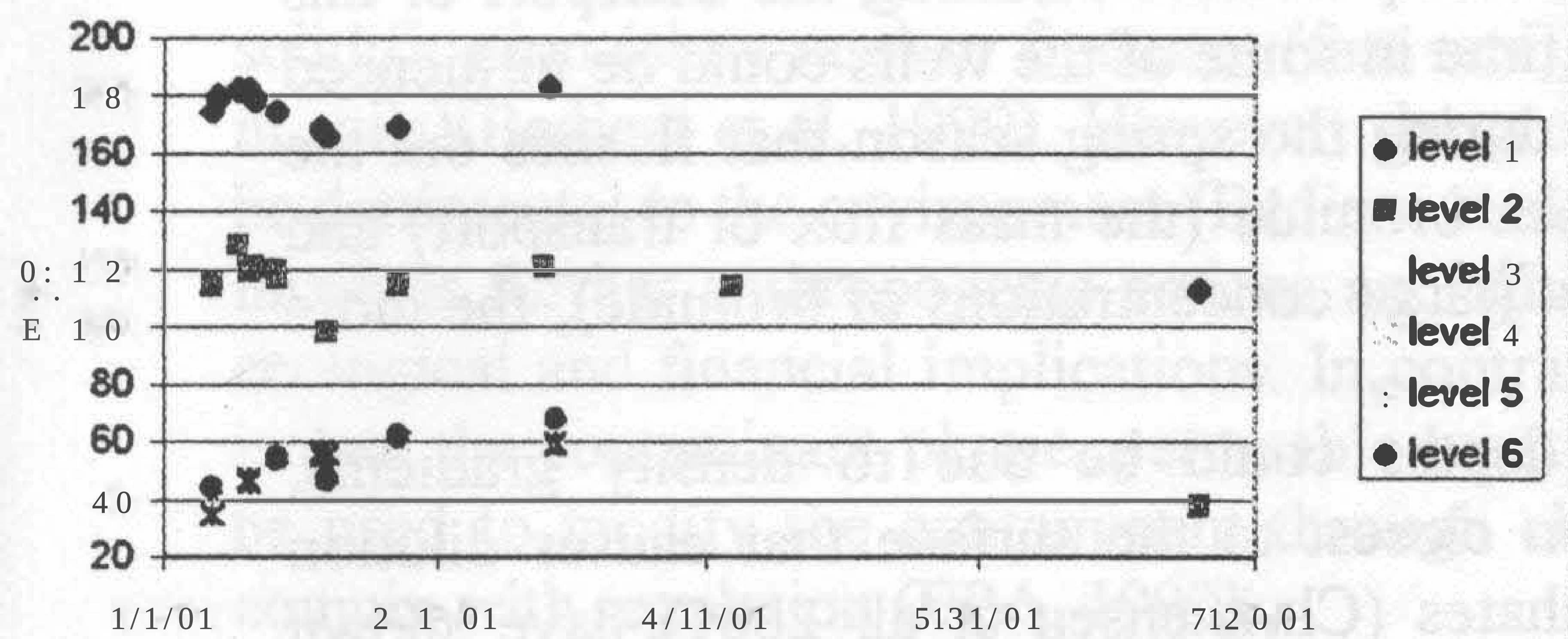


Figure 23

SO4 OW18

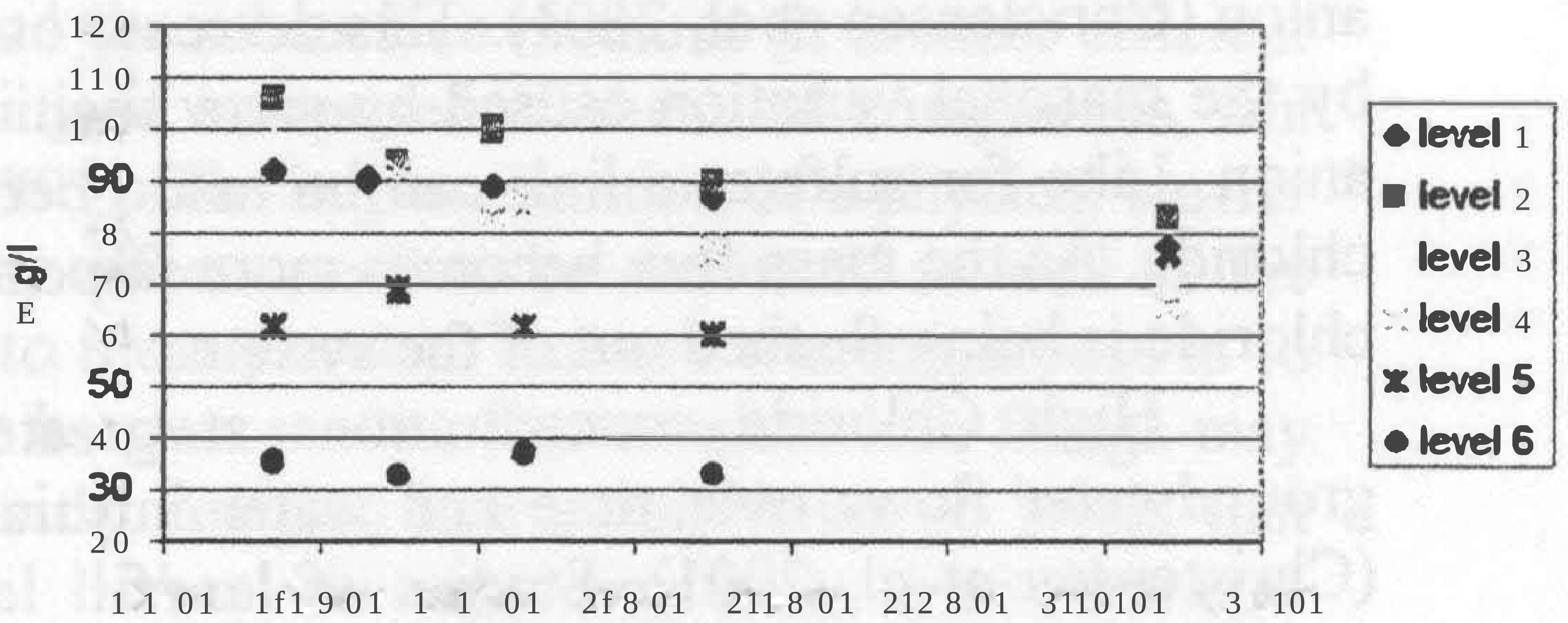
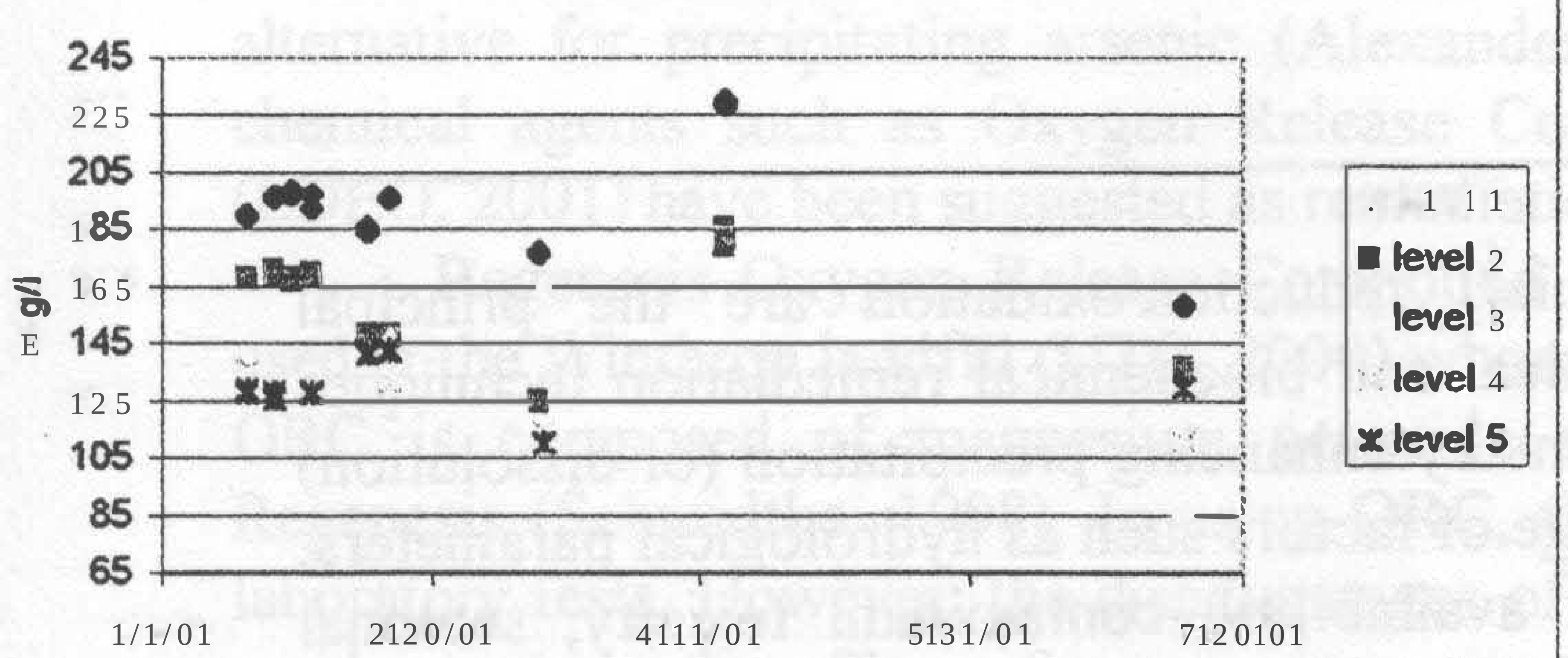


Figure 24

SO4 OW11



sediments), carbon source, and hydrologic parameters are important in defining the dominant microbial population (Christensen et al, 2001; Haack, 1999) and therefore the redox reactions or vice versa, knowledge of the dominant microbial community and concentrations of sulfate in the water samples can help better understand the subsurface when the latter is very complex and difficult to identify. The distribution and constant flow of the landfill leachate, as a source of carbon, has been considered as a controlling factor in enhancing redox reactions (Ludvigsen et al, 1998; Haack, 1999). The identification of redox processes is further complicated by the lack of knowledge on microbial species such as the evolution of microbial population within old landfill in terms of their resistance, adaptation, or modification of what they usually do (Haack, 1999). In addition, less than 10% or possibly 1% of the microbial population have been named and identified (Haack, 1999).

D) Chloride Analysis

Data analysis

The concentrations obtained for chloride are in a smaller range, varying between 15 and 45 mg/l as compared to sulfate in the range of 25 to 350mg/l on average for all wells. As in the case of sulfate, the high concentrations for chloride occur in deeper wells with constant concentrations at each level, although a slight decrease in concentrations can be observed over time. To compare with the Winthrop landfill leachate, typical leachate values have a minimum of 70mg/l of chloride and 55mg/l of sulfate (Manning, 1997).

Chloride has a low reactivity and is not substantially affected by physical reactions such as sorption and precipitation; hence, low or decreasing concentrations of chloride may be caused by leaching and dilution, which are the most important processes affecting the transport of this anion (Christensen et al, 2001). This decrease over time in some of the wells could be influenced by the seasonal variation caused by snow melting during the spring season that flushes out the anion. Like for sulfate, a link can be made between bromide (the mass flux or transport) and chloride. As the mass flux becomes more important (large concentrations of bromide), the more chloride is being flushed out of the system.

High Chloride concentrations at greater depths could be due to density gradients, groundwater flows over time and water infiltration closest to the surface that causes dilution (Christensen et al, 2001). Studies of landfill leachates (Christensen et al, 2001) have shown density to be a major factor that encourages vertical transport since vertical dispersion effect is generally considered to have a minor influence.

REMEDIATION

Since adsorption/desorption and (microbial) reduction/oxidation are the principal processes that dictate the release of arsenic, chemical and biochemical remediation techniques have been suggested to manipulate these mechanisms by enhancing precipitation (or dissolution) of arsenic. During remedial investigation, knowledge of factors such as hydrological parameters, geology, geochemistry, temperature, pH, nutrient availability, contaminant toxicity, seasonal variation, and microbial rate and identification, is necessary to efficiently proceed with the design of an adequate remediation system of groundwater (or soil).

A) Ex-situ Remediation: "Pump and Treat"

At the Winthrop landfill, the "pump and treat" has been used as remediation technology to remove arsenic from groundwater. However, this process has not proved to be effective since a plume of arsenic has been detected in the southern flow path toward the lake. The inefficiency of this technique, evidenced by a number of studies from other sites, has been related to the effect of dispersion, diffusion, adsorption/desorption, and mineral dissolution in the aquifer (Deutsch, 1997).

B) In-situ Remediation

Alternatives to "pump and treat" remediation are the construction of a physical barrier to stop the flow of pollutant, the addition of chemical agents, or bioremediation (Alexander,1999; Bedient, 1999; Deutsch, 1997; Mulligan et al, 2001).

1) Physical barriers

Physical barriers such as "slurry walls", injected "grout" (Bedient et al, 1999), or permeable reactive barriers made of iron (EPA, 1997) can be used to reduce the flow of arsenic. The purpose of the first two barriers is to decrease the permeability and limit the transport of the contaminant throughout the aquifer by isolating the pollutant (Mulligan et al, 2001). "Slurry walls" involve digging trenches but are limited to shallow contamination (Bedient et al, 1999). Injected (liquid) "grout" under pressure from wells followed by solidification of the "grout" in the subsurface decreases the porosity of the aquifer and constitutes a physical barrier that limits the groundwater transport of the contaminant (Bedient et al, 1999). The efficiency of grouting walls depends on the distance between wells, the injection rate that may cause early solidification (slow rate) or fractures (fast rate), and the subsurface medium (it is most efficient in soils)(Bedient et al, 1999). However, the grouting, if composed of chemical compounds, can be detrimental to the environment (Bedient et al, 1999). The implementation of a physical barrier involves further anthropogenic actions and adverse effects need to be evaluated as well as the ecological and financial implications. In contrast to these physical barriers whose purpose is to isolate the contaminant plume, permeable reactive barriers made of zero-valent iron filings may be used to modify the contaminant through chemical reaction and precipitation to levels that comply with regulation (EPA, 1997).

2) Chemical Oxidizing Agents

The oxidation of arsenite to arsenate has been known for decades as a remedial alternative for precipitating arsenic (Alexander, 1999). To create an oxidizing environment, chemical agents such as Oxygen Release Compound (UTC, 2000) and hydrogen peroxide (LDEO, 2001) have been suggested as remediation techniques at Winthrop, Maine.

Regenesis Oxygen Release Compound (ORC) is a recent in-situ remedial technology used at the Winthrop landfill (UTC, 2000) whose purpose is to provide oxygen to the subsurface. ORC is composed of magnesium peroxide and phosphate ions, a product distributed by Regenesis (Schmidtke, 1998). In using ORC, the oxygen evolution rate can be determined by laboratory tests. However, the disadvantages of this technique are the dependence of a catalyst on the system, the effect of temperature on enzyme activity, the atmospheric loss from the system, the microbial demand, and the breakdown of the ORC chemical components, all of which dictate the oxygen release rate (Schmidtke, 1998). The use of ORC at Winthrop has shown little change in the geochemistry of the site, probably due to a high oxygen demand and/or hydrologic parameters (Stute et al, 2001).

As a remedial alternative, hydrogen peroxide is being investigated as a source of oxygen for the Winthrop site (LDEO, 2001). The addition of chemicals in the process is to enhance the precipitation of arsenic in groundwater. The purpose of oxygen injection is to increase the redox potential and precipitate FeOOH, which is insoluble under aerobic conditions (Deutsch, 1997). Arsenic has a strong affinity for FeOOH and is immobilized on the mineral surface (Deutsch, 1997). Laboratory tests of ORC and hydrogen peroxide for at a site in Alaska have shown that the oxygen release rate was much faster for hydrogen peroxide as compared to ORC whose rate was affected by its initial breakdown and presence of a catalyst (Schmidtke, 1998). Hydrogen peroxide has the advantage of being highly reactive and can supply as much as 100 mg/l oxygen compared to other oxygen release methods such as pure "oxygen sparging" (40 mg/l) and "air sparging" (8 mg/l)(National Research Council (NRC), 1993).

However the chemical oxidation of organic and inorganic constituents through hydrogen peroxide creates precipitates that could cause clogging of the aquifer and thereby limits the distribution of oxygen through the system (NRC, 1993). The permeability could further be reduced by bubbles generated by oxygen concentrations exceeding water saturation (NRC, 1993). While hydrogen peroxide is being used to precipitate arsenic, it has also the ability to mobilize metals such as lead and antimony (NRC, 1993) present in the system. Therefore, anthropogenic activities for one remedial purpose (e.g. arsenic decontamination) can have adverse secondary effects that must be evaluated in order to avoid the release of other pollutants.

Hydrogen peroxide, as a strong oxidant, can kill anaerobic bacteria (Chapelle, 1993). Aerobic microorganisms, having the enzyme *catalase*, are capable of catalysing peroxide to oxygen and water and therefore are protected from the toxicity of peroxide in contrast to anaerobic microorganisms that do not have this enzyme (Chapelle, 1993). Hence, hydrogen peroxide can be detrimental to anaerobic bacteria such as sulfate and Fe(III) reducers, but not to aerobic bacteria. Hydrogen peroxide would then inhibit the proliferation of Fe(III) reducers which stimulate the release of arsenic in solution. However, in the presence of sulfides, sulfide oxidation would encourage the release of arsenic. The addition of hydrogen peroxide to the aquifer is further complicated by the adaptation of microorganisms to this chemical agent over time (NRC, 1993).

Although protozoa are generally not present in anaerobic leachate, experiments using hydrogen peroxide for remediation have evidenced large quantities of protozoa due to the presence of oxygen (Haack, 1999). Protozoa, being predators of microbes, increase the aquifer porosity by reducing the microbial mass (Haack, 1999) but can be damaging to microbes, some of which (such as iron oxidizers) are beneficial for the decontamination of groundwater with arsenic. However, the present knowledge about the kinetics of protozoa in leachates is limited (Christensen et al, 2001).

3) Bioremediation

In-situ bioremediation consists of using microorganisms to remove or convert the pollutant into a harmless form either by degradation or immobilization (NRC, 1993). Although microbes contribute to the contamination of groundwater, they can also be used in a beneficial way such as bioremediation to inhibit the release of arsenic in groundwater. Thus, bioremediation can be an inexpensive way of reducing arsenic toxicity. This technique consists way such as bioremediation to inhibit the release of arsenic in groundwater. Thus, bioremediation can be an inexpensive way of reducing arsenic toxicity. This technique consists of selecting the right microbes and growing them by adding the right nutrients and creating the right environment (aerobic/anaerobic) that stimulates their growth. The injection of microbes that favor arsenate, such as *Thiobacillus ferooxidans* which are iron oxidizing bacteria (since arsenate prevails in oxidizing environments), and adsorption of arsenate onto minerals followed by precipitation should favor a subsurface flow that is free of mobile arsenic. In the case of iron and sulfides, iron oxides, on which arsenate sorbed, precipitate under oxidizing environments (but dissolve under reducing conditions) while sulfide compounds precipitate under reducing conditions (but dissolve under oxidizing conditions).

Iron ferrous oxidizing bacteria are very important in controlling the release of iron and arsenic into the environment; experiments on archaean microorganisms with high acid and metal tolerance in iron oxidation have been performed by Banfield et al. (2000). Arsenite oxidation to arsenate mediated by microorganisms, followed by arsenate adsorption on ferryhydrite, can be an alternative way of reducing the mobility of arsenic in groundwater (Banfield et al, 2000). However, bioremediation with oxidizing bacteria requires the right environment (aerobic) and depends on the availability of oxygen.

Another alternative is to favor arsenite instead of arsenate. In reducing conditions, arsenic can be precipitated in the form of arsenic sulfides (Banfield et al, 2000). The reduction of arsenate to arsenite can be mediated by sulfate-reducers *Desulfotomaculum*. The resulting product is a mineral precipitate (As_2S_3); this process is called biomineralization, i.e., a remediation using microbial activity that transforms the toxic form of arsenic into a precipitate that settles out of groundwater flow (Brock, 2000; Newman, 1997). The precipitation of As_2S_3 can be favored by the bacterium *desulfotomaculum auripigmentum* which catalyses two reduction reactions: arsenate to arsenite and sulfate to H_2S (Newman, 1997; Alexander, 1999). Sulfate reducing bacteria have been proposed as a remedial alternative to groundwater contamination of arsenic at Winthrop (LDEO). However, in anaerobic and reducing conditions, the kinetics of Fe(III) reduction dominate over sulfate reduction, in the presence of large quantities of ferric iron (Christensen et al, 2001).

By adding chemical agents, (or through bioremediation) the reactant should immobilize arsenic and stabilize the geochemistry of the area of concern so that the system does not revert in the future (Deutsch, 1997). By providing oxygen to precipitate arsenic, through chemical additives or bioremediation, the metalloid still remains in the system, although in its insoluble form and not as a contaminant to groundwater. Metalloids cannot be destroyed by bacteria, but the latter could modify the reactions or immobilize them into a precipitate form (NRC, 1993). However, if the source of oxygen is no longer delivered and the landfill leachates persist as a source of organic carbon, the system may revert to the original redox state that favors the growth of iron reducers and the release of sorbed arsenic into solution.

Enhanced leaching of sediments/soil to reduce arsenic from the system can be an alternative if arsenic is captured downstream. Bioremediation of soil pollution can be mediated through the arsenic respirer *sulfurospirillum arsen-ophilum*, also known as MIT13. While the previous bioremediation consisted of keeping the arseniferous compounds (arsenate) in soil as a dense precipitate that does not move with groundwater flow, the bioremediation for soil pollution with arsenic consists of favoring arsenite, which is the mobile form of arsenic. In this case the pollution occurs in the soil and the objective is to decontaminate the soil from arseniferous compounds and favor arsenite which will be released from soil to water. This contaminated water can then be treated through oxidation and adsorption on iron oxides and the precipitate disposed of in a secure place (Ahmann, 2001).

However, bioremediation is limited by the lack of practicality and the complexity of the subsurface. In the implementation of bioremediation, increasing the number of samples, modeling biostransformation and establishing safety factors have been suggested to reduce uncertainty (NRC, 1993). In-situ bioremediation as a new remedial approach has been an attractive mean of cleaning up the environment but limited by the lack of understanding microbial processes specific to the site, the complexity and lack of innovative means of providing agents (oxygen, nutrients) that enhance microbial growth and survival, and the uncertainty as to the microbe-pollutant interaction (NRC, 1993).

CONCLUSION

At the Winthrop landfill, the mobilization of arsenic is caused by the landfill leachate and the presence of arseniferous iron and sulfide geology. The patterns of the leachate could be illustrated by the bromide tracer, assuming the latter is conservative. In evaluating the validity of bromide as a conservative tracer, adsorption mechanisms (desorption and anionic competitive exchange with sulfate) can be responsible for the high (low) SF_6/Br ratios which tend to prevail at deep (shallow) levels. However, the identical patterns of bromide and SF_6 time series in a number of wells suggest bromide behaves similarly to SF_6 which is an inert tracer. Assuming, bromide is conservative, the results from the bromide tracer indicate that groundwater fluxes are highly variable from one well to another and at different depths. The tracer tests also help to evaluate transport parameters and the locations where the mass fluxes of the leachate are most influential in constraining the distribution of organic compounds. The latter, which serve as the substrate for iron reducers and sulfide oxidizers, promote the dissolution of arsenic (arsenite) into groundwater under anaerobic and oxic environments respectively. The analysis of sulfate has shown increased sulfate concentration with depth, in the range of 20 to 350 mg/l (of sulfate), or increased sulfate reduction in close proximity to the landfill, at shallow depths. As remedial alternatives, each method offers attractive characteristics as well as disadvantages. Physical barriers such as grout injection into wells constrain the flow of contaminants by decreasing the porosity but are costly and difficult to implement. The addition of chemical agents oxidizes the subsurface and promotes the precipitation of arsenic. However, the oxidation of the aquifer also promotes sulfide oxidation, which is another mechanism by which arsenic is released to groundwater. Although arsenic is immobilized through precipitation, the reversible reaction, that is iron reduction and mobilization of arsenic, is possible if the source of oxidant is no longer available and if the leachate persists, assuming organic compounds can remain for centuries in landfills. Bioremediation through the use of microorganisms is an emerging remedial alternative which is less destructive to the environment but demands additional research and development efforts. To further evaluate the above techniques, the arsenic cycling rate, adsorption/desorption rates, sediment and microbial characterization of the subsurface are required. In addition, more research work is needed on the bacteria that have evolved and adapted in old landfills. Although the pollutant of the groundwater is arsenic, the original source of contamination is the landfill leachate without which organic compounds would not be distributed to catalyze the redox reactions responsible for the dissolution of arsenic. Old landfills are numerous in the U.S. and their detritus will remain there for centuries. Despite the emergence of modern landfills engineered with liners and the monitoring of groundwater, the risk of leakage is permanent and the environmental impact of landfills can be influential on a larger scale, that is on groundwater, soil, and eventually surface water. However, regulation that prevents the installation of landfills in areas of arseniferous iron and sulfide bedrocks and sediments is not currently available.

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APPENDIX A: Major Redox Reaction in Landfill Leachates

(Christensen et al, 2001 [from Stumm & Morgan, 1996])

Reaction		**ΔGo(W)kcal/mol**
Aerobic respiration	$CH_2O+O_2 \rightarrow CO_2+H_2O$	-120
Denitrification	$5CH_2O+4NO_{3^-}+4H^+ \rightarrow CO_2+2N_2+7H_2O$	-114
Manganese reduction	$CH_2O+2MnO_2+4H^+ \rightarrow CO_2+2Mn_{(2+)}+3H_2O$	-81
Iron reduction	$CH_2O+4Fe(OH)_3+8H^+ \rightarrow CO_2+4Fe_{(2+)}+11H_2O$	-28
Sulfate reduction	$2CH_2O+SO_{4(2-)}+H^+ \rightarrow 2CO_2+HS^-+2H_2O$	-25
Methanogenic/ fermentative organic matter mineralization	$2CH_2O \rightarrow CH_3COOH \rightarrow CH_4+CO_2$	-22

APPENDIX B: Physical & Chemical Properties of Arsenic

(EPA, 1998; Smith, 1973)

Table 1: Physical properties of arsenic

Atomic weight	74.92
Melting point (deg.C) at 39.1MPa	816
Latent heat of fusion at melting point (kJ/mol)	21.3
Specific heat (J/mol.K)	24.6
Latent heat of sublimation (kJ/mol.K)	31.974
Vapour pressure: 10E-3 atm at (deg.C)	356
10E-2 atm at (deg.C)	421
10E-1 atm at (deg.C)	502
Boiling point (deg.C)	616
Density (kg/m³)	5780
Hardness	3.5

Table 2: Common arsenic compounds

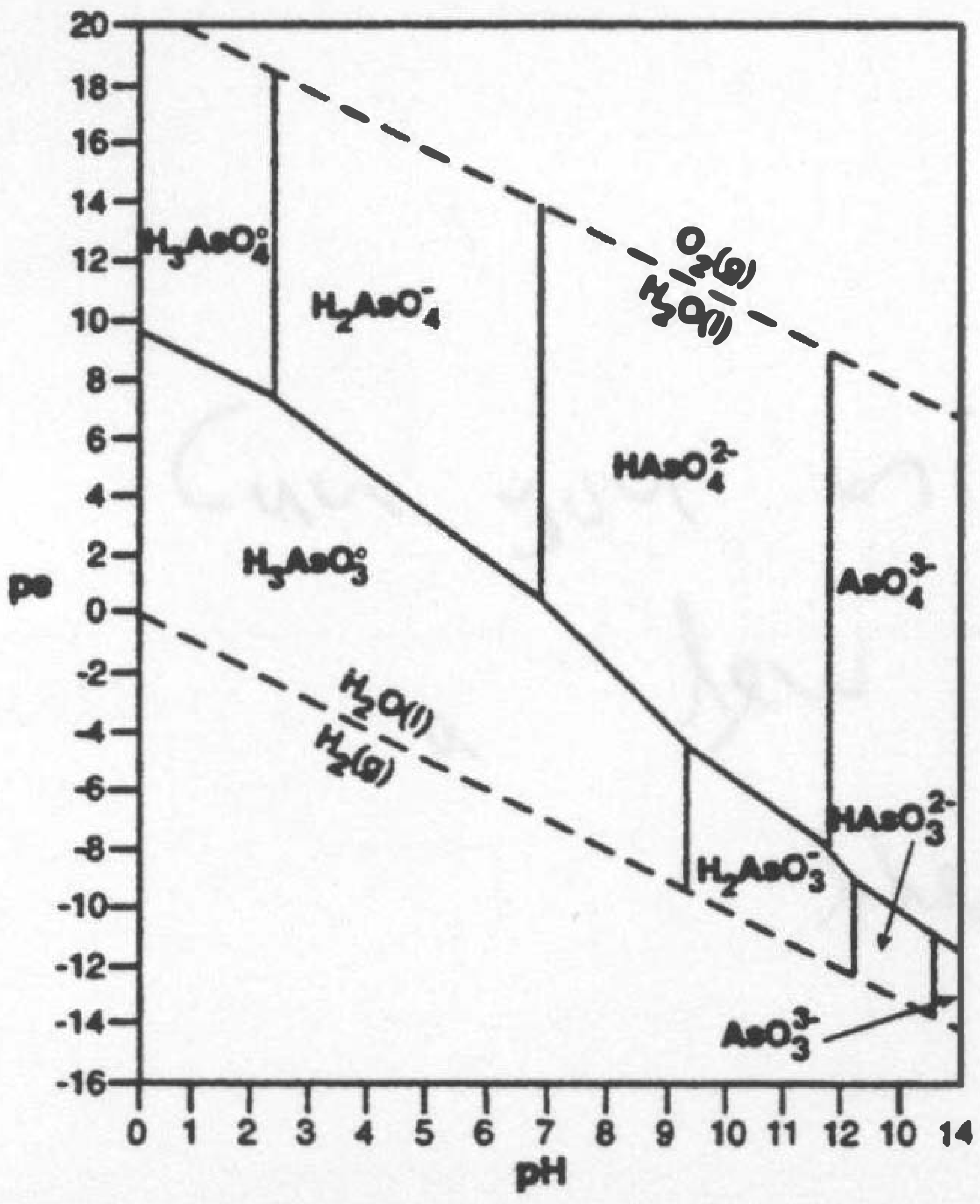
Compounds	Chemical formula
Arsenic acid	H3AsO4 0.5H2O
Arsenic disulfide	As2S2
Arsenic pentoxide	As2O5
Arsenic trioxide	As2O3
Arsenic trisulfide	As2S3
Arsenic hydride (arsine)	AsH3
Some organic arsenic compounds:	
Ethylarsine	C2H7As
Diethylarsine	C5H11As
Methylarsine	CH3AsH
Dimethylarsine	(CH3)2AsH

Table 3: Oxidation potentials

		V
1.	As(s)+3H+ +3e- ↔ AsH3 (g)	-0.239
2.	HasO2 +3H+ +3e- ↔ As(s) + 2H2O	+0.247
3.	1/2As2O3(s) + 3H+ ↔ As(s) + 3/2H2O	+0.234
4.	H3AsO4 + 2H+ + 2e- ↔ HasO2 + 2H2O	+0.559
5.	AsO2(-) + 2H2O +3e- ↔ As(s) +4OH-	-0.68
6.	AsO4(3-) + 2H2O + 2e ↔ AsO2(-) + 4OH-	-0.67

Figure 1: Arsenic Speciation

Arsenic pe/pH diagram (Deutsch, 1997 [modified from Rai and Zachara, 1984])



APPENDIX C: Tracer Injection Calculations (Stute M., LDEO)

minimum required Br concentration (early calculations)

4.30E-06 mol/L	max background Br concentration	
2.14E-06 mol/L	EW2 Br concentration	
1.00E+05	Factor by which we want to exceed the Br background	
4.30E-01 mol/L	Br concentration in injected fluid	
44.29 g/L	NaBr concentration in injected fluid	
100 L	concentrated NaBr/SF6 mixture	
4.4 kg	total	10L per hole

10 x 20L cubitainers were used for tracer injection

NaBr

30	500 g	containers were ordered
	1500 g NaBr	per cubitainer
	15000 g NaBr	total injected (10 * 20L cubitainers)
	145.8 mole	

SF6

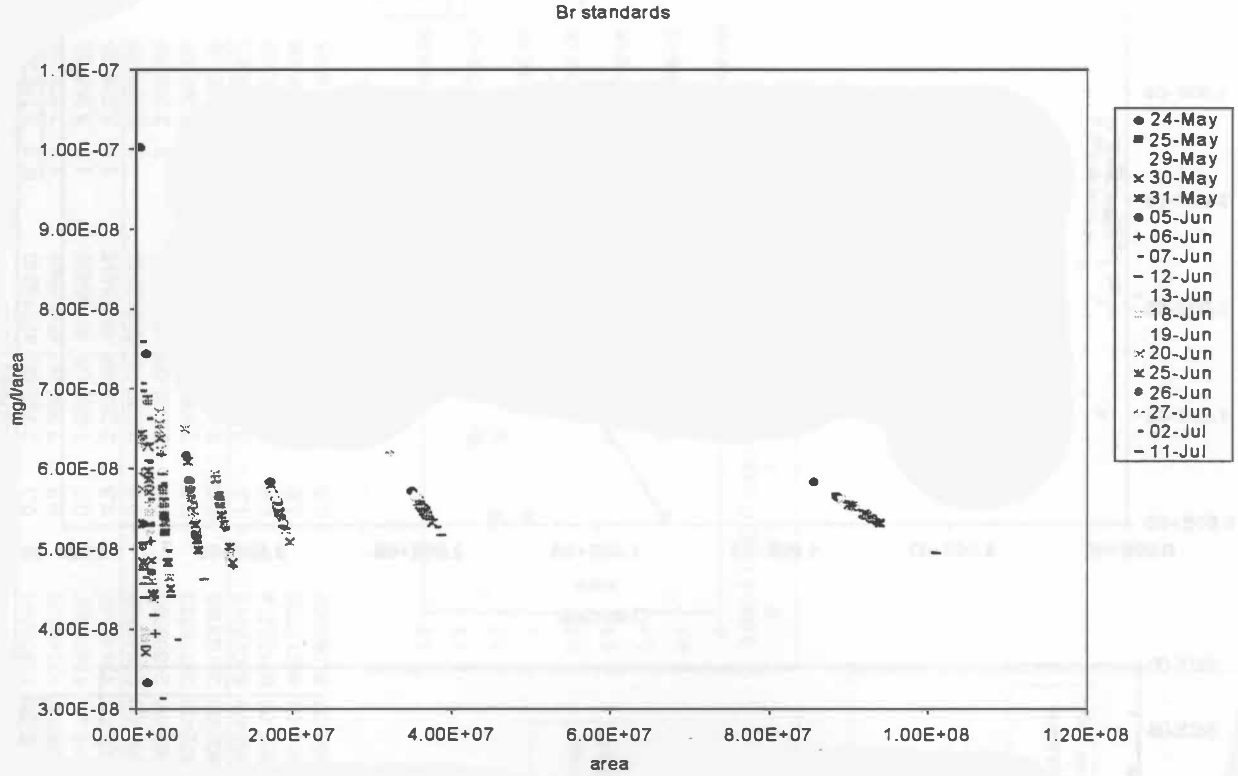
12 μL	total quantity injected during the first experiment
2400 μL	best estimate of total quantity injected during second experiment
1.07E-04 mole	best estimate of total quantity injected during second experiment

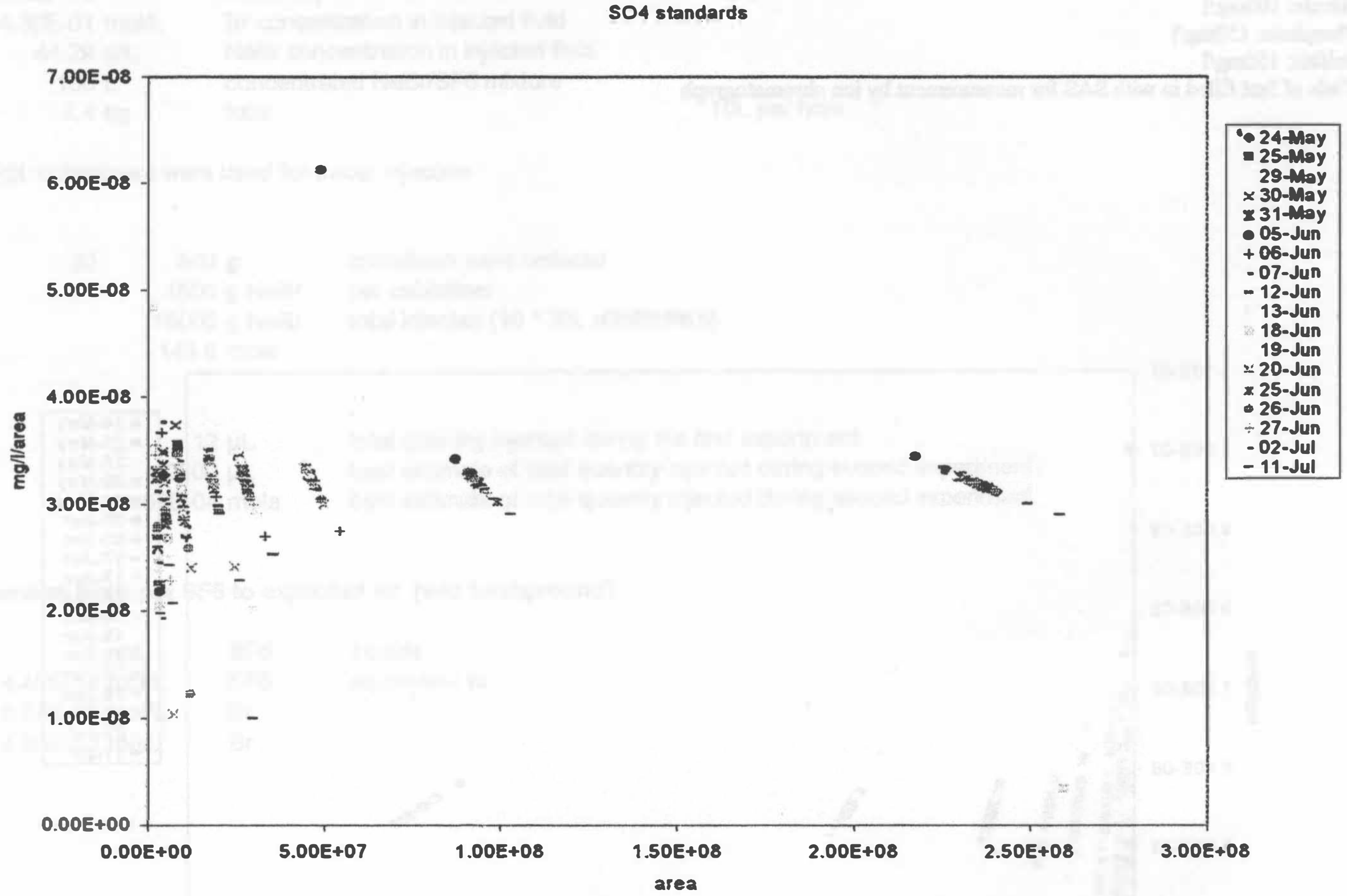
conversion from ppt SF6 to expected Br (w/o background)

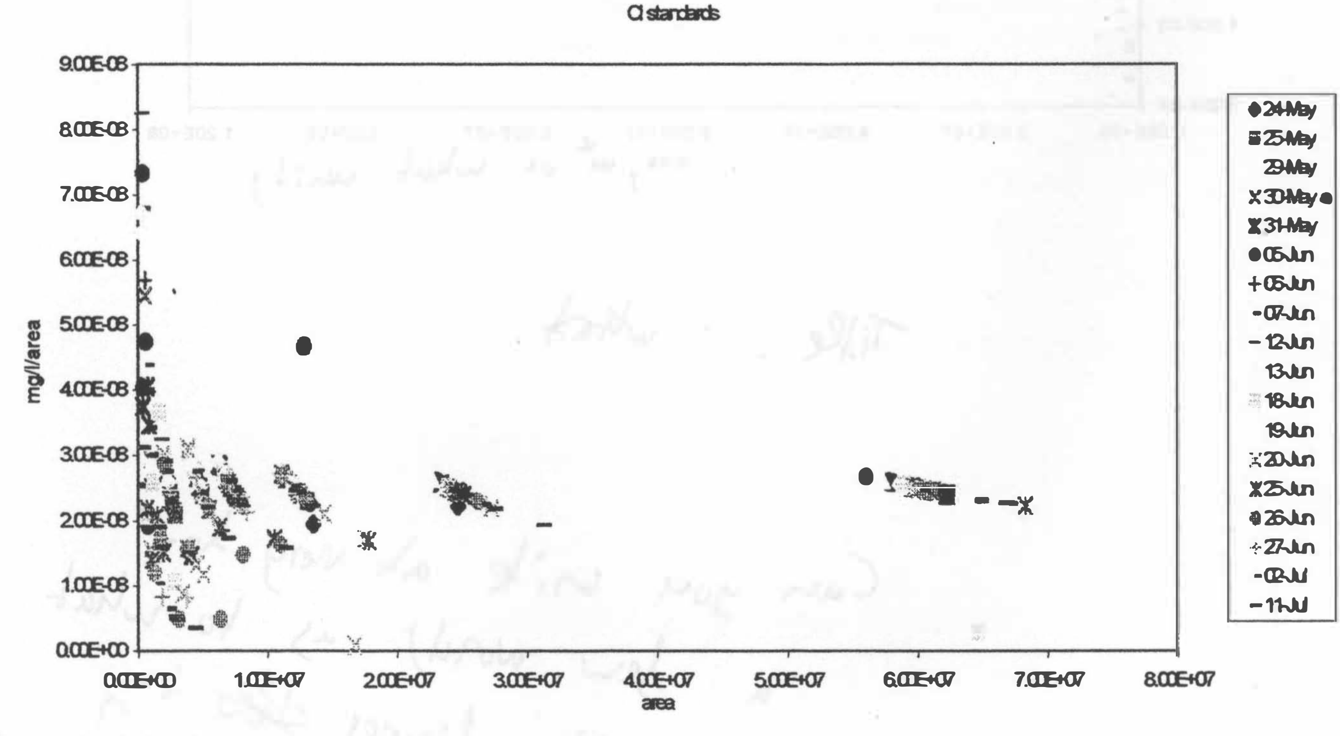
1 ppt	SF6	equals
4.46E-14 mol/L	SF6	equivalent to
6.07E-08 mol/L	Br	
4.85E-03 mg/L	Br	

APPENDIX D: Standard Measurement/Calibration

Standard Anion Solution (SAS) from Dionex:
Fluoride: 20mg/l
Chloride: 30 mg/l
Nitrite: 100mg/l
Bromide: 100mg/l
Nitrate: 100mg/l
Phosphate: 150mg/l
Sulfate: 150mg/l
Vials of 5ml filled in with SAS for measurement by ion chromatograph

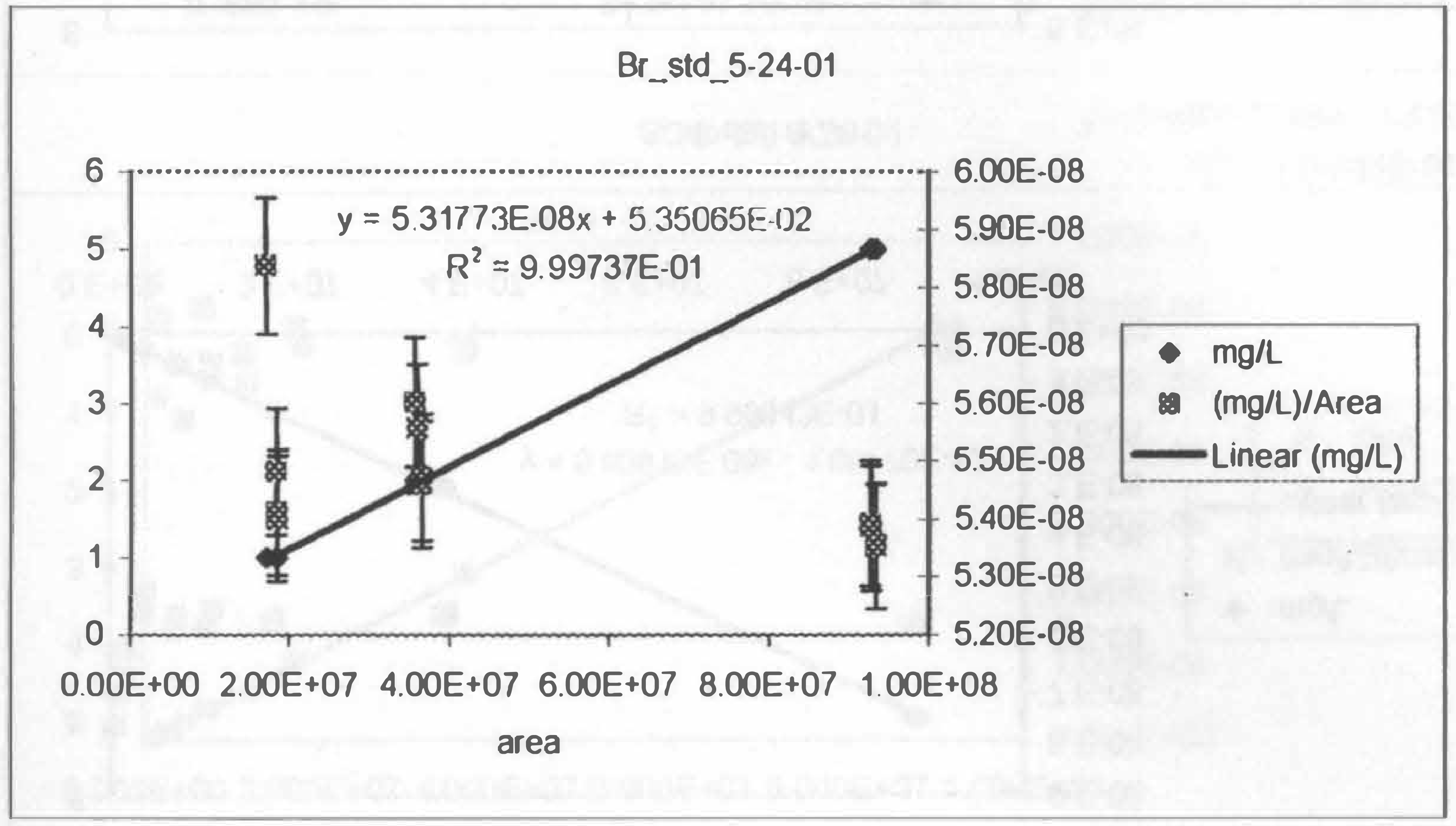


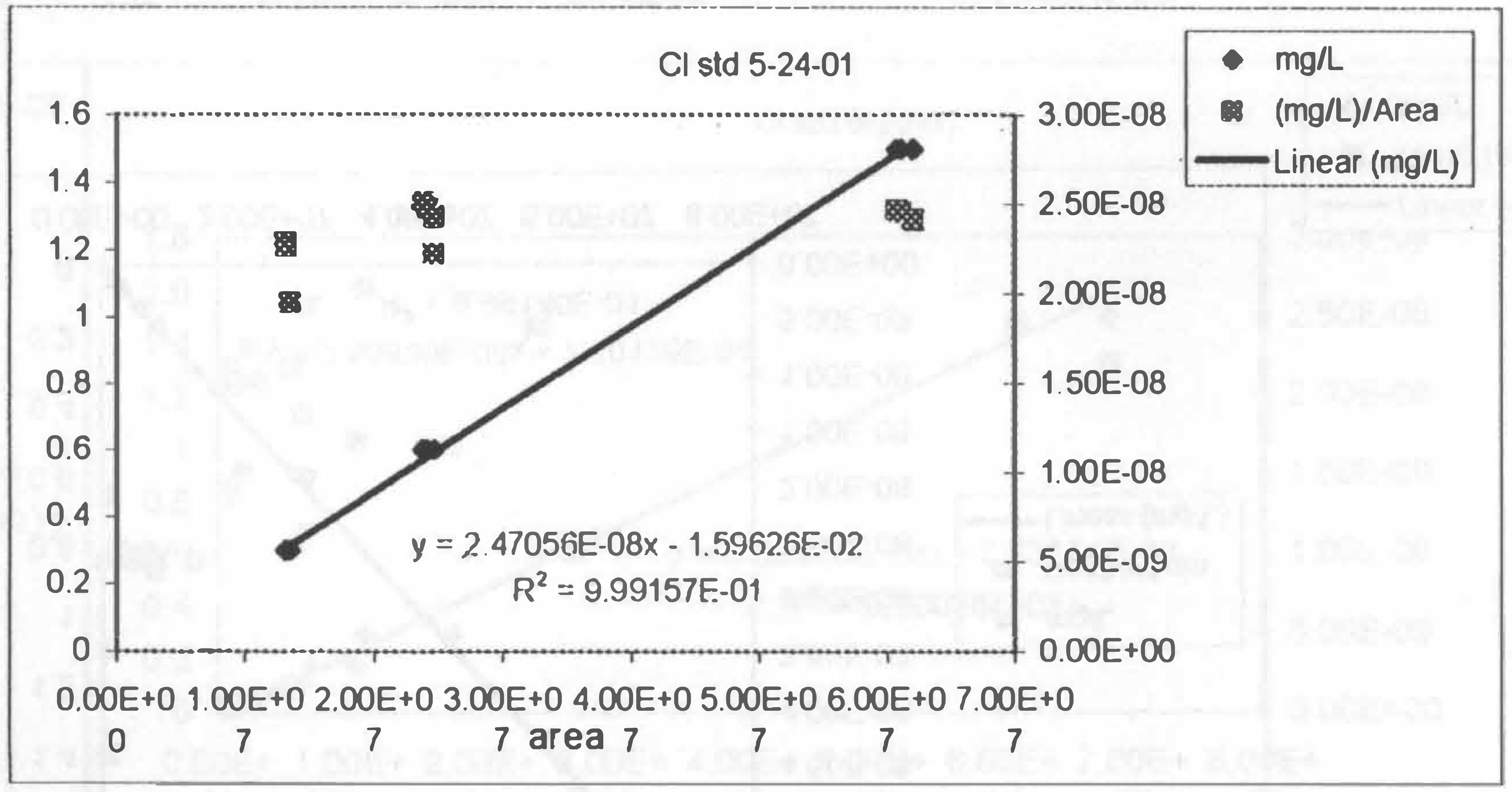

SO4 standards
mg/l/area
7.00E-08
6.00E-08
5.00E-08
4.00E-08
3.00E-08
2.00E-08
1.00E-08
0.00E+00
0.00E+00
5.00E+07
1.00E+08
1.50E+08
2.00E+08
2.50E+08
3.00E+08
area
24-May
25-May
29-May
30-May
31-May
05-Jun
06-Jun
07-Jun
12-Jun
13-Jun
18-Jun
19-Jun
20-Jun
25-Jun
26-Jun
27-Jun
02-Jul
11-Jul

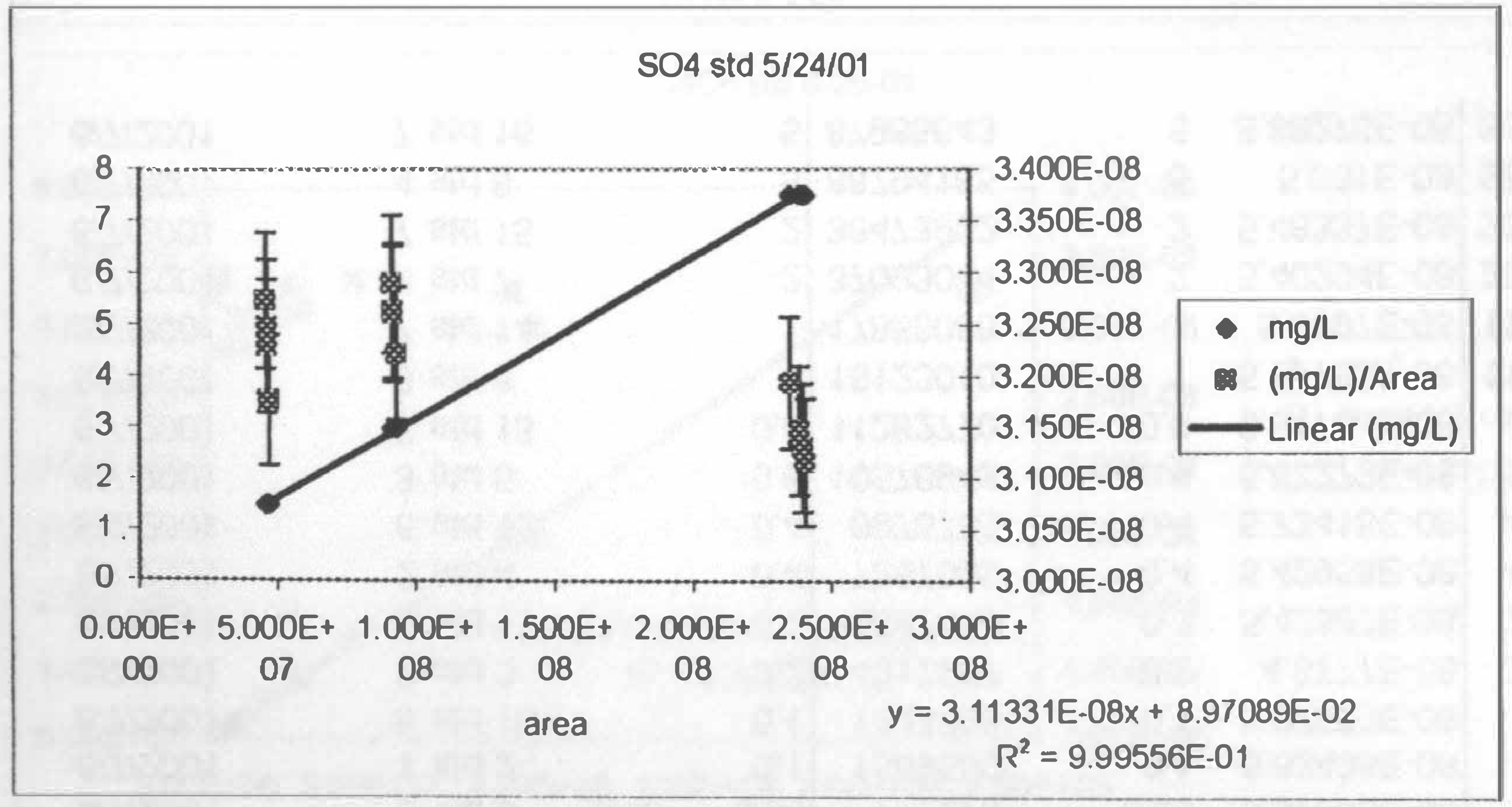

Cl standards
mg/l/area
9.00E-08
8.00E-08
7.00E-08
6.00E-08
5.00E-08
4.00E-08
3.00E-08
2.00E-08
1.00E-08
0.00E+00
0.00E+00
1.00E+07
2.00E+07
3.00E+07
4.00E+07
5.00E+07
6.00E+07
7.00E+07
8.00E+07
area
24-May
25-May
29-May
30-May
31-May
05-Jun
06-Jun
07-Jun
12-Jun
13-Jun
18-Jun
19-Jun
20-Jun
25-Jun
26-Jun
27-Jun
02-Jul
11-Jul

Data from May 24, 2001
SAS as labeled: Br=100mg/l Cl=30mg/l SO4=150mg/l
note: charts are based on labeled SAS

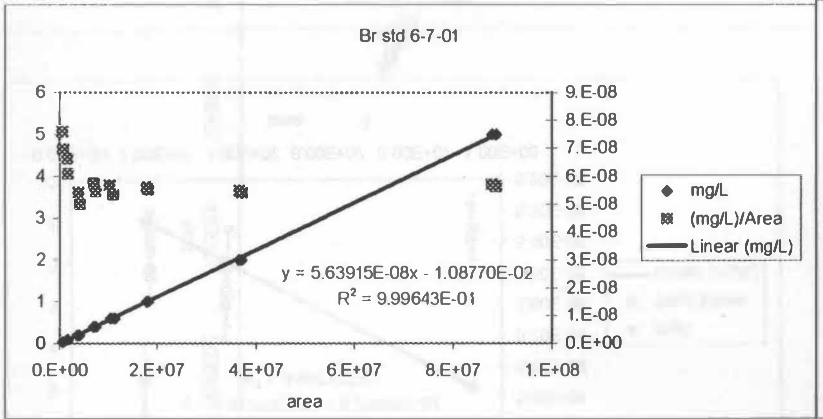
					Br		Cl (base corrected)			SO4		
IC Run	Rack #	Sample	ml SAS	Area	mg/L	(mg/L)/Area	Area	mg/L	(mg/L)/Area	Area	mg/L	(mg/L)/Area
5/24/2001	7	std 1	1	17131081	1	5.84E-08	13109696	0.3	2.29E-08	47216340	1.5	3.18E-08
5/24/2001	7	std 4	1	18243421	1	5.48E-08	13248378	0.3	2.26E-08	45818889	1.5	3.27E-08
5/24/2001	11	std 7	1	18479817	1	5.41E-08	13476507	0.3	1.95E-08	46188420	1.5	3.25E-08
5/24/2001	11	std 10	1	18519602	1	5.40E-08	13140147	0.3	2.28E-08	46445416	1.5	3.23E-08
5/24/2001	7	std 2	2	35706261	2	5.60E-08	23842709	0.6	2.52E-08	91993245	3	3.26E-08
5/24/2001	7	std 5	2	36001009	2	5.56E-08	24669898	0.6	2.22E-08	93093190	3	3.22E-08
5/24/2001	11	std 8	2	36554124	2	5.47E-08	24716733	0.6	2.43E-08	91187632	3	3.29E-08
5/24/2001	11	std 11	2	36639727	2	5.46E-08	24193093	0.6	2.48E-08	91922951	3	3.26E-08
5/24/2001	7	std 3	5	93427938	5	5.35E-08	62027016	1.5	2.42E-08	2.4E+08	7.5	3.13E-08
5/24/2001	7	std 6	5	93400498	5	5.35E-08	62132474	1.5	2.41E-08	2.41E+08	7.5	3.12E-08
5/24/2001	11	std 9	5	92853891	5	5.38E-08	60712026	1.5	2.47E-08	2.38E+08	7.5	3.15E-08
5/24/2001	11	std 12	5	92729113	5	5.39E-08	61060932	1.5	2.46E-08	2.35E+08	7.5	3.19E-08

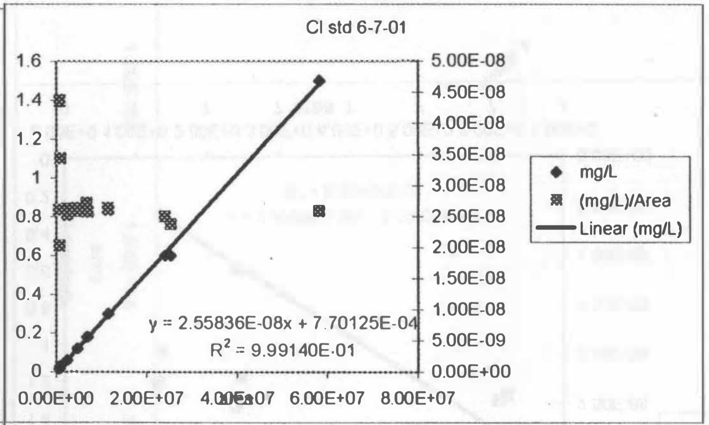


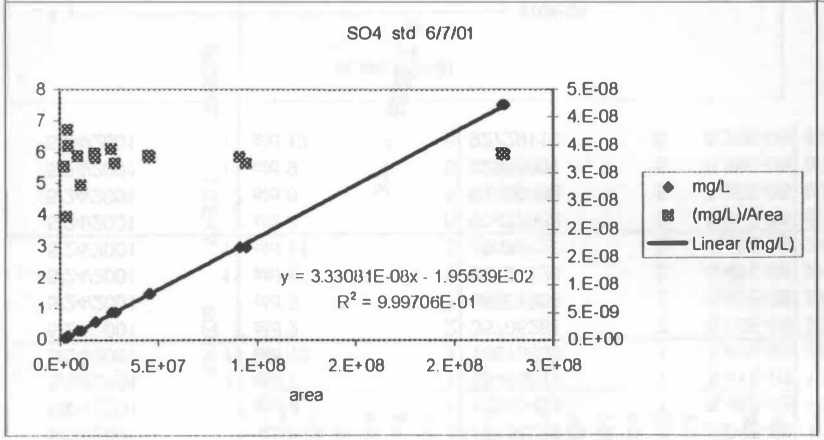




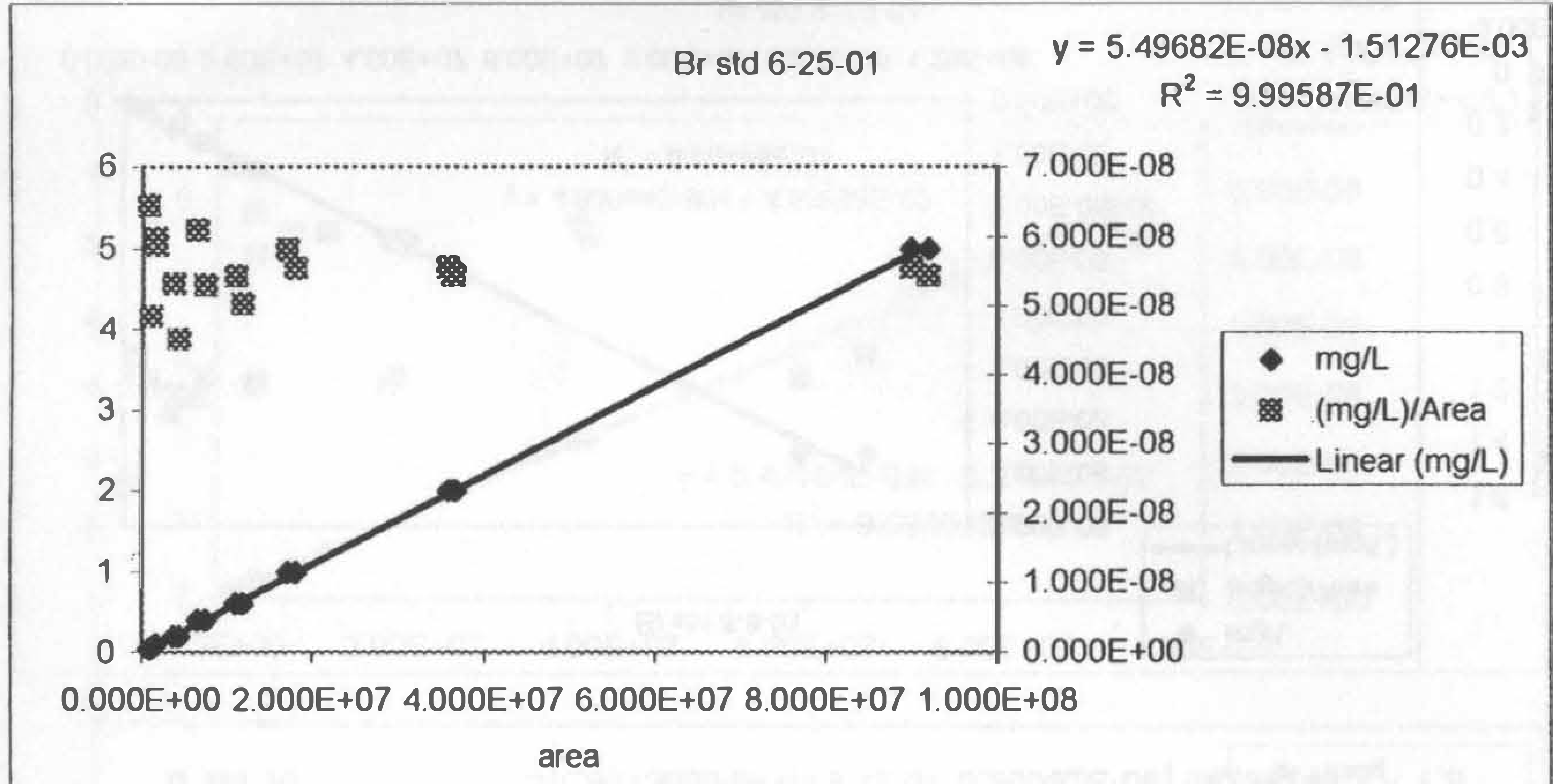
				Br			Cl (base corrected)			SO4		
IC Run	Rack #	Sample	ml SAS	Area	mg/L	(mg/L)/Area	Area	mg/L	(mg/L)/Area	Area	mg/L	(mg/L)/Area
6/7/2001	1	std 1	0.05	658805	0.05	7.5895E-08	738246	0.015	2.03184E-08	3385211	0.075	2.21552E-08
6/7/2001	5	std 9	0.05	717273	0.05	6.97085E-08	575425	0.015	2.60677E-08	2404673	0.075	3.11893E-08
6/7/2001	1	std 2	0.1	1509580	0.1	6.62436E-08	874295	0.03	3.43134E-08	3980434	0.15	3.76843E-08
6/7/2001	5	std 10	0.1	1644793	0.1	6.07979E-08	685933	0.03	4.37361E-08	4311095	0.15	3.47939E-08
6/7/2001	2	std 3	0.2	4017917	0.2	4.9777E-08	2381889	0.06	2.51901E-08	9102410	0.3	3.29583E-08
6/7/2001	6	std 11	0.2	3687405	0.2	5.42387E-08	2288760	0.06	2.62151E-08	10775432	0.3	2.78411E-08
6/7/2001	2	std 4	0.4	7367050	0.4	5.42958E-08	4552259	0.12	2.63605E-08	17903367	0.6	3.35132E-08
6/7/2001	6	std 12	0.4	6975753	0.4	5.73415E-08	4648083	0.12	2.58171E-08	18403591	0.6	3.26023E-08
6/7/2001	3	std 5	0.6	10576943	0.6	5.67272E-08	6619510	0.18	2.71923E-08	26270246	0.9	3.42593E-08
6/7/2001	7	std 13	0.6	11282770	0.6	5.31784E-08	6983808	0.18	2.57739E-08	28319241	0.9	3.17805E-08
6/7/2001	3	std 6	1	18123010	1	5.51785E-08	11510947	0.3	2.60621E-08	45354927	1.5	3.30725E-08
6/7/2001	7	std 14	1	17858088	1	5.5997E-08	11368361	0.3	2.6389E-08	45840481	1.5	3.27222E-08
6/7/2001	4	std 7	2	37023044	2	5.40204E-08	25249479	0.6	2.37629E-08	94408383	3	3.17768E-08
6/7/2001	7	std 15	2	36473922	2	5.48337E-08	23982014	0.6	2.50187E-08	91223747	3	3.28862E-08
6/7/2001	4	std 8	5	88794185	5	5.631E-08	58209015	1.5	2.57692E-08	224317067	7.5	3.34348E-08
6/7/2001	7	std 16	5	87985643	5	5.68275E-08	58131725	1.5	2.58035E-08	225530479	7.5	3.32549E-08

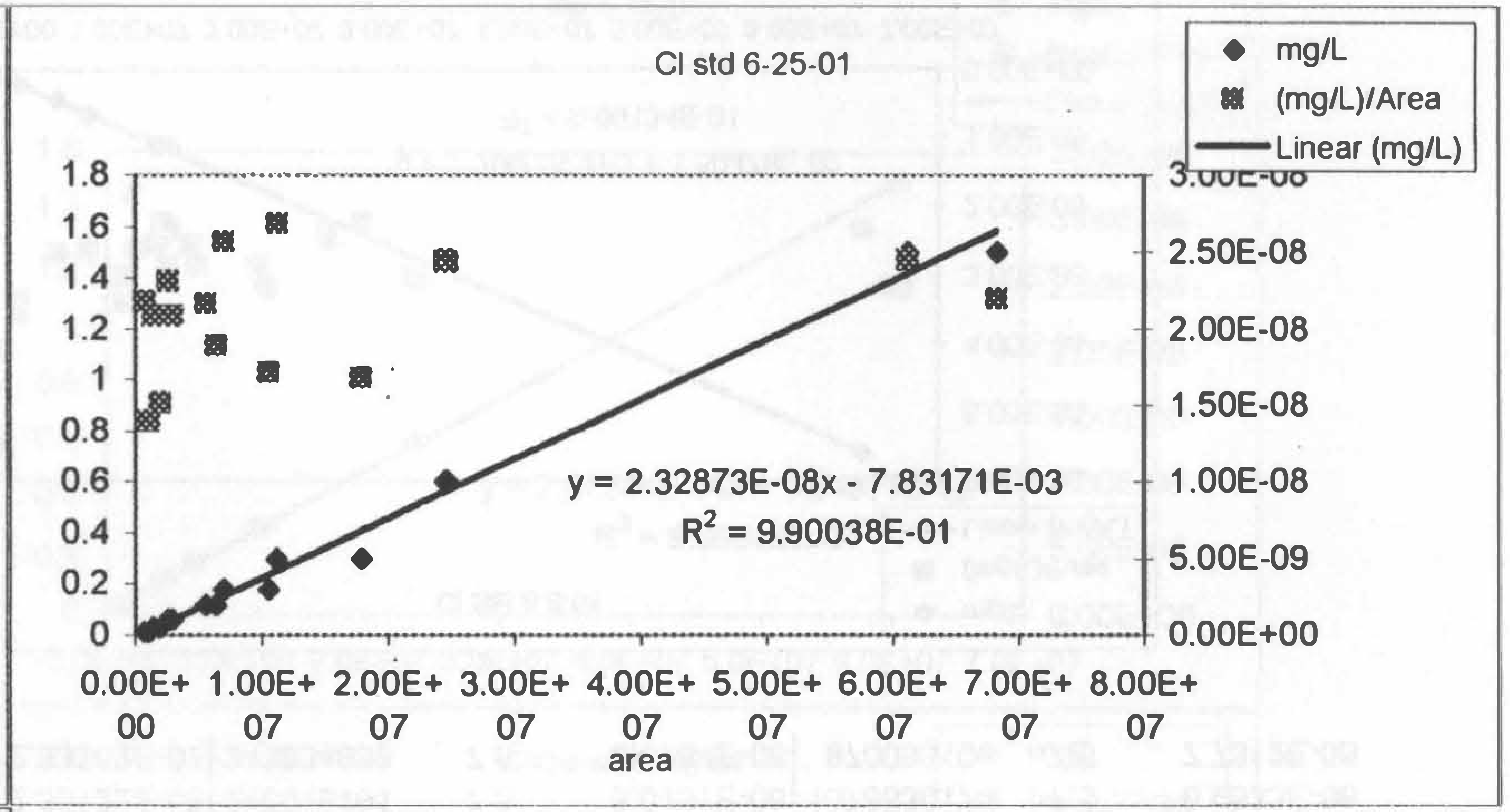


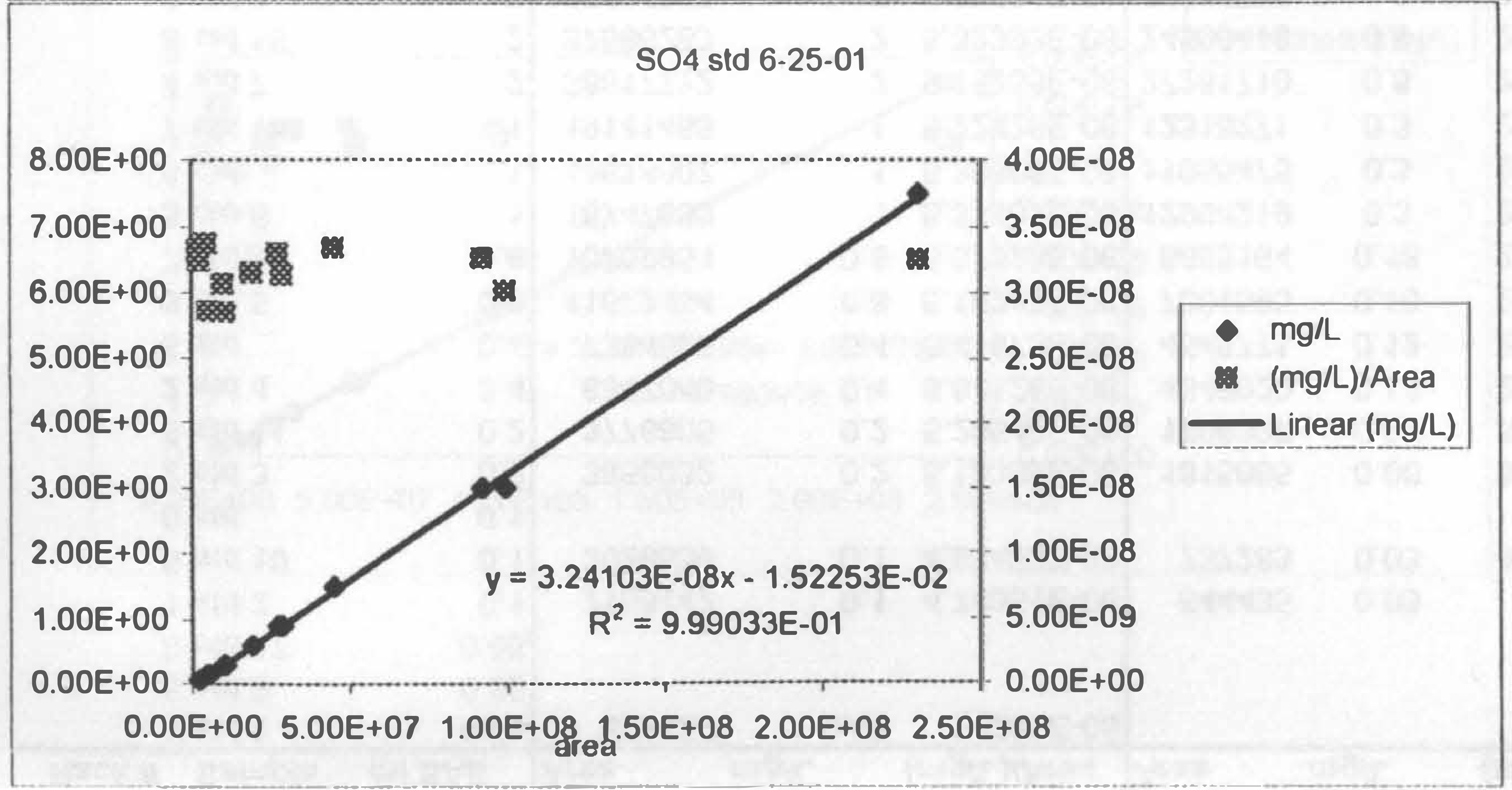




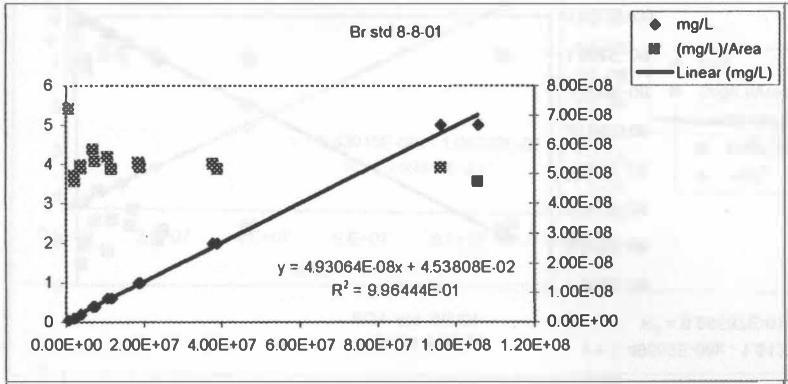
Rack #	Sample	ml SAS	Br Area	mg/L	(mg/L)/Area	Cl Area	mg/L	(mg/L)/Area	SO4 Area	mg/L	(mg/L)/Area
1	std 1	0.05	1029853	0.05	4.85506E-08	1071183	0.015	1.40032E-08	2312806	0.075	3.24281E-08
5	std 9	0.05	776416	0.05	6.43985E-08	686775	0.015	2.18412E-08	2261051	0.075	3.31704E-08
1	std 2	0.1	1674990	0.1	5.97018E-08	1438771	0.03	2.08511E-08	5253577	0.15	2.8552E-08
5	std 10	0.1	1703970	0.1	5.86865E-08	1983569	0.03	1.51243E-08	4455324	0.15	3.36676E-08
2	std 3	0.2	3758215	0.2	5.32168E-08	2592899	0.06	2.31401E-08	10543429	0.3	2.84537E-08
6	std 11	0.2	4434229	0.2	4.51037E-08	2878618	0.06	2.08433E-08	9793476	0.3	3.06326E-08
2	std 4	0.4	7545207	0.4	5.30138E-08	5537400	0.12	2.16708E-08	343376	0.6	1.74736E-06
6	std 12	0.4	6565523	0.4	6.09243E-08	6348891	0.12	1.89009E-08	19048837	0.6	3.1498E-08
3	std 5	0.6	11933049	0.6	5.02805E-08	7007271	0.18	2.56876E-08	27344790	0.9	3.2913E-08
7	std 13	0.6	11047991	0.6	5.43085E-08	10490847	0.18	1.71578E-08	28720874	0.9	3.13361E-08
3	std 6	1	18056953	1	5.53803E-08	17883277	0.3	1.67754E-08	44923768	1.5	3.33899E-08
7	std 14	1	17226772	1	5.80492E-08	11163608	0.3	2.6873E-08	930715	1.5	1.61166E-06
4	std 7	2	36494458	2	5.48028E-08	24597408	0.6	2.43928E-08	91974598	3	3.26177E-08
8	std 15	2	36782683	2	5.43734E-08	24499406	0.6	2.44904E-08	92081692	3	3.25798E-08
9	std 17	2	36007525	2	5.55439E-08	24659817	0.6	2.43311E-08	99364179	3	3.0192E-08
4	std 8	5	90040098	5	5.55308E-08	61234800	1.5	2.44959E-08	230324306	7.5	3.25628E-08
8	std 16	5	91971029	5	5.43649E-08	68311572	1.5	2.19582E-08	1385240	7.5	5.41422E-06

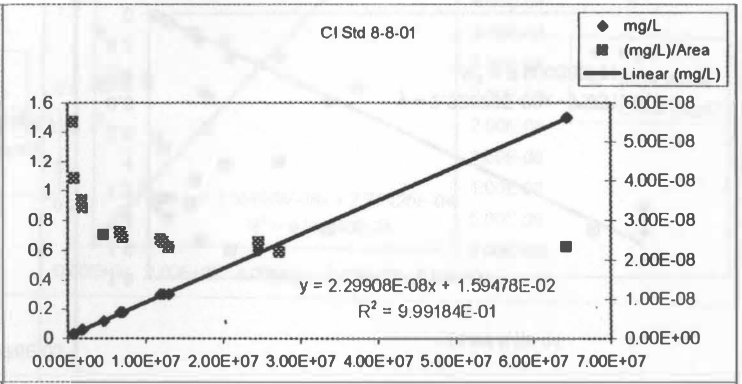


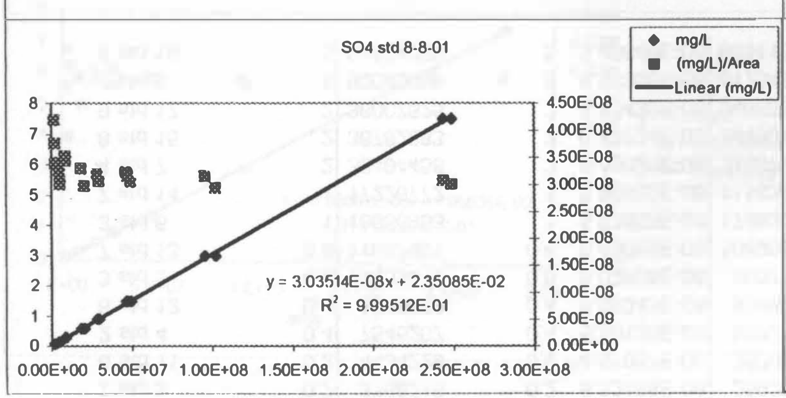


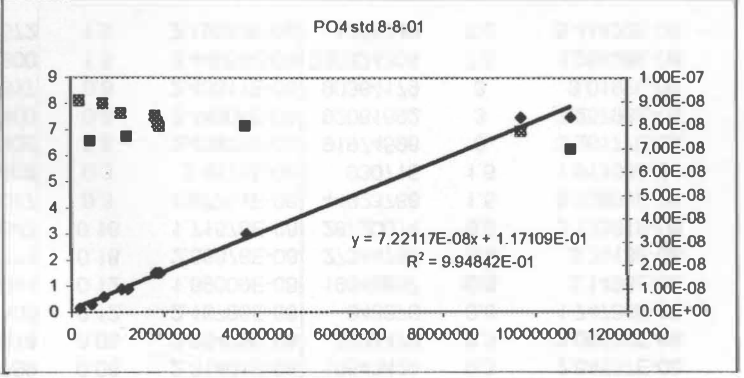


			Br			Cl			SO4			PO4		
Rack #	Sample	ml SAS	Area	mg/L	(mg/L)/Area	Area	mg/L	(mg/L)/Area	Area	mg/L	(mg/L)/Area	Area	mg/L	(mg/L)/Area
1	std 1	0.05	691639	0.05	7.2292E-08				1990530	0.075	3.7678E-08			
5	std 9	0.05							1788635	0.075	4.1931E-08			
8	std 17	0.05							2213984	0.075	3.3876E-08			
1	std 2	0.1	2108142	0.1	4.74351E-08	544435	0.03	5.5103E-08	4986687	0.15	3.008E-08	1661632	0.15	9.0273E-08
5	std 10	0.1	2026536	0.1	4.93453E-08	737283	0.03	4.06899E-08	4658566	0.15	3.2199E-08			
6	std	0.1							4390535	0.15	3.4164E-08			
2	std 3	0.2	3858032	0.2	5.18399E-08	1815685	0.06	3.30454E-08	8707303	0.3	3.4454E-08	4113362	0.3	7.2933E-08
6	std 11	0.2	3776805	0.2	5.29548E-08	1706327	0.06	3.51632E-08	8508729	0.3	3.5258E-08			
2	std 4	0.4	6847840	0.4	5.84126E-08	4546920	0.12	2.63915E-08	18217209	0.6	3.2936E-08			
6	std	0.4	7384525	0.4	5.41673E-08	4545771	0.12	2.63982E-08	20203418	0.6	2.9698E-08	6751571	0.6	8.8868E-08
3	std 5	0.6	11622464	0.6	5.16242E-08	7001595	0.18	2.57084E-08	29316243	0.9	3.07E-08	12029504	0.9	7.4816E-08
7	std 13	0.6	10759954	0.6	5.57623E-08	6685164	0.18	2.69253E-08	28164344	0.9	3.1955E-08	10639853	0.9	8.4588E-08
3	std 6	1	18747630	1	5.33401E-08	12994219	0.3	2.30872E-08	47605293	1.5	3.1509E-08	18939628	1.5	7.9199E-08
6	std	1	18628807	1	5.36803E-08	11955475	0.3	2.50931E-08	46568790	1.5	3.221E-08	17951654	1.5	8.3558E-08
7	std 14	1	19141468	1	5.22426E-08	12318271	0.3	2.43541E-08	49253097	1.5	3.0455E-08	18544317	1.5	8.0887E-08
4	std 7	2	38817212	2	5.15235E-08	27261710	0.6	2.20089E-08	102087117	3	2.9387E-08			
8	std 15	2	37566263	2	5.32393E-08	24598416	0.6	2.43918E-08	95082437	3	3.1552E-08	37708099	3	7.9559E-08
4	std 8	5	105687908	5	4.73091E-08	64344073	1.5	2.33122E-08	248915191	7.5	3.0131E-08	107863017	7.5	6.9533E-08
8	std 16	5	96136891	5	5.20092E-08	64294246	1.5	2.33302E-08	243634636	7.5	3.0784E-08	97009310	7.5	7.7312E-08

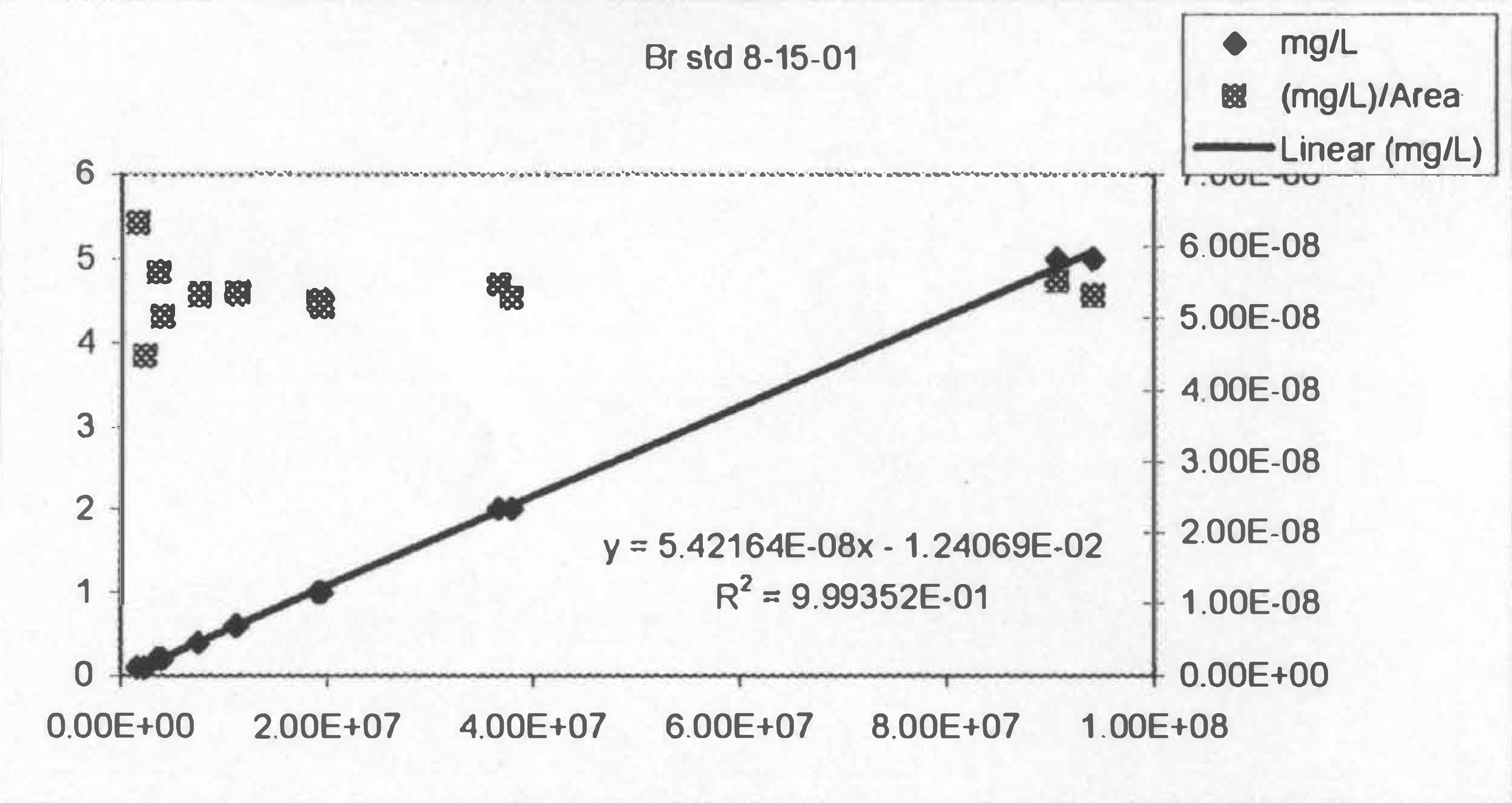


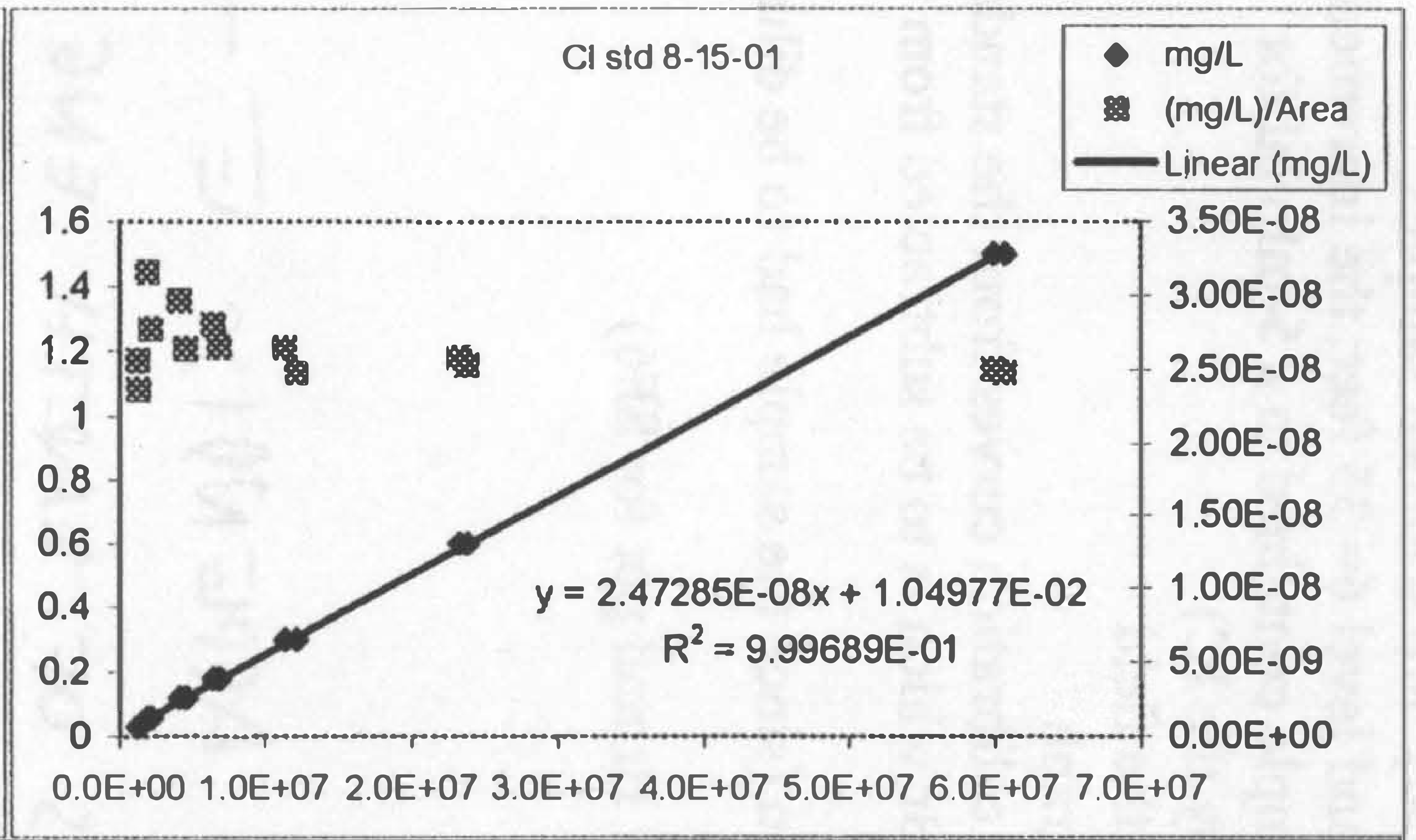


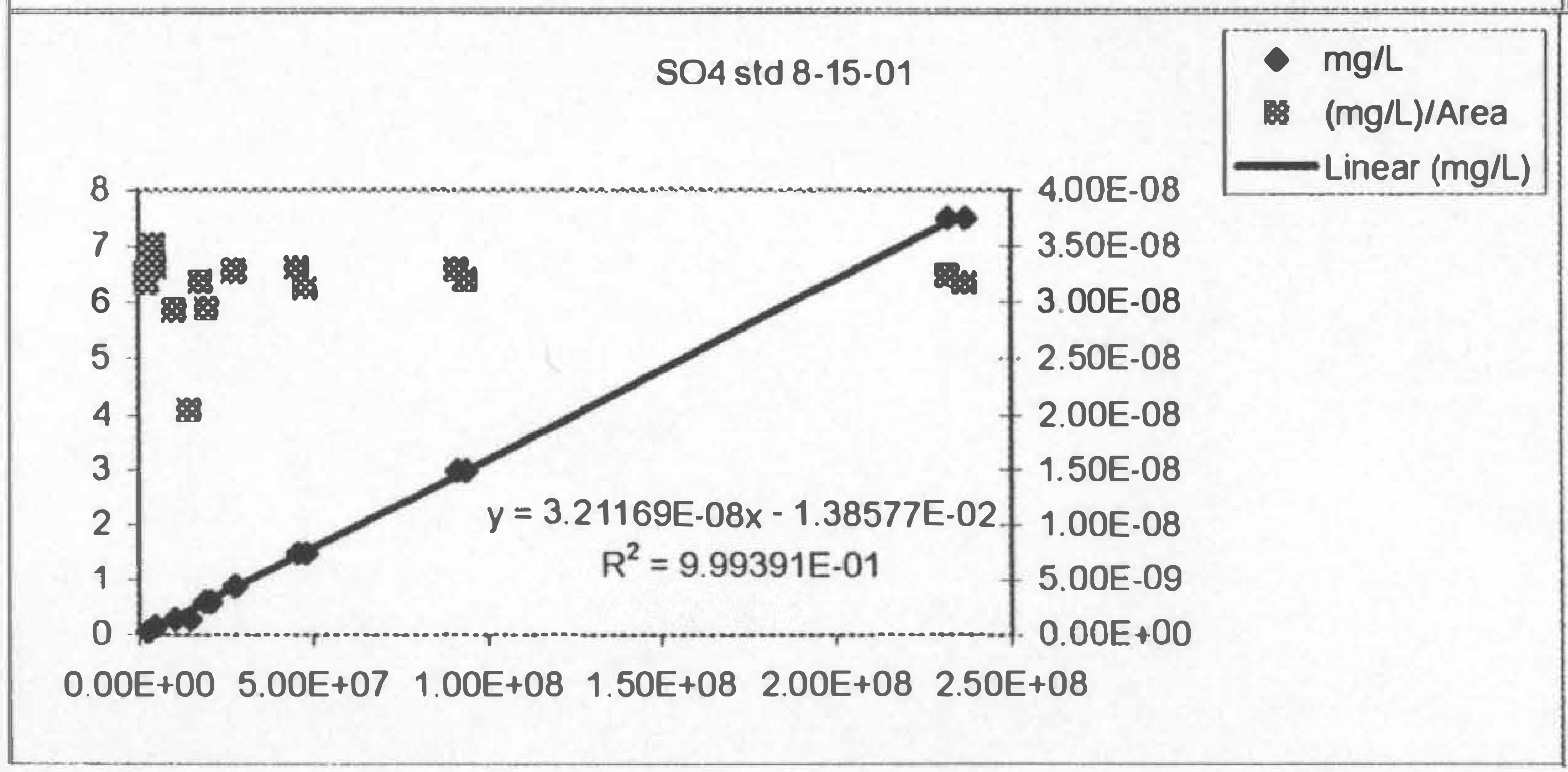


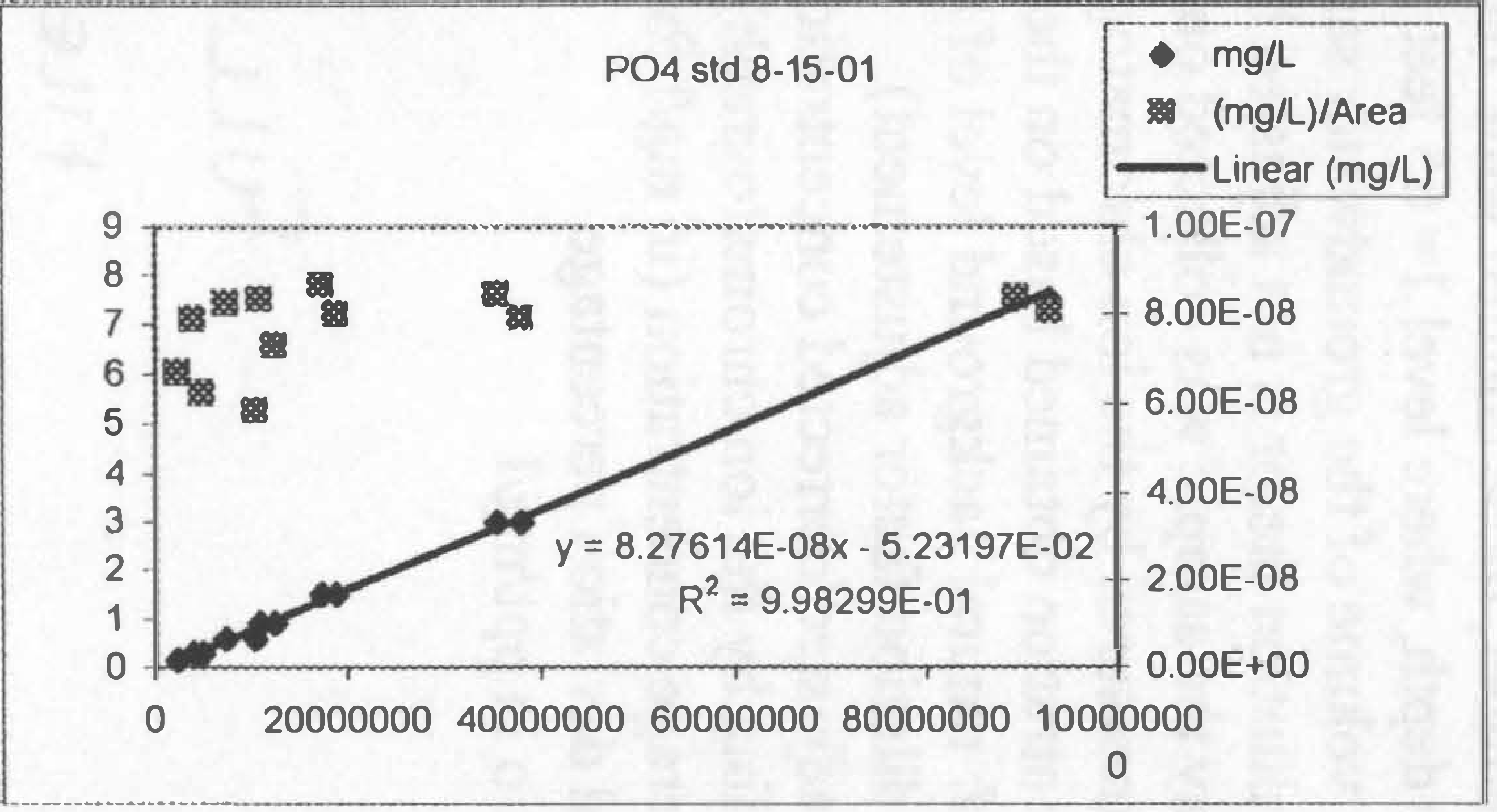


Rack #	Sample	ml SAS	Br Area	Br mg/L	Br (mg/L)/Area	Cl Area	Cl mg/L	Cl (mg/L)/Area	SO4 Area	SO4 mg/L	SO4 (mg/L)/Area	PO4 Area	PO4 mg/L	PO4 (mg/L)/Area
1	std 1	0.05							2369891	0.075	3.1647E-08			
5	std 9	0.05							2303776	0.075	3.2555E-08			
1	std 2	0.1	2228629	0.1	4.487E-08	1172789	0.03	2.558E-08	4540011	0.15	3.304E-08	2238969	0.15	6.69951E-08
5	std 10	0.1	1582596	0.1	6.319E-08	1271558	0.03	2.359E-08	4270874	0.15	3.5122E-08			
2	std 3	0.2	3973971	0.2	5.033E-08	1906014	0.06	3.148E-08	10318358	0.3	2.9074E-08	3809617	0.3	7.87481E-08
6	std 11	0.2	3551988	0.2	5.631E-08	2166528	0.06	2.769E-08	14722413	0.3	2.0377E-08	4792651	0.3	6.25958E-08
2	std 4	0.4	7553904	0.4	5.295E-08	4559444	0.12	2.632E-08	18904440	0.6	3.1739E-08	7274408	0.6	8.24809E-08
6	std12	0.4	7497334	0.4	5.335E-08	4057898	0.12	2.957E-08	20488295	0.6	2.9285E-08	10249193	0.6	5.85412E-08
3	std 5	0.6	11222146	0.6	5.347E-08	6812016	0.18	2.642E-08	27587113	0.9	3.2624E-08	12338404	0.9	7.2943E-08
7	std 13	0.6	11193227	0.6	5.36E-08	6433655	0.18	2.798E-08	27454317	0.9	3.2782E-08	10810867	0.9	8.32496E-08
3	std 6	1	19402734	1	5.154E-08	12141038	0.3	2.471E-08	48009670	1.5	3.1244E-08	18743829	1.5	8.00263E-08
7	std 14	1	19050813	1	5.249E-08	11364266	0.3	2.64E-08	45522030	1.5	3.2951E-08	17290320	1.5	8.67537E-08
4	std 7	2	37820872	2	5.288E-08	23810756	0.6	2.52E-08	93674694	3	3.2026E-08	37957145	3	7.90365E-08
8	std 15	2	36634330	2	5.459E-08	23311930	0.6	2.574E-08	91214915	3	3.2889E-08	35431957	3	8.46693E-08
4	std 8	5	94032538	5	5.317E-08	60741779	1.5	2.469E-08	236847998	7.5	3.1666E-08	93073781	7.5	8.05812E-08
8	std 16	5	90528128	5	5.523E-08	59958017	1.5	2.502E-08	232047641	7.5	3.2321E-08	89508331	7.5	8.37911E-08


Br std 8-15-01


Cl std 8-15-01


SO4 std 8-15-01


PO4 std 8-15-01

APPENDIX E: Data Section

This section contains the measurements obtained from the ion chromatograph (IC) for bromide, chloride, sulfate (and some phosphate) per well and per level. Concentrations of anions are diluted by a factor of 5 except for EW2 well. The SF6/Br ratio only has been adjusted to this factor (see SF6/Br, correction). For exact values of all OW well data, the concentrations should be multiplied by 5; on the spreadsheet, data are presented as diluted (except for EW2).

Abbreviations/Description:

Run date: day the sample was run on the ion chromatograph

Site: well number; those notified with "(acid)" are acidified samples.

L: level (or depth, where level 1= 65 feet and level 6= 35 feet; the increment is a 5-feet interval)

ml sample: volume of the groundwater sample contained in a 5-ml vial for IC measurement (the dilution factor is not adjusted by the IC)

colldate: day the sample was collected on the field

area: area measured by the ion chromatograph

mg/l: concentration obtained based on the calibration curves from the standards (see appendix A).

background: natural background level of Br which is to be subtracted from the "measured" Br (before the dilution factor adjustement)

corrected: adjusted/corrected concentration (since the sample had to be diluted by a factor of 5 for reading by the ion chromatograph)

avconc: average concentration (in mg/l for Br and ppt for SF6)

sd: standard deviation percentage

SF6/Br: ratio in ppt/mg/l