Good Report Received Sept. 6th 83.

CITY OF BURLINGTON

SOLID WASTE MANAGEMENT COMMITTEE

DATE OF MEETING: Friday, September 9, 1983.

PLACE OF MEETING: Committee Room 2, Eighth Floor at 9:00 a.m.

AGENDA

MATTERS FOR CONSIDERATION:

SWM-20-83 Correspondence dated August 29, 1983 from D. Perlin, Regional C.A.O. submitting an update from Dr. Cherry re: the University of Waterloo Research Project - Hydrogeological Investigations; Bayview Park Existing Regional Landfill and Proposed N.S.P. Landfill site.
File: 75.01-1

SWM-21-83 Correspondence dated August 29, 1983 from D. Perlin, Regional C.A.O. submitting a further report from Dr. Cherry, being a draft copy of a paper for a scientific journal (Ground Water).
File: 75.01-1

SWM-22-83 C.A.O. Report 63/83 - Municipal solid waste source separation and recycling financing scheme and sale of 3100 Guelph Line to Halton Recycled Resources.

Note: Report will be delivered on Wednesday, September 7th by courier.

NOTE:

1. Copies of the Halton Environmental Assessment Phase 2 - Stage 2A General Overview Analysis - Final Evaluation Report were delivered to the Clerk's Department by the Region on August 30th and copies were forwarded to members of the Committee.

2. At the September 23rd Solid Waste Management Committee meeting, Dr. J.A. Cherry will appear as a delegation.

ADJOURNMENT:

MC/mbg
0823b

Item SWM-20-83

THE REGIONAL MUNICIPALITY OF HALTON

P.O. BOX 7000
1151 BRONTE ROAD
OAKVILLE, ONTARIO L6J 6E1
416/827-2151

OFFICE OF THE CHIEF
ADMINISTRATIVE
OFFICER

1983 08 29

The City of Burlington
426 Brant Street
BURLINGTON, Ontario

Attn: Mr. Michael Boggs
Chief Administrative Officer

Dear Sir:

Re: University of Waterloo Research Project -
Hydrogeological Investigations: Bayview Park
Existing Regional Landfill and Proposed N.S.P.
Landfill Site

I have now received a further Update from Dr. Cherry of the University of Waterloo updating the situation and indicating in his opinion the desirability to continue to gather further information by way of obtaining funds from the Lottery Fund.

If you have any questions, please feel free to call me.

Yours very truly,

Dennis Y. Perlin
Chief Administrative Officer

DYP*pm

cc: R. Mohammed
R. Moore

RECEIVED
CITY OF BURLINGTON
C. A. O.
AUG 30 1983
M.H.B.
G.V.
S.B.
COPY TO:
S.W.M.C.

Item SWM-20-83

University of Waterloo

Waterloo, Ontario, Canada
N2L 3G1

Faculty of Science
Department of Earth Sciences
519/885-1211

July 4, 1983

Mr. Dennis Y. Perlin,
Chief Administrative Officer,
The Regional Municipality of Halton,
P.O. Box 700,
1151 Bronte Road,
Oakville, Ontario.
L6J 6E1

Dear Mr. Perlin:

During February and March we collected water samples from thirteen of the Morrison and Beatty piezometers at the Bayview Park landfill. These samples were sent to the Department of Environmental Chemistry at the Oregon Graduate Center where they were analysed in May and June for concentrations of organic compounds. Because the groundwater from the fractured shale at the site has a complex chemistry with high concentrations of natural dissolved organic matter, it was necessary to have the analyses done by sophisticated methods i.e. combined mass spectrometry and gas chromatography.

We received the results of these analyses a week ago. More than seventy organic compounds were identified in the samples. The compounds that are of most interest to us are those that are diagnostic of landfill contamination rather than those that can occur naturally in the shale as well as in landfill leachate. We are primarily interested in the diagnostic compounds because they will provide a means of mapping the zone of leachate-influenced groundwater at the site.

Several diagnostic compounds have been identified in the groundwater. These compounds are common chlorinated hydrocarbons produced by the chemical industry. A summary of the results pertaining to three of these compounds is provided in a table included with this letter.

(1) The results indicate that a zone of leachate influence extends from the landfill at least to piezometer nest OW12 and that the zone of influence extends to the deepest piezometers in the nests that were sampled. Of the various nests that were sampled, OW12 is the farthest from the landfill.

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Therefore, we do not know how far beyond OW12 the zone of influence extends. These results are not unexpected because the tritium data and the hydraulic conductivity data included in our April progress report suggested that the groundwater flow system in the fractured shale is moderately active.

(1) cont'd

The chlorinated hydrocarbons can be used to identify groundwater that has been influenced by the landfill, but regardless of their presence or absence, the conclusion reached in earlier studies, which is that the natural groundwater as well as the leachate-influenced groundwater in general have poor quality and are unsuitable for human consumption is valid. At present we do not have sufficient data to predict the fate of the chlorinated hydrocarbons in the hydrologic system.

The $20,000.00 drilling budget that you arranged for us to have access to was consumed during our drilling in the summer and fall of 1982. Our Lottery Fund Grant expired in April, 1983. We have not received word regarding the fate of the Lottery Fund proposal that we submitted in March, 1983. We are continuing our studies of contaminant migration at the site but at a low level of activity supported only by a small NSERC grant. We do not expect to be reporting any significant new information in 1983. If we receive the funds requested in our Lottery Fund proposal, we will be able to do additional sampling and analyses at an earlier date than would otherwise be the case.

Yours sincerely,

John Cherry

JAC/msb

John A. Cherry,
Professor.

Map : p. 29 shows

(Bayview fill)

WELL	COMPOUND CONCENTRATION (ppb)			SAMPLE DEPTH (metres below ground)
	Chlorobenzene	Para-Dichlorobenzene	1,1,1, Trichloroethane	
OW15-2	6.2	1.4	NS	8.7
OW15-3	3.2	0.36	36.0	27.7
OW 1-1	ND	0.013	0.85	1.1
OW 1-2	11.2	1.8	0.35	8.2
OW 1-4	0.066	ND	19.0	20.0
OW 3-2	8.2	1.6	1.2	7.3
OW 3-3	0.79	0.11	8.9	14.3
OW 3-4	0.17	ND	39.0	21.0
OW11-1	2.8	0.55	0.18	3.0
OW11-2	0.025	ND	1.70	14.8
OW11-3	0.041	ND	6.50	22.4
OW12-3	0.80	0.053	10.0	19.4
OW 5	0.050	ND	0.53	7.6

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ND - not detected

NS - no sample collected

Item SWM-20-83

Item SWM-21-83

THE REGIONAL MUNICIPALITY OF HALTON

OFFICE OF THE CHIEF ADMINISTRATIVE OFFICER

P.O. BOX 7000
1151 BRONTE ROAD
OAKVILLE, ONTARIO L6J 6E1
416/827-2151

1983 08 29

The City of Burlington
426 Brant Street
BURLINGTON, Ontario

Attn: Mr. Michael Boggs
Chief Administrative Officer

Dear Sir:

Re: University of Waterloo Research Project - Hydrogeological Investigations: Bayview Park Existing Regional Landfill and Proposed N.S.P. Landfill Site

Enclosed please find a copy of a further Report from the University of Waterloo on the above noted Research Project with the covering letter dated August 23rd, 1983 from Dr. Cherry.

(See p. 7)

This material is submitted to you as in the past for your information.

You will note that Dr. Cherry is very optimistic about the Lottery Fund approving the Fall Sampling Program which he believes should be done and that he is seeking an indication from the City as well as from the Region and National Sewer Pipe that they would be prepared to contribute a few more dollars to the drilling of a few more boreholes.

In discussions with Dr. Cherry, if that circumstance occurred, the cost would be approximately $3,500. per borehole. Dr. Cherry indicates that he can foresee a need for perhaps three - six boreholes; his Lottery Fund funding, he would expect, would provide money for one, thus we should be expecting to receive a request or a contribution for two - five boreholes at a total cost of around $18,000. to be shared three ways.

I would ask you to give some thought to making a further contribution and letting me know so that I would be in a position to indicate to Dr. Cherry once he has his Lottery Fund contribution secured, that I will be in a position to help out in the further research.

You will note that Dr. Cherry invites comments on the Draft Report that has been prepared. If you wish, I can forward those comments through to Dr. Cherry if you send them to me, or else you could send those comments directly through to Dr. Cherry.

Thankyou.

Yours very truly,

Dennis Y. Perlin
Chief Administrative Officer

DYP*pm

cc: R. Mohammed
R. Moore

Item SWM-21-93

University of Waterloo

Waterloo, Ontario, Canada
N2L 3G1

Faculty of Science
Department of Earth Sciences
519/885-1211

August 23, 1984 (See p.5) 1983

Mr. Dennis Y. Perlin,
Chief Administrative Officer,
The Regional Municipality of Halton,
P.O. Box 7000,
1151 Bronte Road,
Oakville, Ontario.
L6J 6E1

Dear Mr. Perlin:

Please find enclosed a draft copy of a paper that we intend in September to submit to a scientific journal (Ground Water) for publication. It is a draft, however I expect that the final manuscript will not be significantly different than this draft. When the editor of Ground Water receives the manuscript, he will send it to two persons that he will select for peer review. This will take a few months. When we receive the review comments, we will make revisions and then, if all goes well, it will be published.

When we make the final revisions, we would take into consideration any comments that we receive from the parties that receive copies of this draft through distribution from your office. This paper contains the data that I sent to you a couple of months ago.

No new data have been acquired in recent months, although work by our students and technicians has been going on at the Bayview site. This work represents preparatory efforts towards a major program of sampling that we intend to conduct in September or October when we receive a grant from the Lottery Fund.

The purpose of the fall sampling program will be to analyse many groundwater samples for concentrations of the diagnostic chlorinated organic compounds that were identified in the results reported on in the enclosed manuscript. The analyses will be done at the Oregon Graduate Center through a cooperative research program that is in effect for 1983-84. I expect that analytical results from this sampling will be available by early 1984. I think that it is quite possible that the results will indicate that there exists a large zone of contaminated groundwater in the shale at the Bayview site. By contamination, I am referring to groundwater that contains above-background level (i.e. above blank levels) of chlorinated organic

compounds such as trichloroethane. Whether or not these chlorinated compounds represent an environmental hazard in terms of possible influences on streamwater or on soil water is not within the scope of our study. This is not a primarily hydrogeologic question.

We have received an informal indication that we will be granted research funds from the Ontario Lottery Fund. These funds will enable us to continue research at a number of landfill sites in Ontario. The Bayview Park landfill is one of the landfills that we want to include in the study. The timing of the grant and its scope will probably be determined in late August. The grant proposal that we made to the Lottery Fund includes a small amount for drilling at all of the sites in our study. The amount that we would be able to allocate to the Bayview site would be small relative to the total. Drilling in shale is expensive relative to drilling at the other sites and this allocation would not accomplish much. Depending on the results of the fall sampling, we may conclude that more drilling at the Bayview Park landfill site is necessary. If we arrive at this conclusion, we will probably request the Region, in conjunction with the City of Burlington and NSPL, to pay for a few more boreholes.

I will continue to keep you informed of the progress of our research at the Bayview Park landfill site.

Yours sincerely,

John Cherry

JAC/msb
Encl.

John A. Cherry,
Professor.

Hem SWM-21-83

A Cartridge and Syringe Method for Down-hole Sampling for Trace Organic Compounds in Groundwater

James F. Pankow and Lorne M. Isabelle

Department of Environmental Science
Oregon Graduate Center
19600 N.W. Walker Rd.
Beaverton, Oregon 97006

and

Janet P. Hewetson and John A. Cherry

Department of Earth Sciences
University of Waterloo
Waterloo, Ontario
N2L 3G1

For Submission to Ground Water

August, 1983

DRAFT

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Item SWM-21-83

ABSTRACT

A newly developed technique which allows the down-hole sampling and subsequent analysis of groundwater for trace organic contaminants was tested during an investigation of contaminant migration at an inactive landfill site in Burlington, Ontario. The sampling device, which is lowered down piezometers with a tube, consists of a small cylindrical cartridge of sorbent material attached to a syringe. Vacuum or pressure applied at the surface controls the movement of the plunger in the syringe. The volume of the syringe determines the volume of sample water that passes through the cartridge. The cartridge is removed from the syringe at the surface. One cartridge is used for each sampling. The syringe is reusable. The residual water in the cartridge is removed in the laboratory, and the cartridge is desorbed to a fused silica capillary column for analysis by gas chromatography (GC). The analyses discussed here were performed on a GC/mass spectrometer/data system (GC/MS/DS). Of the many organic compounds that were identified in the samples, three compounds were clearly landfill-related: 1,1,1-trichloroethane, chlorobenzene, and para-dichlorobenzene. The three compounds were found at levels substantially above blank levels in 9, 5, and 5 piezometers, respectively. The average concentrations were 14., 5.3, and 0.88 ug/L (ppb) respectively. The pooled relative standard deviations for the analyses for the three compounds were 25., 6.9, and 6.3% respectively. The volatility of 1,1,1-trichloroethane was probably the cause of the greater variability in its analytical data. The main advantages of the technique over most conventional sampling methods include: 1) down-hole sampling in a manner which minimizes the potential for volatilization losses; 2) the avoidance of the passage of the sample through long sections of tubing that may contaminate the sample or cause adsorptive losses; and 3) convenience of sample handling, storage, and shipping.

Item SWM-21-83

INTRODUCTION

The number of groundwater systems which are recognized as having become contaminated with trace organic compounds is steadily increasing. In many cases, the compounds of interest are relatively volatile, often being members of the list of "purgeable" U.S. Environmental Protection Agency (EPA) priority pollutants (Keith and Telliard, 1979). Such compounds are usually present in groundwaters at low levels (ng/L (ppt) to mg/L (ppm)). Their typically low concentrations as well as their high volatilities places stringent requirements upon the sampling and analytical method(s) selected for groundwater monitoring programs.

When attempting to obtain a sample for analysis by a method such as purge and trap (Bellar and Lichtenberg, 1975), many of the procedures used to bring samples of groundwater to the surface can lead to the formation of bubbles and/or the exposure of the sample to a headspace. The volatilization losses which may then occur can cause artifacts. Landfill leachates high in methane and carbon dioxide are particularly troublesome in this regard. A possible means of circumventing this volatilization loss problem is provided by the adsorption/thermal desorption (ATD) method developed for water samples by Pankow et al. (1982a, 1982b, 1982c, 1983), and for air samples by Zlatkis et al. (1973) and Pellizzari (1975a, 1975b).

Aqueous ATD involves the: 1) passage of a water sample through a pre-prepared cartridge of sorbent material (e.g., Tenax-GC); 2) drying of the cartridge; 3) thermal desorption of the cartridge to a fused silica capillary gas chromatography (GC) column at approximately -80 C; and 4) a temperature program GC run with some type of detector. Tenax-GC is an attractive sorbent for this type of work since it is very thermally stable. Its possible use for water sampling was first considered by Bertsch et al. (1975). Although this sorbent has been shown to be effective in trapping

aqueous chlorinated benzenes and other similar non-polar compounds (Pankow et al., 1982a, 1982b, 1982c), its efficiency in sorbing the very volatile purgeable compounds is as yet unknown. Recovery studies are now underway in the laboratory of one of the authors (JFP) to determine these efficiencies.

Regardless of whether or not Tenax-GC proves to be the aqueous ATD sorbent of choice for all compounds of interest, the ATD method in general is attractive for certain groundwater sampling situations. This is the case because it is both sensitive and easily adaptable to down-hole sampling procedures. The sensitivity of the method arises from the fact that 100% of the sorbed organics are transferred to the GC column. Within the limits posed by breakthrough losses (Pankow, Rosen and Wojcik, 1983), the mass amount of analyte sorbed can be increased by increasing the volume sampled. The adaptability of ATD to down-hole sampling is due to the fact that the cartridge alone and not the actual water sample is returned to the laboratory. Therefore, it is not necessary to bring a sample to the surface and risk volatilization losses: passage of the sample through the cartridge can occur down-hole.

(2) The ATD-based down-hole sampling technique discussed here was developed in response to a need to obtain reliable measurements of trace organic contaminant levels in groundwater down-gradient of the Bayview Park Landfill in Burlington, Ontario. This 18 hectare landfill (Figure 1) began to receive waste from the City of Burlington in 1960. It was closed and covered over with earth in 1970. It is situated on the edge of the Niagara Escarpment where bedrock is either exposed at the surface, or covered by a thin veneer of clay till. The bedrock is fractured, red Paleozoic shale of the Queenston Formation which extends to depths of over 100 m.

Groundwater movement is to the southeast and towards Lake Ontario (3.5 2.1 miles

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See "Map 2 - Property Ownership"

of Dillon Draft report "Burlington Landfill Site Proposed Continued Use", Feb. 1984

(Region application to MoE)

km away). It flows in the fractured shale along the slope of the escarpment which corresponds to the regional slope in the water table. Down-gradient of the landfill there is a 1 km long expanse of land that is partly forested and is unoccupied. The land surface further down-gradient is characterized by industrial and urban areas of the City of Burlington which extend to the shore of Lake Ontario.

(2) cont'd

The fact that the Bayview Park Landfill is situated on fractured shale makes it particularly interesting. This is the case because many groundwater systems that are receiving waste materials or have received them in previous years are fractured in a manner which makes them quite permeable to groundwater and solute transport. For example, fractured shale of the Queenston formation also exists within the stratigraphic sequence at landfill and hazardous waste disposal sites in the Niagara Falls area where leakage of contaminants through the shale and other formations is of concern. Furthermore, compared to porous media where much information exists on the theory of contaminant migration (Bear, 1972; Fried, 1975; Freeze and Cherry, 1979) and on behavior at field sites (e.g. MacFarlane, 1983; Cherry et al., 1983a; Egboka et al., 1983, Sudicky et al., 1983; Dance et al., 1983; Nicholson et al., 1983; and Greenhouse and Harris, 1983), contamination migration in fractured systems is relatively poorly understood.

Initial attempts at the Bayview Park Landfill by Cherry et al. (1983b) and Hewetson and Cherry (1983) to delineate a zone of contamination on the basis of inorganic parameters (major ions, transition metals and heavy metals) and organic indicator parameters (dissolved organic carbon (DOC), chemical oxygen demand (COD), phenols, and organic nitrogen) were unsuccessful due to the naturally high levels of these parameters: typical chloride and DOC concentrations in the area of the site are 12,500 and 500 mg/L, respectively. It was hoped that: 1) the ATD method with detection by mass

spectrometry would provide the sensitivity necessary to allow the conclusive determination of landfill-derived organic contaminants in zone of contamination; and that 2) the study would provide a perspective on the applicability of ATD to groundwater sampling and analysis. Once a suite of landfill-derived organic compounds are identified at representative sampling locations, it should be possible with much more extensive sampling to use the occurrence of these compounds to delineate the full extent of the zone of organics contamination and the rates of migration.

II. EXPERIMENTAL

ATD Cartridge Preparation.

The cartridge bodies were of Pyrex glass (Figure 2). The bed length, I.D., and O.D. were 5.4, 0.40, and 0.46 cm, respectively (bed volume = 0.68 mL). A 2.5 cm piece of 2.0 mm I.D., 0.46 cm O.D. glass tubing was fused to the inlet end of the cartridge main body, and a 1.5 cm piece was fused to the outlet end. The cartridges were packed with 0.11 g of resieved 35/60 mesh Tenax-GC (Alltech Assoc., Inc., Los Altos, CA). The Tenax-GC was held in place with silanized glass wool (Supelco, Inc., Bellefonte, PA). Cartridge conditioning was carried out by passing 0.5 L of glass distilled acetone through each cartridge, vacuum drying for 20 min, then thermally desorbing for 3 h at 300 C with 30 mL/min of nitrogen gas which had been pre-cleaned by passage through a Supelco oxygen trap and then through a molecular sieve trap in liquid nitrogen.

The cartridges were then capped on the inlet end with clean brass Swagelok (Crawford Fitting Co., Solon, OH) endcaps with Teflon ferrules. Following Krost et al. (1982), prior to use, all Teflon parts were degassed under a vacuum at 110 C for 2 h. The outlet end of the cartridge was fitted with a brass Swagelok 0.25 in. to 0.125 in. reducing union which was silver soldered to a 3.0 cm long, 25 gauge needle with a Luer hub (Figure 2). The latter served as a flow restrictor. The dimensions of the needle were

selected so that the flow rate through the cartridge would not exceed 0.1 mL/s with a total pressure differential of 1 atmosphere (10.3 m of water column) across the cartridge/needle system. The flow rate of 0.1 mL/s was selected based on the dimensions of the cartridge and the recommendations of Pankow et al. (1982b). For piezometers which had more than 10 m of water column above the desired sampling interval, additional flow restriction was achieved by placing a 3.25 cm long pre-cleaned section of 0.15 mm O.D. piano wire inside of the needles of the cartridges. Cartridges were prepared in sets, one blank cartridge to a set.

Prior to shipment to the field, each entire cartridge system was evacuated, then forcibly wetted by releasing the vacuum with water which had been pre-cleaned by: 1) passage through an activated carbon bed; and 2) boiling with simultaneous sparging with nitrogen which had been pre-cleaned by passage through a molecular sieve trap in liquid nitrogen. The Luer hub was then sealed with a Teflon plug, and the entire cartridge system stored in a muffle-furnaced Pyrex culture tube with a Teflon cap liner. The cartridges were prepared in groups so that each group contained one blank cartridge. After preparation, all of the cartridges were shipped (together with the down-hole syringe sampling devices to be described below) via overnight air courier from OGC to U. Waterloo.

Syringe Sampling Device.

The syringe sampler (Figure 2) was a glass and Teflon version modelled after a similar polyethylene and rubber device developed by Gilham (1982) for sampling for inorganic constituents in groundwater. Concerns about contamination and losses associated with polyethylene and rubber led to their replacement. Glass syringes with a 50 mL capacity and Luer-lock fittings were obtained from Popper and Sons (New Hyde Park, NY). The top

rim was removed from each syringe with a glass cutting wheel. In this manner, the O.D. of the device was reduced to that of the syringe body (3.3 cm). The device could then pass down sample piezometers constructed from schedule 40, 4.0 cm I.D. PVC tubing. The sharp edges were ground smooth with the wheel, but could not be fire-polished since this type of glass cracks easily when heated due to its high coefficient of thermal expansion. A movable plunger and an upper tube coupling were machined from Teflon. O-ring grooves were included on both parts. Since the O-rings would not contact the sample, conventional Buna-N O-rings were used. Prior to assembly, each syringe was washed with warm laboratory detergent, rinsed with deionized water, sonicated in acetone, then hexane, then acetone again, rinsed with deionized water, then baked at 110 C for 1 h. The O-rings were washed with warm detergent, rinsed with deionized water, rinsed with acetone, then vaccum-outgassed at 110 C for 1 h.

Item SWM-21-83

Sample Piezometers and Sampling Procedures.

The sampling points used were the OW ("observation well")) sample piezometer nests installed between 1979 and 1981 by Morrison Beatty, Ltd. (1981) (Figure 1). These piezometers are conventional PVC standpipe piezometers with 0.7 m long slotted screens. They were installed and sealed in holes drilled by the hollow-stem auger method. While most of these piezometer tubes were 4.0 cm I.D., some were 3.2 cm I.D.. The samples reported on in this paper were acquired in February and March, 1983. A few days prior to sampling, the piezometers were bailed to dry prior to sampling to remove nearly all of the standing water. For the 4.0 cm I.D. casings, sampling was carried out by: 1) connecting a polyethylene tube to the Teflon coupling on the upper end of the syringe; 2) pressurizing the tube with a hand vacuum/pressure pump (Model 7090, Cole-Parmer, Chicago, IL) so that the moveable plunger was forced to the zero volume position; 3) locking a cartridge onto the Luer fitting; 4) lowering the cartridge/syringe down the piezometer tube to the slotted interval; 5) releasing the pressure and/or

pulling a vacuum on the tubing to allow sample to pass through the cartridge and into the syringe; 6) bringing the device to the surface; and 7) removing the cartridge, resealing it with the Swagelok endcap and Teflon Luer plug, and replacing it in the culture tube for air courier shipment back to OGC. It should be noted that the low pressure portion of the sampler occurred in the exit end of the cartridge. In this manner, the needle served to control the flow rate as well as eliminate degassing prior to or in the cartridge. At the point in time during which cartridges from a given set were used in sampling, the endcaps on the blank cartridge from that set were removed, the cartridge thereby opened to the atmosphere. The blank cartridge was then immediately closed again, and returned to its culture tube for shipment.

For the 3.2 cm I.D. PVC casings, it was not possible to sample down-hole. Approximately 1 L of groundwater was brought to the surface with a stainless steel bailer previously rinsed with methanol and sample water. The sample was then transferred to a glass erlenmeyer flask. The syringe and cartridge were prepared and assembled as described above. The cartridge was then partially submerged. A vacuum was then applied with the pump to allow sample to be pulled through the cartridge. Further handling of the cartridge proceeded as described above for down-hole sampling.

Cartridge Desiccation, Desorption, and Analysis

Upon arrival at OGC, each cartridge was dried according to a two-step centrifugation/vaccuum desiccation method. This desiccation does not cause losses for the analytes of interest. The cartridges were then resealed and refrigerated for a maximum of two weeks before desorption and analysis occurred. The desorption procedure began with the addition of 2.0 uL of a standard solution in methanol (containing 10 ng/uL each of toluene-d8 and 2-

bromo-meta-xylene) directly to the sorbent at the sampling inlet end. The cartridge was then placed in a thermal desorption block described in detail elsewhere (Pankow et al. 1983a). Briefly, the oxygen and the majority of the methanol were purged from the cartridge with 10 min of 10 ml/min of helium carrier flowing into the cartridge inlet. The flow was reversed, and the cartridge desorbed for 20 min at 250 C with 30 psi helium directly to a 30 m 0.35 mm I.D. SE-54 fused silica capillary column (J&W Scientific, Rancho Cordova, CA) mounted in a Finnigan 4000 GC/MS/DS (by passing it through a transfer line to within 5 mm of the source), and held at -80 C during the desorption. The high efficiency of the drying procedure served to prevent the plugging of the column with ice during the desorption step. The analyses were carried out using a carrier gas linear velocity of 45 cm/s, MS scanning from 35 to 450 in 0.5 s, and a GC temperature program of -80 to 250 at 10 C/min. The transfer line, source, and MS manifold temperatures were maintained at 225, 225, and 100 C, respectively. The electron multiplier was maintained at 1600 V during the chromatographic runs.

GC/MS/DS Identification Procedures

The procedures utilized in the analysis of the data were designed so that all identifications reported would be of a "confirmed" nature (Christman, 1982). Following the analysis of a standard containing known amounts of each of the target and internal standard compounds, relative retention times (RRT) and relative response factors (RRF) were calculated using the GC/MS/DS software. The internal standard compounds toluene-d8 and 2-bromo-m-xylene eluted in the early and late portions of the chromatogram, respectively, and each was used in the RRT and RRF calculations in its respective chromatographic region. The mass spectral ions used for

peak area quantitation of toluene-d8 and 2-bromo-m-xylene were 98 and 184, respectively. The 26 target analytes which were specifically sought in the samples (and the ions used for peak area quantitation) included: 1,1-dichloroethene (61), dichloromethane (84), trans-1,2-dichloroethene (61), 1,1-dichloroethane (63), chloroform (83), 1,1,1-trichloroethane (97), 1,2-dichloroethane (98), tetrachloromethane (carbon tetrachloride) (117), benzene (78), 1,2-dichloropropane (63), trichloroethene (trichloroethylene) (130), bromodichloromethane (83), trans-1,3-dichloropropene (75), toluene (91), cis-1,3-dichloropropene (75), 1,1,2-trichloroethane (83), dibromochloromethane (129), tetrachloroethene (129), chlorobenzene (112), ethylbenzene (91), bromoform (171), 1,1,2,2-tetrachloroethane 83), 1,3-dichlorobenzene (meta-dichlorobenzene) (146), 1,4-dichlorobenzene (para-dichlorobenzene) (146), 1,2-dichlorobenzene (ortho-dichlorobenzene) (146), and hexachloroethane (117).

The identification of the compounds in a sample data file was carried out by manual means to avoid misassignments. To this end, the system software was first used to plot the extracted ion current profiles (EICPs "ion chromatograms", or "mass chromatograms") for up to seven characteristic ions of each target compound in a narrow (+/- 25 s) window. The center of the window was predicted on the basis of the predetermined RRT of the compound and the observed internal standard RT. An identification was considered to be confirmed if: 1) the EICPs all maximized within +/- 1 s of each other, and very near to the predicted RT; and 2) the intensities of all of the plots relative to the most intense EICP were within +/- 20% of those observed in a standard run which had been carried out within 6 h of the sample run under consideration. Computer matching of the background-subtracted spectrum at the peak maximum was used to further confirm the assignment.

RESULTS

Of the over 26 compounds were specifically sought in the samples, the only ones which were detected (or detected at levels above blank levels) were 1,1,1-trichloroethane, chlorobenzene, and para-dichlorobenzene. A variety of naturally-present compounds were also identified in the samples. Some of these identifications are given in Figure 3 which is the chromatogram obtained for piezometer OW 3 - 2 with Cartridge 415. The concentrations of 1,1,1-trichloroethane, chlorobenzene, and para-dichlorobenzene together with the associated blank levels are presented in Table I. The volumes sampled are also given. Volumes substantially greater than 50 mL (the nominal capacity of the syringes) occurred when the O-ring on the moveable plunger leaked somewhat allowing water to pass up into the tube which led to the surface. This problem may be overcome through the adjustment of the O-ring groove tolerances. Although breakthrough for 1,1,1-trichloroethane is of general concern, it is encouraging (though not statistically convincing) to note that there is no dependence on the sample volume for the data (above blank levels) obtained for piezometer OW 11-3.

The gas chromatographic mean retention times for the compounds 1,1,1-trichloroethane, chlorobenzene, and para-dichlorobenzene were 402, 585, and 720 s, respectively. The means of the absolute values of the deviations between the predicted and observed retentions times were 7.7, 3.1, and 1.5 s, respectively. The corresponding standard deviations of the latter were 6.6, 2.9, and 1.7 s, respectively. Thus, 95% of the analyses reflected retention time deviations which were less than ~(mean +/- 1.96 s) = 21., 8.9, and 4.9 s, respectively. The fact that 1,1,1-trichloroethane and chlorobenzene displayed greater variability is due to the fact that they were relatively more influenced by a certain amount of unavoidable variability in the low temperature portion of the GC temperature program.

Although it is known that the value of the relative standard deviation (coefficient of variation, or CV) for the concentration of an analyte as given by an analytical method is a function of the concentration of the analyte (Glaser et al., 1981), we will assume that to a first approximation it is independent of concentration for these analyses. This assumption allows one to pool replicate data and obtain estimates of the CV (Davies and Goldsmith, 1972). The data sets which were included in this pooling process, marked with an asterisk in Table I, were limited to those piezometers for which the concentrations were substantially above blank levels. The blank values (calculated by dividing the ug amounts of each compound found on a blank cartridge by smallest sample volume employed = 0.050 L) were not subtracted from the data prior to the calculation of individual standard deviations. The pooled CV were therefore observed to be 25., 6.9, and 6.3% for 1,1,1-trichloroethane, chlorobenzene, and para-dichlorobenzene, respectively.

In view of its substantially higher volatility, it is not surprising that the 1,1,1-trichloroethane data should exhibit the highest CV. If the surface samples are excluded from the calculation of the pooled CV for this compound, the result is 23% rather than 24%. There are too few data points to allow a statistical distinction to be made between those samples which could be obtained down-hole and those which had to be obtained at the surface. Some of the variability may reside in errors associated with the cartridge handling and analysis which occurred after the sampling.

The average blank values for 1,1,1-trichloroethane, chlorobenzene, and para-dichlorobenzene were 0.30, 0.38, and 0.011 ug/L, respectively. A blank cartridge prepared by exposing it to a section of the type of O-ring used in the syringe device showed no contamination from these compounds. It is

probably significant that the two compounds with the highest blank levels are also the two compounds with the higher vapor pressures (96.0 and 11.7 torr vs. 1.2 torr for para-dichlorobenzene (Callahan et al., 1979) In view of the fact that we have never seen such high 1,1,1-trichloroethane and chlorobenzene blank levels in conjunction with other, generally lower level trace analyses by aqueous ATD underway in our laboratories (Pankow et al., 1983b), it appears that a portion of the contamination is cross-contamination from samples to blanks. It will therefore be possible to lower this contamination level by increasing the isolation which each cartridge receives subsequent to sampling.

The down-hole cartridge technique provides some unique advantages over conventional methods for obtaining groundwater samples for analysis for trace organic compounds. In effect, each cartridge is a dedicated sampler. The technique is convenient for acquiring samples from depths near the piezometer tip or well screen. Since the cartridge itself is quite small in diameter (0.64 cm), the possibility exists for modifying the method for very narrow piezometers such as those developed by Cherry et al. (1983a, 1983b) and Hewetson and Cherry (1983) for multi-level sampling. If the piezometer is pumped or bailed prior to sampling, the sample will represent groundwater which recently flowed into the piezometer and also travelled only a short distance upward in the piezometer. This water will contact only a small percentage of the total, potentially adsorptive casing surface. If the sample is taken at the piezometer tip after a freshly pumped well has been allowed to recharge, the sample will not be exposed to pressures lower than the in situ pressure, and volatilization will be minimized.

Sampling down-hole also allows the possibility of not pumping or bailing many water columns prior to sampling. This is of particular interest in view of the controversy that currently exists regarding the

number of water column volumes that should be removed from a well or piezometer before sampling can occur. Since most pumping methods cause the mixing of fresh formation water with water which previously existed in the water column, it is generally desirable to pump considerably more than one column volume when sampling permeable formations. Down-hole sampling techniques such as those described in this paper have the advantage of allowing the sampler to be placed near the bottom of the piezometer when the pump is operating near the top of the water column. While the low permeability of the shale at the Bayview Park Landfill prevented the use of this configuration in this study, its application in higher permeability formations would allow the sample to represent new formation water even when a only small total volume is removed from the water column.

While the same water could be sampled conventionally by placing a pump at the piezometer tip, losses by adsorption and volatilization may be problematic as the sample rises in the tube leading to the surface. The use of a conventional bailer equipped with a one-way valve may eliminate the sorption loss problem, but volatilization at the surface remains a source of uncertainty. If a pump/tube assembly or a bailer is not dedicated to each piezometer, a process which involves additional expense, cross-contamination may also occur.

Disadvantages associated with the cartridge down-hole sampling technique as developed here with the sorbent Tenax-GC are: 1) the cost in labor time in preparing the cartridges as compared to cleaning glass sample vessels; and 2) the potential for less than quantitative sorption for very volatile compounds such as 1,1,1-trichloroethane. For many sampling applications, the many advantages of the technique outweigh the cost of preparation. Furthermore, it is likely that the first problem will be reduced in the

future as the method develops. Uncertainties with regard to the magnitude of the second problem are currently under field investigation by this group and may be reduced through the use of several cartridges in series. Studies are also currently underway in the laboratory of one of the authors (JFP) concerning how the magnitude of the problem may be reduced through the variation of sorbent type and sampling conditions.

CONCLUSIONS

A down-hole cartridge sampling technique based on the analytical method ATD and analysis by GC/MS/DS has been developed for the determination of ug/L levels organic contaminants in groundwater. The convenience of the technique for field use and the reproducibility of the results were encouraging during an application of the technique to the study of the zone of contamination down-gradient of a landfill located on fractured shale in Burlington, Ontario. The technique enables samples to be obtained from any depth in piezometers or wells in a manner that minimizes losses due to volatilization and sorption on sampling equipment. In essence, each cartridge is a dedicated sampler in that it is not used in more than one piezometer or well. Because the sample exists as a small, light-weight porous cartridge regardless of the water volume that is sampled, the sample is in a form that is very convenient for packaging and shipping by mail or by courier from field sites to distant analytical laboratories. Further work is underway in our laboratories to improve the technique.

ACKNOWLEDGEMENTS

Funds for the development of the sampling technique and its application at the Bayview Park Landfill were obtained from grants provided by the National Science and Engineering Research Council of Canada. We gratefully acknowledge the permission to conduct research at the site provided by The City of Burlington, Ontario and by National Sewer Pipe Ltd., owners of the land in the vicinity of the landfill. Assistance with equipment preparation and field sampling by Toni J. Kristensen and Paul E. Johnson is also gratefully acknowledged.

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Table I. Concentrations of selected organic compounds in ug/L (ppb) in Bayview Park Landfill samples from OW sample well series. Volume sampled data are given in mL.

Well	Slotted Depth (m)	Cartridge Number	Volume Sampled	1,1,1-Trichloroethane	Chloro-benzene	Para-dichlorobenzene
OW 15-3 down-hole	27.7	419	50	* 35.	* 3.4	* 0.37
		421	50	38.	2.9	0.35
	Blank	409	-0-	0.17	0.89	0.041
OW 1-2 down-hole	8.2	402	56	* 0.30	* 11.	* 1.8
		404	58	0.41	12.	2.0
	Blank	409	-0-	0.17	0.89	0.041
OW 1-4 down-hole	8.0	570	65	* 25.	0.080	0.003
		580	60	13.	0.051	ND
	Blank	640	-0-	0.18	0.042	0.001
OW 3-2 surface	7.3	415	54	* 0.94	* 8.0	* 1.5
		416	50	1.6	8.3	1.6
	Blank	418	-0-	0.40	0.91	0.011
OW 3-3 down-hole	14.3	411	54	* 7.6	0.90	0.013
		412	56	11.	0.74	0.011
		413	57	8.4	0.72	0.008
	Blank	418	-0-	0.40	0.91	0.011
OW 3-4 surface	21.0	559	54	* 48.	0.19	ND
		560	50	30.	0.16	ND
	Blank	640	-0-	0.18	0.042	0.001
OW 11-1 down-hole	3.0	554	60	0.24	* 2.8	* 0.52
		555	105	0.12	2.9	0.57
	Blank	505	-0-	0.25	0.029	ND
OW 11-2 down-hole	14.8	552	62	* 1.4	0.025	0.001
		553	68	2.0	0.026	ND
	Blank	505	-0-	0.25	0.029	ND
OW 11-3 down-hole	22.4	591	61	* 5.7	0.044	0.005
		593	188	6.1	0.027	0.009
		596	58	7.7	0.050	0.007
	Blank	505	-0-	0.25	0.029	ND
OW 12-3 down-hole	19.4	558	56	* 11.	* 0.84	* 0.051
		600	46	9.3	0.75	0.057
	Blank	505	-0-	0.25	0.029	ND
OW 5 surface	7.6	650	50	0.50	0.053	ND
		680	50	0.53	0.051	0.002
	Blank	780	-0-	0.50	0.045	0.001
Average concentration on * data sets:				14.	5.3	0.88
Average blank level (ug/L):				0.30	0.38	0.011
CV based on pooling of * data sets:				25.%	6.9%	6.3%

LIST OF FIGURES

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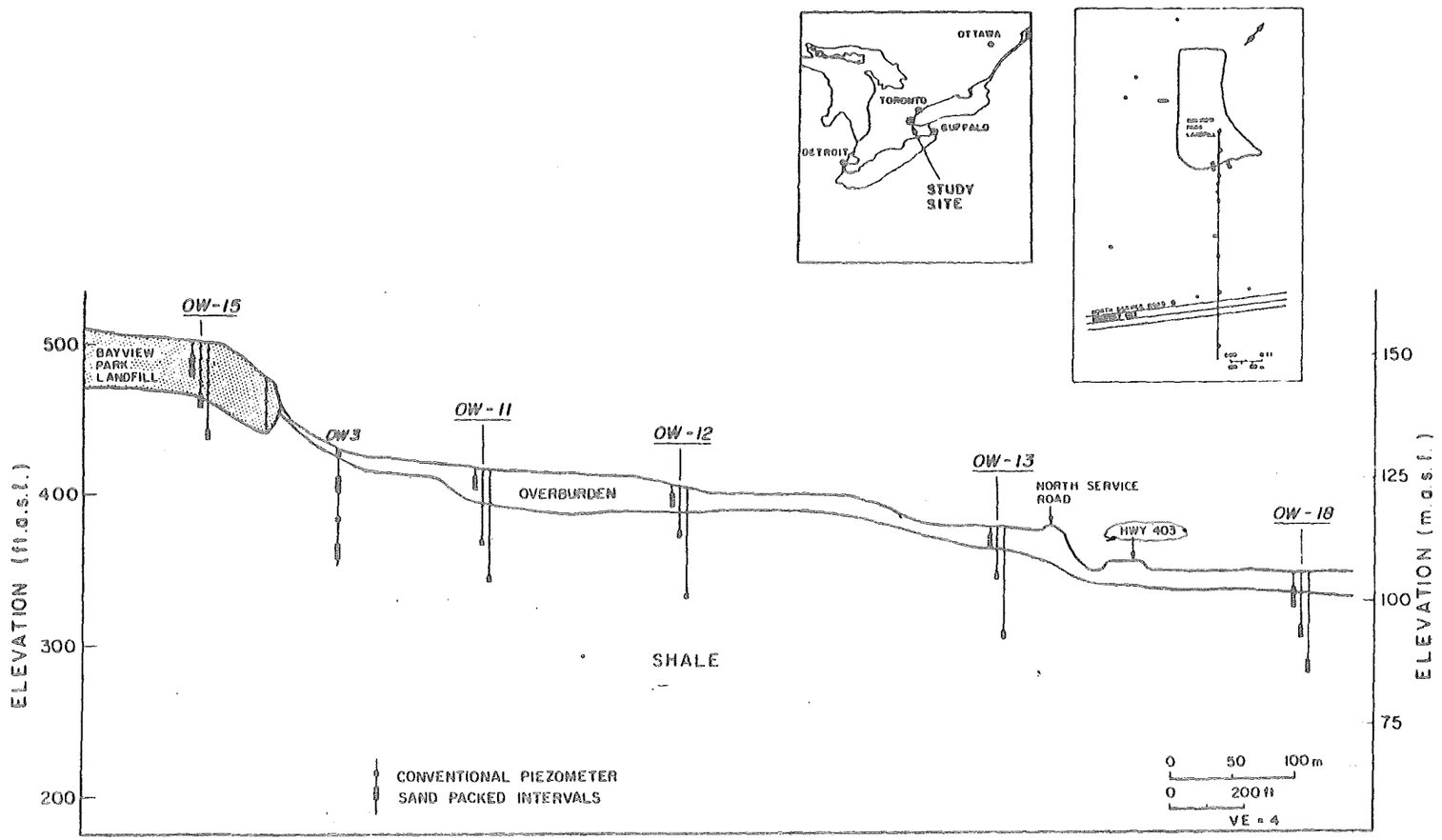

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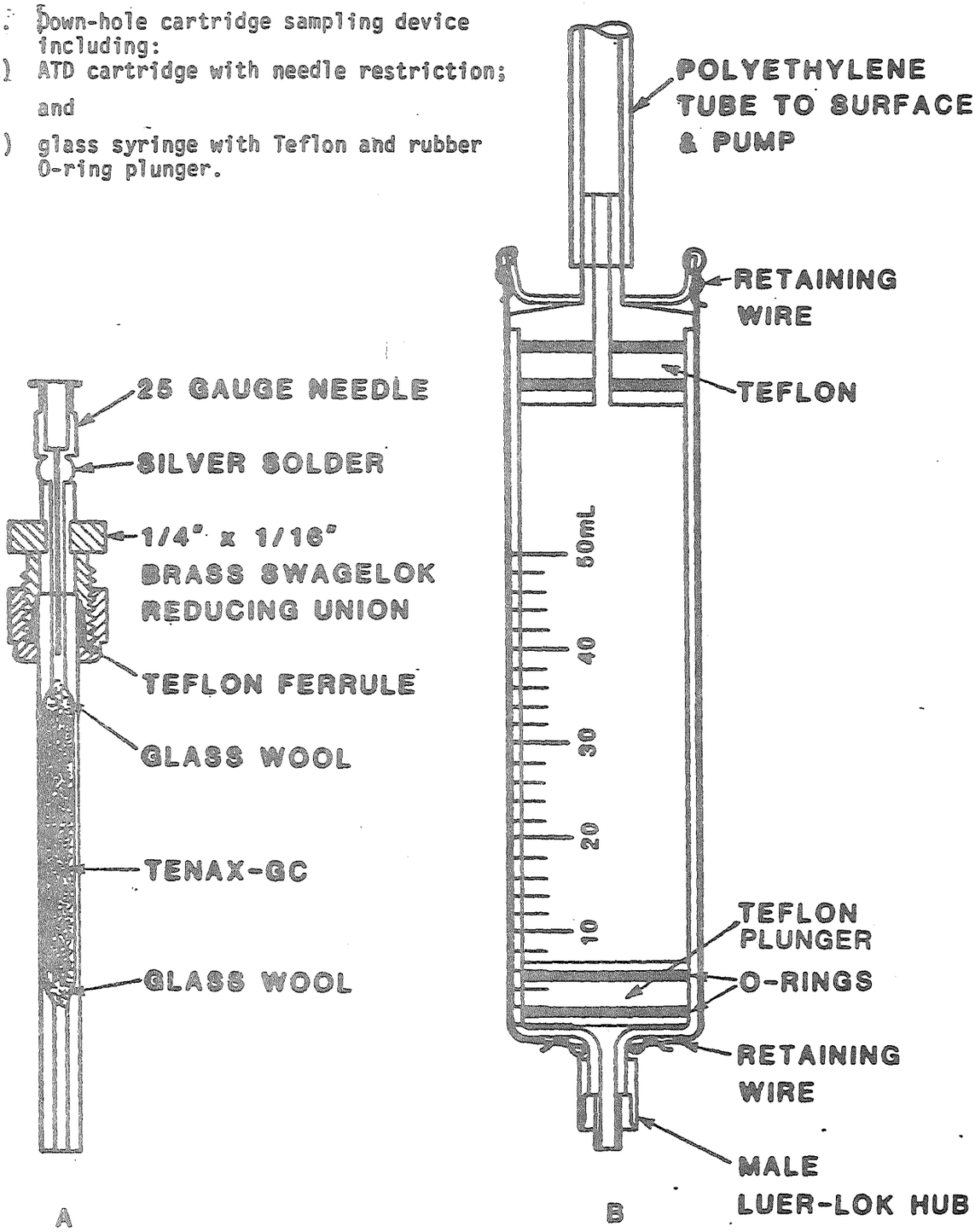
Figure 2. Down-hole cartridge sampling device including:
A) ATD cartridge with needle restriction; and
B) glass syringe with Teflon and rubber O-ring plunger.



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03/26/83 20:53:00
DATA: CH415032683 #1 SCANS 1 TO 2000
CALI: FC430323831 #1
SAMPLE: WELL OW3-2, CART 415.1 UL IS PPD 3/18/83 BY TJK, EM 1600
CONDS.: PRG 10 @ 30/M, DSRB 15 @ 250 & 15 PSI, - 80 TO 250 @ 15/M
RANGE: G 1.3000 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

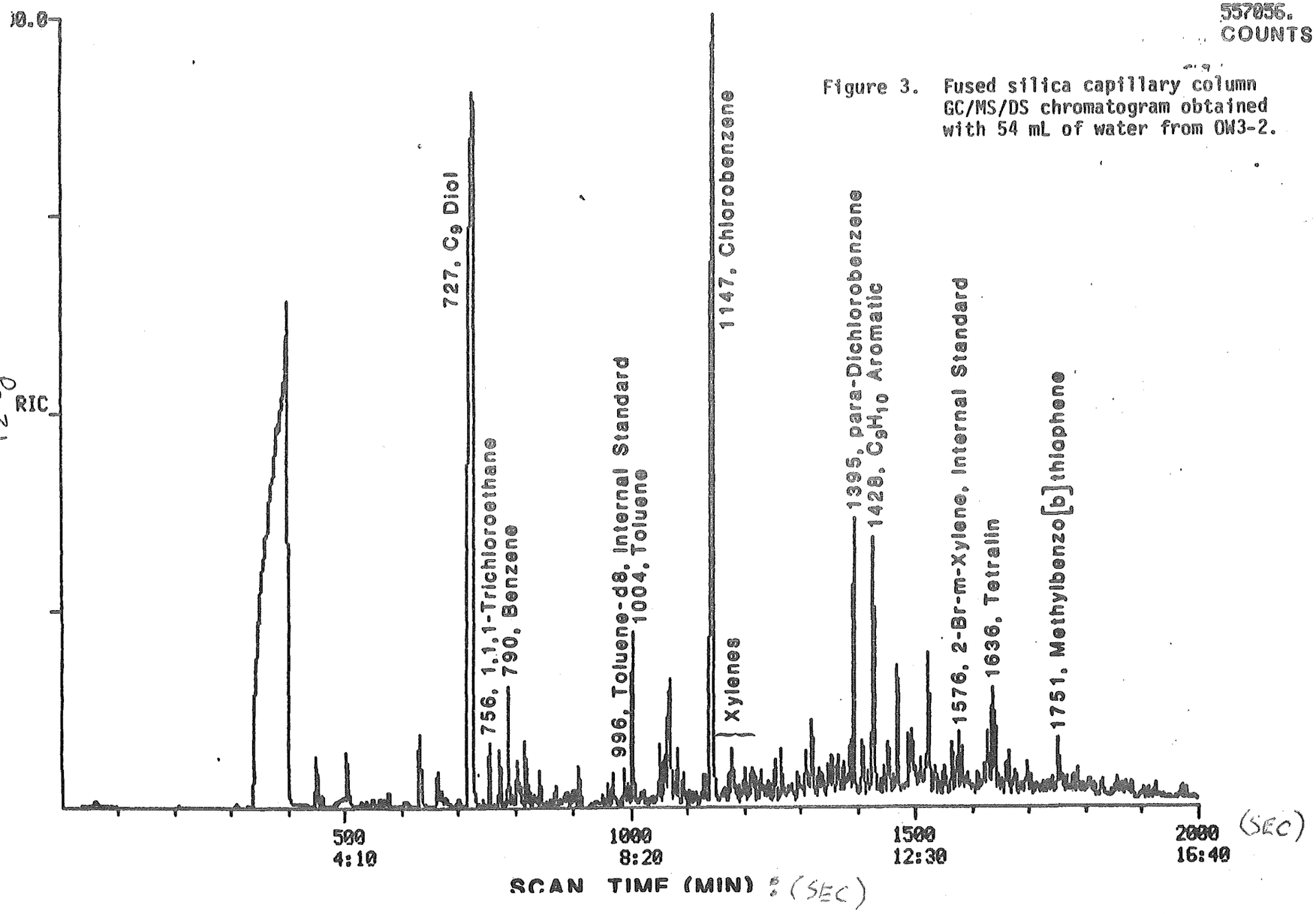

Figure 3. Fused silica capillary column GC/MS/DS chromatogram obtained with 54 mL of water from OW3-2.

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