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DIFFERENTIATION OF THE ORIGINS OF BTEX IN GROUND WATER USING MULTIVARIATE PLOTS

by

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ABSTRACT

Multivariate plots were utilized to create fingerprints of aromatic hydrocarbon residues in groundwater. The technique allows hydrogeologists to distinguish between benzene, toluene, ethyl benzene and total xylene residues originating from ground water contact with petroleum in natural deposits and refined petroleum waste products. Examples are taken from deep-well injection of refinery waste waters, natural petroleum deposits, municipal and industrial landfill leachates, coal tar and creosote contaminated waters, and varnish industry contaminated ground water. The data was plotted from ASCII files generated through either Lotus 123™ or a database (The Manager™) report program, using a simple Fortran interactive program with Plot88™ subroutines.

RESUME

Des graphiques à variables multiples ont été utilisés pour créer des empreintes des résidus de composés aromatiques dans l'eau souterraine. Cette technique permet aux hydrogéologues de distinguer les résidus de benzène, toluène, éthylbenzène et xylènes totaux provenant du contact de l'eau souterraine avec des dépots naturels de pétrole d'avec ceux qui proviennent des déchets de raffinage. Les exemples proviennent de l'injection dans le roc de décharges de raffineries, de dépots naturels de pétrole, de lexiviats de dépotoirs municipaux et industriels, de créosote et de goudron et de la manufacture des vernis. Les graphiques sont générés à partir de données contenues dans de filières ASCII produties par Lotus 123^MD ou un logiciel de banque de données (The Manager^MD) en utilisant un programme interactif en Fortran avec des sous-routines de Plot88^MD.

MANAGEMENT PERSPECTIVE

A method that allows the differentiation of sources of aromatic hydrocarbons (benzene, toluene, ethyl benzene, xylenes or BTEX) in ground water is described. It is important to be able to recognize benzene residues that arise from ground water contamination through spills or seepage from hazardous waste sites and petroleum storage tanks, from similar residues that occur from natural petroleum deposits. A simple interactive computer program was written to plot data stored in ASCII files using an inexpensive graphics package. The plots generated are fingerprints of the ground water contamination and several examples are given where the fingerprints are sufficiently specific to differentiate between natural and anthropogenic sources of BTEX.

POINT DE VUE POUR LA GESTION

On décrit une méthode qui permet de différencier les sources d'hydrocarbures aromatiques (benzène, toluène, éthylbenzène et xylènes, ou BTEX). Il est important de pouvoir reconnaître les résidues de benzène dus à la contamination des eaux souterraines lors de décharges accidentelles, de fuites dans les citernes ou par lessivage des dépotoirs, de ceux qui proviennent des dépots pétrolifères. Un programme interactif simple permet de générer des graphiques à partir de données en format ASCII en utilisant un logiciel commercial peu coûteux. Les graphiques servent d'empreintes de la contamination des eaux souterraines et plusieurs exemples démontrent que ces empreintes sont suffisamment spécifiques pour différencier le BTEX d'origine naturelle de celui d'origine anthropogénique.

INTRODUCTION

Aromatic hydrocarbons such as benzene, toluene, ethyl toluene and xylenes (termed collectively BTEX) enter ground water from a variety of sources. They are of environmental concern because of their presence in ground waters contaminated by landfills, leaking storage tanks and spills. However, these compounds also occur naturally in petroleum deposits (Hunt, 1979). It is therefore often difficult to distinguish between anthropogenic and naturally occurring BTEX (Barker et al., 1988).

The problem was initially encountered in the assessment of the deep-well disposal of wastes from the petrochemical industry in Sarnia, Ontario. A 300 m multilevel borehole was installed near the injection wells and water samples from various levels were analysed for volatile organic compounds. The concern was that the injected wastes could potentially migrate upwards and contaminate the shallow ground waters. Analyses showed high BTEX concentrations at most sampling levels in the bedrock (Intera Technologies, 1988). Because several of the formations contain natural petroleum deposits, it was not possible, a priori, to eliminate the possibility of an upward migration of the wastes.

Multivariate plots have been used by Meyerhein (1987) to evaluate data obtained from several monitoring wells at a gasoline contaminated site and to compare the mobility of the different gasoline components. By plotting the analytical data for the different depths in the borehole on multiple axes, it was possible to discern a distinct pattern difference between the zones of disposal and the zones situated above it. A computer routine was written allowing the use of an ASCII file generated either as a Lotus 123™ print file or from a database to input directly into a plotting program. Patterns from several different types of contaminated ground waters including those from natural petroleum deposits, municipal landfill, industrial dumpsites, coal tar and creosote sites, and solvents from varnish manufacturing, were compared to verify the general applicability of the concept.

METHODS

Chemical Analysis

Ground water analyses were carried out using a Unacon model 810 purge and trap apparatus (Envirochem Inc., Kemblesville, PA) interfaced directly to a Hewlett-Packard model 5970 GC-MSD. The analytical column was a 30 m DB-624 J&W™ column (Chromatographic Specialties, Brockville, Ontario). Samples size was generally 10 mL except for heavily contaminated samples where 100 µL was diluted to 10 mL with uncontaminated water.

Computer Program

The program used to generate the plots was written in FORTRAN with PLOT88™ (Plotworks Inc., La Jolla, CA) subroutines. The plots in this paper were created using a COMPAQ portable III microcomputer and a Roland DG, DXY-990 plotter. Data is read into the program from fixed format ASCII files, which are easily created from available spreadsheet packages such as LOTUS 123™ or from a database such as The Manager™ (BMB Compuscience, Milton, Ontario). An interactive portion of the program allows the user to plot one or more data sets from the same or different files and control the output of the graph. The measured concentration of each compound is plotted from the origin on a separate axis. The axis units and line characteristics are user-defined. A multi-colour plot can be generated for diagnostic purposes or a differing line type plot can be created for inclusion in reports. The program is flexible, and while the plots in this paper use six variables, the program can be easily modified to display several more.

RESULTS

Multivariate plots were prepared to display analytical chemical results for ground water samples containing benzene, toluene, ethyl benzene, 1,2,4-trimethyl benzene, the sum of o,m and p-xylenes, and the sum of ethyl toluenes that were collected at different depths in the multilevel borehole installed in Sarnia, Ontario, Canada (Intera Technologies, 1988). The results obtained are shown in Figure 1. To facilitate the visual comparison, the results for the top four levels of sampling (depth of 200 (61 m), 250 (75 m), 405 (123 m) and 440 ft. (133 m)) were grouped in Figure 1a; the results for the disposal zone

(635 (192 m) and 685 ft (207 m)) in Figure 1b; and the results for the lower part of the disposal zone (752 ft (228 m) and 792 ft (240 m)) in Figure 1c. Although the total BTEX concentrations were similar in the two upper zones, their fingerprints were very distinct. Also, even if the total concentration was much lower at 685 ft (207 m), the pattern was still typical of the one found in the main disposal zone. In the lower portion of the disposal zone, yet a different pattern was observed. These results are consistent with those reached on the basis of phenol levels in the well (Intera Technologies, 1988). Elevated levels of phenols were found at 635 ft. This fact was, however, not sufficient evidence of waste disposal since phenols are also associated with natural petroleum deposits (Hunt, 1979).

The pattern observed in the upper part of the borehole (Figure 1a) was compared to that obtained with data from a site located in Niagara Falls, N.Y., which was not contaminated, but contained petroleum deposits (Figure 2). The two fingerprints were very similar and may be indicative of typical natural petroleum derived ground water.

The fingerprints obtained from a municipal landfill (Guelph, Ontario) and an industrial dumpsite (Ville Mercier, Quebec) are shown in Figures 3a and b respectively. In the municipal landfill, toluene, ethyl benzene and the xylenes were predominant, whereas the industrial site showed a more mixed distribution, somewhat more similar to the crude oil contacted ground water (Figure 1a). This may be because the municipal landfill received predominantly light petroleum distillates such as gasoline, whereas waste oils were deposited in the dumpsite.

Coal tars are another potential source of BTEX groundwater contamination (Speight, 1983; Enzminger and Ahlert, 1987). Samples were collected on the site of a former coke oven works associated with a steel plant. Several storage tanks and disposal pits for the coal tar distillates and wastes were found in an area of approximately 1 mile^2. The results obtained from the analysis of ground water collected in a monitoring well located near a coal tar pit are shown in Figure 4a and those from two monitoring wells close to a storage tank containing coal tar distillates in Figure 4b. The product distributions are sufficiently different in the two to conclude that the contamination was indeed from two different sources although the monitoring wells were located only 500 ft from each other. It is interesting to note the similarity between Figures 1a, 2 and 4a that all arose from unprocessed petroleum-contacted ground water.

Finally, data from contaminated ground water under a varnish plant (Mantica, 1983) resulted in a totally different pattern from which benzene is absent (Figure 5). It was difficult to find other such examples from data contained in the literature, because only in very few instances were all the compounds used in our comparisons, measured. This is in part due to the tendency to restrict measurements to the EPA list of priority pollutants which are not always the best indicators of ground water contamination (Sabel and Clark, 1984).

The contaminants to be plotted were selected on the basis of their general prevalence in petroleum products and as significant groundwater contaminants based on their solubility (Koehn and Stanko, 1988). The higher alkylated benzenes offered the best diagnostic value. Parameters such as benzene/toluene ratios were not sufficiently different to be useful as discriminating criteria. Xylenes and ethyl toluenes were summed to allow the use of the program with data of various sources, where, depending on the analytical methodology, some isomers were not resolved. Other minor constituents such as cumene and styrene were rejected because they were present in much lower concentration than the others and could not be visually distinguished on the same scale.

The method proved useful in comparing residues of samples that were very close to their respective source. As the distance of monitoring wells from the source increases, it is expected that these fingerprints would be altered slightly to reflect the mobility of the individual contaminants in groundwater (Meyerhein, 1987). An example of this is given in Figure 6, which is from the same site as 3b, but taken from a pumping well situated 200 ft from the source. The concentrations are all lower, and that of benzene, which is the most soluble compound of the group, is proportionally higher.

CONCLUSION

Multivariate plots are very useful diagnostic tools because they allow for the simultaneous plotting of several data sets, and on-screen comparisons before plotting. They are also superior to ratios, since they allow for the visual comparisons and the combination of several ratios. Data sets can be assessed rapidly through a very simple interactive program which uses as input ASCII files generated from either a Lotus 123™ spreadsheet or a database report. This approach allowed for the differentiation of BTEX residues in ground water originating from natural petroleum deposits and petrochemical waste disposal by deep well injection.

ACKNOWLEDGEMENTS

Thanks to Mr. Richard Noll, Syracuse University, for providing samples from the USGS borehole in Niagara, to Mr. Mark Priddle for collecting the Sarnia samples and to Ms. Anne Masson of Laval University for providing samples from the Ville Mercier site. Thanks also to Dr. Allan Crowe for his help with the computer program.

REFERENCES

Barker, J.F., J.E. Barbash and M. Labonte. 1988. Groundwater Contamination at a Landfill Sited on Fractured Carbonate and Shale. J. of Contaminant Hydrology, 3:1-25.

Intera Technologies. 1988. Hydrogeologic Study of Freshwater Aquifer and Deep Geologic Formations, Sarnia, Ontario. Report to the Ontario Ministry of the Environment. Contract H87-039-05, Toronto, Ontario.

Enzminger, J.D. and R.C. Ahlert. 1987. Environmental Fate of Polynuclear Aromatic Hydrocarbons in Coal Tar. Environmental Technology Letters, 8:269-278.

Hunt, T.M. 1979. Petroleum Chemistry and Geology. W.H. Freeman and Co., San Francisco.

Koehn, J.W. and G.H. Stanko. 1988. Groundwater Monitoring: Accurate assessment and reasonable economy are achievable. ES&T, 22(11):1202-1204.

Mantica, E. 1983. Analytical Techniques for the Monitoring of Water Contamination by Organic Compounds. International Conference on Ground Water Contamination with Organo-Chlorine Compounds of Industrial Origin. Milan, Italy. Jan. 26-29.

Meyerhein, R.F. 1987. Introduction to Ground Water Geochemistry. National Water Well Association. Sept. 29-Oct. 1, San Diego, CA. Course notes module 10.

Sabel, G.V. and T.P. Clark. 1984. Volatile Organic Compounds as Indicators of Municipal Solid Waste Leachate Contamination. Waste Management and Research, 2:119-130.

Speight, J.G. 1983. The Chemistry and Technology of Coal. Marcel Dekker, Inc. New York.

FIGURES

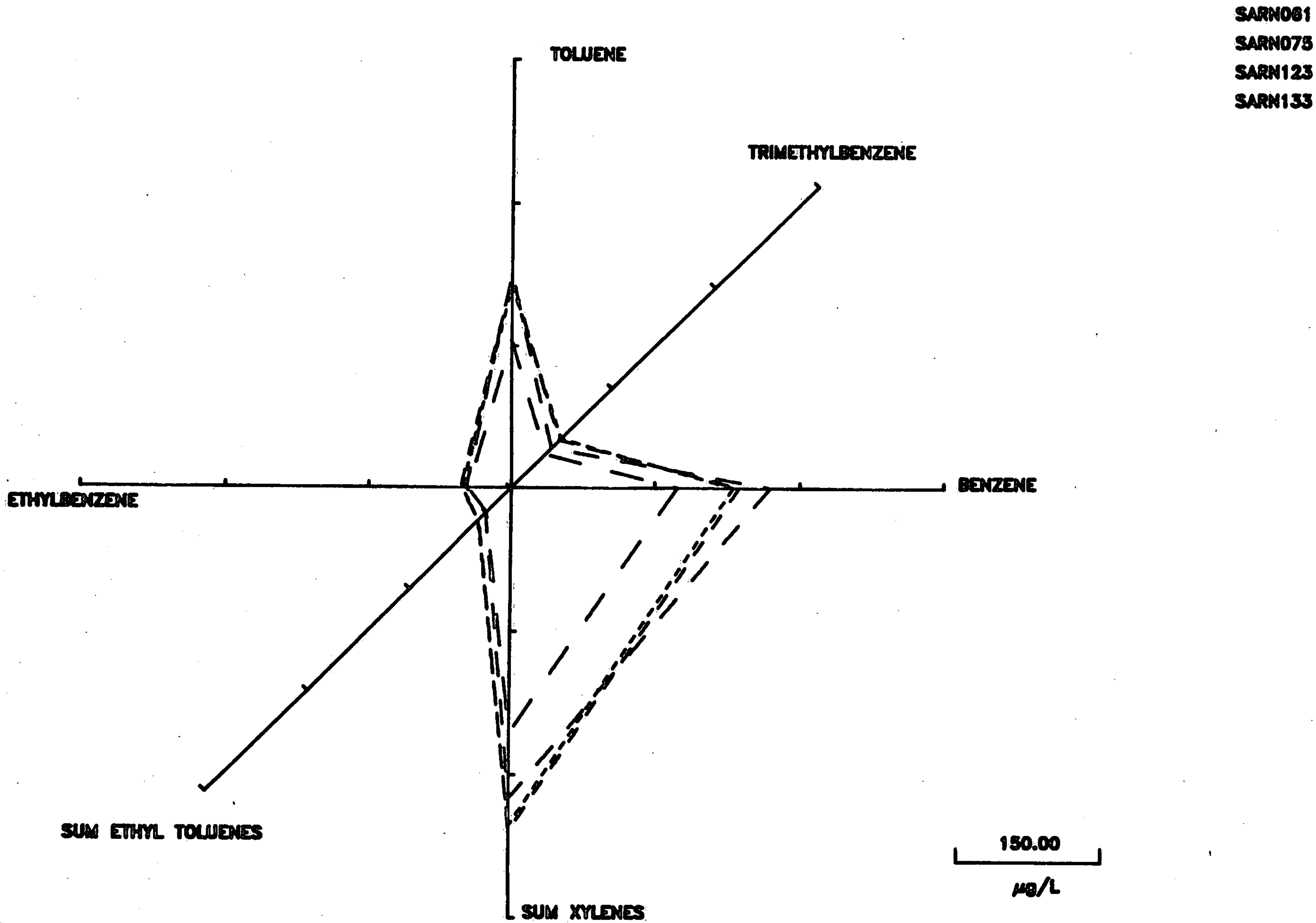

Figure 1a) Sarnia multilevel borehole: Depths of 200, 250, 405 and 440 ft.

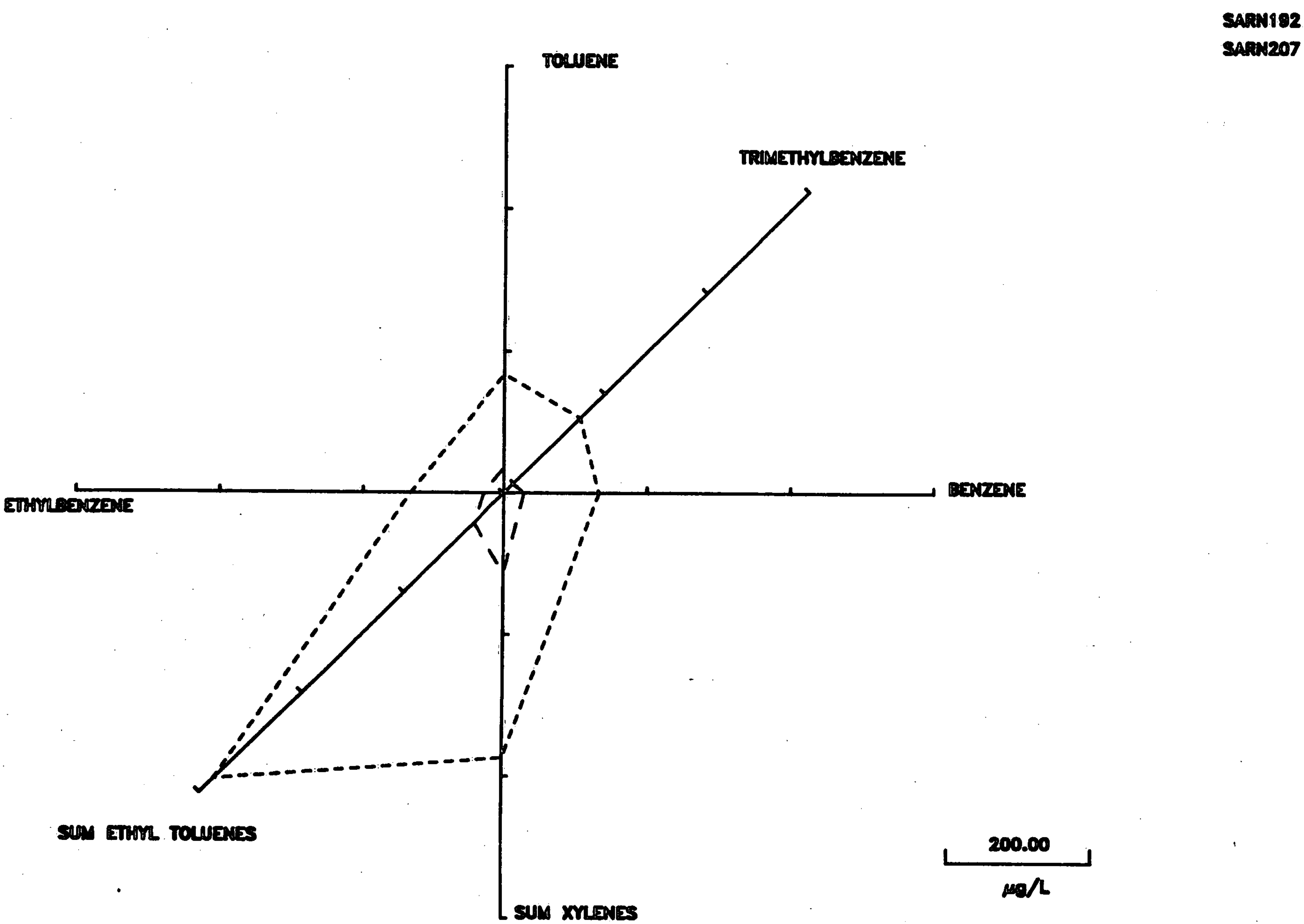

Figure 1b). Sarnia multilevel borehole: Depths of 635 and 685 ft.

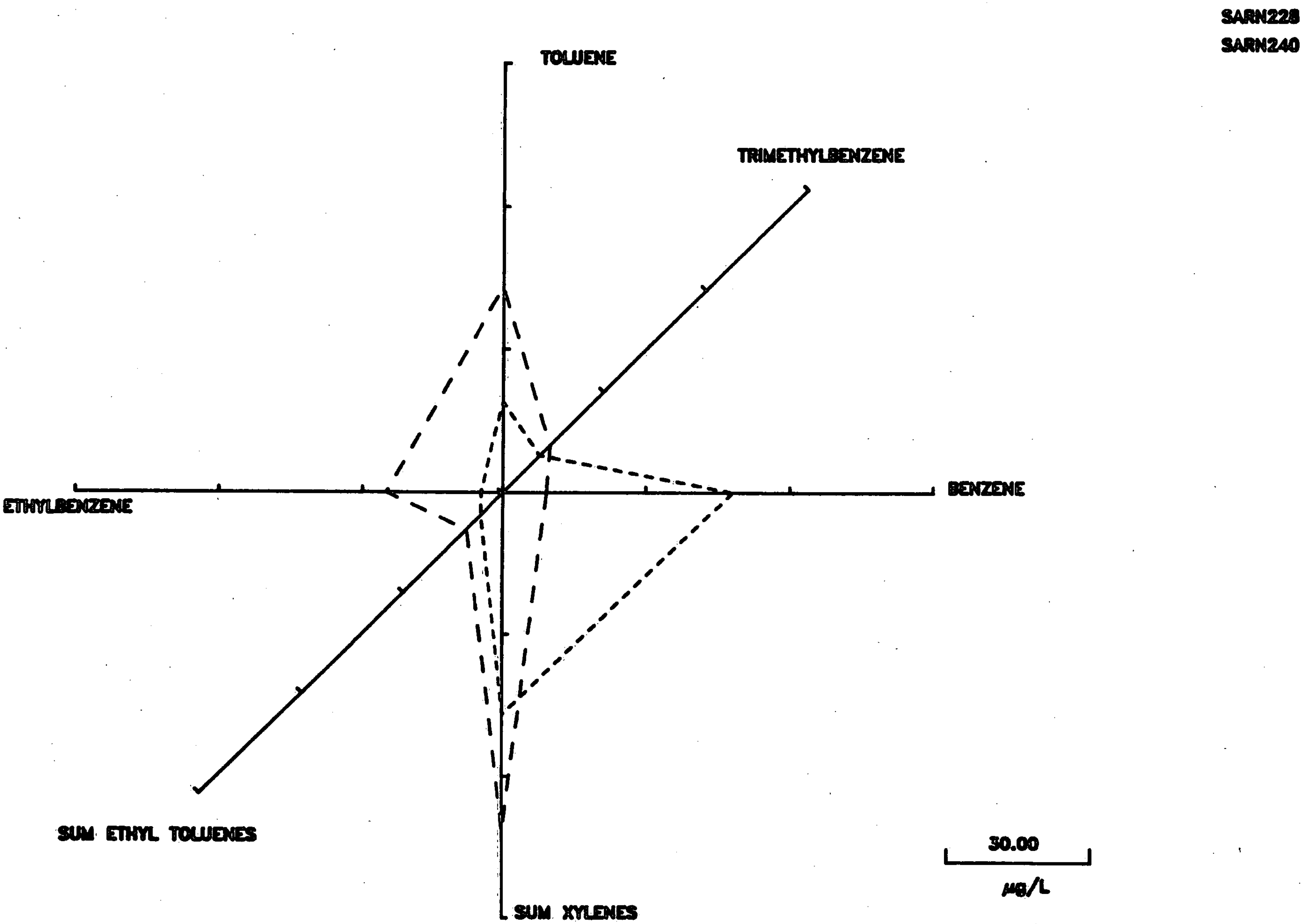

Figure 1c) Sarnia multilevel borehole: Depths of 752 and 792 ft.

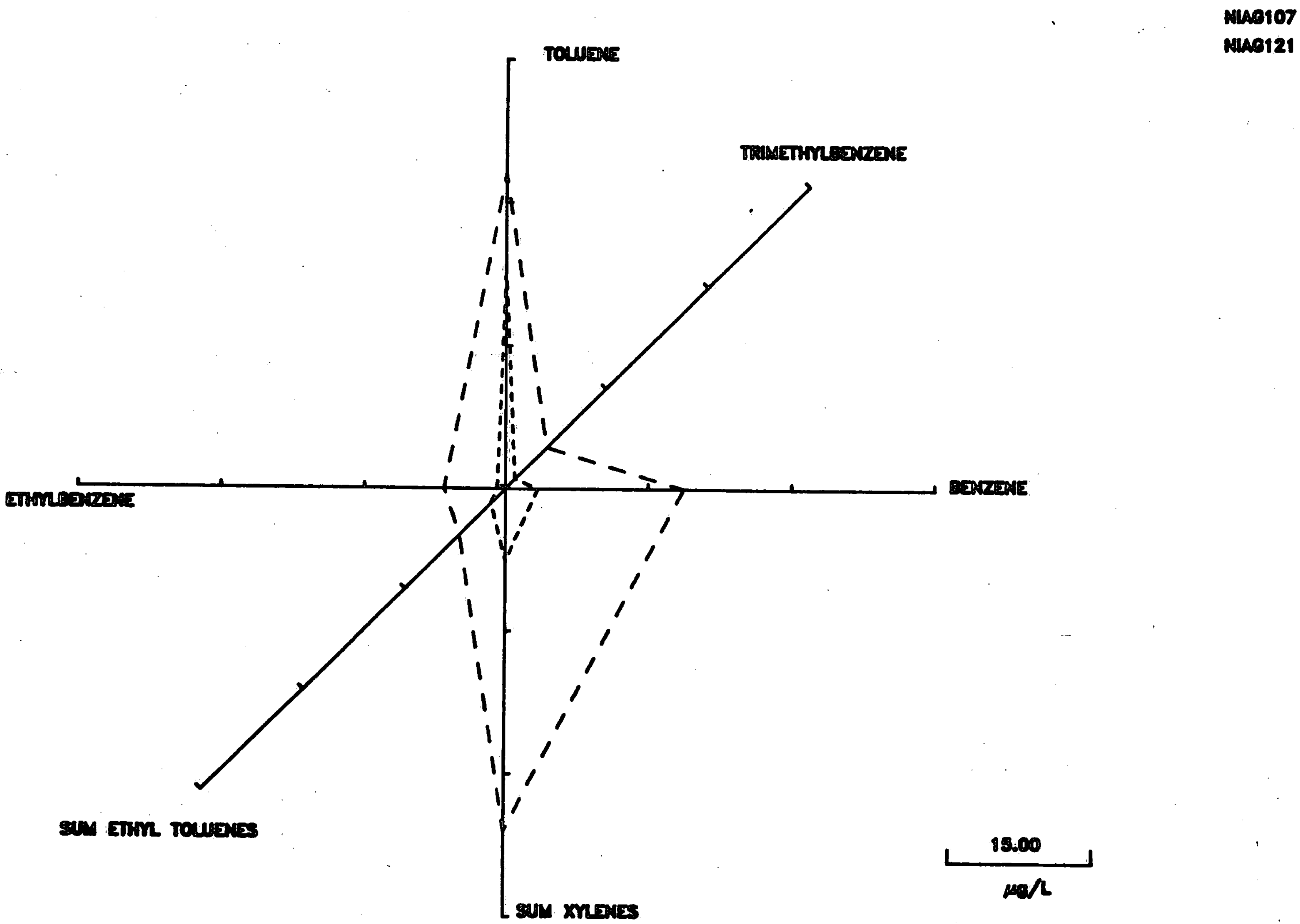

Figure 2. Niagara Falls, USGS multilevel borehole. Depths of 107 and 121 ft.

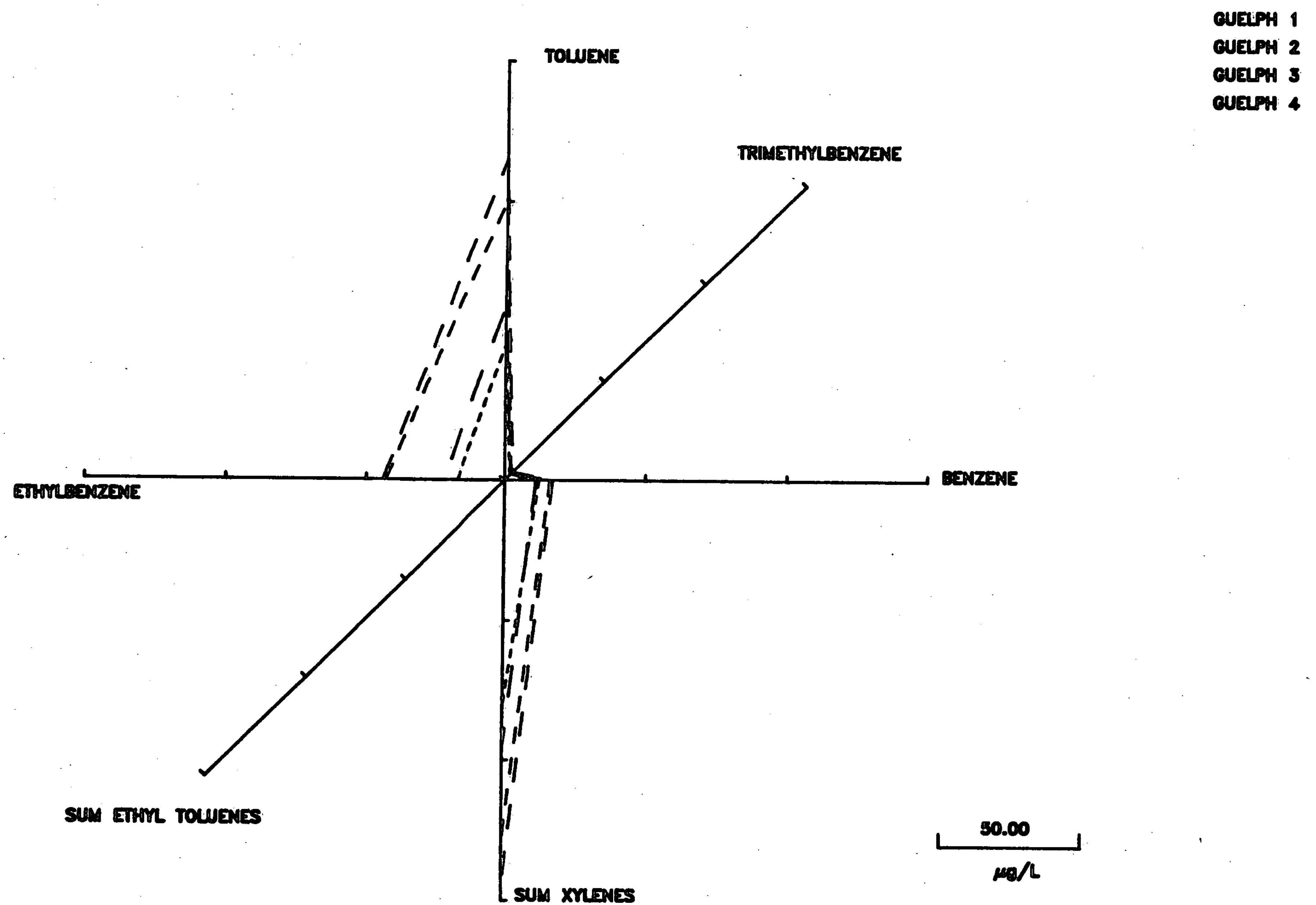

Figure 3a) Municipal landfill leachate.

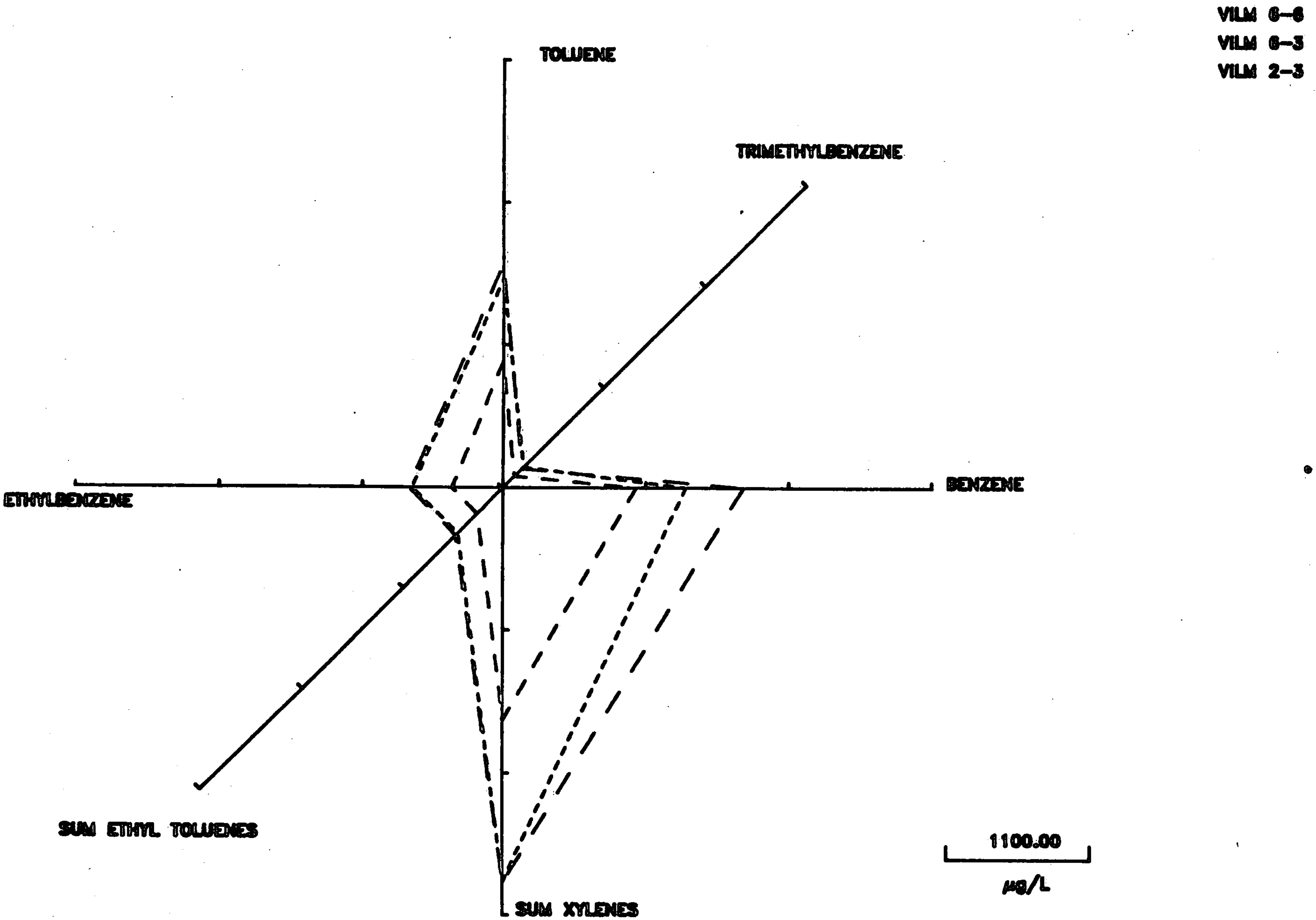

Figure 3b) Industrial dumpsite, Ville Mercier, Quebec, monitoring well R-2, 10 ft; well R6 at 10 and 20 ft.

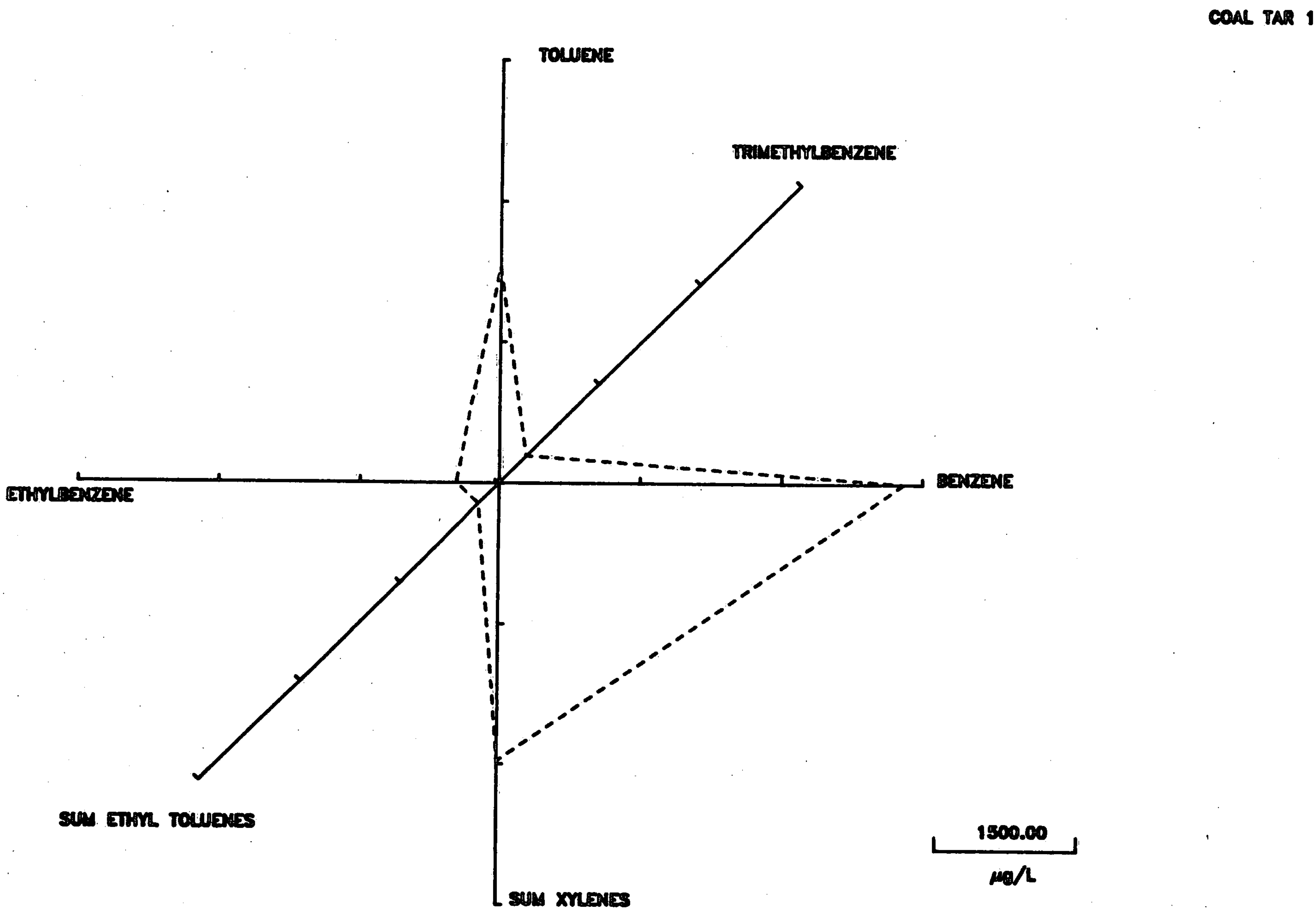

Figure 4a) Coke oven/steel foundry near coal tar pit at 30 ft.

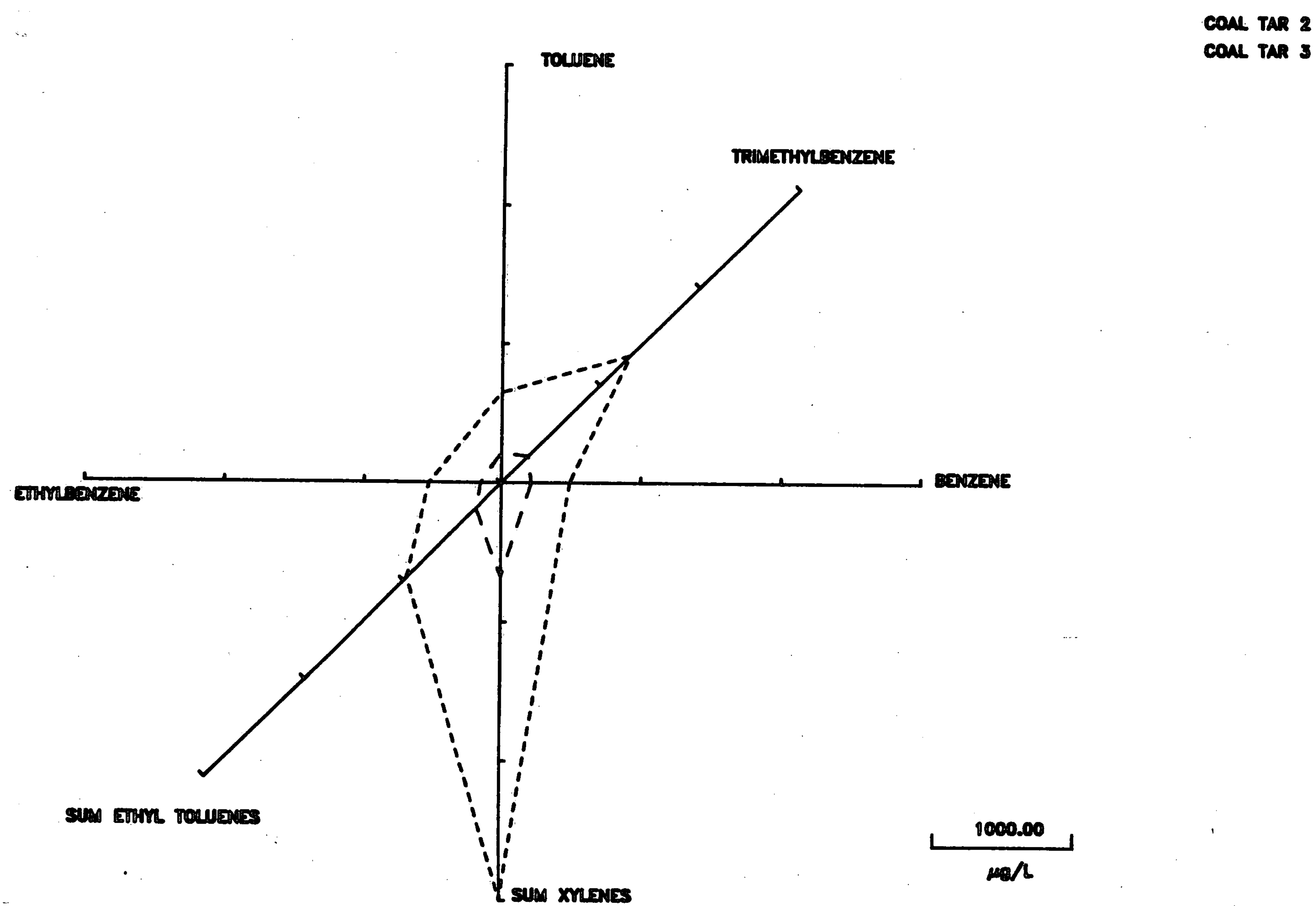

Figure 4b) Coke oven/steel foundry near storage tank at 12 and 32 ft.

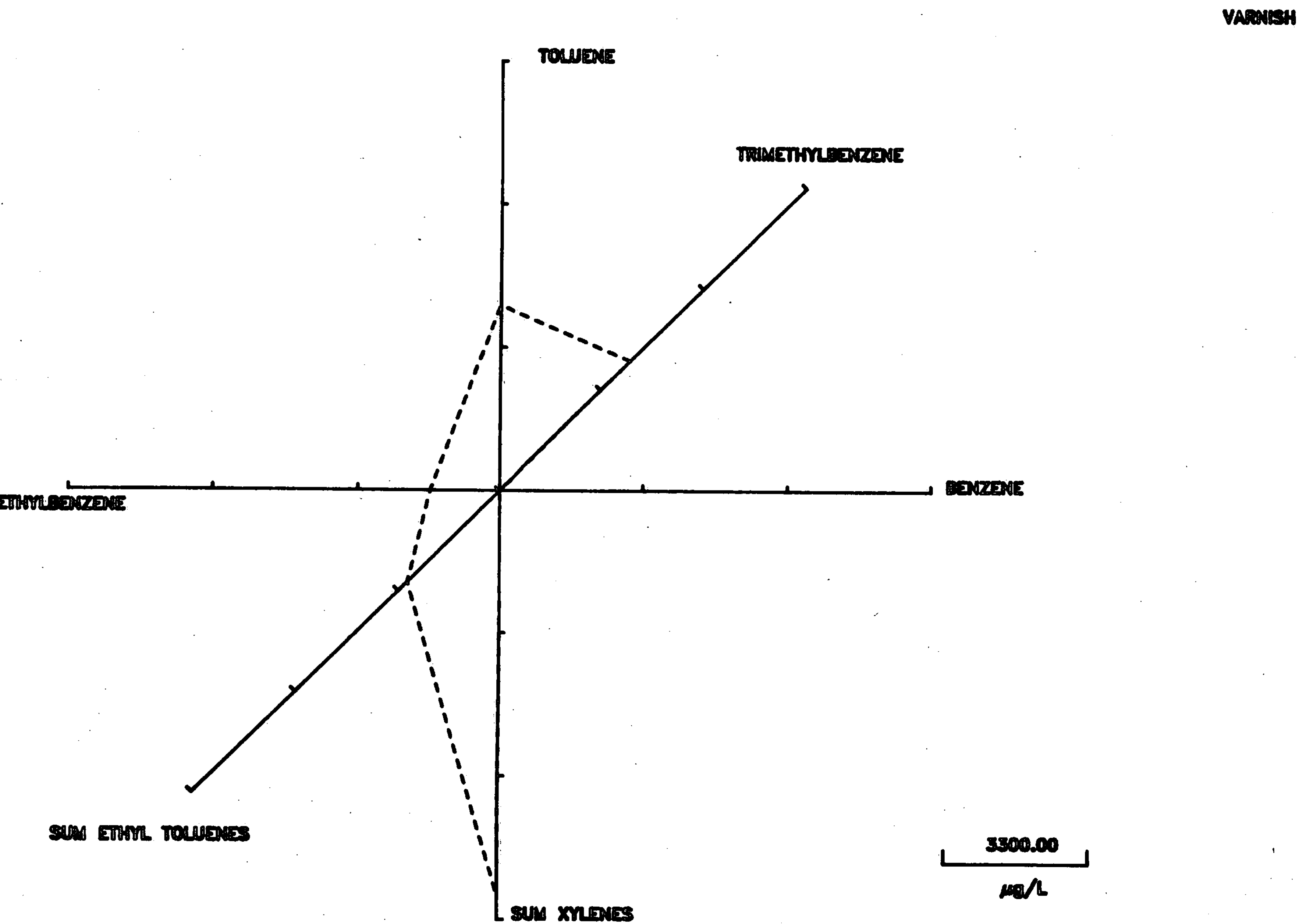

Figure 5. Varnish plant (Mantica, 1983).

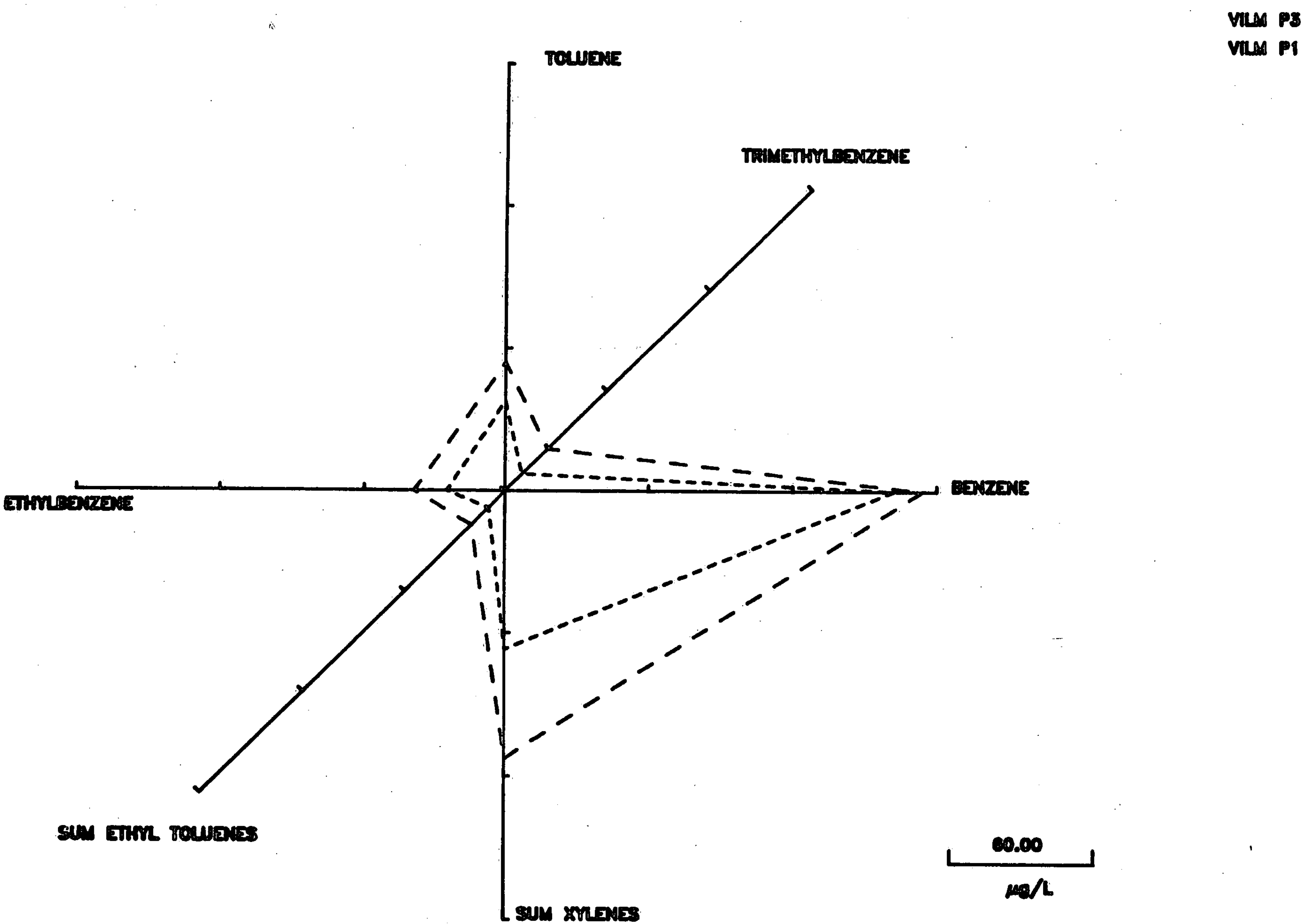

Figure 6. Ville Mercier dumpsite from a pumping well 200 ft from the source.