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Distinguishing Natural Hydrocarbons from Anthropogenic Contamination in Groundwater

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MANAGEMENT PERSPECTIVE

Groundwater contamination by petroleum hydrocarbons is a widespread environmental problem. Anthropogenic contamination is mainly caused by the leakage of underground storage tanks, spills during transport and leaching from landfill sites Estimates from Environment Canada (1987) indicate that as many as 7,500 to 20,000 existing underground storage tanks are leaking and the number of leaking tanks will increase with time.replaced. The environmental and economic consequences of leaking underground tank storage systems are very significant because of the impact on drinking water resources and the cost for the cleanup. Differentiation of groundwater contamination by petroleum hydrocarbons from natural or anthropogenic sources is important in terms of legal responsibility and remediation plans. In areas where petroleum is naturally occurring, it is important to identify the source of hydrocarbons in groundwater because it would be futile to attempt cleaning up if the source was indeed natural, on the other hand, some responsible parties could use this as an excuse to shun their obligations.

The naturally occurring hydrocarbons in groundwater can be produced during by biodegradation of organic matter such as in landfills. Hydrocarbons are also present in natural gas deposits. In some areas of southern Ontario and western New York, the petroleum hydrocarbons in shallow groundwater migrated from deep underground natural gas reservoirs due to the presence of large vertical fractures in the bedrock

Because of the similarity in composition between natural and refined petroleum, the use of statistical techniques to discern trends become essential. In this study both multivariate plotting techniques and principal component analysis were used. The objective of this study was to develop protocols and methods for the differentiation of groundwater contamination by natural or anthropogenic sources and to identify which chemical paramater or group of chemicals were the most appropriate for this task. Groundwater and gas samples were collected from Niagara Falls area and from three gasoline stations where leaking underground storage tanks had been found.

Propane and pentene were found to be the most useful chemical parameters in discriminating between the natural and anthropogenic sources: propane because it is the dominant species for groundwater contaminated by natural gas and it is absent from gasoline, and 1-pentene because it is present only in the light fraction of refined petroleum. These chemicals are not usually measured in groundwater contamination investigations, yet they are accessible to most environmental laboratories using conventional methods.

Introduction

Groundwater contamination by petroleum hydrocarbons is a widespread environmental problem. Anthropogenic contamination is mainly caused by the leakage of underground storage tanks, spills during transport and leaching from landfill sites. Estimates from Environment Canada (1987) indicate that as many as 7,500 to 20,000 existing underground storage tanks are leaking and the number of leaking tanks identified increases as they gradually are being dug up and replaced. The environmental and economic consequences of leaking underground tank storage systems are very significant because of the impact on drinking water resources and the cost for the cleanup. Differentiation of groundwater contamination by petroleum hydrocarbons from natural or anthropogenic sources is important in terms of legal responsibility and remediation plans. In areas where petroleum is naturally occurring, it is important to identify the source of hydrocarbons in groundwater because it would be futile to attempt cleaning up if the source was indeed natural, on the other hand, some responsible parties could use this as an excuse to shun their obligations.

The naturally occurring hydrocarbons in groundwater can be produced during biochemical or chemical processes. Methane can be produced by methanobacteria using carbon dioxide and hydrogen (Bryant, 1974) and can also be generated in the subsurface by the biodegradation of buried peats (Aravena and Wassenaar,1993). Biogenic gas can be distinguished from that found in volcanic systems and petroleum deposits using ^{13}C isotopic data (Barker and Fritz, 1981). Benzene, toluene and xylenes can be generated in groundwater where bituminous or petroliferous sedimentary rocks are used as the aquifer resource. Slaine and Barker (1990) found that benzene concentrations were commonly in the 50 to 200 ug/l range with a maximum concentration of 500 ug/l in the shaly bedrock. In some areas of southern Ontario and western New York, the petroleum hydrocarbons in shallow groundwater migrated from deep underground natural gas reservoirs due to the presence of large vertical fractures in the bedrock (Novakowski and Lapcevic, 1988; Noor *et al.*, 1992). Worldwide, relative oil and gas richness of petroleum deposits vary with their respective age and diagenetic process (Tissot and Welte, 1984, page 658). The possiblity of migration depends on the prevalence of faults to act as vertical conduits. The Gulf Coast and Niger Delta have been identified as such areas (Tissot and Welte, 1984, page 355). It is therefore possible for relatively heavier molecules such as BTEX to be entrained as part of the migration of the light petroleum hydrocarbons (e.g. methane, ethane, propane, butane and pentane, etc.). The question then arises as to whether these compounds would be found simultaneously and whether gas surveys could be used as indicators of natural sources of heavier hydrocarbons.

Anthropogenic contamination, on the other hand, mostly results from leaking of underground storage tanks and spills of petroleum and petroleum products (Beach and Cloutier, 1987; Barker et al., 1988). In the case of suspected accidental petroleum releases, monitoring for the aromatic hydrocarbons, such as benzene, toluene, ethylbenzene and xylenes (termed collectively BTEX) in groundwater is a common method of evaluating the contamination sources and contaminant migration. However, identifying the contamination sources in groundwater is a complex problem because many factors can change the distribution of the individual compounds in the mixture. After a surface spill, hydrocarbons can be removed by volatilization, sorption onto soil, dissolution into groundwater or biological degradation.

A plethora of analytical methods mostly based on gas chromatography are available to analyse the individual components of petroleum in contaminated soil and groundwater (Potter, 1989). Several U.S. EPA methods were used in case studies to differentiate between crude oil and refined products in soil (Baugh and Lovegreen, 1990). Total Recoverable Petroleum Hydrocarbons by Infra-Red (TPRH, method 418.1), Total Petroleum Hydrocarbons by gas chromatography (TPH, method 8015), BTEX (method 8020), Volatile Organic Compounds (VOCs, method 8270) Semi-Volatile Organic Compounds (method 8270) and Organic Lead by ICP-MS were used simultaneaously and in most cases. The samples were all relatively unweathered yet, the authors concluded to the need for some more simple method. Such a method based on the presence of petroporphyrins in crude has been developed for soils (Xu, 1994). For groundwater, where the concentrations are lower and only a portion of the petroleum dissolves, the identification task is an even more substantial challenge.

With such potential variability in the data, the use of statistical techniques to discern trends becomes essential. Application of multivariate plotting techniques to BTEX data in groundwater has been explored by a few researchers. Meyerhein (1987) utilized multivariate plots to evaluate data obtained from several monitoring wells at a gasoline contaminated site and to compare the mobility of the different gasoline components. Lesage and Lapcevic (1990) demonstrated the different patterns of BTEX from natural petroleum deposits and refined petroleum waste products. These findings were useful for samples very close to the source and for a limited number of variables. However, the multivariate plotting techniques cannot handle large sets of data with many variables in different pattems. By using principal component analysis Barker *et al.* (1988) reported that recognition of leachate contamination in landfill sites was somewhat improved.

Principal component analysis (PCA) is a statistical technique used to approximate the multivariate data of each class by a separate principal component model. It classifies the data according to their degree of fit to the different class models. The PCA has been applied for the study of pollution sources of acid rain (Finzi et al., 1991; Prada-Sanchez et al., 1993) and dioxin (Brakstad, 1992), and for evaluation of the leaching of contaminants in landfill sites (Barker et al., 1988). However, information on using PCA for differentiation of petroleum contamination sources of groundwater is still scarce (Saenz and Pingitore, 1991).

The objective of this study was to develop protocols and methods for the differentiation of groundwater contamination by natural or anthropogenic sources and to identify which chemical paramater or group of chemicals were the most appropriate for this task. Groundwater and gas samples were collected from Niagara Falls area (an area with supemormal gas pressure) and from three gasoline stations. Volatile hydrocarbons were analyzed in both groundwater and gas samples. Concentrations of aromatic hydrocarbons, anions and cations were measured in the groundwater samples only. The data was analyzed using a multivariate plotting technique and by principal component analysis.

The study is divided into four parts: A) analysis and comparison of hydrocarbons in gas samples from natural and anthropogenic sources; B) analysis and comparison of hydrocarbons in groundwater samples from natural and anthropogenic sources; C) pattem recognition using multivariate plots ; D) principle component analysis.

Material and Methods

1. Study area

The study was conducted in the Niagara Falls area where natural gas occurs and three gasoline stations, located in Scarborough, Aurora and Flamborough County, Ontario (Figure 1).

The Niagara Falls region is located between two major Paleozoic sedimentary basins, the Michigan Basin to its west and the Appalachian Basin to its southeast. The two basins are separated by the Algonquin and Findlay Arches and the Niagara Falls are situated to the south of the Arches. The area is underlain by Paleozoic sedimentary strata of Cambrian to Devonian age. Natural gas is produced in varying quantities in high porosity stratigraphic zones and permeability pinchouts developed in Lower to Middle Silurian Whirlpool, Grimsby, Thorold and Irondequoit Formations (Koepke and Sanford, 1965). The basement rocks of the region has a vertical displacement fault and supernormal gas pressure in the region has been reported (Novakowski and Lapcevic, 1988; Noor *et al.*, 1992). Six boreholes with multilevel piezometers originally installed by Ontario Hydro, U.S. Geological Survey and National Water Research Institute were used. In addition, five shallow boreholes were drilled for this project. At the gasoline stations, existing monitoring wells were used for sampling.

2. Sampling

A total of fifty-six groundwater samples were collected. The samples were divided into three groups according to contamination sources and their geological locations and depths.

Group I included samples from bedrock wells located in Niagara Falls. These wells were instrumented with Westbay casings, which allow sampling at various depths (from 32 to 197 M). Thirty-six gas samples were collected in the Niagara Falls: 7 samples from boreholes NF28, 8 from NF3, 5 from NI1, 8 from CH1, 6 from ANI1 and 2 from ANI3. Twenty-seven groundwater samples were collected: 7 samples from NF28, 6 from NF3, 3 from NI1, 6 from CH1 and 5 from ANI1.

Group II included 4 samples from overburden wells located in Niagara Falls (CH2, CH4, CH5 and CH6). No groundwater sample was available in well CH3. In addition, two groundwater samples from ANI3 were also categorized into the Group II because the samples were collected from very shallow layers (Oak Orchard at 18 M and Eramosa at 26 M).

Group III included all the samples from overburden wells located at gasoline stations. Twelve gas samples were collected from these stations: 6 samples from Scarborough, 3 from Aurora and 3 from Flamborough County. Twenty-three groundwater samples were collected: 8 samples from Scarborough, 7 from Aurora and 8 from Flamborough County.

In the Niagara Falls, gas samples were collected by connecting an evacuated 200 ml stainless steel bottle with the underground measurement port under in-situ pressure. Each sample was then transferred into an evacuated 250 ml glass sampling vessel and from which aliquots ranging from 2 to 100 µl, depending on the concentration of hydrocarbons, were analyzed on site. At the gasoline stations, the evacuated glass vessel was used for sampling immediately after opening the cap of the wells and 100 µl of gas was analyzed.

All the water samples were collected in 40-ml glass vials sealed with teflon lined septa. The total volume of 160 ml (in 4 vials) was taken for analysis of volatile hydrocarbons, anions and cations. The samples were refrigerated prior to analysis.

3. Analytical procedure

Gases

Hydrocarbon gases (C1 to C6) were analyzed on a portable Organic Vapour Analyser (OVA 128, Foxboro, Massachusetts) equipped with a flame ionization detector and a Chemipack C_{18} column (0.31cm X 1.8 m) at ambient temperature (10-20 °C). Hydrocarbon standards used were: hydrocarbon mixtures (16.5 and 1000 ppm) in helium, containing methane, ethane, propane, n-butane, n-pentane and n-hexane; 99% methane; 99% ethane (Scott Specialty Gases, Troy, Michigan).

Unleaded gasoline was used as a reference material. A 100 µl of gasoline was injected into a 43 ml-vial containing 30 ml of water. The vial was shaken for a few minutes and 10 µl of headspace was injected into the OVA for the analysis of the volatile hydrocarbons.

Groundwater

Volatile hydrocarbons The analysis of volatile hydrocarbons were performed on a GC/MS (Hewlett-Packard model 5890-5970) with purge-and-trap (Envirochem Unacon 810). A groundwater sample (2.0 to 8.0 ml) was taken by a PTA autosampler (Dynatech) and diluted to 10 ml with 0.04 M NaOH solution to neutralize the H_2S in the samples. The sample was then injected into a purge cell of the purge-and-trap, separated on the GC and quantitatively identified on the MS. A DB-624 fused silica capillary column (J&W, 30 m, 0.32 mm i.d., 1.8 µm film thickness) was used for the separation. The oven temperature of the GC was started at -15 °C in a CO_2 cooled oven and increased to 35 °C at a rate of 10 °C/min and to 135 °C at 4 °C/min. The standards of aromatic hydrocarbons and internal standards (bromochloromethane, 1,4-difluorobenzene and chlorobenzene-d5) were from Supelco (Mississauga, Canada).

Inorganics Anions were analyzed by ion chromatography (Waters, Millipore, Miford, MA) with an electrochemical detector (Waters 460) and a conductivity detector (Waters 430). An anion HC column (4.6 x 150 mm, IC-pak™, Waters) was employed for the separation. The mobile phase is a mixture of 2 % lithium borate (V/V) and 12 % acetonitrile (V/V) in water. Cations were analyzed by ICP by the National Laboratory for Environmental Testing (Environment Canada, Burlington ON).

RESULTS AND DISCUSSION

A. Hydrocarbon Gases

1. Composition of hydrocarbon gases from natural sources

1.1 Niagara Falls

The compositions of the hydrocarbon gases for the samples from Niagara Falls are listed in Table 1. Methane was the predominant species with the mean concentration of 94.1% (84.3-98.1%). Mean concentration for ethane was 4.8% (1.2-10.9%), propane 0.89% (0.04-2.2%), iso-butane 0.11% (0-0.57%) and n-butane 0.11% (0-0.61%). Pentane was detected in 8 samples at a concentration less than 0.03% and no hexane was detected in any of the samples.

1.2 Variability of gas composition in relation to source material

Natural gases, because of differences in the maturation level of the source material, vary widely in hydrocarbon composition. The variability is also affected by gas migration processes. Knowledge of the variability of the naturally occurring gases is essential if they are to be used as indicators. The source material can be classified by its maturation level using relative hydrocarbon ratios (Table 2):

C_1/C_n ratio The C_1/C_n (C_n defined as $C_1+C_2+C_3+C_4$) ratio has been considered to be related to the maturation level of petroleum. A low C_1/C_n ratio (<0.4) was related to the immature petroleum and a high C_1/C_n ratio (>0.7) to overmature petroleum in western Canada (Evans and Staplin, 1971). In the present study, the C_1/C_n ratio in the Niagara Falls area was 0.94, which is an indication of a mature to overmature petroleum. This result is consistent with earlier studies in southern Ontario by Barker and Pollock (1984) and Lollar (1990) .

C_2/C_3 ratio The C_2/C_3 ratio in natural gas may also reflect its degree of thermal maturation. It was found to decrease between the immature to mature stages, then increase as

overmature thermal maturation levels are reached (Erdman and Morris, 1974; Heroux *et al.*, 1979). The high ratio (8.9) in the present study suggests the gas in the Niagara Falls area has been generated at the overmature stage.

iC_4/nC_4 ratio The iC_4/nC_4 ratio has also been used for the evaluation of the maturation level. A high ratio (>1.0) was found in the absorbed gases in Labrador sediments of the immature to marginally mature (Heroux et al., 1979). However, this ratio is also affected by other factors, e.g., oil associated or non-oil associated gases, and the interpretation from the iC_4/nC_4 ratio is not always consistent with other indicators, such as, non-hydrocarbon gas composition (Barker and Pollock, 1984). The iC_4/nC_4 ratio in the Niagara Falls area is 1.13, a sign of thermal immaturation level. The ratio is larger than that of samples from southern Ontario, which may indicate an immature local source in the Niagara Falls.

Barker and Pollock (1984) have reported that gases from the Appalachian and Michigan Basins can be distinguished on the basis of a ratio R, where $R = (C_2/C_3)/(iC_4/nC_4)$. The gases from the Appalachian Basin have R > 3.5, while the gases from the Michigan Basin have R < 3.5. The R value for the samples from Niagara Falls is 7.82, from 2.79 to 21.63, which indicates the gases have probably migrated from the Appalachian Basin.

Thus, using various hydrocarbon ratios give conflicting results as to the classification of the Niagara Falls gases. Considerable weight must be given to the C_1/C_n ratio, because methane is the dominant component. The natural gases in the Niagara Falls may have the same source material as other area in southern Ontario (mature and overmature gases from Appalachian or Michigan basins) but mixed with less mature local gases generated from the Paleozoic sedimentary strata. The variability in the ratios suggest than while they may be useful indicators of petroleum maturity, their usefulness as environmental discriminators will always be limited.

2. Composition of hydrocarbon gases from anthropogenic source - Gasoline stations

Gasoline is composed of hydrocarbons with carbon numbers from 4 to 12 (C_4 - C_{12}). Therefore only hydrocarbons with 4 and 5 carbons were detected in an unleaded gasoline sample used as reference. Figure 2 shows the composition of hydrocarbon gases of a sample from the Scarborough gasoline station (BH7). Four hydrocarbon peaks were detected: methane (C_1, 0.8min), C_4 (4.8 and 9 min) and C_5 (12 min). It is very interesting to note that in addition to the C_4- and C_5-hydrocarbons, a fairly large proportion of methane is detected in the sample. In the absence of ethane and propane it is most likely that the methane is of biogenic origin, possibly due to the biodegradation of petroleum hydrocarbons or humic substances present in groundwater. At the Flamborough gasoline station, only the methane peak could be detected, although the total hydrocarbons (butane, pentane, benzene, toluene, ethylbenzene and xylenes) in the groundwater were found at 100 ppb level. Qualitative gas composition data of all the samples from the three contaminated gasoline stations are summarized in Table 3.

3. Differentiation of hydrocarbon contamination from natural and anthropogenic sources using gases.

In spite of the variability in natural gas compositions, hydrocarbons could still be used in some cases because of the total absence of ethane and propane from gasoline contaminated samples. There are however some limitations. The gases from Niagara Falls contain methane at 94.1% and ethane at 4.8% of the total hydrocarbon gases. If the total hydrocarbon concentration is low, for example, below 50 ppm, only methane would be detected and could be mistaken form methane of biogenic origin.

The interference by heavier hydrocarbons in gas measurements at gasoline stations is another problem. Because gasoline contains hydrocarbons with carbon numbers from 4 to 12, the larger molecular weight hydrocarbons are eluted very slowly at field temperatures. This causes a baseline problem in later analysis. In addition, hydrocarbons in gasoline contain numerous isomers and the portable OVA could not resolve all the peaks. Therefore, the gas composition data in gasoline stations can not be quantified accurately.

Natural gases could be a mixture of thermogenic and biogenic origins. To distinguish between these two natural sources, the evaluation of the maturation level must be done by carbon and hydrogen isotope analysis in addition to hydrocarbon relative ratios. In her study, Lollar (1990) reported that the gases of the Silurian strata in southwestern Ontario have a typical thermogenic origin. However, a significant component (15-45%) of bacterial gas was mixed with the thermogenic gases. Therefore, one should be very cautious in drawing conclusions solely based on hydrocarbon gas composition data.

Thus, although the hydrocarbon composition of gas samples is a useful tool for the differentiation of contamination sources, the sole use of the composition data from gas samples could lead to misleading conclusions.

B. Hydrocarbons in Groundwater Samples

1. Volatile hydrocarbons (C_3 - C_6)

Volatile hydrocarbons, including propane, butane, pentane, and pentene, were detected in most of the groundwater samples. Values of median and range for samples from different monitoring wells are listed in Table 4.

Propane is the smallest hydrocarbon compound that can be detected by purge & trap-GC/MS. The groundwater samples from five sites (Bedrock wells in Niagara Falls) were found to contain propane at concentrations ranging from 13 to 70 mg/L (median values). These very high conccentration were not unexpected, because recent hydrogeological investigations in Niagara Falls area have documented the existence of supernormal gas pressure in sedimentary rocks (Novakowski and Lapcevic, 1988; Raven et al., 1992). Results from gas analysis have showed that methane is the dominant component (84 - 99 %) and the concentration of propane is from 4 to 6800 ppm. Since the aqueous solubility of propane has been estimated at about 112 ppm at 753 mm Hg and 17.8°C (Merk Index), it is reasonable to observe such a high concentration of propane in the groundwater. A large variation in propane concentrations in the samples from the same borehole can be attributed to differences in the geological formations and in the depth of sampling points. The propane concentration in the gas was different for samples from the different geological formations (e.g., from 9 to 1310 ppm for NF 28) although it cannot be simply explained by either local production or the migration process through the faults. A linear relationship between the concentration of propane in the gas samples and in the groundwater samples was observed ($P < 0.05$). The depth of sampling sites will also affect the propane concentration in groundwater because an increase in pressure can increase the aqueous solubility. An increase in the propane concentration with depth was observed although this relationship was not statistically significant.

Butane was detected in most of the groundwater samples. The median values were from 5.9 ppm to 29 ppm for the bedrock wells samples from the Niagara Falls and from 0 to 3.5 ppm for the overburden wells at the gasoline stations. The ratio of n-butane to iso-butane was from 1.0 to 1.5 for the samples from Niagara Falls and 3.3 to 3.5 for those from the gasoline stations. The lower ratio of n-butane to iso-butane in the bedrock wells is consistent with the ratio observed in the gas samples from the same wells (from 0.9 to 1.2). This ratio is not available for the gas samples from gasoline stations because of sampling and analytical problems.

Concentrations of pentane and hexane were very low in most of the groundwater samples because of their low aqueous solubility. However, a relatively higher concentration of pentane was observed in the samples from heavily contaminated gasoline stations (Scarborough and Aurora). Pentene was not detected in any samples from Niagara Falls but was found in most of the gasoline stations samples. The median values for pentene were 160 ppb and 180 ppb for Scarborough and Aurora station, respectively. Alkenes are produced during the petroleum refining process known as cracking. A high content of alkenes is one of the characteristics of refined petroleum and low molecular weigth alkenes are absent from natural gas and natural gasoline (Kalichevsky and Peters, 1960). The presence of pentene corroborates the fact that groundwater in the Scarborough and Aurora gasoline stations had been contaminated by a light refined petroleum product. In Flamborough, pentene was only present in one of the monitoring wells.

2. Monocyclic aromatic hydrocarbons

Monocyclic aromatic hydrocarbons are a group of chemical compounds often used as an indicator of anthropogenic petroleum contamination. Many are toxic, they are relatively water-soluble and represent a substantial portion of gasoline and diesel fuel. Table 5 lists concentrations of benzene, toluene, ethylbenzene, m- and p-xylenes, o-xylene, ethyltoluenes, trimethylbenzenes and the total monocyclic aromatics in groundwater samples. The aromatic hydrocarbons were found in most of the samples from Group I with the total concentration of aromatics up to 346 ppb, which is consistent with the early studies by Barker et al. (1988) and Novakowski and Lapcevic (1988). No aromatic hydrocarbons were detected in any of the samples from Group II. The concentrations were extremely high in the groundwater samples from Scarborough and Aurora stations, up to 38,000 ppb and 60,000 ppb, respectively. This is typical of groundwater samples near the source of contamination by gasoline, diesel fuel or other petroleum products. The samples from the Flamborough station contain relatively low concentration of the aromatic hydrocarbons (from not detectable to 138 ppb).

3. Inorganic chemistry

Anions (Cl^-, SO_4^{2-}, HCO_4^-, NO_3^-) were analyzed in all the groundwater samples and cations in the samples from the Niagara Falls area, to provide supplementary information on groundwater geochemistry. The results of chloride, sulfate, alkalinity and the total dissolved solid are shown in Table 6. Chloride is the dominant anion in the groundwater from bedrock wells (Group I) with a median value of 50000, 49950, 24010, 14240 and 5040 ppm for the well NF3, ANI1, NF28, NI1 and CH1, respectively. The highest concentrations were found in the Clinton and Cataract Groups in Niagara Falls. For the Group II (overburden wells in Niagara Falls), sulfate prevails in groundwater of ANI3 while chloride is predominant in CH2, CH4, CH5 and CH6. Carbonate is the dominant anion for the groundwater of the gasoline stations (Group III).

Nitrate was not detected in any of the samples from Niagara Falls (Group I and II). However, it was found in three samples from the gasoline stations, i.e., Scarborough-BH4 (5 ppm), Aurora-BH5 (23 ppm) and Flamborough-BH6 (42 ppm). The presence of nitrate at ppm level may imply a certain amount of surface water infiltration into the groundwater.

The total dissolved solid (TDS) was determined in the Group I and II samples. The concentration of TDS was 18.4-90.9 g/L for the bedrock wells and 2.5-9.3 g/L for the overburden wells. In the present study, TDS was also used as a quality control for samples in the wells with multilevel sampling ports. All the samples with TDS below 2.0 g/L were suspected of having been diluted with casing water and were therefore retaken.

4. Sulfide hydrocarbons

As shown in Table 6, sulfate is also an important anion in the groundwater from the Niagara Falls area. Since these bedrock wells contain high level of hydrocarbons and have a reduced condition (Eh around -400 mV), it was expected to detect sulfide hydrocarbons in the groundwater. Dimethyl sulfide, 1,1-thiobisethane, 1-methylthiopropane, 2-methylthiobutane, dimethyl disulfide, methyl ethyl disulfide and methyl propyl disulfide were found in several samples.

No attempt was made to use these compounds as an indicator of petroleum contamination sources because these compounds are also often found in landfills (Lesage et al. 1990) and their presence depends also on the concentration of sulfate in an aquifer. They cannot therefore be used as specific indicators.

C. Multivariate plots

Multivariate plots were prepared to display the distribution of the C_3-C_5 hydrocarbons in the groundwater samples. To facilitate the visual comparison, the plots were grouped according to their geological formations and location. Figure 3 (a-d) shows the plots for the samples from Niagara Falls. Propane and butane are the dominant species and the proportion of propane increases with the increase in formation depth (Nottawasaga > Cataract > Clinton ≈ Lockport). The distribution of C_3- to C_5-hydrocarbons in the samples from the gasoline stations, on the other hand, are very different from that of the Niagara Falls because butanes are the predominant species (Figure 4 a-c). This results in multivariate patterns that are very consitent within the groups and dramatically different between the natural and anthropogenic sources.

Groundwater in Group I has been contaminated by naturally occurring petroleum hydrocarbons that migrated from deep gas reservoirs through vertical fractures in the bedrock. Propane as the predominant species and a low ratio of n-butane to iso-butane (1 to 1.5) in the groundwater are indicators of this type of contamination. Groundwater in Group II has been contaminated by the same source as the Group I but to a lesser extent. Concentration levels of C_1- to C_5-hydrocarbons in gas samples from Group II were very low and no hydrocarbons could be detected in the groundwater samples. Groundwater in Group III, on the other hand, has been contaminated by gasoline and fuel oils. The presence of pentene and a high ratio of n-butane to iso-butane in the groundwater samples is indicative of this type of contamination.

As was done with the C_3- to C_5-hydrocarbons, the distribution of benzene, toluene, ethylbenzene, xylenes, ethyltoluene and trimethylbenzenes were also plotted on multiple axes. The Group I samples were combined (Figure 5 a-d). BTEX are the predominant compounds in most samples. Unlike what was observed for the C_3- to C_5-hydrocarbons, however, it seems that the distribution of the aromatic hydrocarbons is not related to the geological formations. In Group III, samples from the same gasoline station were plotted together (Figure 6 a-c). Different patterns are observed for the samples from the same gasoline station. This is probably because there are multiple sources of contamination at the gasoline stations (diesel, leaded & unleaded gasolines of different grades). Because of the high variability between samples at each locations, it is not possible to conclude to a distinctive pattern for naturally occurring or anthropogenic sources of aromatic hydrocarbons.

In summary, multivariate plots are a useful visualization technique to discern trends in concentration data. The distribution of C_3- to C_6-hydrocarbons in groundwater was found to be one of the most useful parameters for distinguishing petroleum contamination from natural or anthropogenic sources. Patterns of the aromatic hydrocarbons in groundwater appear not to be related to the contamination sources.

D. Principal Component Analysis

1. Method

PCA is a multivariate statistical technique used for the analysis and ranking of many variables. PCA can be generally described as a model of similarity between objects. The objects are classified as belonging to a certain group or class and ranked as to their degree of fit in the class. In this study, the aim of using PCA was to find out which chemicals or group of chemicals were characteristic of the locations and which paramaters had the least similarity between to the sample locations and therefore would be the best discriminating tools for these locations.

The basic principle of PCA is that multivariate data, X_{ik}, observed in a group of similar objects (k) can be well described by a simple empirical model. If the variables (i) are related to the similarity between the objects (k), the data X_{ik} can be approximated by the PC model with A product terms (components):

$$X_{ik} = \alpha_i + \sum_{a=1}^{A} \theta_{ak} \beta_{ia} + \epsilon_{ik}$$

Here, α, β and θ describe the systematic part of X and ε, the residual, describes the "random" part of X, including errors of measurement and modelling. In this application, the variables i represents the chemical parameters and the objects k, the sampling points.

In matrix notation, the equation can be expressed as

$$X = 1 * \overline{X} + T P' + E$$

where T is a matrix of scores for each sample, which summarizes the X-variables and describes the degree of fit of a sample to its class, P is a matrix of loadings which shows the influence and the weight of the variables to the model, and E is a matrix of residuals, the errors.

The PCA uses a projection method to model the systematic part of the data (α, β and θ), the part that contains information about the formulated problem. It is based on approximating the data by fitting a line (A = 1), plane or hyperplane (A ≥ 2) to the data represented as points in the multidimensional space. The results of the projections can then be expressed as observation parameters ($t_{(a)}$) and variable parameters ($p_{(a)}$).

Thus, a score plot (two columns of T against each other, e.g., t_1 vs t_2) shows a picture where each observation is a point. This plot allows one to see "patterns" in the observation space. On the other hand, a loading plot (two rows of P against each other, e.g., p_1 vs p_2) informs how the variables combine to form the patterns seen in the score plot. The loading plot also provides information about which variables have a similar effect on the model and which have not.

In the present study all the chemical data were analyzed by principal component analysis (PCA) using SIMCA software from UMETRICS (MA, USA). The data matrix consists of the chemical parameters (variables) for every sampling point (object). Because there was a very large variation in the concentration for each chemical compound between the samples, the raw data were transformed to percentage (%) before being analyzed. The data were then autoscaled by SIMCA software with unit variance as their weight factors, i.e., dividing the data by standard deviation.

To evaluate usefulness of different groups of chemical parameters for differentiation of contamination sources, PCA was performed upon 4 data sets:

Set 1: C_3 - C_6 hydrocarbons with 8 variables;
Set 2: Monocyclic aromatic hydrocarbons with 7 variables;
Set 3: The total hydrocarbons (set 1 and 2) with 15 variables;
Set 4: All the chemical parameters with 18 variables.
The number of objects was 56 for all of the 4 data sets.

2. Results and Discussion

Eigenvalues, which describe the principal components of the total variance within the analyses, are obtained from principal component analysis. Typically, 3 or 4 components account for more than 75 % of the total variance (Table 7). Because of a large variation in the data, many of these eigenvalues are not statistically significant. However, the results can be used for visual examination of the data containing many variables in different patterns. This kind of analysis could have been used to decide which data set would be best plotted together in the multivariate plotting technique described above. Without PCA this decision is made empirically.

Results of the first two principal components are being presented and discussed in the following parts. Similar results were observed in the third and higher principal components which carry less weight than the first two components in the model.

1. C_3 - C_6 hydrocarbons

Figure 7 shows a score plot of the first two principal components (t_1 vs t_2) for C_3 - C_6 hydrocarbons (Data Set 1). On Figure 7, #1 represents all the samples from bedrock wells in the Niagara Falls area (natural source), #2, all the samples from overburden wells in the Niagara Falls (natural source) and #3, all the samples from the gasoline stations (anthropogenic source). It is interesting to note that the projected position (t_1 vs t_2) for each sample does correspond to its contamination source and geological location. As expected, Group I included all the #1 samples, Group II, all the #2 samples, and Group III, all the #3 samples. Unlike Group I and II, however, samples in Group III are widely spread, which indicates the similarity between the samples in Group III is lower than that in Group I or Group II.

Figure 8 shows a loading plot of the first two components (p_1 to p_2). As discussed above, the loading plot can provide information on similarity of each variable to a PC model. Eight variables can be divided into 4 groups according to their positions on Figure 8. Group A only has one variable, propane, and Group B include pentene and n-pentane, Group C, iso- and n-butane, and Group D, iso-pentane, iso- and n-hexanes.

Thus, PCA of the C_3 - C_6 hydrocarbon data can supply some information for differentiation of groundwater petroleum contamination from a natural source or an anthropogenic source. Amongst the eight variables, some of them have a similar effect on the model, e.g., iso- and n-butane, and some have not, e.g., propane.

2. Monocyclic aromatic hydrocarbons

Figure 9 illustrates a score plot of the first two principal components (t_1 vs t_2) for the data of monocyclic aromatic hydrocarbons (Data Set 2). As discussed in the part of C_3 - C_6 hydrocarbons, the number 1, 2 and 3 stand for samples from different contamination sources and geological locations. However, unlike what was found in the C_3 - C_6 hydrocarbon analysis (Figure 7), the result from the monocyclic aromatic hydrocarbon analysis cannot help to distinguish groundwater petroleum contamination from a natural source or from an anthropogenic source. As was found using multivariate plotting, the distribution of monocyclic aromatic hydrocarbons in groundwater appears not to be related to petroleum contamination sources. In this case, neither PCA nor multivariate plotting can supply information for the differentiation. The only advantage of PCA is that it can show all the 56 samples on a single figure, which is easier for the comparison.

Figure 10 shows a loading plot of the first two components (p_1 vs p_2) for the monocyclic aromatic hydrocarbons. Seven variables can be divided into 3 groups on the basis of their positions. Group A includes 3 variables (benzene, toluene and ethylbenzene), Group B, 2 variables (o-xylene and m+p-xylenes), and Group C, 2 variables (ethyltoluene and trimethylbenzene).

Monocyclic aromatic hydrocarbons have been widely used as an indicator for groundwater contamination by accidental petroleum releases. Although the monocyclic aromatic hydrocarbons could be found in many "non-gasoline-contaminated" groundwater samples, extremely high concentration levels of the aromatics (up to 60 mg/L) could only be found in the samples from the gasoline stations. In this application, because the percentage of the individual aromatic hydrocarbon was used, the position of each sample was determined by the distribution of the aromatics, not by their total concentration.

3. The total hydrocarbons (C_3 - C_6 & aromatic hydrocarbons)

Taking the total hydrocarbons as one data set (i.e., C_3-C_6 hydrocarbons + aromatics=100 %) has the advantages of a larger data set (15 variables) and of giving weight to the concentration of the aromatics. Figure 11 illustrates a score plot of the first two principal components (t_1 vs t_2). Samples from different locations and depth were marked by the number 1, 2 and 3, as above. The samples of #1 (Group I, bedrock wells in the Niagara Falls) were projected together and so were the samples of #2 (Group II, overburden wells in the Niagara Falls). The samples of #3 (Group III, overburden wells in the three gasoline stations), on the other hand, were spread widely. The result is very similar to that shown on Figure 7 except that there is a greater similarity between Group I and II on Figure 11. These results were as hoped for, that is the hydrocarbon composition is correlated to the sample locations. Because the samples in Group I and II have the same contamination source (natural source) and geological location (Niagara Falls) they seem to have the same hydrocarbon distribution. The only difference of the samples between Group I and II is the depth of the wells.

Figure 12 shows a loading plot of the first two components (p_1 vs p_2). The 15 variables can be divided into 4 groups based on their positions. Group A includes all the variables of the monocyclic aromatic hydrocarbons, Group B, all the variables of the C_3 - C_6 hydrocarbons except for propane and pentene, Group C, pentene and Group D, propane. This clearly identifies propane and pentene as the individual parameters which can best be used to discriminate between natural and anthropogenic sources of hydrocarbons.

4. All the chemical parameters (C_3 - C_6 & aromatic hydrocarbons, anions)

In addition to the total petroleum hydrocarbons, three anions were analyzed in the groundwater samples, i.e., chloride, sulfate and bicarbonate. The anion analysis supplies supplementary information on groundwater geochemistry, which could be useful for differentiation of contamination sources in certain cases.

The result with a total of 18 variables was very similar to that from the total hydrocarbon analysis. In addition, the #2 samples could be further divided into two groups, 2 samples from ANI3 and 4 samples from CH2, 4, 5 and 6. This is because groundwater from ANI3 has sulfate as a dominant species while groundwater from CH2, 4, 5 and 6 has chloride as a dominant species. The loading plot of the hydrocarbon variables was very similar to that observed on Figure 12. For the anions, chloride or sulfate were different from all the other variables while bicarbonate was similar to the Group A variables (the aromatic hydrocarbons). Therefore, while the addition of inorganic data helped to recognize the difference between samples from different aquifers, the weight of this result did not change what would be obtained using hydrocarbon analysis only.

Plotting of eigenvalues of the first two components did illustrate the similarity between the samples or between the variables. The effectiveness of PCA depends on the chemical parameters selected. The PCA can help to differentiate an anthropogenic contamination source from a natural source on the basis of the chemical data of C_3- to C_6-hydrocarbons in groundwater. However, it cannot provide any information for the differentiation if using the data of aromatic hydrocarbons only. Combination of the two sets of chemical parameters provided better information on contamination sources. PCA is therefore a very useful technique for identifying the most important parameters to be analysed. When these are selected, the technique could be applied to other data sets to establish the source of contamination as natural or anthropogenic.

Conclusion

In summary, because of the difficulty in getting representative gas samples from conventional groundwater monitoring wells and because of the interference from the numerous other volatile components in gasoline, gas surveys are of limited use in differentiating between natural and anthropogenic sources of contamination in groundwater. The dissolved gases in groundwater samples on the other hand provide much more reliable information.

Multivariate plots are a useful visualization technique to discern trends in concentration data. The distribution of C_3- to C_6-hydrocarbons in groundwater was found to be one of the most useful parameters for distinguishing petroleum contamination from natural or anthropogenic sources. Patterns of the aromatic hydrocarbons in groundwater appear not to be related to the contamination sources.

Principal component analysis was the most useful tool for the identification of petroleum contamination sources of groundwater. The strength of PCA resides in its ability to identify which variables are the most different and thus the best for discriminating between sources. In this study, propane and pentene were found to be the most useful chemical parameters in discriminating between the natural and anthropogenic sources: propane because it is the dominant species for groundwater contaminated by natural gas and it is absent from gasoline, and 1-pentene because it is present only in the light fraction of refined petroleum. These chemicals are not usually measured in groundwater contamination investigations, yet they are accessible to most environmental laboratories using conventional methods.

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TABLE 1. Hydrocarbon composition of gas samples from Niagara Falls.

No	Site	Formation	Depth(m)	Hydrocarbon gas composition (%)				
				C1	C2	C3	iC4	nC4
1	NF28	Gasport	31	95.42	3.60	0.27	0.36	0.35
2	NF28	Rochester	39	91.93	7.02	0.94	0.05	0.05
3	NF28	Irondequoit	57	97.70	2.10	0.21	0.00	0.00
4	NF28	Grimsby	80	98.15	1.72	0.06	0.04	0.03
5	NF28	Whirlpool	93	97.40	2.43	0.11	0.03	0.03
6	NF28	Whirlpool	112	91.11	7.71	0.89	0.12	0.17
7	NF28	Queenston	196	98.59	1.37	0.04	0.00	0.00
8	NF3	Gasport	31	95.49	3.71	0.80	0.00	0.00
9	NF3	Gasport	36	92.13	7.25	0.62	0.00	0.00
10	NF3	Decew	46	97.46	2.32	0.21	0.00	0.00
11	NF3	Rochester	54	97.82	1.76	0.11	0.16	0.17
12	NF3	Thorold	69	87.71	9.86	2.07	0.17	0.19
13	NF3	Cabot Head	91	98.78	1.08	0.11	0.02	0.01
14	NF3	Whirlpool	100	95.06	3.51	1.26	0.09	0.09
15	NF3	Queenston	102	96.48	3.09	0.36	0.03	0.04
16	ANI1	Rochester	47	92.41	5.87	1.22	0.28	0.22
17	ANI1	Irondequoit	67	96.54	2.80	0.51	0.08	0.08
18	ANI1	Thorold	76	87.94	9.51	1.97	0.29	0.29
19	ANI1	Cabot Head	94	87.19	11.54	1.11	0.08	0.09
20	ANI1	Whirlpool	106	95.54	3.22	0.95	0.14	0.15
21	ANI1	Queenston	111	94.85	4.00	1.15	0.00	0.00
22	ANI3	Oak Orchard	16	94.85	4.00	0.44	0.40	0.31
23	ANI3	Eramosa	28	94.72	3.59	0.61	0.57	0.50
24	NI1	Eramosa	52	97.41	2.28	0.31	0.00	0.00
25	NI1	Irondequoit	96	97.60	1.76	0.64	0.00	0.00
26	NI1	Grimsby	120	98.65	1.21	0.12	0.01	0.01
27	NI1	Cabot Head	132	96.83	2.36	0.62	0.10	0.09
28	NI1	Queenston	148	96.91	2.76	0.32	0.00	0.00
29	CH1	Guelph	36	88.65	9.76	1.59	0.00	0.00
30	CH1	Eramosa	43	84.28	13.82	1.90	0.00	0.00
31	CH1	Goat Island	64	89.00	8.81	1.81	0.14	0.24
32	CH1	Gasport	73	85.91	10.93	2.16	0.39	0.61
33	CH1	Rochester	82	91.63	6.72	1.42	0.13	0.09
34	CH1	Irondequoit	99	96.42	2.85	0.61	0.05	0.06
35	CH1	Grimsby	108	97.39	2.06	0.39	0.07	0.08
36	CH1	Whirlpool	138	94.82	3.83	0.90	0.21	0.22

TABLE 2. Comparison of composition of hydrocarbon gases from Niagara Falls with that from other areas in southern Ontario.

Indicator	The present study[a]	Barker & Pollock, 1984[b]	Lollar, 1990[c]
C_1/C_n[d]	0.94 (0.84-0.99)	0.88 (0.70-0.95)	0.85 (0.66-0.96)
C_2/C_3	8.86 (2.79-35.56)	2.22 (0.86-3.80)	2.19 (1.00-3.79)
iC_4/nC_4	1.13 (0.60-3.01)	0.54 (0.32-1.50)	0.69 (0.13-1.24)
R[e]	7.82 (2.79-21.63)	7.28 (1.27-30.0) <3.5[f] >3.5[g]	4.45 (0.39-26.26)

[a] 36 samples collected from the Middle Silurian-Lower Silurian and Upper Ordovician strata in Niagara Falls.

[b] 43 samples collected from the Silurian strata in southern Ontario.

[c] 42 samples collected from commercial gas wells in the Ordovician-Cambrian strata in southern Ontario.

[d] $C_1/C_n = C_1/(C_1+C_2+C_3+C_4)$.

[e] $R = (C_2/C_3)/(iC_4/nC_4)$

[f] Michigan Basin gas pool.

[g] Appalachian Basin gas pool.

TABLE 3. Qualitative hydrocarbon composition of underground gases at three gasoline stations, Ontario.

No	Sample	C_1	C_2	C_3	C_4	C_5
Scarborough						
1	ScarBH1	Y	N	N	N	-
2	ScarBH4	Y	N	N	Y	Y
3	ScarBH5	Y	N	N	Y	Y
4	ScarBH6	Y	N	N	Y	Y
5	ScarBH7	Y	N	N	Y	Y
6	ScarBH8	Y	N	N	Y	Y
Aurora						
7	AuroBH1	Y	N	N	Y	Y
8	AuroBH2	N	N	N	Y	Y
9	AuroBH4	Y	N	N	Y	Y
Flamborough						
10	FlamBH2	Y	N	N	N	N
11	FlamBH3	Y	N	N	N	N
12	FlamBH4	Y	N	N	N	N

Table 4. Median (Range) concentrations (mg/L) of C_3- to C_5-hydrocarbons in groundwater samples.

Sites	n	Propane C_3H_8	Butane C_4H_{10}	Pentane C_5H_{12}	Pentene C_5H_{10}
NF 28	7	13.3 (2.1-41.9)	10.2 (0.1-32.9)	0.04 (n.d.-0.38)	n.d. (n.d.)
NF 3	6	20.1 (0.3-56.6)	5.9 (0.03-18.5)	n.d. (n.d.-0.14)	n.d. (n.d.)
CH1	6	35.5 (14.6-106)	17.6 (3.7-30.2)	0.08 (0.01-0.11)	n.d. (n.d.)
NI 1	3	69.8 (13.6-128)	12.9 (3.2-33.5)	n.d. (n.d.)	n.d. (n.d.)
ANI 1	5	70.1 (29.8-90.3)	29.4 (5.3-34.8)	0.06 (n.d.-0.15)	n.d. (n.d.)
ANI 3	2	n.d. (n.d.)	n.d. (n.d.)	n.d. (n.d.)	n.d. (n.d.)
CH2, 4, 5, 6	4	n.d. (n.d.)	n.d. (n.d.)	n.d. (n.d.)	n.d. (n.d.)
Scarborough	8	n.d. (n.d.)	1.8 (n.d.-37.0)	0.16 (0.01-2.72)	0.16 (n.d.-1.61)
Aurora	7	n.d. (n.d.)	3.5 (n.d.-98.9)	0.81 (n.d.-3.15)	0.18 (n.d.-1.62)
Flamborough	8	n.d. (n.d.)	n.d. (n.d.-0.3)	n.d. (n.d.-0.01)	n.d. (n.d.-0.01)

[a] Not detected. The detection limit is 0.01mg/L for propane and butane, 0.001mg/L for pentane and pentene.

Table 5. Median (Range) concentrations (μg/L) of aromatic hydrocarbons in groundwater samples.

Sites	n	Benzene	Toluene	Ethylbenzene	m+p-Xylenes	o-Xylene	Ethyltoluenes	TMB	Total aromatics
NF 28	7	16 (0-49)	12 (4-79)	3 (1-16)	2 (n.d.-63)	n.d.[a] (n.d.-29)	n.d. (n.d.-6)	n.d. (n.d.-16)	30 (11-256)
NF 3	6	5 (n.d.-21)	8 (n.d.-53)	1 (n.d.-16)	2 (n.d.-53)	n.d. (n.d.-15)	n.d. (n.d.-2)	n.d. (n.d.-5)	16 (n.d.-164)
CH1	6	38 (n.d.-89)	39 (n.d.-118)	2 (n.d.-15)	18 (n.d.-58)	2 (n.d.-50)	n.d. (n.d.-4)	n.d. (n.d.-12)	107 (n.d.-346)
NI 1	3	9 (9-109)	16 (5-19)	3 (2-6)	14 (12-21)	n.d. (n.d.-4)	n.d. (n.d.-2)	2 (n.d.-7)	54 (30-156)
ANI 1	5	12 (3-25)	11 (n.d.-19)	2 (n.d.-4)	4 (1-15)	n.d. (n.d.-5)	n.d. (n.d.-1)	n.d. (n.d.-2)	38 (4-55)
ANI 3	2	n.d. (n.d.)	n.d. (n.d.)	n.d. (n.d.)	n.d. (n.d.)	n.d. (n.d.)	n.d. (n.d.)	n.d. (n.d.)	n.d. (n.d.)
CH2, 4, 5, 6	4	n.d. (n.d.)	n.d. (n.d.)	n.d. (n.d.)	n.d. (n.d.)	n.d. (n.d.)	n.d. (n.d.)	n.d. (n.d.)	n.d. (n.d.)
Scarborough	8	176 (51-12300)	122 (46-11700)	111 (16-2580)	278 (50-8360)	77 (n.d.-4165)	45 (n.d.-575)	122 (n.d.-1151)	938 (162-38060)
Aurora	7	400 (6-6630)	86 (17-8850)	541 (16-2340)	1750 (68-39300)	764 (14-7680)	741 (24-3009)	1201 (17-6796)	7739 (177-60109)
Flamborough	8	2 (n.d.-71)	n.d. (n.d.-1)	1 (n.d.-10)	2 (n.d.-19)	n.d. (n.d.-7)	n.d. (n.d.-29)	n.d. (n.d.-31)	4 (n.d.-138)

[a] Not detected. The detection limit is 1 μg/L for the aromatic hydrocarbons.

Table 6. Median (Range) Concentrations (mg/L) of chloride, sulfate, alkalinity and the total dissolved solid (TDS) in groundwater samples.

Sites	n	Cl^-	SO_4^{2-}	Alkalinity	TDS
NF 28	7	24010 (4774-65450)	1170 (921-1774)	37 (7-122)	55400 (10600-108700)
NF 3	6	50000 (160-67900)	1220 (749-1473)	105 (14-220)	90900 (2300-110000)
CH1	6	5040 (906-23520)	1899 (144-2377)	115 (5-169)	18400 (1700-59400)
NI 1	3	14240 (3345-44533)	1221 (308-1411)	73 (70-128)	27100 (7100-71900)
ANI 1	5	49950 (239-50000)	1016 (703-1800)	96 (27-285)	77700 (2000-89000)
ANI 3	2	235 (193-277)	1223 (1107-1339)	266 (179-352)	2450 (2400-2500)
CH2, 4, 5, 6	4	4553 (1690-7510)	2060 (0-3468)	not available	9300 (2500-14100)
Scarborough	8	452 (119-948)	7 (0-119)	547 (320-960)	not available
Aurora	7	407 (60-938)	23 (0-375)	655 (339-769)	not available
Flamborough	8	76 (25-335)	97 (31-168)	424 (288-632)	not available

Table 7 Eigenvalues (%) of principal components from PCA.

Data set	No. of variables	No. of components	Comp.1	Comp.2	Comp.3	Comp.4	Total
C_3-C_6 Hydrocarbons	8	3	0.42	0.21	0.13	-	0.76
Arom. hydrocarbons	7	3	0.34	0.18	0.17	-	0.69
Total hydrocarbons	15	4	0.35*	0.21	0.14	0.08	0.78
All chemicals	18	4	0.34*	0.18	0.14	0.09	0.75

* Statistically significant, $P<0.05$

Figure Text

Figure 1 Map of the study areas.

Figure 2 Chromatogram of hydrocarbon gases of a sample from the Scarborough gasoline station (BH7).

Figure 3 a-d. Multivariate plots of hydrocarbon gases in groundwater from bedrock samples (Group I)

Figure 4 a-c Multivariate plots of hydrocarbon gases in groundwater from the gasoline stations (Group III).

Figure 5 a-d Mutlivariate plots of aromatic hydrocarbons for bedrock samples (Group I)

Figure 6 a-c Mutlivariate plots of aromatic hydrocarbons at gasoline stations (Group III)

Figure 7 A score plot of the first two principal components (t_1 vs t_2) resulting from PC analysis of data on groundwater C_3-C_6 hydrocarbons (Observations = 56, Variables = 8).

Figure 8. A loading plot of the first two principal components (p_1 vs p_2) resulting from PC analysis of data on groundwater C_3-C_6 hydrocarbons (Observations = 56, Variables = 8).

Figure 9. A score plot of the first two principal components (t_1 vs t_2) resulting from PC analysis of data on groundwater monocyclic aromatic hydrocarbons (Observations = 56, Variables = 7).

Figure 10. A loading plot of the first two principal components (p_1 vs p_2) resulting from PC analysis of data on groundwater monocyclic aromatic hydrocarbons (Observations = 56, Variables= 7).

Figure 11. A score plot of the first two principal components (t_1 vs t_2) resulting from PC analysis of data on the total hydrocarbons in groundwater (Observations = 56, Variables = 15).

Figure 12. A loading plot of the first two principal components (p_1 vs p_2) resulting from PC analysis of data on the total hydrocarbons in groundwater (Observations = 56, Variables = 15).

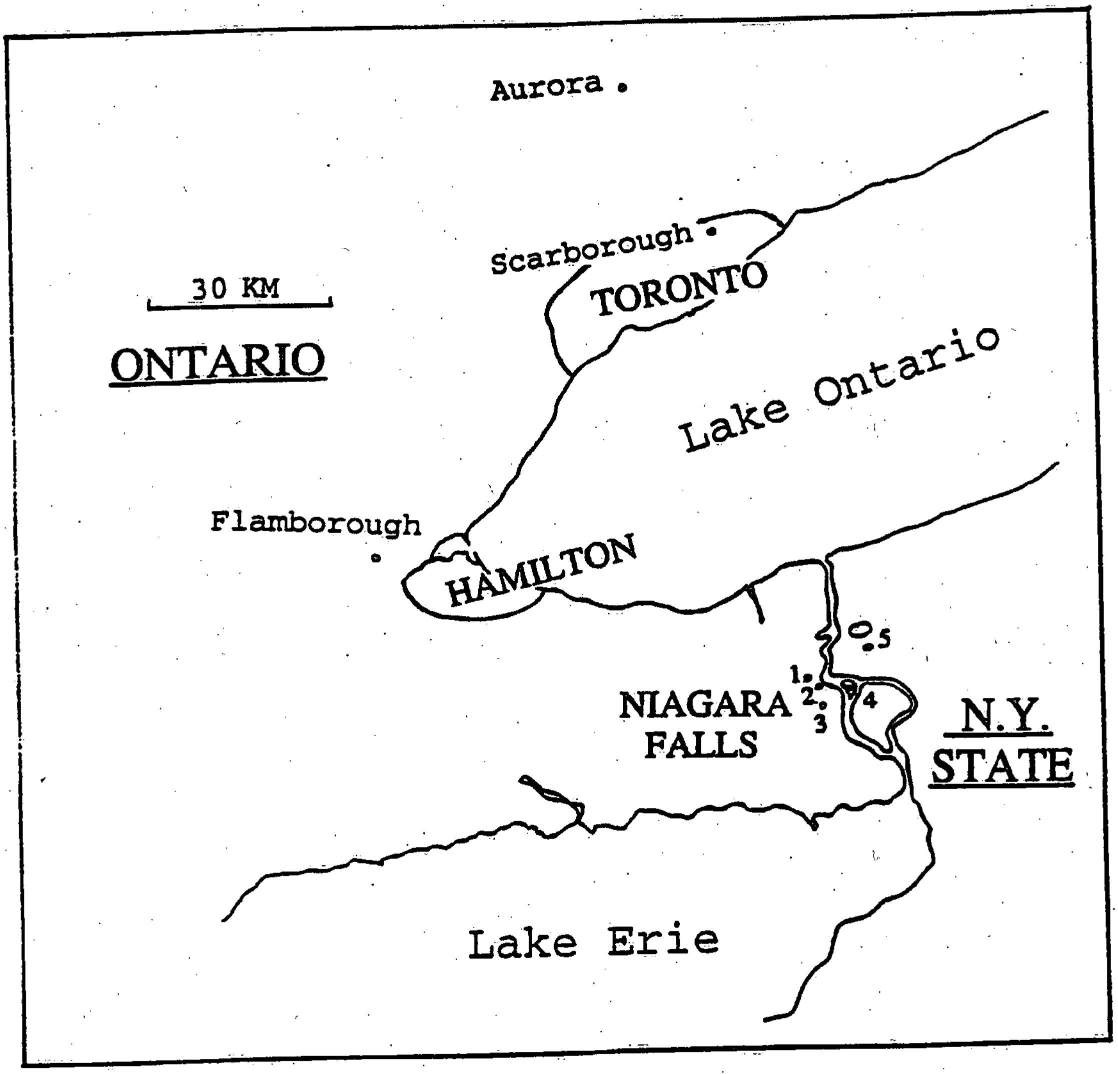
Aurora
Scarborough
TORONTO
30 KM
ONTARIO
Lake Ontario
Flamborough
HAMILTON
5
1
2
3
4
NIAGARA FALLS
N.Y. STATE
Lake Erie

Figure 1

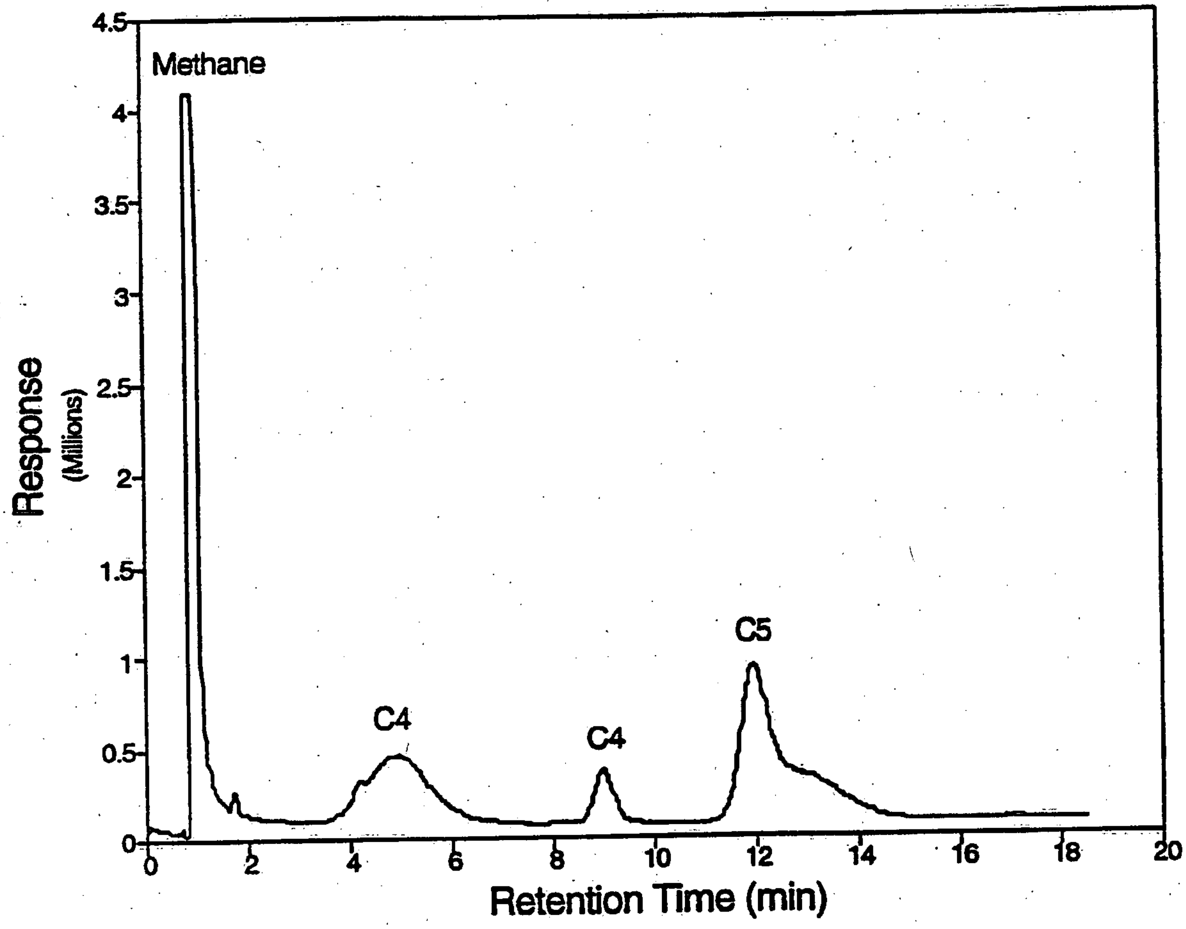
Methane
C4
C4
C5
Response
(Millions)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
2
4
6
8
10
12
14
16
18
20
Retention Time (min)

Figure 2

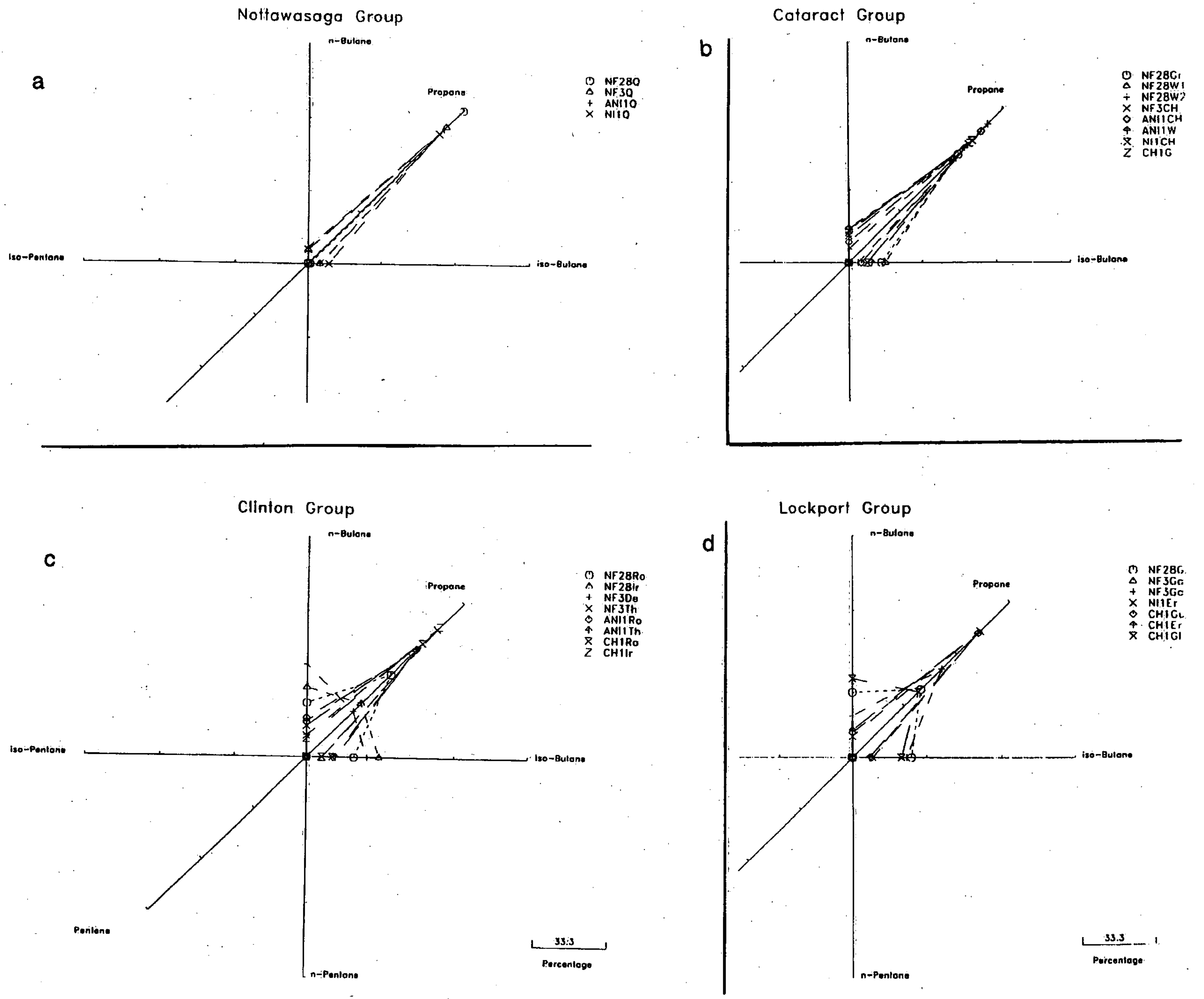
Nottawasaga Group
a
n-Butane
Propane
Iso-Pentane
iso-Butane
ϴ NF28Q
△ NF3Q
+ ANI1Q
× NI1Q
Cataract Group
b
n-Butane
Propane
Iso-Butane
ϴ NF28Gr
△ NF28W1
+ NF28W2
× NF3CH
◇ ANI1CH
↑ ANI1W
X NI1CH
Z CH1G
Clinton Group
c
n-Butane
Propane
Iso-Pentane
Iso-Butane
Pentane
n-Pentane
ϴ NF28Ro
△ NF28Ir
+ NF3De
× NF3Th
◇ ANI1Ro
↑ ANI1Th
X CH1Ro
Z CH1Ir
33.3
Percentage
Lockport Group
d
n-Butane
Propane
iso-Butane
n-Pentane
ϴ NF28G
△ NF3Ga
+ NF3Gc
× NI1Er
◇ CH1Gu
↑ CH1Er
X CH1Gl
33.3
Percentage

Figure 3

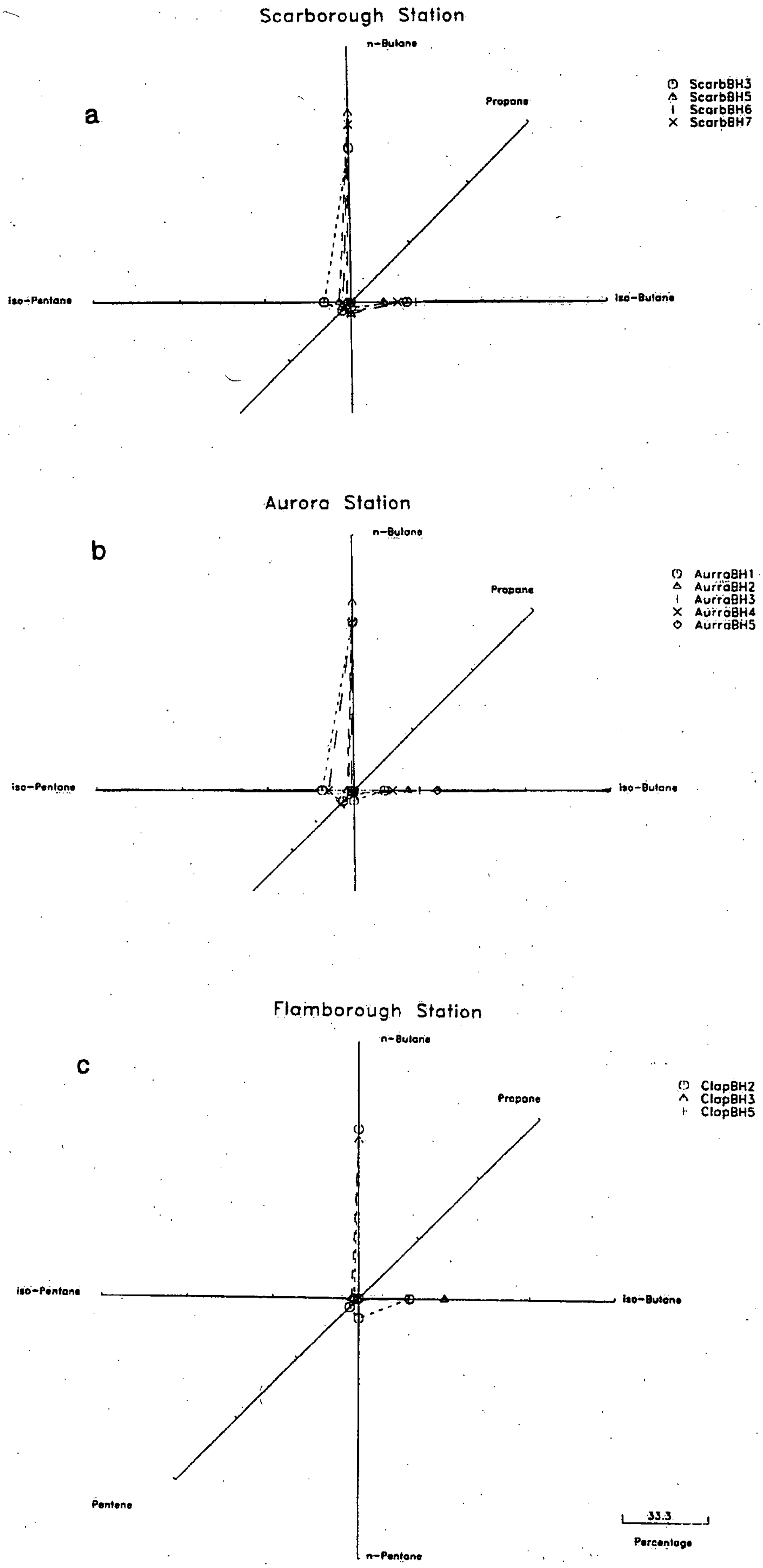
Scarborough Station
a
n-Butane
Propane
iso-Pentane
iso-Butane
ScarbBH3
ScarbBH5
ScarbBH6
ScarbBH7
Aurora Station
b
n-Butane
Propane
iso-Pentane
iso-Butane
AurraBH1
AurraBH2
AurraBH3
AurraBH4
AurraBH5
Flamborough Station
c
n-Butane
Propane
iso-Pentane
iso-Butane
Pentene
n-Pentane
ClapBH2
ClapBH3
ClapBH5
33.3
Percentage

Figure 4

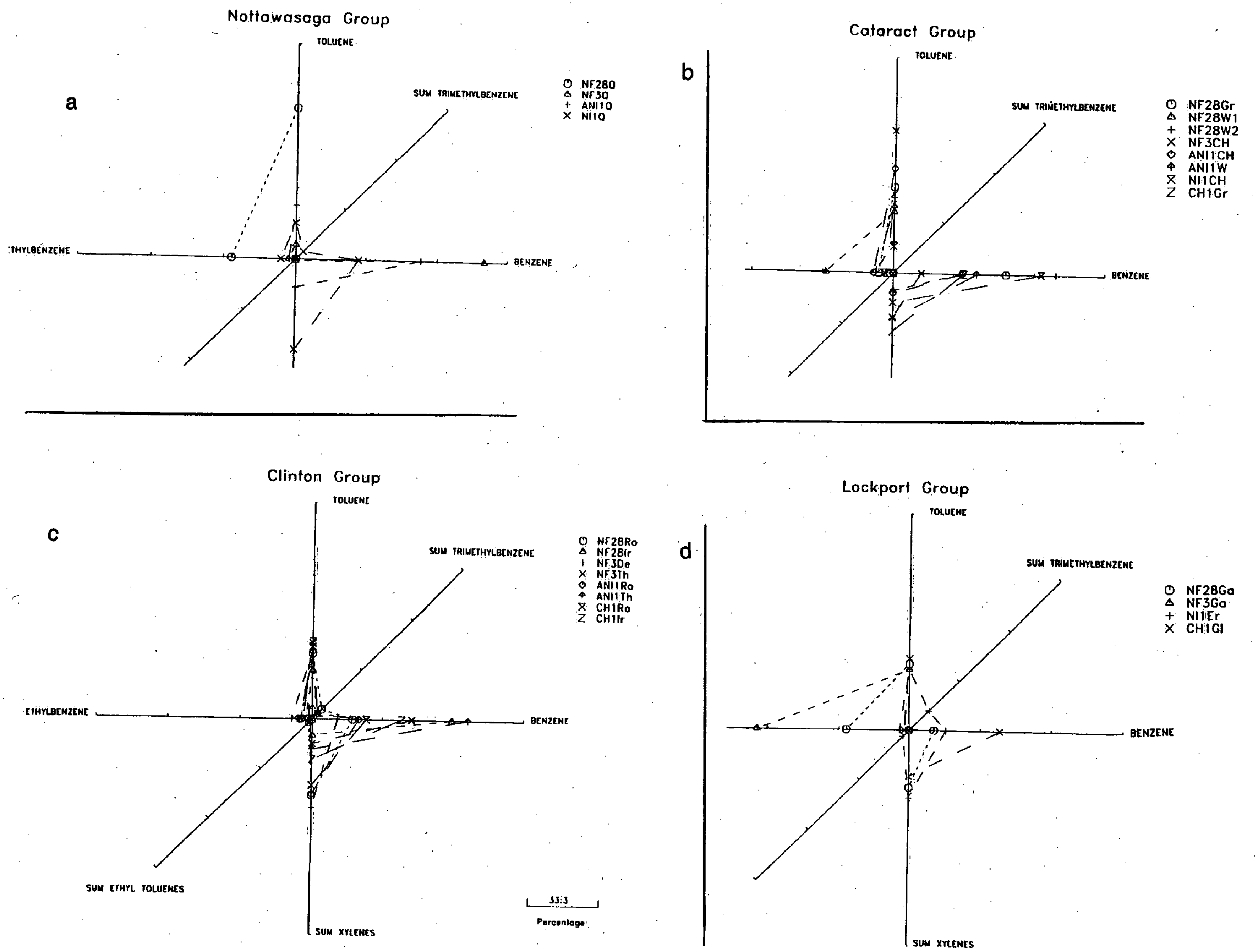
Nottawasaga Group
a
TOLUENE
SUM TRIMETHYLBENZENE
THYLBENZENE
BENZENE
O NF28Q
Δ NF3Q
+ ANI1Q
× NI1Q
Cataract Group
b
TOLUENE
SUM TRIMETHYLBENZENE
BENZENE
O NF28Gr
Δ NF28W1
+ NF28W2
× NF3CH
◇ ANI1CH
✦ ANI1W
X NI1CH
Z CH1Gr
Clinton Group
c
TOLUENE
SUM TRIMETHYLBENZENE
ETHYLBENZENE
BENZENE
SUM ETHYL TOLUENES
SUM XYLENES
O NF28Ro
Δ NF28Ir
+ NF3De
× NF3Th
◇ ANI1Ro
✦ ANI1Th
X CH1Ro
Z CH1Ir
33.3
Percentage
Lockport Group
d
TOLUENE
SUM TRIMETHYLBENZENE
BENZENE
SUM XYLENES
O NF28Ga
Δ NF3Ga
+ NI1Er
× CH1Gl

Figure 5

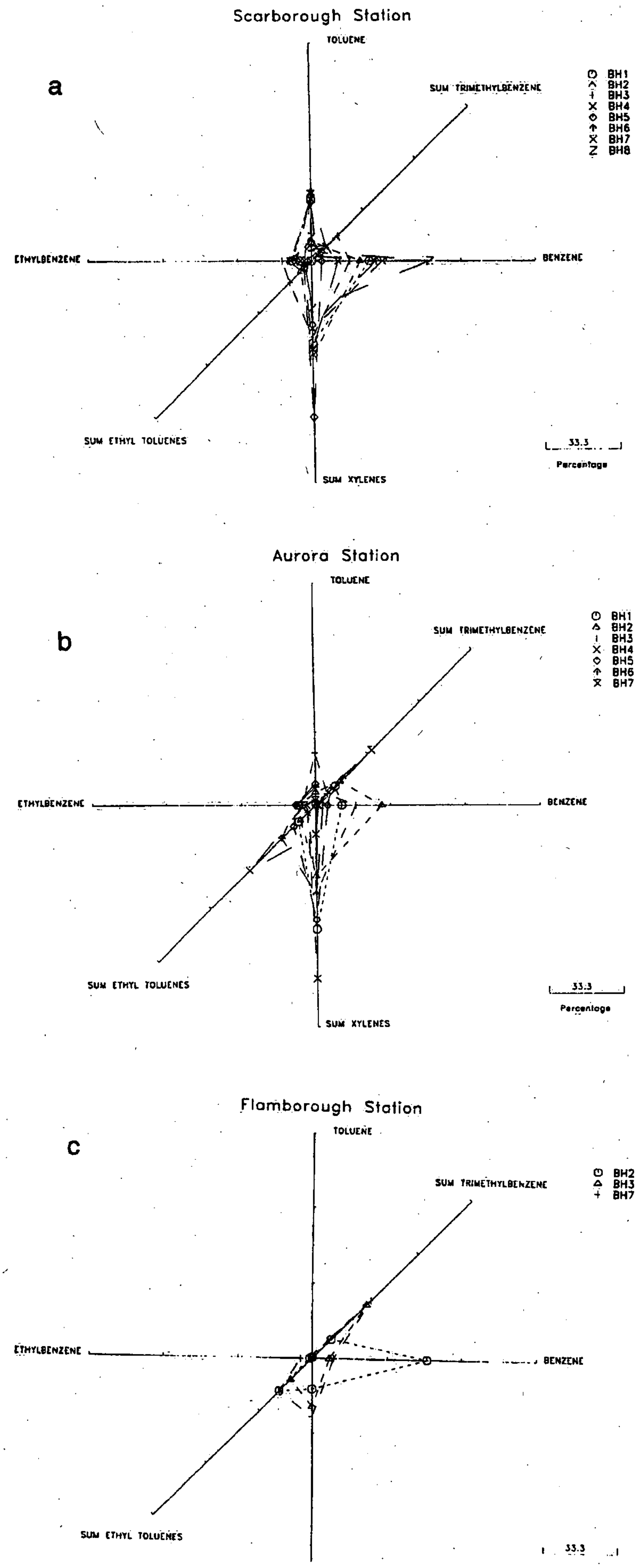
Scarborough Station
a
TOLUENE
SUM TRIMETHYLBENZENE
BH1
BH2
BH3
BH4
BH5
BH6
BH7
BH8
ETHYLBENZENE
BENZENE
SUM ETHYL TOLUENES
SUM XYLENES
33.3
Percentage
Aurora Station
b
TOLUENE
SUM TRIMETHYLBENZENE
BH1
BH2
BH3
BH4
BH5
BH6
BH7
ETHYLBENZENE
BENZENE
SUM ETHYL TOLUENES
SUM XYLENES
33.3
Percentage
Flamborough Station
c
TOLUENE
SUM TRIMETHYLBENZENE
BH2
BH3
BH7
ETHYLBENZENE
BENZENE
SUM ETHYL TOLUENES
33.3

Figure 6

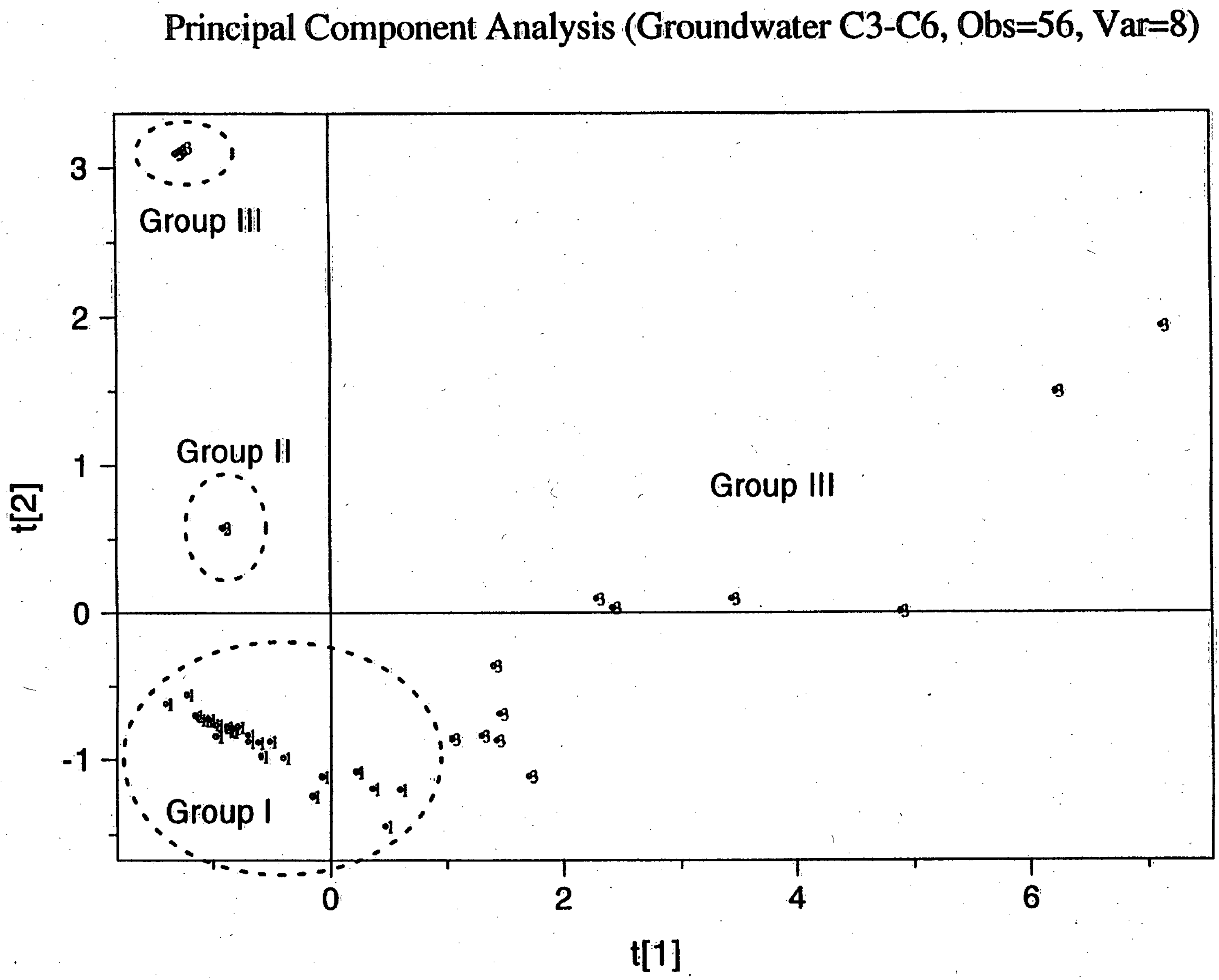

Figure 7 A score plot of the first two principal components (t_1 vs t_2) resulting from PC analysis of data on groundwater C_3-C_6 hydrocarbons (Observations = 56, Variables = 8).

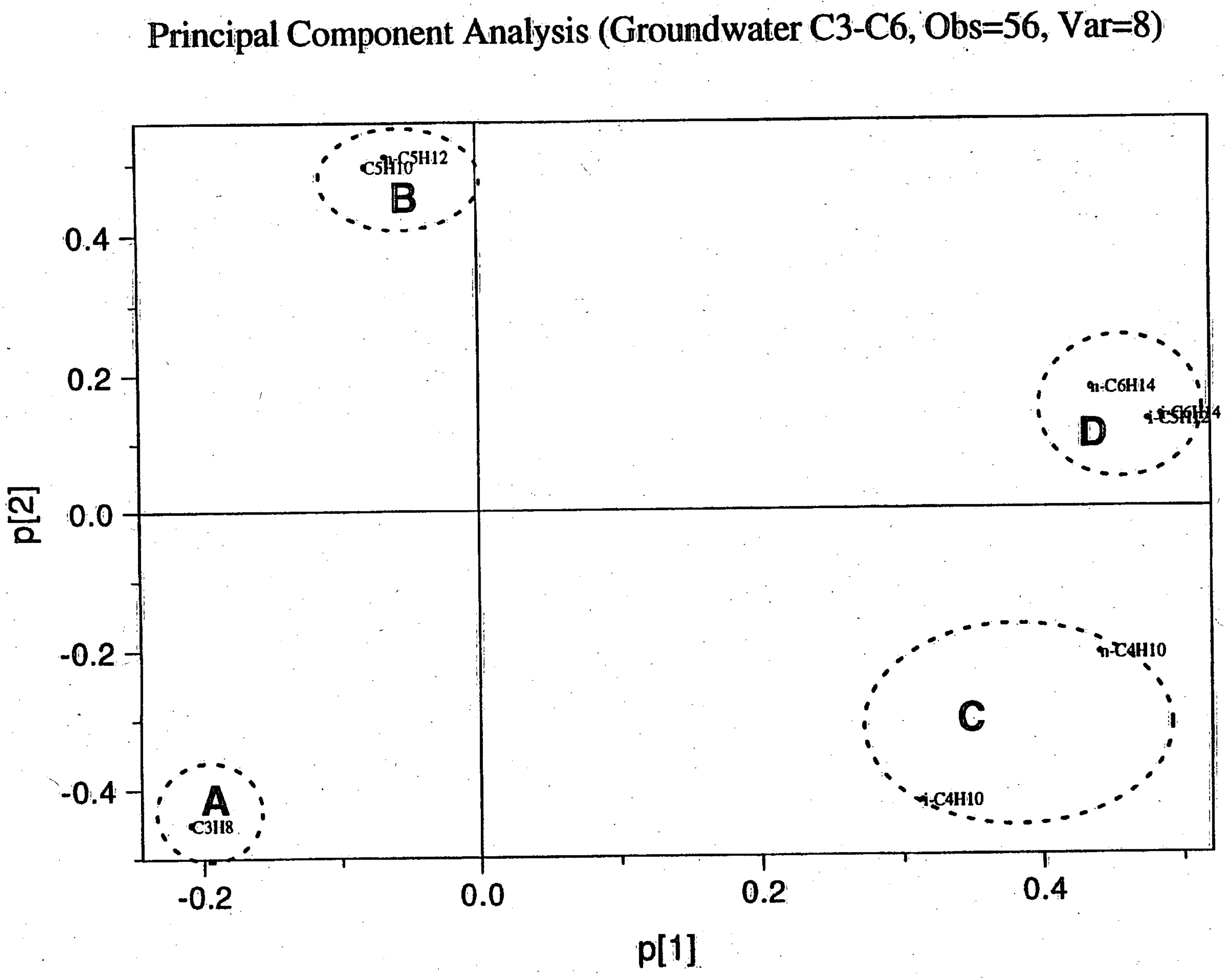

Figure 8 A loading plot of the first two principal components (p_1 vs p_2) resulting from PC analysis of data on groundwater C_3-C_6 hydrocarbons (Observations = 56, Variables = 8).

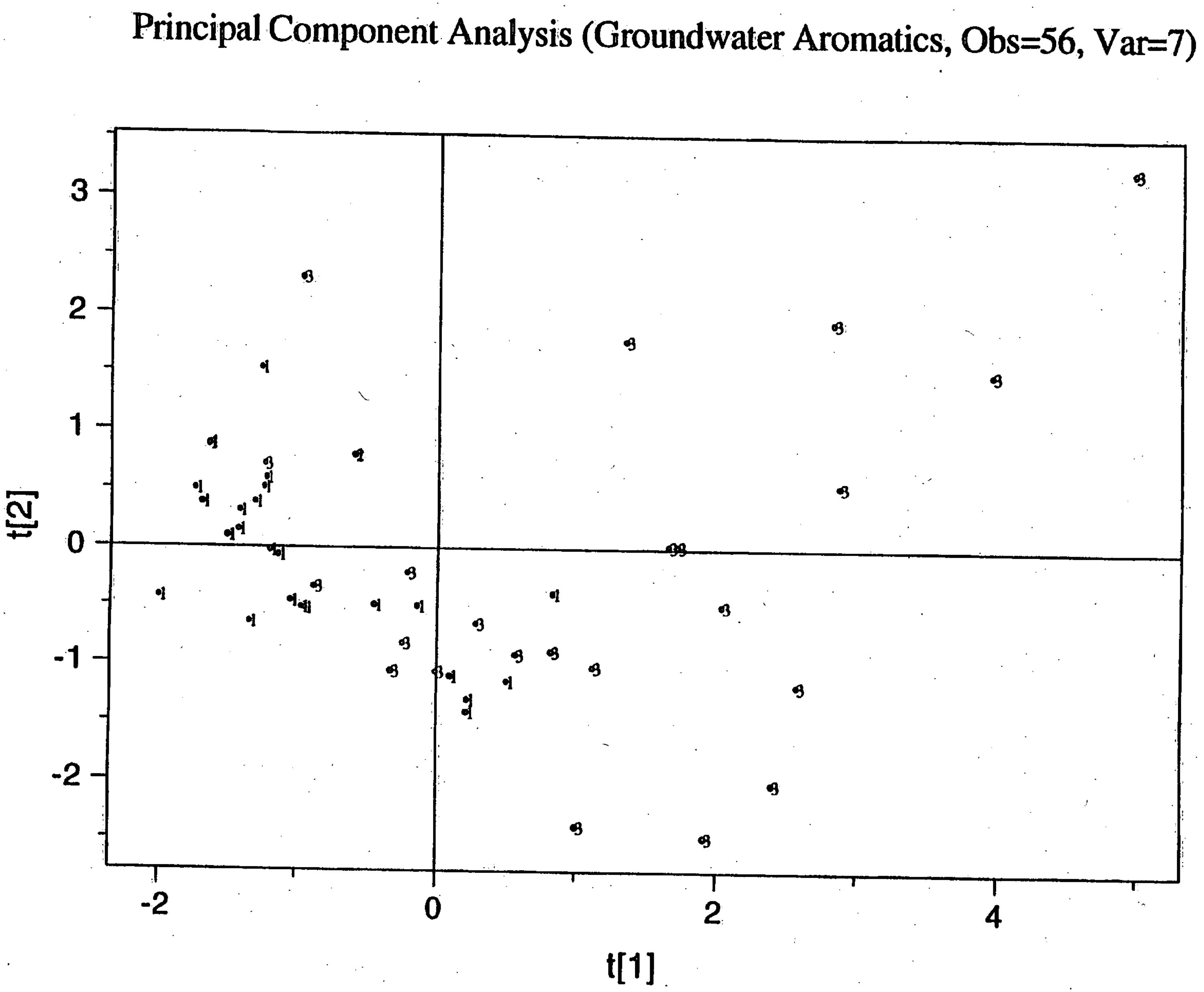

Figure 9 A score plot of the first two principal components (t_1 vs t_2) resulting from PC analysis of data on groundwater monocyclic aromatic hydrocarbons (Observations = 56, Variables = 7).

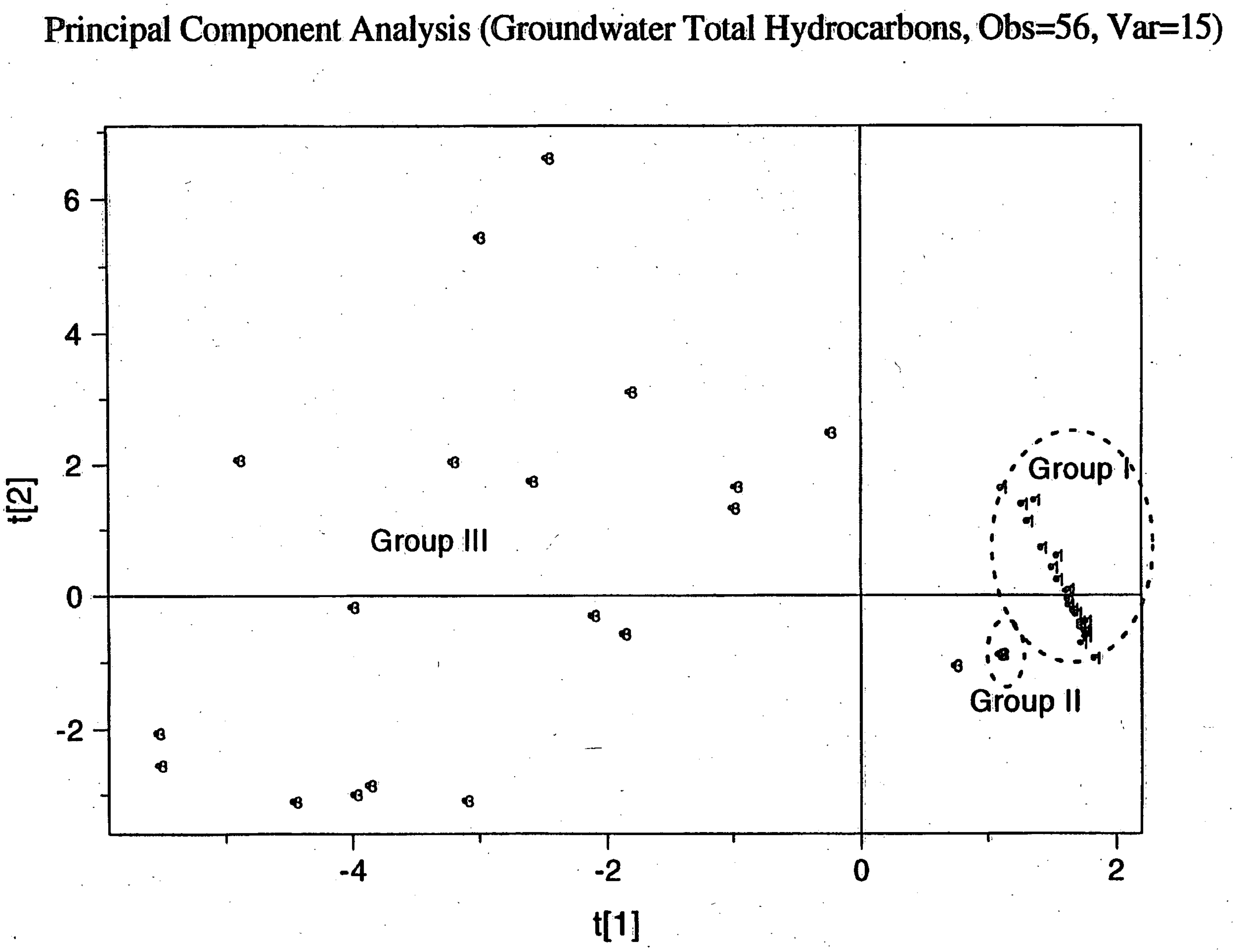

Figure 11 A score plot of the first two principal components (t_1 vs t_2) resulting from PC analysis of data on the total hydrocarbons in groundwater (Observations = 56, Variables = 15).

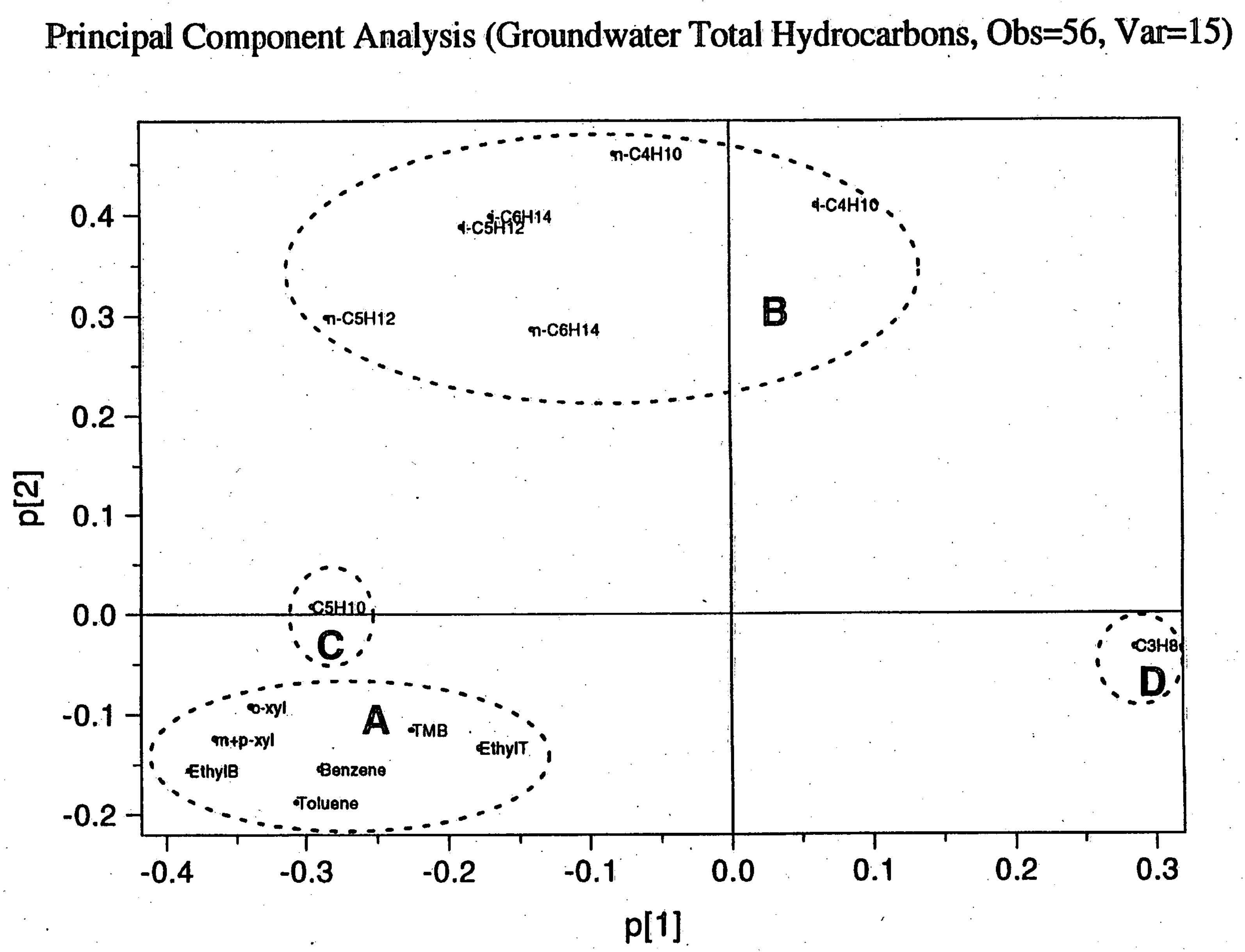

Figure 12 A loading plot of the first two principal components (p_1 vs p_2) resulting from PC analysis of data on the total hydrocarbons in groundwater (Observations = 56, Variables = 15).

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