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# Results from the Canister Sampling Program Conducted During the 1990 Atlanta Precursor Study

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# INTRODUCTION

Control of NMOC compounds is the current approach to reduce ozone levels in cities that exceed the National Ambient Air Quality Standard (NAAQS) level of 0.12 ppm (1). The Clean Air Act requires that ozone non-attainment cities reduce hydrocarbon emissions 15 percent over a 6-year period (2). Several cities have reported reduced nonmethane organic carbon (NMOC) emissions with little impact on observed ozone exceedances. These reductions in emission levels were determined by the preparation of revised source emission inventories. Inconsistencies and inaccuracies in the methods used to estimate NMOC source emissions are thought to lead to incorrect emission inventories. An active ambient air monitoring program in which the effectiveness of control procedures can be directly measured may provide a better approach to verify reduced NMOC emissions. This approach is used successfully for other regulated criteria pollutants using continuously operating monitoring instrumentation. However, reliable and accurate monitoring instruments for ambient NMOC measurements are currently not available. Because the number of ozone non-attainment cities increased to 120 in 1988, EPA initiated an ambient air NMOC measurement program using sophisticated methodology to obtain a baseline data base. The 1990 Atlanta Ozone Precursor Study was designed to serve this purpose. In addition to the development of a representative baseline data base, the measurement program was designed to support other on-going programs that require NMOC measurements. These programs included ozone model development and testing, and development of a source-receptor model to verify the NMOC emissions data base.

The 1990 Atlanta Ozone Precursor Study primarily addressed the measurement of the speciated NMOC compounds was conducted during the July-August, 1990 period. Automated gas chromatographic systems were used at 6 ground sites in the Atlanta metropolitan area and were setup to measure the speciated NMOC compounds each hour during the 24-hour period. The sampling sites consisted of one upwind, three urban and two near urban downwind sites. In addition to the speciated NMOC compounds, measurements were also obtained for ozone, the nitrogen oxides and carbon monoxide. At the present time data validation efforts are underway for the ultimate development of a retrievable data base.

An important component of the monitoring study was the canister sampling program that was conducted in parallel to the operation of the automated gas chromatographs. The objectives for collecting canister samples included:

1. QA/QC comparisons with the automated gas chromatographic system using established gas chromatographic procedures to measure the speciated NMOC compounds.
2. Enhancement and expansion of the spatial coverage of the sampling network by periodic sampling at six additional ground sites.
3. Collection air samples near known emission sources to determine source signatures.

4. Confirmation of the identity of known GC peaks and to provide identification to persistent unknown compounds using GC-mass spectrometric analysis.

This paper presents the status of the canister sampling components of the 1990 Atlanta Precursor Study and provides some preliminary results.

## EXPERIMENTAL

For the QA/QC comparison program between the automated GC (Chrompack International, The Netherlands) and the established laboratory GC system, air samples were collected in SUMMA polished stainless steel canisters using automated collection systems (Anderson Model 87-100, Atlanta, GA) installed at each of the 6 ground sampling sites (See Figure 1 for site location). Air samples were collected in evacuated canisters (initial pressure less than 0.1 torr) and filled to a final pressure of 15 to 20 psig. Canister samples were collected over the identical 30 minute period that the automated GC was taking an ambient air sample. Samples were collected every other day at all six ground sites using rotating collection time periods of 0800, 1000, 1200, 1500, 1800, and 2400. Collected samples were sent via air freight to the central AREAL laboratory facility in Research Triangle Park, North Carolina for detailed GC analyses. During the course of the study a system audit was performed on the canister collection systems at the 6 ground sampling sites. During this audit, humidified zero hydrocarbon air was passed through the sampling device to evaluate system contamination.

For enhancement sampling, a portable collection systems consisting of a mass flow controller unit and a canister were used. The collection system did not include a pump to fill the canister with sample air. Rather, the evacuated canister (initial pressure less than 0.1 torr) pulled air sample into the canister at a flow rate of 120 $cm^3$ $min^{-1}$ for a 30-minute period. The pressure differential between the evacuated canister and ambient pressure maintained the sample flow rate over the collection period. Final sample pressure in the canister ranged from 500 to 550 torr. The enhancement sampling program consisted of 2 three-consecutive-day experiments in which canister samples were collected at 9:00 am and 3:00 pm at six ground sites. The location of the enhancement sites are shown on the map in Figure 1.

Canister samples were collected at source area locations using a 12 volt battery-operated pump (Model 158, Metal Bellows Corporation, Sharonville, MA) and a throttle valve to control sample flowrate to approximately 1.2L $min^{-1}$. Evacuated canisters (initial pressure less than 0.1 torr) were filled with sample air for an integrated 12 to 15 minute time period to a final pressure of approximately 25 psig. These samples were collected at selected source areas to obtain some insight into the VOC emission compositions affecting the Atlanta air quality. Sample sites included: the shoulder of the combined I-75 and I-85 roadway going north at the I-20 intersection; an underground garage in the State of Georgia Building Authority building, 1 M.L. King, Jr. Drive, the tarmac areas of the Hartsfield Airport, forested areas near the 6 ground sampling sites, and several industrial sites identified as point sources in Georgia, Department of Natural Resources VOC Emission Inventory. A total of 63 samples were collected at these source sites including 9 roadway, 14 underground garage, 11 airport samples, 16 vegetation areas, and 13 industrial area samples.

In order to determine the source signatures for vehicular evaporative emissions, samples of the three octane grades of 6 major gasolines sold in the Atlanta area were analyzed. The fuels consisted of the Octane Grades 87, 89, and 92 manufactured by Texaco, Gulf, Exxon, Amoco, Shell, and Chevron. Three canister samples were prepared for each fuel including headspace samples collected over the fuels at 24 and 32°C and a fuel aliquot in humidified zero HC air. This amounted to a total of 54 samples.

Two separate GC analyses were performed on each canister sample to analyze for the $C_2$-$C_{12}$ nonmethane hydrocarbon (NMHC). The $C_2$-$C_{12}$ compounds were separated on a 60 m X 0.32 mm ID DB-1 fused silica column with a 1 $\mu$m liquid phase film thickness (J&W Scientific, Folsom, CA). The column temperature conditions included a -50°C initial temperature held for 2 minutes followed by an 8°C per minute temperature program rate to a final temperature of 200°C held for 11.75 minutes. The $C_2$-$C_3$ hydrocarbons were analyzed on a 30 m X 0.53 mm ID GSQ gas solid fused silica column (J&W Scientific). Column temperature conditions included a 40°C initial temperature held for 4 minutes followed by a 10°C per minute temperature program rate to a final temperature of 200°C held for 5 minutes. A cryogenic preconcentration procedure was used to prepare a 500 cc aliquot of sample air for injection onto the GC column. Details of the GC system, preconcentration procedure and calibration approaches are published elsewhere (3).

## RESULTS AND DISCUSSION

The primary purpose of the canister program during the 1990 Atlanta Ozone Precursor Study was to provide support and complement the data base obtained from the automated gas chromatographs (Chrompack) at the six ground sites. The Chrompack systems were recently developed and considered to be new technology with no previous field operation experience for the measurement of the $C_2$-$C_{10}$ hydrocarbons. Consequently, the comparison analysis of air samples in canisters collected in parallel to the operation of the Chrompack systems using established laboratory GC analysis procedures was critical to the development of a credible data base. Two important differences between the Chrompack and laboratory GC systems included the preconcentration approach and the GC column liquid phase loading. The Chrompack system used a two-stage preconcentration approach to remove organic compounds from sample air and prepare the trapped compounds for injection onto the GC column. The first stage trap contained absorbent material that removed the organic compounds from sample air. The second stage trap cryogenically focused the organic compounds that were heat vaporized off the primary adsorbent trap prior to injection onto the GC column. The laboratory GC system did not use an adsorbent and operated in a more direct approach using only one stage of cryogenic preconcentration prior to injection onto the GC column. The other important difference between the two GC systems was the use of a 5 $\mu$m liquid phase column in the Chrompack. The laboratory GC system used a 1 $\mu$m liquid phase column. The selection of a 5 micron phase column for the

Chrompack system was based upon the desire to obtain resolution of the $C_2$ to $C_4$ hydrocarbons. The resolution of the more complex $C_5$ to $C_{10}$ hydrocarbons, however, are quite different between the 1 and 5 μm columns. Because of these significant differences, a more concerted laboratory approach was used in the analysis of the collected canisters. In addition to the laboratory GC system, the canister samples were also analyzed with a laboratory Chrompack system identical to the field systems but set up to operate in the manual mode. By comparing the results obtained from the laboratory and field Chrompack systems affects due to canister storage can be determined . Effects due to the use of the 5 μm GC column can be determined by comparison of the laboratory GC with both Chrompack results.

To verify that the canister collection systems were properly operating and not providing contaminants to the collected canister sample, field audits were conducted at all 6 sampling sites. The audits consisted of both a visual check of the collection system and the collection of a humidified zero HC air sample through the sampling device. The chromatographic results for the blank zero HC air prior to and after passing through the canister collection system at the Tucker site are shown in Figure 2. From the figure it is observed that a minor increase in the number and magnitude of the peaks appeared in the sample air after passing through the canister collection device. The total NMOC concentrations measured for the "prior to" and "after" GC analyses were 1.7 and 8.8 ppbC respectively. Such differences are considered to be quite small and much below the typical total NMOC concentration levels observed in the ambient air samples. Actually from the test it is difficult to rule out the possibility that the increase is not due to canister itself. Similar results were observed for the canister collection systems at the other 5 sites indicating that the canister sampling devices were not contaminating the collected samples.

A total of 184 canister samples were collected at the 6 sites during the July-August, 1990 study period. These samples were returned to the central laboratory facility in the Research Triangle Park, NC and analyzed on both GC systems. This data base is currently in the development stage but should be more than adequate to evaluate the operational performance of the Chrompack system. One serious problem that has delayed data base development is GC peak identification by the Chrompack system. The Chrompack system contained a fused silica GC column with the column carrier gas exit flow split to 2 detectors, i.e., flame ionization (FID) and electron capture (ECD). The computer controlled system contained standard data integration and peak identification programs to prepare results files that contained named peaks and concentrations. Correct peak identification depended upon finding selected reference peaks and adjusting the retention times of all other observed peaks based upon these compounds. If reference peaks were not located, a message to that effect was also placed in the results file. During the preliminary review process, this message was observed in many of the results files obtained from the 6 monitoring sites and the laboratory Chrompack systems. As a consequence, the GC result files are currently being reprocessed to correctly name the GC peaks. Some preliminary results that compare field monitoring and canister analyses for 3 of the Atlanta sites are given in Table I. The table includes concentrations for 15 hydrocarbon compounds obtained from the laboratory GC and the Chrompack laboratory and field monitoring systems. In the table both good and poor comparisons between GC analyses are observed for the 15 compound peaks. For example the comparisons between propylene, isoprene, and 3-methylpentane appear to be quite reasonable; however, those for isopentane, benzene, and n-butane indicate significant differences between the GC systems. The benzene results for the laboratory Chrompack system at the Mars Hill and Georgia Tech sites are significantly different than the laboratory GC and the field Chrompack systems which demonstrate excellent agreement. Other compound comparisons suggest that at times the laboratory GC system or the field Chrompack unit appears to have produced the outlier result. It is expected that the on-going data reprocessing activity will significantly improve these comparisons.

The other important role of the canister program was to obtain hydrocarbon component compositions at important source areas in Atlanta. From review of the Atlanta VOC emission inventory, volatile organic compounds come primarily from vehicles and vehicular related sources. Consequently a canister sampling program was designed to collect samples at sites dominated by these sources. Two such sites were identified including a roadway and underground parking facility. The roadway location was along interstate I-75 and I-85 near the I-20 intersection. The roadway at this complex intersection was covered by an overpass that extended approximately 100 ft. This extensive overpass provided what could be termed a "mini-tunnel" along the I-75 and I-85 roadway. Canister samples were collected on the shoulder of this roadway approximately in the middle of this overpass. The overpass served to restrict air ventilation and provided higher sample concentrations. Likewise, air samples were collected during morning periods when vehicular traffic densities were high.

The underground parking facility also presented the opportunity to collect samples at locations dominated by vehicular traffic. The influence of parked vehicles were expected to affect observed composition, consequently, canisters were collected at three different time periods: morning, late morning, and afternoon. The morning and afternoon periods corresponded to times vehicles entered and left the parking facility. The late morning period represented a condition of limited vehicular traffic.

Canister samples were collected at other source areas that were expected to have an impact on the hydrocarbon air quality in Atlanta. One such site included the forested areas near the 6 monitoring locations. Air samples collected at these sites were intended to give qualitative compositional information of hydrocarbon compounds coming from these natural sources. Since these forested areas contained mostly mixed deciduous vegetation, isoprene was expected to be a principal component of the observed mixtures. Downwind and upwind canister samples were collected at a few of Atlanta's largest VOC point source emitters in an effort to determine their compositions. Like the forest area samples, the intent of these samples was to obtain a qualitative picture of hydrocarbon compositions. Sufficient samples were not collected to obtain any useful source signature composition.

The last source area sampled was Hartsfield International Airport. Canister samples were collected on the airport tarmac near jet aircraft activities. Several samples were collected between and during periods of aircraft loading and departure. Sample collection times occurred during the morning period to maximize aircraft activity and minimize ambient air ventilation conditions. The possibility of using the collected samples for major airport source signature development was re-enforced when it was learned that all aircraft and airport support vehicles used the same jet fuel. Source signatures of selected compounds for the airport, roadway, and underground parking facilities are given in Table II. The hydrocarbon composition observed at the airport ranged from $C_2$ to $C_{14}$. It was interesting to note that the most abundant compounds observed consisted of those measured from gasoline-powered vehicular sources (like those found in the roadway source signatures). These compounds include ethylene, acetylene, n-butane, isopentane, toluene, ethylbenzene and m- and p-xylene. Air samples were collected some distance from the airport parking facilities. Consequently major influence from this source was not expected. The major difference between airport and roadway sources is observed in the $C_{10}$-$C_{14}$ normal paraffins where a near order of magnitude difference is observed. Whether this source signature is valid requires testing in receptor model calculations and additional sample collection programs.

To complete the source signature development program analyses of liquid and headspace vapor at 24 and 32°C were made for the 3 octane grades of six major gasolines used in the Atlanta area were determined. Results for the 87 octane grade gasolines are provided in Table II. Little difference is observed in these headspace profiles at the two different temperatures which suggest that this fingerprint is probably independent of temperature. Source signatures consisting of all gasolines analyzed will be used in combination with gasoline sales estimates to determine the source signature most appropriate for the Atlanta area.

The source signatures reported in Table II were obtained with the laboratory GC system. All source samples were likewise analyzed on the laboratory Chrompack system and will be available for use with the field Chrompack data base. From Table II large differences in the source signatures are noticed for the underground garage; only the afternoon composition compares well with the roadway source signature. Obviously evaporative emissions from the large number of parked vehicles observed during the morning collection periods strongly affected the hydrocarbon compositions. During the afternoon sampling period, fewer parked cars were in the facility; also traffic activity was more frequent - particularly cars leaving the facility. The roadway source signatures agree reasonably well with those reported by Scheff et. al. (4). The gas vapor compositions are somewhat different in that our source signatures were more abundant in isopentane rather than n-butane.

## CONCLUSIONS

The large speciated hydrocarbon data base obtained from the 6 monitoring sites during the 1990 Atlanta Precursor Study is unique and provides the opportunity to evaluate VOC emissions activities at various sites and at different times of the day. The companion canister program will serve as a valuable tool to both validate the continuous data base and provide source source signatures unique to Atlanta. Data base validation and development efforts are currently underway. After these activities are completed, more definitive comparisons of the field and canister data will be performed.

## REFERENCES

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### NOTE TO EDITORS

TABLE I. HYDROCARBON COMPOUND RESULTS OBTAINED FROM THE LABORATORY AND FIELD SITE GC SYSTEMS FOR THE AUGUST 28, 1990, 10:00 AM SAMPLE

| | MARS HILL | | | GEORGIA TECH | | | MARTIN LUTHER KING | | |
|---|---|---|---|---|---|---|---|---|---|
| Compound | $GC_1$[a] | $GC_2$[b] | $GC_3$[c] | $GC_1$ | $GC_2$ | $GC_3$ | $GC_1$ | $GC_2$ | $GC_3$ |
| Ethylene | 7.1 | 6.7 | 9.3 | 12.6 | 10.7 | | 3.6 | 13.4 | |
| Ethane | 7.7 | 5.5 | 7.4 | 11.1 | 10.9 | 11.9 | 6.7 | 9.6 | |
| Propylene | 3.3 | 5.6 | 3.4 | 4.7 | 7.4 | 4.7 | 5.4 | 4.1 | 3.5 |
| Propane | 10.7 | 8.8 | 10.7 | 21.4 | 19.5 | 24.3 | 6.3 | 9.9 | 11.9 |
| n-Butane | 12.1 | 9.6 | 12.3 | 27.7 | 25.1 | 30.7 | 7.5 | 24.3 | 29.9 |
| isoPentane | 21.0 | 20.3 | 23.1 | 53.0 | 35.6 | 40.1 | 11.1 | 65.3 | 50.6 |
| n-Pentane | 10.3 | 6.3 | 7.3 | 10.7 | 9.7 | 10.7 | 7.4 | 11.9 | 14.8 |
| isoPrene | 21.5 | 16.5 | 20.0 | 12.9 | 10.5 | 13.2 | 8.1 | 9.1 | 8.4 |
| 3-Methylpentane | 4.0 | 3.1 | 4.0 | 5.8 | 5.2 | 6.3 | 8.5 | 10.1 | 8.1 |
| Benzene | 5.8 | 43.3 | 5.6 | 9.0 | 45.4 | 9.1 | 11.8 | 8.0 | 10.1 |
| n-Heptane | 1.7 | 1.7 | 1.1 | 2.6 | 1.6 | 2.2 | 8.9 | 2.1 | 2.8 |
| Toluene | 15.0 | 12.5 | 13.8 | 32.1 | 29.5 | 35.4 | 21.5 | 26.8 | 30.2 |
| Ethylbenzene | 3.2 | 2.0 | 2.4 | 6.9 | 6.7 | 6.5 | 10.4 | 5.0 | 5.2 |
| m- + p-Xylene | 8.1 | 6.3 | 6.7 | 18.7 | 16.9 | 19.4 | 12.4 | 13.8 | 15.3 |
| o-Xylene | 3.7 | 2.7 | 2.8 | 8.3 | 8.2 | 6.9 | 19.9 | 6.3 | 6.0 |

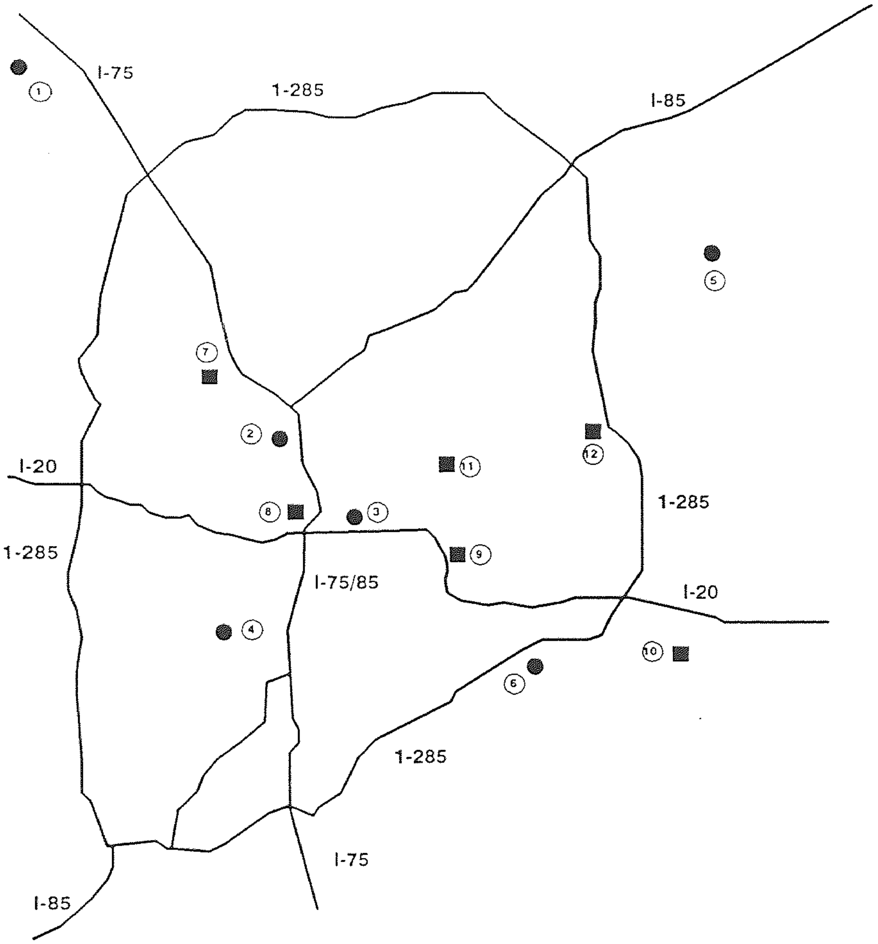
[a] $GC_1$ is the field site Chrompack GC system data, ppbC

[b] $GC_2$ is the laboratory Chrompack GC system data, ppbC

[c] $GC_3$ is the laboratory standard GC system data, ppbC

TABLE II. 1990 ATLANTA SOURCE SIGNATURES FROM VARIOUS SOURCES (wt%)

| | | Underground Parking Facility | | | | | |
|---|---|---|---|---|---|---|---|
| Compound | Roadway | Morning | Late Morning | Afternoon | Gas Vapor 24C | Gas Vapor 34C | Airport |
| Ethane | 1.79 | 0.83 | 0.59 | 1.14 | 0.86 | | 1.39 |
| Ethylene | 4.51 | 2.17 | 1.89 | 5.62 | | | 3.40 |
| Acetylene | 3.62 | 1.67 | 2.40 | 3.43 | | | 2.22 |
| Propylene | 2.00 | 0.86 | 0.82 | 2.69 | 0.13 | 0.12 | 0.83 |
| Propane | 1.17 | 0.78 | 0.69 | 0.38 | 1.17 | 1.00 | 1.42 |
| isoButane | 1.26 | 1.71 | 2.06 | 0.71 | 4.85 | 4.53 | 0.85 |
| n-Butane | 4.57 | 6.10 | 7.48 | 3.38 | 20.13 | 18.72 | 2.72 |
| isoPentane | 9.35 | 12.92 | 12.44 | 7.20 | 28.21 | 27.26 | 5.28 |
| n-Pentane | 2.86 | 3.71 | 3.70 | 2.13 | 8.89 | 8.51 | 1.99 |
| 2-Methylpentane | 2.62 | 3.02 | 3.21 | 2.30 | 4.17 | 4.11 | 1.95 |
| 3-Methylpentane | 1.56 | 1.74 | 1.88 | 1.34 | 2.28 | 2.27 | 1.03 |
| n-Hexane | 1.18 | 1.32 | 1.45 | 1.03 | 1.42 | 1.41 | 1.10 |
| 2,4-Dimethylpentane | 0.76 | 0.68 | 0.77 | 0.74 | 0.46 | 0.51 | 0.45 |
| Benzene | 2.63 | 2.02 | 2.18 | 2.92 | 0.92 | 0.93 | 1.42 |
| Toluene | 6.50 | 6.62 | 7.65 | 7.53 | 1.17 | 1.35 | 4.48 |
| Ethylbenzene | 1.28 | 1.20 | 1.37 | 1.60 | 0.10 | 0.15 | 3.40 |
| m-& p-Xylene | 4.33 | 4.07 | 4.31 | 5.03 | 0.31 | 0.46 | 3.21 |
| o-Xylene | 1.67 | 1.58 | 1.68 | 1.96 | 0.11 | 0.17 | 1.15 |
| n-Decane | 0.27 | 0.30 | 0.27 | 0.30 | | | 2.04 |
| n-Undecane | 0.28 | 0.35 | 0.27 | 0.53 | | | 2.94 |
| n-Dodecane | 0.27 | 0.34 | 0.19 | 0.29 | | | 2.33 |
| n-Tridecane | 0.10 | 0.12 | 0.07 | 0.06 | | | 1.46 |



● CONTINUOUS SITE

1 - MARS HILL
2 - GA. TECH
3 - MLK
4 - FT. MACPHERSON
5 - TUCKER
6 - SO. DEKALB

■ ENHANCEMENT SITE

7 - FIRE STATION #8
8 - HEALTH DEPT.
9 - BAPTIST CHURCH
10 - FLAT SHOALS RD.
11 - MORNINGSIDE PARK
12 - GDNR

FIGURE 1. ANALYSIS OF HYDROCARBON FREE AIR