



Air monitoring of a coal tar cleanup using a mobile TAGA LPCI–MS/MS

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Received 29 July 2001; received in revised form 11 December 2001; accepted 13 December 2001

Abstract

Real-time detection of air toxics is becoming increasingly important in understanding the sources and constituents of air pollution. The detection of low levels of air contaminants requires reliable sampling and calibration techniques, as well as sophisticated analytical instrumentation. Recently, a new low pressure chemical ionization (LPCI) source was developed for ambient air monitoring of benzene, toluene, xylene (BTX) and gas-phase polycyclic aromatic hydrocarbons (PAH) in real-time. This ion source in conjunction with a triple quadrupole (Q1, Q2, Q3) mass spectrometer (trace atmospheric gas analyzer (TAGA IIe)) has been proven highly useful for measuring selected air pollutants. The ion chemistry under LPCI conditions involves charge transfer reactions yielding parent ions which are selected in the first quadrupole, Q1, dissociated in the second quadrupole, Q2, and the resultant daughter ions are then identified by the third quadrupole, Q3. Monitoring of specific parent/daughter (P/D) ion pairs is used to measure concentrations of BTX and selected PAH. The response of the TAGA IIe is characterized through multi-point calibration curves. Detection limits (DL) as low as $0.5 \mu\text{g}/\text{m}^3$ for BTX and PAH were accomplished by optimizing various TAGA IIe operating parameters. This unique method was applied in November 1999 to monitor emissions released during the cleanup of a historical coal tar site in Kingston, Ontario. This information was used by local officials for enhancing abatement activities or in some cases temporarily halting the excavation when levels of air toxics were higher than allowable provincial guidelines. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Mobile TAGA IIe; Air monitoring; LPCI–MS/MS; Coal tar cleanup; Aromatic hydrocarbons

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1. Introduction

The ability to perform real-time, on-site chemical analysis is very important in the evaluation of emissions from sites containing hazardous chemical waste. Situations where fast response and assessment is critical include monitoring of chemical fires, chemical spills, or accidental chemical releases especially when the public may be at risk due to exposure to elevated levels of toxic airborne contaminants. Information on the types and levels of the toxic chemicals around a spill site is needed immediately by medical officers of health, fire department personnel, police department and public officials. This on-site information could then be used for assessment of the environment and, if necessary, plan for remedial action to limit the release of chemicals and the exposure to the population including evacuating of residents from the affected areas. In such cases, the best approach is to bring a mobile air monitoring unit to the affected areas and conduct real-time air quality analysis and monitoring. Collection of discrete air samples and analysis at a laboratory usually takes several hours or days and such conventional methods are generally not useful for the minute-by-minute decisions that may have to be made at a spill site. The mobile TAGA (trace atmospheric gas analyzer) technology has been used by the Ontario Ministry of the Environment (OMOE) since 1980 for on-site analysis of numerous contaminants from a variety of industrial sources in Ontario and during environmental emergencies. The first mobile TAGA (model 3000) used from 1980 to 1988 was a single quadrupole mass spectrometer equipped with an atmospheric pressure chemical ionization (APCI) source and cryogenic vacuum pumping system. The second generation TAGA (model 6000) was a triple quadrupole system (also with a cryogenic vacuum pumping system) and was used by the Ministry for 10 years starting in 1988. In 1998 the two TAGA 6000 models were replaced by the latest model, TAGA IIe: a state-of-the-art triple quadrupole mass spectrometer with turbo molecular vacuum pumps. In this paper, we describe the monitoring results obtained by a mobile TAGA as it was used to monitor air quality at a cleanup site of the buried remnants of a historical coal gasification plant in Kingston, Ont.

Coal tar contains mainly benzene, toluene, xylene (BTX), naphthalene and other polycyclic aromatic hydrocarbons (PAH). Naphthalene is the major constituent of coal tar which makes up to 11% of the total volume [1]. A large area at a prime location in downtown Kingston, Ont. was contaminated by coal tar which had been buried in large underground tanks since the late 1950s. The list of air toxics to be monitored included benzene, a known carcinogen, and naphthalene, an irritant, readily recognizable for its characteristic mothball odour.

2. The mobile TAGA IIe

The TAGA IIe MS/MS is a real-time, direct-air sampling, analytical instrument which is mounted in a 10 m “Orion” coach [2] shown in Fig. 1. It is a completely self-contained mobile air monitoring unit, capable of monitoring hundreds of different air contaminants “on the fly”. The coach accommodates the TAGA IIe (Fig. 2) and other essential pieces of equipment: two computer stations for complete TAGA IIe automated control, data acquisition and data analysis, a fume hood, a refrigerator, various storage compartments and work



Fig. 1. External view of the mobile TAGA IIe unit "Explorer".

benches. A telescopic 10 m meteorological tower equipped with a combination anemometer/wind vane, is used for recording ambient air temperature, wind direction and wind speed. Meteorological data is recorded once every minute and displayed on real-time basis. A communication link to other vehicles and home base offices is facilitated by two-way radios, cellular phone, digital phone and facsimile. Four roof-mounted air conditioners provide the necessary environmental control to the interior of the mobile unit. All power requirements of the mobile are supplied by an on-board 17.5 kW generator, interfaced with a four-cylinder water-cooled diesel engine, providing stable voltage and frequency. The mobile is equipped with an automated system to permit unattended generator and TAGA IIe start-up. The mobile TAGA IIe can be fully functional in 30 min from a complete shut-down mode.

3. Experimental

3.1. TAGA IIe mass spectrometer

The main components of the TAGA IIe include an air inlet system, a chemical ionization source, a mass analyzer consisting of a series of mass filters and focusing elements, an ion detector, and two MAC-based computer systems (Fig. 3). The operation of the TAGA IIe is based on the principles of tandem mass spectrometry. A triple quadrupole mass spectrometer is used to differentiate and quantitate thousands of different chemicals in the gas phase. Ambient air is sampled continuously at a flow rate of 90 l/min directly into the



Fig. 2. The TAGA IIe mass spectrometer housed inside the mobile unit, known as the “Explorer”.

ion source. The high sampling rate, and the direct link to the heated ionization chamber, assures that sample adsorption or degradation is negligible.

Earlier mass spectrometry methods for real-time detection of air pollutants used a well established atmospheric pressure chemical ionization (APCI) technique involving a corona discharge for ionization of chemicals [3]. Chemical reagents such as water vapour were used for highlighting alcohols and ketones while ammonia highlights amines through proton transfer reactions, benzene was used to focus on some aromatics through charge transfer reactions and oxygen to highlight electronegative compounds such as organic and inorganic acids. This method while excellent for polar compounds was not conclusive for monitoring benzene at low parts-per-billion (ppb) levels. For several years, the most common method for sampling volatile organic pollutants (VOCs) involved cartridge sampling and analysis at a later time using gas chromatography/tandem mass spectrometry (GC-MS/MS); this method is particularly useful for low levels ($\mu\text{g}/\text{m}^3$) [4]. However, when ambient VOC concentrations are higher than approximately $300 \mu\text{g}/\text{m}^3$, adsorbent cartridges become overloaded, breakthrough may occur and consequently ambient pollutant levels cannot be reliably quantified. With the assistance of SCIEX, the manufacturer of the TAGA systems, a new low pressure chemical ionization (LPCI) source was developed and has been applied in several situations, including the coal tar cleanup in Kingston, Ont., to measure aromatic air pollutants.

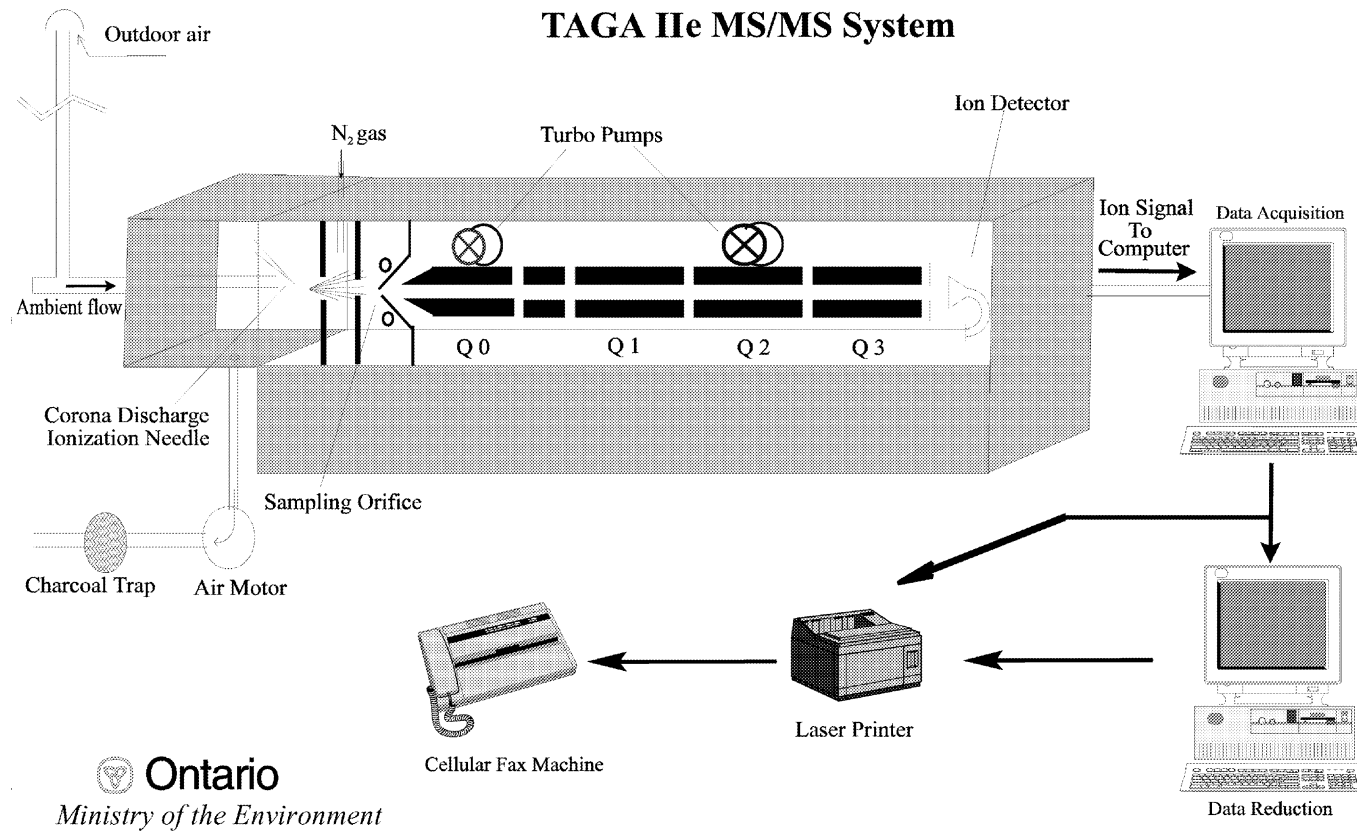


Fig. 3. Schematic of the TAGA IIe tandem quadrupole mass spectrometer.

3.2. LPCI

The ionization of airborne chemicals emitted from the coal tar is accomplished through a series of gas-kinetic, chemical ionization reactions, initiated in the LPCI source. The LPCI consists of a stainless steel rod to which a current is applied to produce a glow discharge in a small volume of ambient air allowing for the formation of positive and negative reagent ions by donating or removing an electron. The LPCI source is normally operated at a pressure of 3 Torr and 100 μ A. Airborne chemicals undergo charge transfer reactions with reagent ions (typically NO^+ , N_2^+ , and O_2^+) to yield parent ions which are mass analyzed in the first quadrupole, Q1.

3.3. Identification

A Q1 only, or single MS spectrum obtained downwind of the coal tar cleanup site in Kingston, Ont. is shown in Fig. 4. The major parent ions observed in Q1 were at 78, 92, 104, 106, 116, 118, 120, 128, 134, 142 and 154 amu. Selected parent ions are then subjected to collision activated dissociation (CAD) with an inert gas, nitrogen, and produce fragment ions better known as daughter ions in Q2. By comparing the parent/daughter (P/D) ion frag-

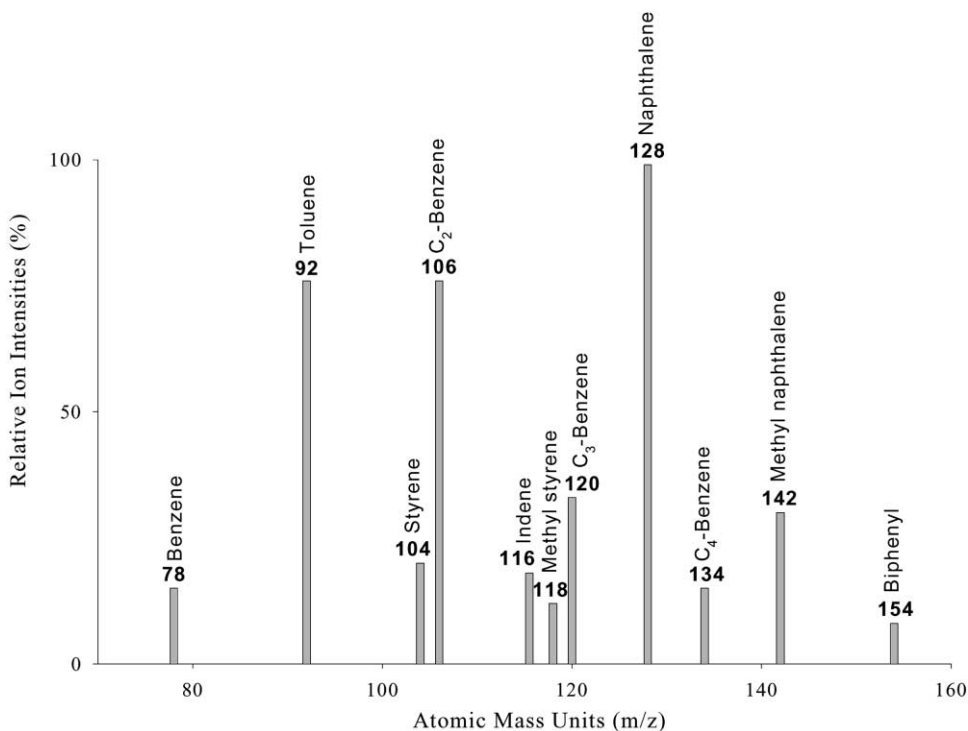


Fig. 4. TAGA IIe single MS spectrum obtained downwind of the coal tar cleanup site.

Library Search Results (TAGA IIe LPCD)

Library File: Parent ion = 128

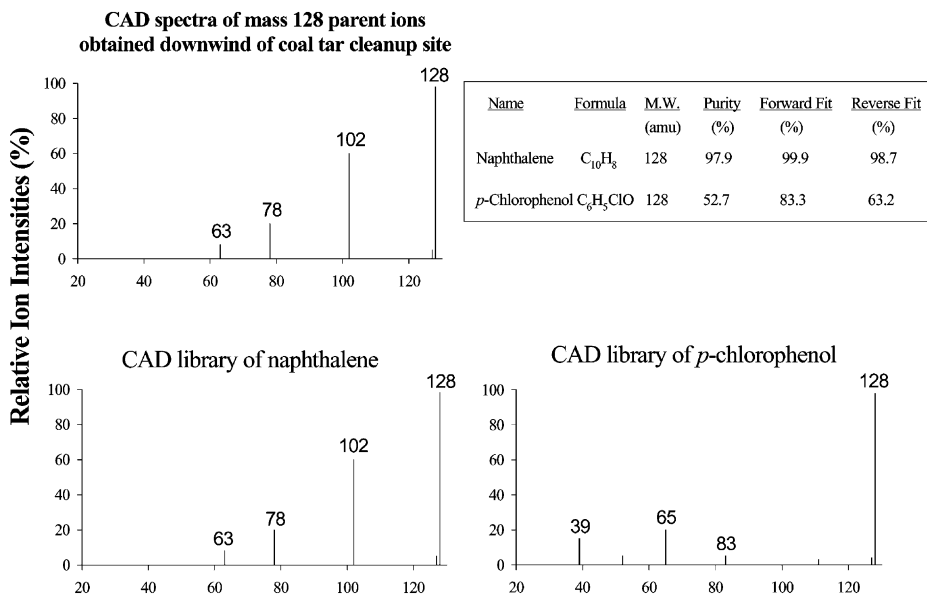


Fig. 5. TAGA IIe MS/MS library search of molecular ion at 128 amu.

mentation pattern with the library of known chemicals the contaminants were identified. The major parent ions shown in Fig. 4 correspond to the following contaminants: benzene, toluene, styrene, C₂-benzene (including xylene isomers and ethyl benzene), indene, methyl styrene, C₃-benzene isomers, naphthalene, C₄-benzene isomers, methyl naphthalene and biphenyl.

A good example of library matching is shown in Fig. 5. A standard TAGA IIe CAD library containing the common air contaminants has been created using 20 eV of collisional ion energy and nitrogen as the collision gas. The CAD fragmentation pattern of the “unknown” parent ion at 128 amu obtained downwind of the coal tar cleanup site, shown in Fig. 5 (top left), is dominated by three daughter ions at 63, 78 and 102 amu. Fig. 5 also shows the CAD spectra for $m/z = 128$ amu from our standard library; one for naphthalene (bottom left) and one for *p*-chlorophenol (bottom right). The spectrum of the “unknown” is compared with the standard CAD library spectra; agreement between the “reverse” and “forward” library search results and their closeness to unity, indicate the degree of certainty for compound identification. In this case, the “best” search results match with naphthalene.

3.4. Quantitation

Quantitation is accomplished by multiple reaction monitoring (MRM) involving data acquisition of selected P/D ion pairs, for example the 128/63, 128/78 and 128/102 ion pairs

are used to monitor ambient naphthalene levels. In order to quantitate levels of ambient air toxics, the response of the TAGA IIe is calibrated using known chemical standards. A calibration method developed by our group involves injecting an aqueous standard into the inlet air flow via a heated nebulizer [5]. The nebulizer used on the mobile unit consists of a capillary tube for liquid sample injections and two outer concentric stainless steel tubes for nebulizing and purging gases; this configuration ensures uniform sample atomization thus providing for addition of controlled amounts of standards into TAGA IIe LPCI source. The standard solution is injected into the nebulizer with a 1 ml, 22 s gauge Hamilton Gastight syringe mounted in a Harvard (model 22) syringe infusion pump. The flow rates of the liquid standard are controlled by the speed of the syringe pump. For example, flow rates between 0 and 20 $\mu\text{l}/\text{min}$ allow for naphthalene concentrations in the range of 0–200 $\mu\text{g}/\text{m}^3$ to be generated in the LPCI source. Five-point calibration curves of naphthalene were performed by simultaneously recording the responses of three P/D ion pairs. An example of a calibration of naphthalene, in the concentration range of 0–200 $\mu\text{g}/\text{m}^3$ is shown in Fig. 6. Note that calibrations are performed in situ, i.e. ambient air is used as the carrier gas to automatically account for any matrix effects. The slopes of the response curves are measures of the sensitivity of the LPCI–MS/MS system to naphthalene. A linear response for naphthalene was observed up to 400 $\mu\text{g}/\text{m}^3$ (to avoid system contamination, the saturation points for response non-linearity was not determined beyond 400 $\mu\text{g}/\text{m}^3$). Another calibration is achieved by introducing a gas mixture of known concentration from a certified standard gas cylinder. The response of TAGA was observed to be linear up to 2000 $\mu\text{g}/\text{m}^3$ for benzene using this method.

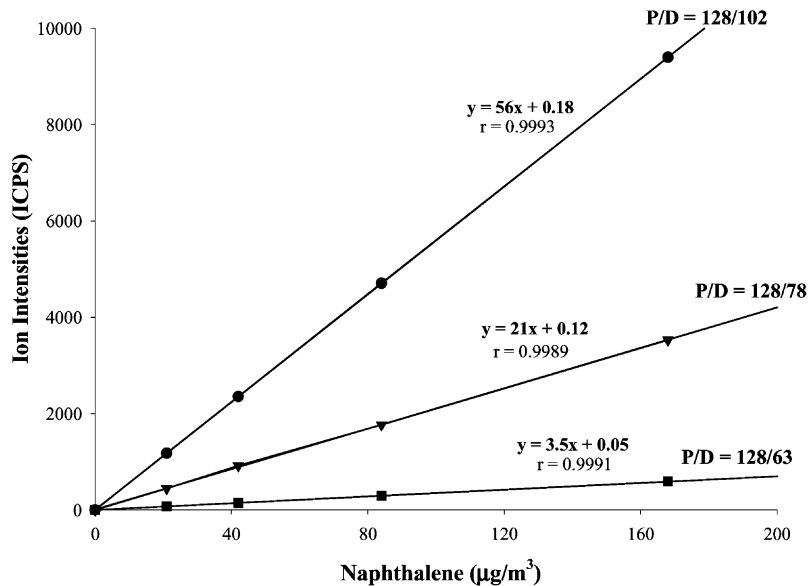


Fig. 6. TAGA IIe calibration plot of naphthalene using three P/D ion pairs: 128/102, 128/78 and 128/63.

During this survey, the calibration response factors and detection limits (DL) were determined twice daily at upwind locations for each of the BTX and PAH compounds. Each of these compounds have a unique DL which is defined as three times the standard deviation of the background signal (usually immediately upwind of the site) divided by the slope of the calibration curve. DL vary from day to day due to variations in the air matrix which effect the sensitivity and/or the background levels. The DLs ranged from 0.5 to 3 $\mu\text{g}/\text{m}^3$ with a mean value of 2 $\mu\text{g}/\text{m}^3$ and a standard deviation of 0.3 $\mu\text{g}/\text{m}^3$ for each of the BTX and PAH compounds monitored.

3.5. Strategy of mobile TAGA air monitoring

Upon arrival at a site to be investigated the mobile unit determines the background levels and performs calibrations of the target chemicals (if they are known) upwind of the emission source. Following upwind measurements, “plume tracking” is conducted by driving the mobile TAGA downwind of the source while monitoring for selected target compounds to obtain the maximum instantaneous levels. Monitoring includes, “chemically fingerprinting” the air to identify as many chemicals as possible and determining the levels of the predominant chemicals and/or those known to be the most toxic. Depending on wind direction shifts, monitoring is performed at several downwind locations. During surveys, weather forecasts for the region being monitored are used to assist with the air monitoring. The information is collected by the computer which includes minute-by-minute meteorological data and instantaneous levels of target compounds over pre-selected half-hour periods. At times when levels exceed provincial standards, the TAGA crew immediately notifies the local staff or city officials. If some contaminants are detected which currently do not have a provincial criteria, then the Standards Development Branch of the OMOE provides additional information on toxicity and proposes an interim guideline for triggering abatement actions.

4. Results and discussion

LPCI–MS/MS method was field-tested in November of 1999 during a 3 week air monitoring survey in the vicinity of a historical coal tar site. An area map of the coal tar contamination site in Kingston, Ont. is shown in Fig. 7. A total of 168 half-hour concentrations were determined at several different locations upwind and downwind of the site. Fig. 8 shows real-time measurements of naphthalene recorded every 5 s for a period of 30 min at a fixed location downwind of the cleanup site. Rapid changes in naphthalene levels were primarily due to local air eddies or turbulence, as well as changes in the wind direction. Note that the downwind response profiles of the three P/D ion pairs (128/63, 128/78 and 128/102) were similar indicating the presence of naphthalene. For simplicity the major P/D ion pair 128/78 is shown in Fig. 8.

BTX and PAH were measured concurrently while the mobile TAGA was driven slowly along the streets surrounding the cleanup site. Fig. 9 shows an example of plume tracking. As the location of the mobile TAGA changes the real-time concentration of naphthalene varies. During this time frame the prevailing wind was from southwest and the mobile TAGA was

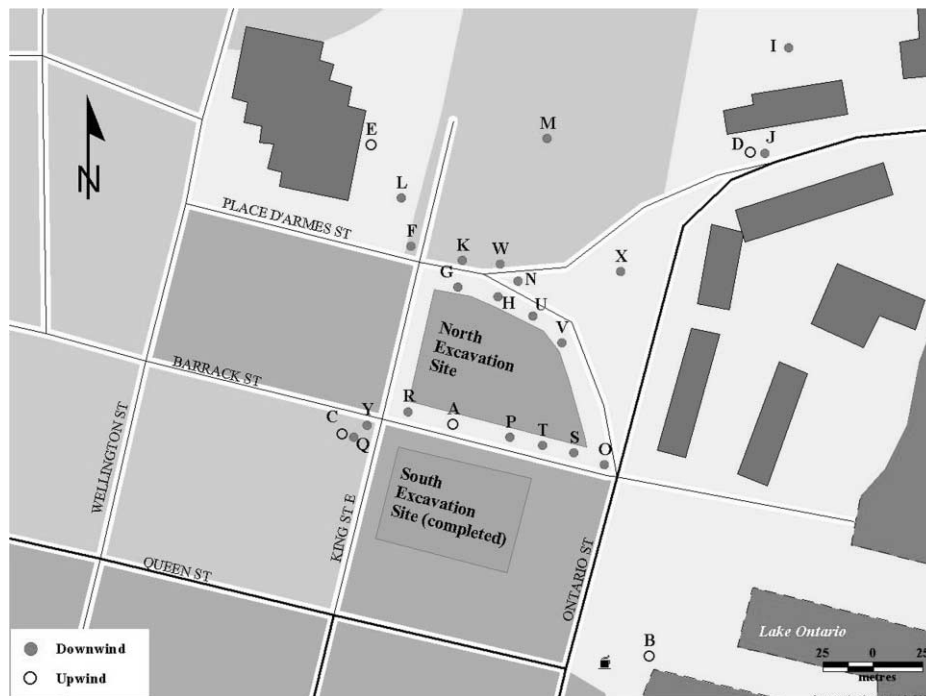


Fig. 7. The upwind and downwind monitoring locations of the TAGA IIe in the vicinity of the coal tar cleanup site in Kingston, Ont. during November 1999.

driven from an upwind location (Site B) to downwind location (Site G) to determine the highest ground-level concentration of naphthalene. The plume tracking technique showed the real-time concentrations of naphthalene peaking at Site G. Plume tracking results such as these were used in the selection of downwind monitoring locations and to isolate the target emission source from other potential sources.

4.1. Contaminants detected

During cleanup activities eleven chemicals were identified by the TAGA IIe. Eight contaminants were selected for more comprehensive monitoring: naphthalene, methyl naphthalene, biphenyl, benzene, toluene, C₂-benzene (xylene isomers), C₃-benzene (trimethyl benzenes) and styrene. In total, 168 half-hour concentration measurements of these eight contaminants were determined over 16 days that the mobile TAGA monitored.

4.2. Naphthalene

The highest recorded half-hour average concentration for naphthalene was 250 µg/m³. In 75 of the 168 (45%) half-hour samples, the concentration of naphthalene exceeded the

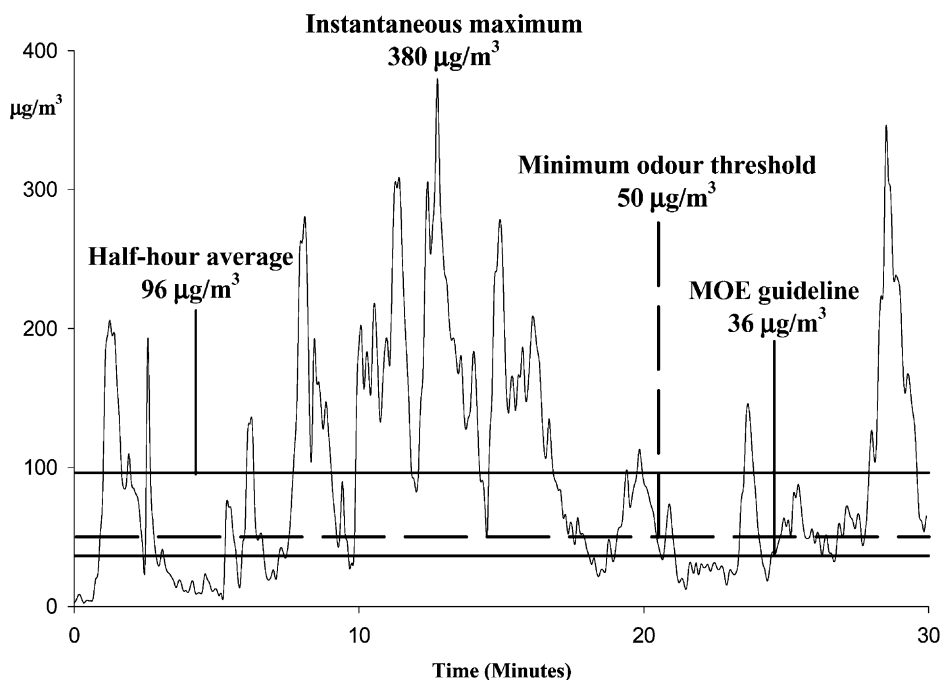


Fig. 8. A real-time half-hour sample of naphthalene using the P/D ion pair of 128/78 obtained by the TAGA II downwind of the coal tar cleanup site (Site G, Fig. 5) in Kingston, Ont. during November 1999.

Ministry guideline of $36 \mu\text{g}/\text{m}^3$. Fig. 10 shows all half-hour concentrations for naphthalene measured during 16 days in November 1999. During the first few days only clean top soil was being removed from the cleanup site and the naphthalene levels were low. Over the last few days of the cleanup, coal tar was being removed from the bottom of the buried tanks and the naphthalene levels were the highest. On numerous occasions, during each half-hour sampling period, instantaneous levels of naphthalene were as high as $380 \mu\text{g}/\text{m}^3$ compared to the odour threshold of only $50 \mu\text{g}/\text{m}^3$ [6].

4.3. Benzene

Benzene is a known carcinogen and its emissions to the environment are to be prevented or limited to the greatest extent possible [7]. Fig. 11 shows all the half-hour concentrations for benzene downwind of the cleanup site during the 16 days in November 1999. Typical urban levels of benzene are about $1\text{--}5 \mu\text{g}/\text{m}^3$ [8]. Only a few times during the removal of liquid coal tar and transferring it to trucks, were the ambient benzene levels above $5 \mu\text{g}/\text{m}^3$. The overall average half-hour concentration of benzene was $3.6 \mu\text{g}/\text{m}^3$. The highest half-hour average concentration for benzene measured during the cleanup of coal tar was $51 \mu\text{g}/\text{m}^3$.

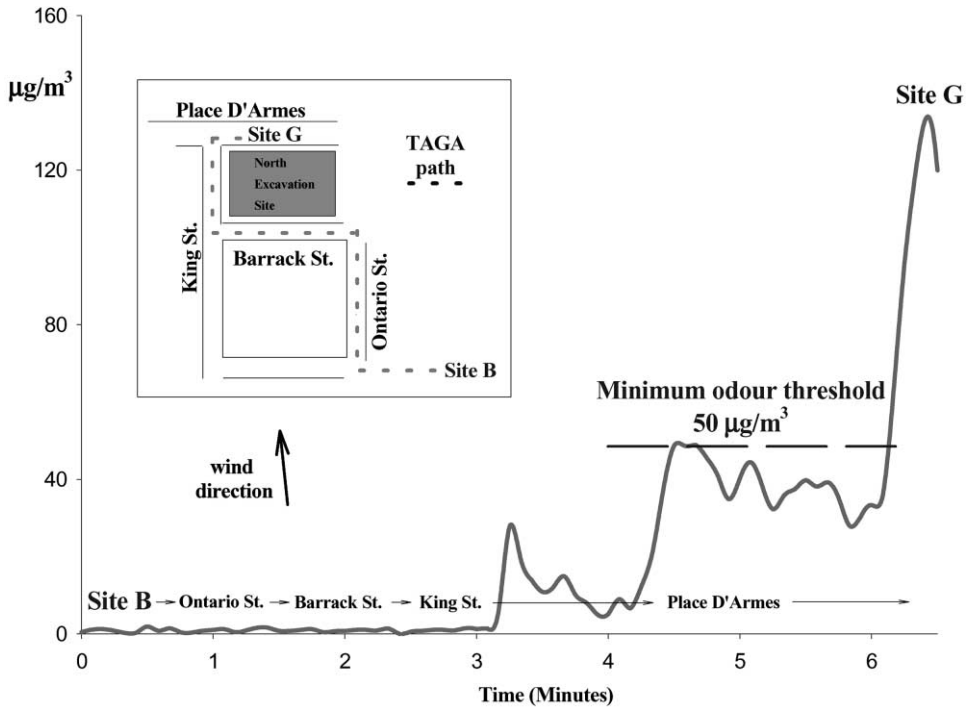


Fig. 9. Real-time plume tracking for naphthalene from Site B (upwind) to Site G (downwind) by the TAGA IIe in the vicinity of the coal tar cleanup site in Kingston, Ont. on 25 November 1999 from 12:59 to 13:06.

4.4. Concentration versus distance

The mobile capability of the TAGA unit was also utilized in determining BTX and PAH concentrations versus distance from the cleanup site. The concentrations of the target compounds were the highest near the perimeter of the cleanup site which was less than 25 m from the excavation area containing the tanks. The ambient concentration of BTX and PAH dropped off rapidly as the mobile TAGA moved further away from the cleanup site. At distances of 100 m or more the target compounds were essentially at background levels.

4.5. Action taken

The air monitoring results that are obtained using this method are unique and the speed with which they are made available allows for rapid decisions to be made concerning on-site activities. The information obtained during on-site surveys are used by the local environmental staff and engineers for assessing the effectiveness of the abatement activities, i.e. the use of odour suppressing foam, wood chips and charcoal vapour filtration. This information can also be used by the Medical Officer of Health to temporarily halt or alter the cleanup activities.

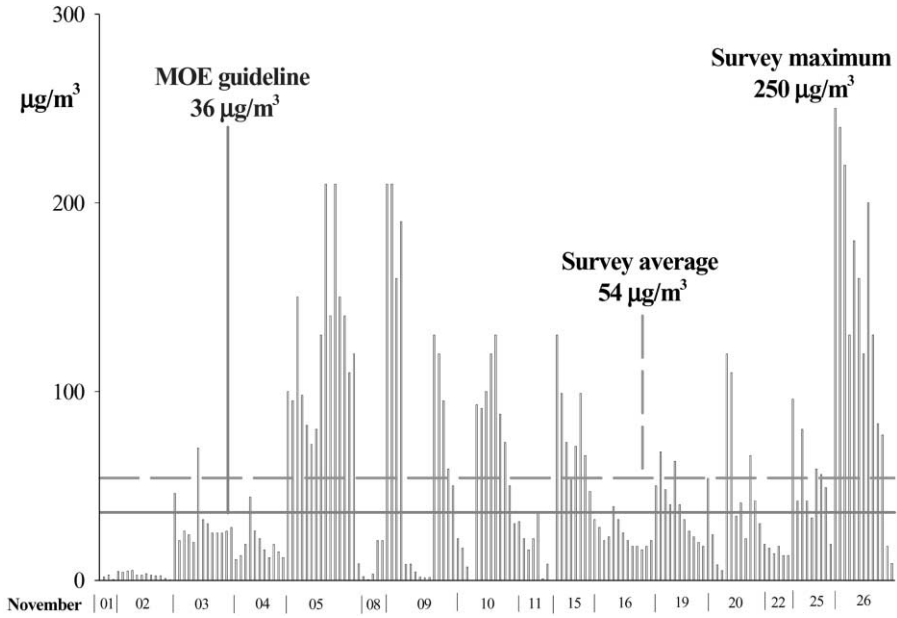


Fig. 10. A survey summary of the naphthalene half-hour concentrations measured by the TAGA IIe at several sites downwind of the coal tar cleanup site in Kingston, Ont. during November 1999.

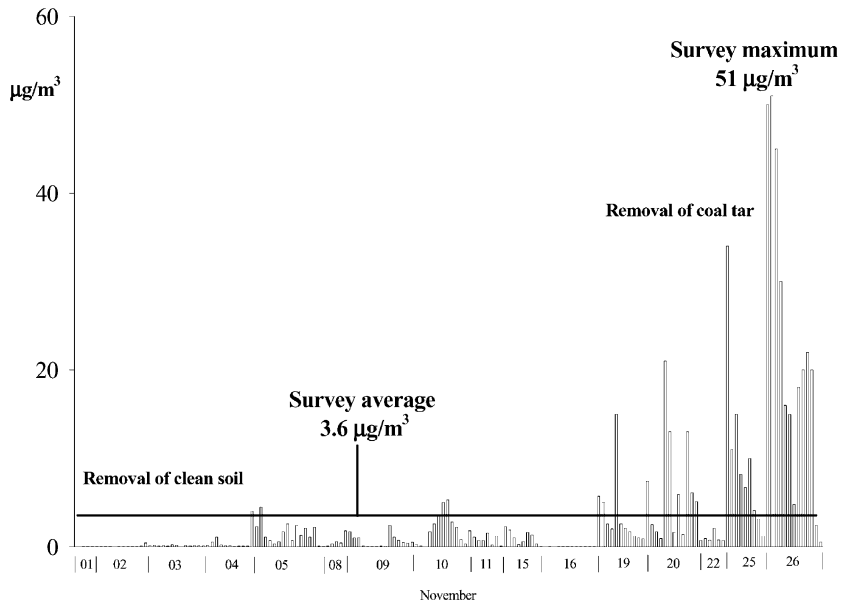


Fig. 11. A survey summary of the benzene half-hour concentrations measured by the TAGA IIe at several sites downwind of the coal tar cleanup site in Kingston, Ont. during November 1999.

5. Summary

A mobile TAGA unit monitored, in real-time, several chemicals emitted during the cleanup of a coal tar site in Kingston, Ont. For this, a new LPCI–MS/MS method was developed based on the mobile TAGA IIe. This new method gave relatively low “background” levels and lower DL than previous APCI–MS/MS methods. This unique technique, proved very useful in the real-time monitoring and reporting of measurements of ambient BTX and naphthalene. Benzene half-hour concentrations up to 51 $\mu\text{g}/\text{m}^3$ and naphthalene levels as high as 250 $\mu\text{g}/\text{m}^3$ were recorded during this survey. Levels of emitted chemicals were monitored daily for 3 weeks during cleanup activities. The information was given to local Ministry of the Environment and health officials for altering or halting the cleanup activities in order to minimize risk to the public.

Acknowledgements

The authors express their appreciation to Ontario Ministry of the Environment TAGA staff (John Merritt and George Rioual), Bill Stott of MDS Sciex and the local Ministry of the Environment staff (Robert Michea and Vic Huggard).

References

- [1] S. Budavari, *The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals*, 11th Edition, Merck & Co. Inc., Rahway, NJ, 1989.
- [2] SCIEX, *Model TAGA IIe MS/MS System Operators Manual*, 1999.
- [3] (a) N.S. Karellas, G.B. De Brou, J.V. Merritt, A.C.W. Ng, Research and method development for real time detection of HCl in ambient air using a mobile APCI/MS system, in: *Proceedings of the 38th ASMS Conference on Mass Spectrometry and Allied Topics*, Tuscon, Arizona, 1990, p. 1479;
(b) N.S. Karellas, A.C.W. Ng, G.B. De Brou, Real-time detection of airborne pentachlorophenol (PCP) by mobile APCI MS/MS, in: *Proceedings of the 40th ASMS Conference on Mass Spectrometry and Allied Topics*, Washington, DC, 1992, p. 989;
(c) N.S. Karellas, A.C.W. Ng, G.B. De Brou, Measurements of hazardous PAHs in ambient air using SFE/LC/MS, in: *Proceedings of the 88th Annual Air and Waste Management Association*, San Antonio, TX, USA, 1995.
- [4] M.D. Corbridge, A.C.W. Ng, G.B. De Brou, On-site analysis of landfill hazardous air pollutants, in: *Proceedings of the 88th Annual Air and Waste Management Association*, San Antonio, TX, USA, 1995.
- [5] N.S. Karellas, G.B. De Brou, A.C.W. Ng, Application of a mobile MS/MS air monitoring system during PCB incineration in Smithville, Ont., in: *Proceedings of the 8th Technical Seminar on Chemical Spills*, Vancouver, BC, 1991, p. 189.
- [6] (a) L.J. Van Gemert, A.H. Nettenbreijer, *Compilation of Odour Threshold Values in Air and Water*, The Netherlands, 1977;
(b) *Odour Characteristic: Reference Guide to Odour Thresholds for Hazardous Air Pollutants Listed in the Clean Air Act Amendments of 1990*, US-EPA, March, 1992.
- [7] Standards Development Branch, *Summary Point of Impingement Standards, Point of Impingement Guidelines, and Ambient Air Quality Criteria (AAQC)*, Ontario Ministry of the Environment, November 1999.
- [8] *Air Quality in Ontario—A Concise Report on the State of Air Quality in the province of Ontario*, 1997, ISBN 0-7778-9169-7.