

# Real Time On-Site Odor and VOC Emission Measurements Using a zNose™

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## Remediation Site Description

Remediation of contaminated soil from where coal-fired power generators dating back to the mid-1800s once operated is an environmental priority for present day utility companies. Contaminated soil is excavated and removed to a remote location where hydrocarbons are removed and the clean soil returned for use as landfill. As a result of on-site excavation, hydrocarbons from coal tars are released into the air. Some are toxic and their concentration is regulated by the US EPA while others are just perceived by humans as noxious odors. Because of the negative impact of these emissions on the surrounding community, site managers need to monitor and minimize the release of volatile organic compounds and odors.



Figure 1- Excavation at remediation site involves removal of coal tar contaminated soil

## Odor Chemistry

Odor chemistry can be estimated from an analysis of soil samples by an independent laboratory. The names and concentration of the individual compounds contaminating the soil are then known. Physical properties of each compound, such as molecular weight or boiling point provide an estimate of the odor chemical signature. For a site contaminated with coal tar, the major VOC is naphthalene which has an odor threshold of 27 ppbv.

Compound	Mol. Wt.	ug/m3
Benzene	79	100
Toluene	93	100
Styrene	104	450
Ethylbenzene	106	400
o-Xylene	107	350
1,3,5 Trimethylbenzene	121	300
1,2,4 Trimethylbenzene	122	720
Naphthalene	129	11800
2-Methylnaphthalene	143	2700
Acenaphthalene	153	3800
Dibenzofuran	168	1000
Phenanthrene	178	7200
Anthracene	179	1800
Fluorene	187	1800
Benz[anthracene	193	2000
Fluoranthene	202	6000
Pyrene	206	4600
Chryzene	229	3600

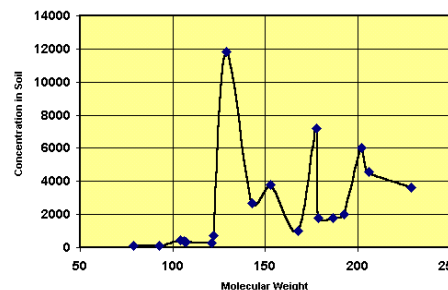


Figure 2- Laboratory analysis of contaminated soil provides a first order approximation of odor signature based upon molecular weight.

## Odor Measurement Method

A new type of portable electronic nose, called the zNose™, can now perform on-site chemical measurements of VOC emissions and odors in near real time. This electronic nose separates and quantifies the hydrocarbon chemistry of odors in 10 seconds. Using a new solid-state detector, part per trillion sensitivity and universal selectivity is achieved.

Performance of the technology has been validated by the US EPA's Environmental Technology Verification (ETV) program. Quality control of odor measurement methods is the same as used in laboratory testing. The instrument also uses an optional GPS receiver allowing an odor measurement to be linked to a specific time and location. On-site and off-site measurements of VOC emissions and odors provides real-time information to site managers and is a useful tool for monitoring and controlling the impact of such emissions on the surrounding community.



Figure 3-Model 4100 zNose™ ultra-high speed gas chromatograph

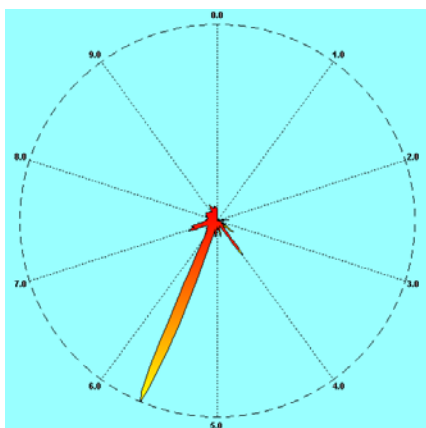
To characterize only the odors from the soil, a 10 gallon bucket was half filled with soil and covered with aluminum foil. After waiting 5 minutes, headspace vapors were sampled and measured. A side-ported GC needle was attached to the inlet of the zNose™ and inserted through the aluminum foil. One milliliter of headspace vapor was removed in 2 seconds and the concentrations of the individual chemicals within the odor measured in 10 seconds. Although 27 different compounds were separated, the major hydrocarbons and their concentrations were Benzene (9.5 ppm), Toluene (5.7 ppm), m,p-Xylene (12.6 ppm), Naphthalene (17 ppm) and methyl-naphthalene (2.5 ppm). Interference or background odors were not a problem due to the high concentration of VOCs in the soil headspace vapors.



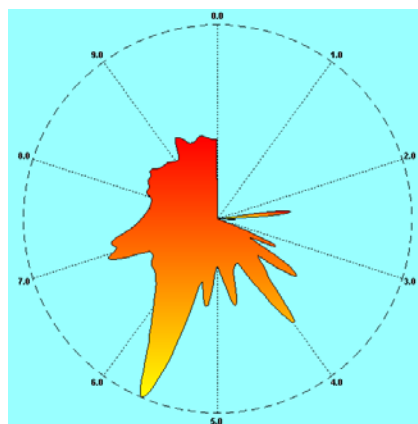
**Figure 4- Soil odors were tested in foil covered buckets. A characteristic odor signature for the site was obtained by measuring the headspace vapors.**

## On-Site Odor Measurements

A patented solid-state detector directly measured odor intensity Vs elution time from a GC column which was temperature programmed from 40°C to 200°C at rates as high as 20°C per second. Sensitivity was controlled by (1) the temperature of the detector and (2) the amount of the vapor sampled. The concentration of chemical vapors from contaminated soil in a closed environment was high and odors could easily be evaluated using only a 1-milliliter vapor sample and a relatively hot 80°C detector. Background odors from ambient air was not a factor at these high odor concentrations.



**Figure 5- Linear odor intensity (radial direction) vs elution time from GC column (angle) with start and stop time at 12 o'clock position.**



**Figure 6- Logarithmic odor intensity (radial direction- 100 to 1 span) vs elution time from GC column (angle) with start and stop time at 12 o'clock position**

Olfactory images, called VaporPrints™, are high-resolution 2-dimensional images based entirely upon the relative concentrations of the individual chemicals making up an odor. The image is a polar plot of the odor intensity (radial direction = sensor signal) and retention time (volatility). Complex odors can be recognized by their characteristic shapes based upon the odor's unique chemistry. In effect the olfactory image allows the olfactory response to be transferred to a visual response. Humans and computers are well suited to the analysis and recognition of visual patterns. In addition, computer processing of olfactory images allows for identification, quantification and comparison of individual chemicals within the odor.

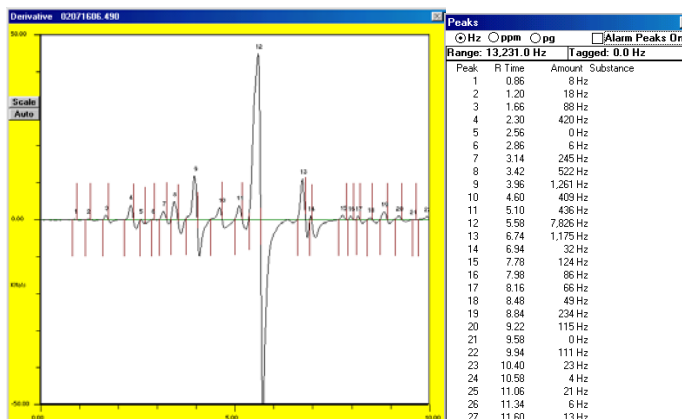
## Odor Chemistry

The solid-state detector measures the concentration of the odor chemicals directly and retention times for each of the chemicals detected are determined by identifying peaks in the GC column flux. Column flux is computed in real time by mathematically performing the time derivative of the detector signal. The result is a chromatogram spanning 10 seconds and representing the rate of adsorption and desorption of vapors onto the detector. The compounds are separated and identified by their unique retention times. Tabulating the retention times together with the individual and total concentration counts (cts) provides a quantitative measure of the chemicals within an odor.

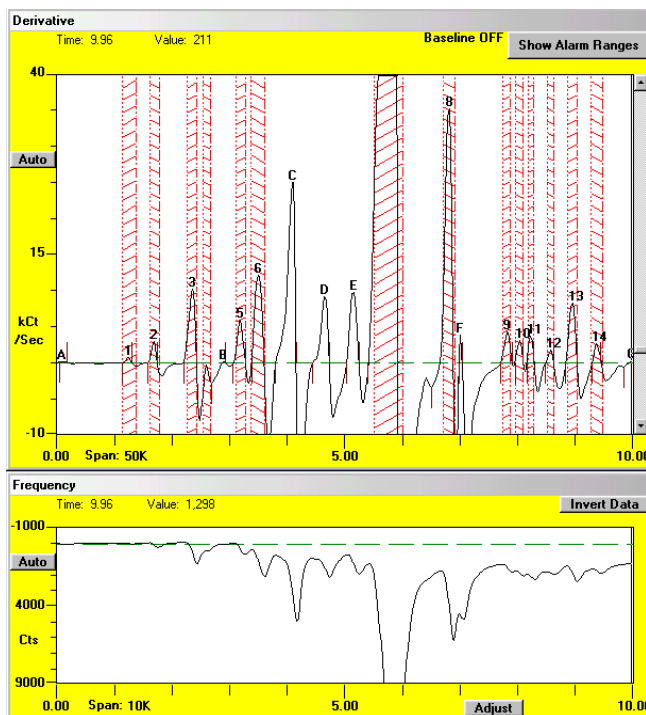
Automatic quantification and tabulation of individual chemicals within an odor is achieved by defining alarm bands centered on the individual retention times of each chemical peak. A narrow range in time is defined for each compound to be measured. Defining bands and alarm levels for specific chemicals within an odor results in a virtual array of chemical sensors specific to that odor. Using alarm bands, each peak is automatically

Peaks				
Range: 13,231.0 Hz Tagged: 0.0 Hz				
Peak	RT	Amount	Substance	
A	0.080	5 Cts		
1	1.240	69 Cts	Benzene	
2	1.680	289 Cts	Toluene	
3	2.340	1,373 Cts	m,p Xylene	
B	2.880	111 Cts		
5	3.180	642 Cts	135 TMB	
6	3.480	1,599 Cts	124 TMB	
C	4.080	3,787 Cts		
D	4.640	1,077 Cts		
E	5.140	1,174 Cts		
7	5.860	23,276 Cts	naphthalene	
8	6.800	4,474 Cts	2M-Naphthlene	
F	7.000	109 Cts		
9	7.800	459 Cts	Acanaphthalene	
10	8.020	256 Cts	Dibenzofuran	
11	8.220	255 Cts	Fluoranthene	
12	8.560	143 Cts	Phenanthrene	
13	8.940	903 Cts	Anthracene	
14	9.360	239 Cts	Fluoranthene	
G	9.960	41 Cts		
H	10.160	140 Cts		

**Figure 8- Peak identification table listing identified compounds in RED together with their retention time and concentration counts.**



**Figure 7- The derivative of odor intensity is a chromatogram used to determine chemical retention times. Using a 10-second analysis of the soil odor, 27 different compounds, their individual intensity, and the total of all intensities is tabulated.**



**Figure 9- Top trace shows alarm bands (in RED) which are used to identify individual chemicals and compare their concentration (lower trace) to a user defined alarm level.**

identified, measured, and compared with a user defined alarm concentration level. Identified peaks are displayed in a peak list in RED together with their retention time and concentration counts.

## Naphthalene Calibration

A known vapor concentration of target chemicals (standard vapor) is used to calibrate the detector response. Injecting a container of a known volume with a known amount of a volatile chemicals creates a standard vapor. Calibration response factors can be single point or multi-point and are linked to specific instrument sensitivity settings. Variable sensitivity is achieved by changing the vapor sample size (sampling time) or the temperature of the detector. Using a one milliliter vapor sample of naphthalene standard vapor, the response factor is 0.5 counts per ppbv with an 80°C detector. Cooling the detector to 20°C increases the response factor to 7.5 cts/ppbv. Increasing the sample size to 15 milliliters gave a response factor of 300 cts/ppbv and a minimum detection level of 100 parts per trillion.



Figure 11- Calibrating with standard vapor concentration.

T (°C)	Response	Counts/ppb
10	6456	12.4
20	3881	7.5
30	2378	4.6
40	1467	2.8
50	901	1.7
60	597	1.2
70	352	0.7
80	250	0.5

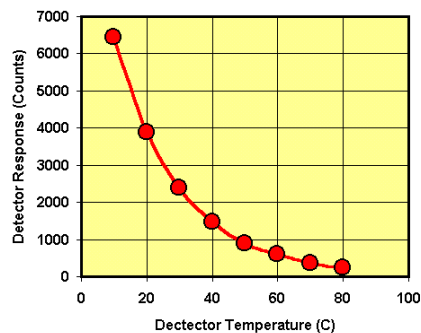


Figure 10- Naphthalene sensitivity Vs detector temperature with a 1-milliliter vapor sample.

## N-Alkane Calibration

Often vapor standards for all chemicals at a site are not available. Many times too, the exact chemical name of a detected compound is unknown, yet it is still possible to identify the compound by indexing its retention time to that of a known chemical. Identification is most often done by indexing the unknown compound's retention time to that of the n-alkanes and then searching a library of indices for a match. An expandable library of chemical smells and indices, called Kovats indices, is part of zNose™ software and is based upon the measured retention times from a n-alkane vapor standard. This is a convenient method of calibrating and tentatively identifying unknown odors in the field because it requires only one calibration standard for all compounds contained within the user library of smells and Kovats indices.

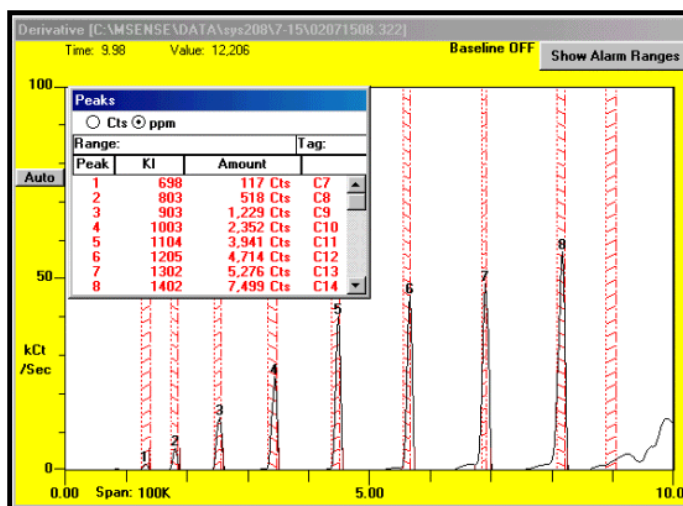


Figure 12- System response to a vapor standard containing n-alkane vapors C7 to C14. Indexed compound retention times relative to that of an n-alkane is called Kovats Indices.

## BTXX and BTEX Calibration

Calibration vapor standards for benzene, toluene, ethylbenzene, and the m,p, and o-xylene were created by filling tedlar bags from gas canisters with certified concentrations of these compounds. One standard vapor, BTEX, contained 1 ppm of benzene, toluene, ethylbenzene, and o-xylene. Another standard vapor (BTXX) contained 1 ppm benzene, toluene, and 1 ppm of each of the three xylenes.



Figure 13- Tedlar bags make constant concentration vapor standards for calibration of the zNose™.

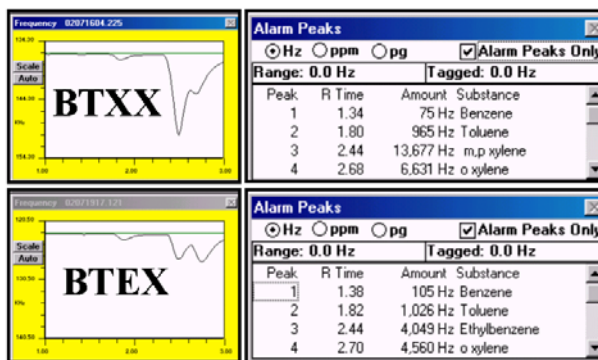


Figure 14- Expanded response to BTXX and BTEX calibration vapors.

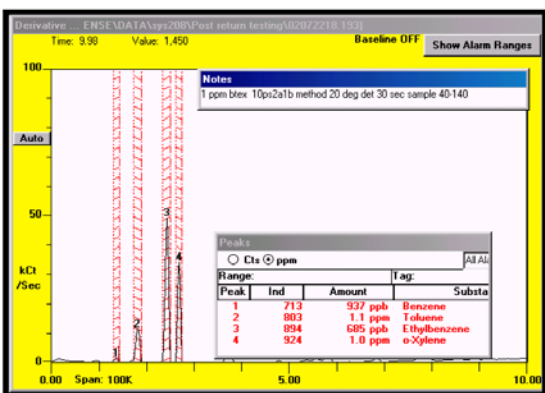


Figure 15- Response and alarm window settings for 1 ppm BTEX.

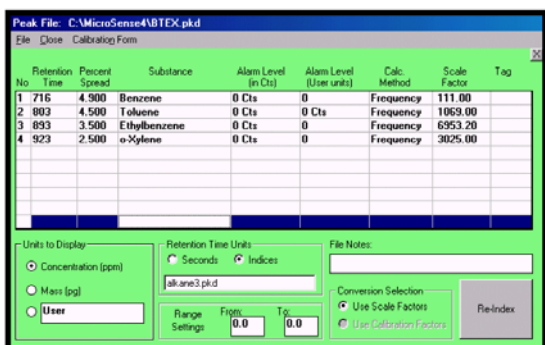


Figure 16- Peak identification file for BTEX standard vapors. Retention times are listed as Kovats indices and response factors are per ppm.

Because m and p-xylene co-elute they cannot be separated easily from each other or from ethylbenzene. Two other compounds at this site, benzene and thiophene, also had identical retention times. However, because co-eluting compounds have similar response factors, total concentrations were measured and calibrated as total m-,p-xylene. Software allows the user to graphically select alarm bands, retention time, alarm levels or odor thresholds for selected chemicals within an odor. Peak identification and response factor data is stored in files containing all relevant calibration information for specific odors.

Sensitivity to the BTXX and BTEX standard vapors was characterized by response factors in counts (cts) per ppm. For the lightest compound, benzene, the response factor was approximately 100 cts/ppm using a 15 milliliter vapor sample (30 second sample time) and a 20°C detector. Using replicate measurement methods, the minimum detection level was approximately 300 ppb. Lowering the detector temperature to 0°C increased sensitivity and lowered the minimum detection level for benzene to 40 ppbv. Response factors were proportionally larger for higher molecular weight compounds such as 3000 Cts/ppm for o-Xylene and 30,000 cts/ppm for naphthalene. Retention times were expressed in seconds or as Kovats indices referenced to a file containing the system response to n-alkane vapors.

## Outside Air Measurements

Odors and their intensity within and surrounding the remediation site were measured in real time at several locations. One location, downwind from the site, was next to an entrance gate approximately 100 feet from where active excavation was being carried out. Ambient air was sampled by placing the zNose™ on top of a 3 foot high concrete wall facing into the site.

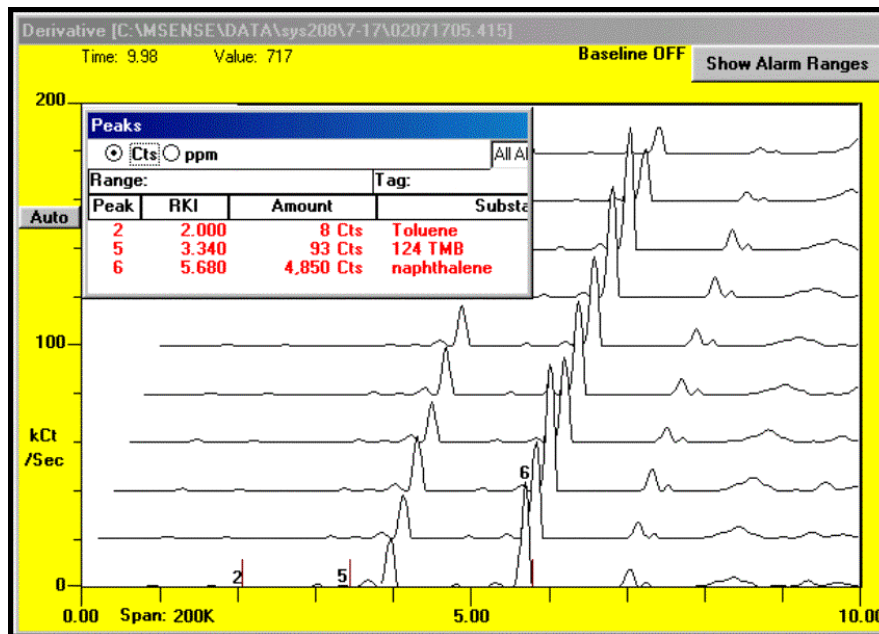


**Figure 18- Downwind location (arrow) near active excavation of contaminated soil.**



**Figure 17- Real time monitoring of site odors located at street entrance (downwind).**

Repetitive measurements of the site odors were taken every 80 seconds using a 30 second vapor preconcentration (15 milliliters) followed by a 10 second analysis time and 30 second recovery. Offset chromatograms in Figure 19 show a sequence of 10 analysis runs which began at approximately 9 am, shortly after active work on the site had started. Over a 50 minute period 35 measurements were taken.



**Figure 19- Consecutive measurements were taken every 80 seconds using a 30 second sample time, 10 second analysis, and 30 second recovery time. The prominent peak at 5.7 seconds is naphthalene.**

Since site odor chemistry was dominated by naphthalene and methyl naphthalene these two compounds were used to monitor the odors being released from the site. Other, trace elements within the odor, are expected to vary in proportion to the concentration of these compounds.

The intensity of site odors showed considerable short term variation in odor concentration and in the warm afternoon concentrations were higher than during the cooler morning hours. During a one hour period in the morning the concentration of naphthalene varied from 15 to 10 ppbv with an average of 11.4 ppbv. The variability of the odor concentration was reflected in a standard deviation of 43% for 35 consecutive measurements. Since the odor threshold for naphthalene is 27 ppbv, morning odors at this time and location might be undetectable.

Measurements taken at the same downwind location over a 10 minute period in the late afternoon indicated a substantial increase in the concentration of naphthalene odors. Following an upward trend, naphthalene concentrations as high as 60 ppbv, well above the odor threshold of 27 ppb, were measured.

Ambient air within 10 feet of contaminated soil showed high odor concentration as expected. Soil piles arranged into open bins and awaiting treatment with chemical and biochemical odor reducing agents was tested over a 1 hour period in the late morning. Although the location was somewhat sheltered from winds, the concentration of naphthalene and methyl naphthalene still showed large short term variations and routinely exceeded the odor threshold.



Figure 22- Ambient odors were measured near soil being treated to reduce odors.

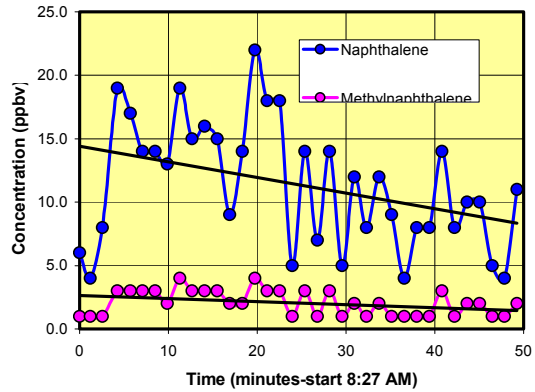


Figure 20- Concentration of Naphthalene and Methyl Naphthalene at downwind location.

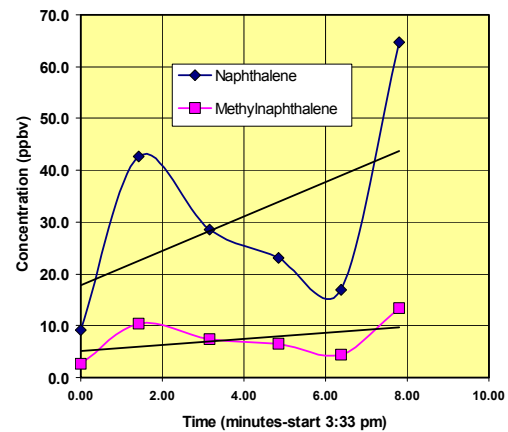


Figure 21-Concentration of Naphthalene at downwind location in afternoon

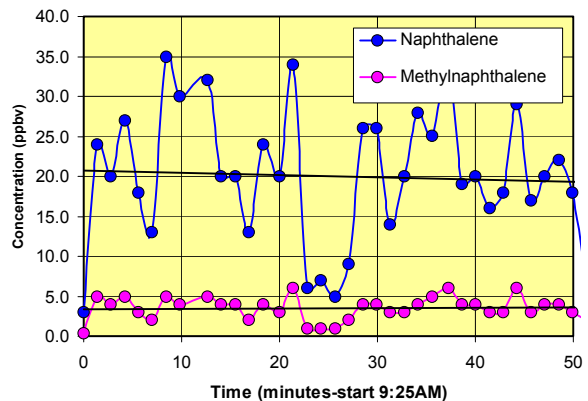


Figure 23- Naphthalene odor concentration near soil bins.

## Summary of Results

A new type of electronic nose based upon ultra high-speed gas chromatography now allows the chemistry of odors to be quantified in near real time with laboratory precision and accuracy. Over a 3 day period more than 800 odor measurements were performed at different locations in and around a soil remediation site contaminated with coal tar. A visual olfactory image based upon chemical measurements clearly indicated naphthalene was the dominant chemical compound in the site odor, although many other hydrocarbon elements were also present at lower concentrations. The sensitivity of the instrument allowed odor chemical concentrations at low ppt levels to be measured quickly and easily.

Headspace vapors in foil-covered bucket samples of contaminated soil showed vapor concentrations at part per million levels. Chemical vapor concentrations of benzene (9.5 ppm), toluene (5.7 ppm), m,p-Xylene (12.6 ppm), naphthalene (17 ppm), methyl naphthalene (2.5 ppm), and numerous trace elements were measured and their relative concentrations defined the odor signature (VaporPrint™) of the site.

Ambient air vapor concentrations in close proximity to contaminated soil (less than 1 foot) were in the low 1-10 ppm concentration range. Odor concentrations at a downwind location next to the site (approximately 200 feet from active excavation) were in the 10 to 50 ppb range. Upwind odor concentrations were much lower, typically in the part per trillion range. Replicate odor samples (30 second) taken at 80 second intervals showed considerable short term variability e.g. 43% standard deviation for 35 samples. Morning levels of naphthalene were slightly below odor threshold levels (27 ppbv) while afternoon levels were substantially higher, typically 60 ppbv downwind adjacent to the site.

Because the electronic nose is based upon the science of gas chromatography, odor measurements can be easily confirmed and validated by independent laboratory measurements taken on quality control samples collected at the site. The ability to rapidly perform analytical measurements on-site in real time provides site managers with a cost effective new tool for monitoring volatile organic compounds and minimizing the impact of site odors on the surrounding community.