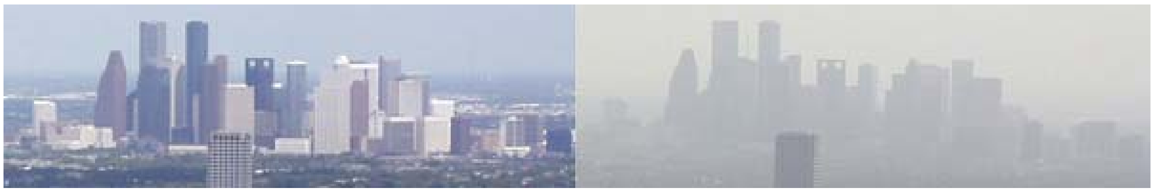


# Galveston Houston Association for Smog Prevention
# Air Monitoring Activities
# 2005-2008

## Introduction

The Houston region is the location of some of the most extensive ambient air monitoring anywhere in the world. Only the Los Angeles region even comes close. Nevertheless, many of us believe that the air monitoring done here is insufficient to protect the health of our region's citizens.

Starting in the spring of 2005, the Galveston-Houston Association for Smog Prevention (GHASP) began evaluating monitoring technologies that could be deployed by citizens. This effort was financially sponsored by a private donor to GHASP. The executive director at that time decided to focus on ozone at unmonitored locations. Some locations stood out not merely because they were unmonitored, but because models suggested they might have elevated levels of ozone.

After discussing monitoring with local experts who described newer, less-expensive and less-complicated methods, the executive director decided to expand GHASP's monitoring evaluation to include other forms of air pollution, especially air toxics and particulate matter. While the Houston region is in compliance for particulate matter, levels at some monitoring sites have long hovered near non-compliance. Air toxics have no federally enforced levels, so non-compliance is not the issue. Houston has a reputation for having some of the highest levels of some air toxics anywhere. Health effects attributed to some of this category of pollutants are known to occur in the Houston region in numbers larger than most other parts of the U.S.

Building a case for a causal relationship between air pollution and disease requires, at the very least, extensive monitoring data. This data must be gathered where humans spend their time or it must include information that will allow reasonable inference about pollutant concentrations in these places. Otherwise inferences about human exposure will not likely be meaningful and may include unmanageable levels of error.

The Houston regulatory air monitoring network was initially designed for purposes that at best only marginally include health effects inquiry. The city of Houston alone is spread out over six hundred square miles. Therefore the significant gaps in the region's comparatively extensive ozone monitoring network should be no surprise. Regulatory monitoring of air toxics is done at only a few of these air monitoring sites.[1] Also, while monitoring of particulates is comparatively more extensive, the network is also limited and cannot provide data about particulate concentrations where some of the most at risk Houstonians breathe most of their air. GHASP wanted to see if monitoring near homes or other unmonitored areas would confirm expectations derived from data collected at existing monitoring sites. GHASP also wanted to test models, especially those created by the University of Houston's Institute for Multidimensional Air Quality Studies. GHASP began recruiting volunteers to conduct this monitoring. GHASP contacted local experts, including researchers at Rice University and the University of Texas Houston Health Sciences Center School of Public Health (UT-SPH), to discuss method options.

Citizen-based monitoring is not a new concept. As early as 1890, the National Weather Service accepted weather data from non-professional citizens.[2] In the early part of the 20$^{th}$ century, citizens gathered and maintained data about birds in the United States under the Audubon Society's Christmas Bird Count program. In the early 1960s, many U.S. citizens participated in monitoring of water quality. Citizen-based air quality monitoring has also been conducted in the US, notably in New York and Massachusetts.[3] GHASP became interested in this approach because it could be used to check regulatory performance, especially in areas where regulatory agencies didn't have much data, as a tool for educating the public, and, most of all, as a tool for rapid warning of susceptible populations.

To meet this last goal, GHASP began seeking instrumentation that could provide closer to real-time concentration estimates of pollutants under the assumption that public health is significantly impacted by delayed information. Regulatory agencies typically do not provide real-time data because they have time-consuming quality control and quality assurance regimens. To be fair, this is due to a high standard of data integrity required for data used for permit enforcement. There exists also a portion of the populace who believe that minimization of costs associated with health warnings should be paramount. GHASP adopted the position that real-time data, even if it has not been subjected to rigorous validation, allows more opportunity for health conscious responses to air quality events. If cost is the primary concern, GHASP believes, it should include expenses related to health outcomes such as lost school or work time and emergency room visits or hospitalization.

Citizen-based environmental monitoring is often regarded with suspicion by the regulatory and scientific communities. Neutrality cannot be assumed for what are often activist citizens, and scientific and statistical methods can be extremely complex. Nevertheless, numerous regulators and scientists take a more activist role and attempt to sponsor citizen-based efforts.[4,5] These professionals have been described as “experts who are willing to support communities in their efforts to seek recognition and assistance from industry or government.’’ [5]

After discussions with scientists, regulatory personnel and instrument vendors, GHASP was able to locate technologies that were relatively cheap and could be used to obtain ambient concentration estimates for ground-level ozone and ultra-fine particulate matter ($PM_{2.5}$). A third method, for sampling and analysis of gas-phase toxics, was suggested by a GHASP volunteer who had done research into alternative methods for toxics sampling and analysis while working as an intern at the city of Houston’s Bureau of Air Quality Control (BAQC).

For ozone, GHASP selected products designed and manufactured by a company out of Auckland, New Zealand. This company, Aeroqual, Ltd., manufactures a variety of ozone devices including hand-held personal monitors as well as stationary industrial units. Their monitors are based on a proprietary gas sensitive semiconductor, and they are widely regarded as accurate and reliable. Hand-held units were priced in the $900-$1500 range. Stationary units were slightly cheaper.

For $PM_{2.5}$ monitoring, an expert at Rice University recommended a technology called beta-attenuation. This technology utilizes an industry standard ultra-fine particle cyclone to selectively “grab” a $PM_{2.5}$ sample. The sample is then quantified using Beer’s Law applied to attenuation by the sample of a stream of beta particles aimed at a calibrated detector. One manufacturer of this type of instrument, Met-One Instruments, had already been selected by the US Environmental Protection Agency (EPA) as a vendor of particulate monitors. The EPA had favorably evaluated one of their units, which sold at around $10,000.

For air toxics, GHASP selected a technology called “solid phase microextraction” or SPME. Many methods for quantification of air toxics exist, but most are either exorbitantly expensive (meaning in the greater than $100,000 range) or extremely complex and labor intensive. SPME offers many simplifications, has been demonstrated to be deployable in the less than $25,000 range, and numerous scientific papers attest to its sensitivity to a variety of toxics at levels similar to those observed by the EPA and the Texas Commission on Environmental Quality (TCEQ) in the Houston-Galveston area.

### Ozone Project

As many Houston residents know, the city has never met the ozone standard set with the United States Clean Air Act Extension of 1970. Almost 40 years after the extension was passed, ozone continues to be a significant air quality problem for Houston and is considered a health risk for a number of susceptible populations living in the region. While the EPA, TCEQ, the city of Houston (COH), and Harris County maintain an extensive ozone monitoring network and an email ozone event warning system, many citizens are not adequately and appropriately protected. GHASP decided to evaluate methods for some of the following goals:

- To give citizens access to real-time ambient ozone concentration estimates.
- To do this in a manner affordable for individuals, school districts, and citizen sport leagues.
- To locate a method that yields ambient ozone concentration estimates that correlate without significant bias to estimates generated by more rigorous regulatory methods.
- To have durable devices with operation simple enough for use by non-professionals.
- To have devices portable enough to be carried where the users go during their daily activities.

In the spring of 2005, GHASP purchased three Aeroqual, Ltd. Series 500 handheld ozone monitors and one series 300. The units all used the same sensing technology, but the more expensive series 500 had data-logging capability. The series 500 units were purchased for $1,358 apiece, while the series 300 unit cost $890.

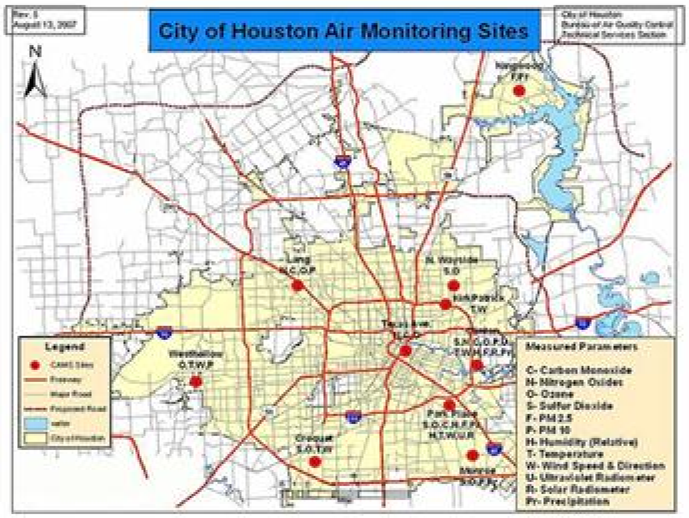



**Figure 1. City of Houston CAMS sites.**
Source: http://www.houstontx.gov/health/Environmental/BAQCnewmap2.jpg. Dowloaded 2/25/08

Before these units could be recommended to the public, they had to be certified against proven methods. GHASP contacted the staff at the city of Houston's BAQC and was given permission to collocate the three series 500 units at city ozone monitoring stations. The series 300 monitor was given to a GHASP volunteer who suffered from chronic obstructive pulmonary disease (COPD) and who liked to call himself an "ozone canary." He was asked to carry the unit with him during his normal daily activities and to keep a journal of this use.

The COH maintains ten "continuous air monitoring stations" (CAMS). From this group, GHASP selected the Texas Avenue, Monroe, and Clinton monitors. These were selected because the three sites each had exhibited a wide range of ozone concentrations including some of the highest observed in the region. The sites were also representative of interesting categories of the Houston landscape: The Texas Avenue site is close to downtown, Clinton is near the Houston Ship Channel, and Monroe is in a suburban setting not far from Houston's Hobby Airport.

Because GHASP wanted to evaluate the Aeroqual units as devices that would be carried by people, a model of a person holding one of the units and standing near a City monitor was adopted. The Aeroqual handheld units do not come with protective housings. Because one potential use was as a device carried to outdoor athletic events, GHASP chose to design an inexpensive, easy to construct protective housing that could cheaply be replicated. This housing could not significantly alter the ozone concentration entering the monitor. GHASP chose a polycarbonate laboratory jug, typically referred to as a "carboy", fitted with an aluminum residential water heater stack cap, and a couple of aluminum bars.

**Figure 2. Polycarbonate carboy with Aeroqual Series 500 ozone monitor.**

Three such containers were constructed, and they were then mounted at the three COH sites during the summer of 2005 between 6/24/05 and 8/15/05. They ran continuously except during major rain events when they were temporarily taken down for protection.

Like many regulatory sites in the EPA's network of ozone of monitors, the COH sites used Dasibi 1008 ultraviolet photometric ozone analyzers. These are listed in the EPA's Reference "List of Designated Reference and Equivalent Methods" as method EQOA-0383-056.[6] They operate under a different principal than the Aeroqual units, and they are large, metal enclosure units that must be installed in a controlled environment with inlet and outlet tubes used to bring in and exhaust outside air. Regulatory agencies conduct rigorous quality control and assurance (QA/QC) on data taken from these devices, and they are regularly calibrated using a National Institute of Standards and Testing (NIST) traceable ozone generator.

Every week or so, a GHASP volunteer downloaded data from the Aeroqual monitors. The Aeroqual units were configured to generate five minute interval average ozone concentration estimates. These units are capable of storing 8,000 data points, so they could theoretically be downloaded once every 27 days.

At the end of the study period, both parametric and non-parametric statistical tests were used to compare hourly concentration estimates generated by the Aeroqual units to those generated by the regulatory agency Dasibis. These tests demonstrated excellent correlation between the Aeroqual units and the Dasibis. The third Aeroqual unit demonstrated more variability in relation to the proximate Dasibi, but overall the Aeroquals were recommended as an acceptable substitute method for the COH Dasibis. A linear regression of data from one monitor compared to its adjacent COH monitor is displayed in Figure 3. A summary of the statistical tests is:

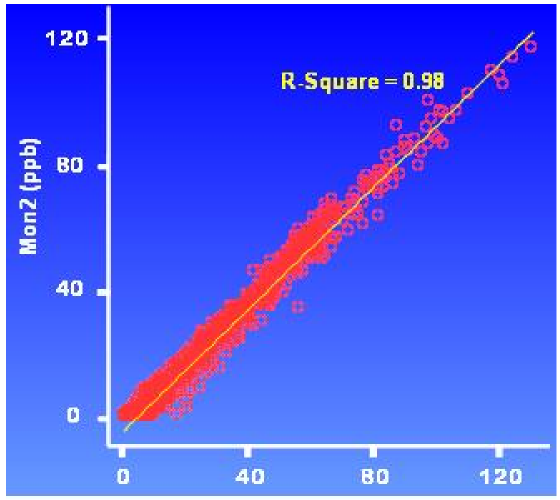



**Figure 3. Regression of Aeroqual to Dasibi at COH Monroe CAMS site 06/24/05 – 08/15/05.**

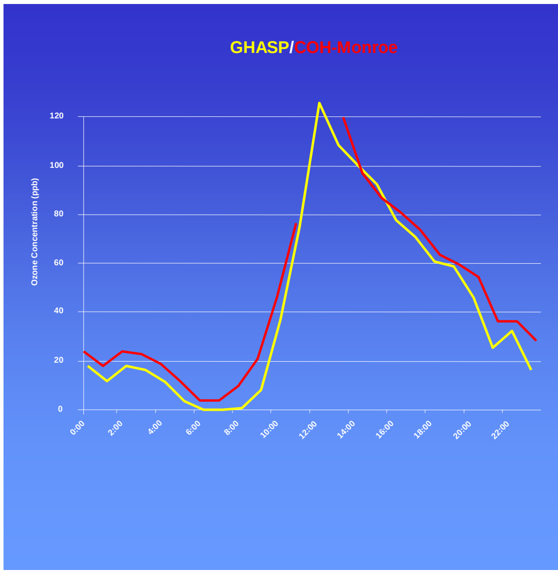
- The handheld monitors were significantly correlated (Pearson's coefficients of .980, .991 and .945 for monitors 1, 2 and 3, respectively) with regulatory monitors (*p*-values <0.01 for monitor 1 and 2 and ~0.05 for monitor 3).
- No trend in change of the difference between monitor 2 and the regulatory Monroe monitor over time was noted. Significant trends over time of increasing Δ between methods (monitor 1 to Texas Ave.) and decreasing Δ (monitor 3 to Clinton Ave.) were noted.

Subsequent analysis of the data collected by GHASP volunteers by David E. Williams, PhD. of the Department of Chemistry of the University of Auckland (New Zealand) offered a possible reason for the drift observed at two of the monitors: The Aeroqual sensor semiconductor is composed largely of tungsten and tungsten exhibits reactivity with hydrogen sulfide. The reaction results in a sulfiding of the sensor material which may decrease the sensor signal. This suggestion is currently being evaluated by Aeroqual scientists. At least in the vicinity of the Clinton monitor, industrial activity is known to produce sulfur gas emissions. Nevertheless, Dr. Williams' conclusion was:

> *Overall, the instrument based on a WO3 semiconductor device matches the performance of a reference spectrometer of many times the size and cost. These simple instruments offer the possibility of very wide-spread, low-cost urban air monitoring.*[7]

Concurrent to the collocation study, a GHASP volunteer carried the series 300 unit with him. The volunteer was a noted local inventor who held more than 50 patents, most obtained when he worked as an engineer for a multi-national oil exploration, drilling and refining company. The volunteer was thus considered more technically competent than most citizens and able to make qualitative judgment about the functionality of the Aeroqual instrument. As stated earlier, the volunteer suffered from COPD and was susceptible to debilitating shortness of breath if he encountered high levels of ozone in his breathing air. The volunteer found the Aeroqual monitor to be an essential item whenever he ventured out of his house. He relied on it to protect him from encountering overwhelming levels of ozone, and he discovered that difficult breathing and general weakness often preceded elevated ozone. This suggested sensitivity to other air components, but this will never be determined because the volunteer succumbed to his disease about six months after the evaluation ended.

In addition to confirming the Aeroqual unit's ability to accurately measure ambient ozone in the Houston area, the collocation study unearthed interesting facts about the regulatory monitoring network. For example, on one day of the study, both the regulatory monitor and the Aeroqual were showing an increasing trend in ambient ozone concentrations that suggested a likely exceedance of the one hour standard. Interestingly, the regulatory monitor was put into maintenance mode and missed the exceedance event. The hourly concentration estimates of the two methods for this day are summarized in Figure 4.




| Hour | GHASP | COH |
|---|---|---|
| 0:00 | 18 | 25 |
| 1:00 | 12 | 19 |
| 2:00 | 18 | 25 |
| 3:00 | 16 | 24 |
| 4:00 | 11 | 20 |
| 5:00 | 4 | 13 |
| 6:00 | 0 | 5 |
| 7:00 | 0 | 5 |
| 8:00 | 1 | 11 |
| 9:00 | 8 | 22 |
| 10:00 | 37 | 47 |
| 11:00 | 75 | 77 |
| 12:00 | 126 | PMA |
| 13:00 | 108 | 121 |
| 14:00 | 100 | 98 |
| 15:00 | 93 | 88 |
| 16:00 | 78 | 82 |
| 17:00 | 71 | 75 |
| 18:00 | 61 | 65 |
| 19:00 | 59 | 61 |
| 20:00 | 46 | 56 |
| 21:00 | 26 | 38 |
| 22:00 | 32 | 38 |
| 23:00 | 16 | 30 |

**Figure 4. GHASP Handheld vs. COH Monitor 8 July 2005 (All Values in Parts Per Billion)**

In February of 2006, the results of GHASP's study of the Aeroqual monitor were accepted for presentation at the 2006 National Air Quality Conference in San Antonio, Texas.[8] This presentation generated quite a bit of interest in the Aeroqual units, and GHASP periodically receives requests for information about the 2005 evaluation from state and municipal regulatory agencies.

The success of the handheld monitor evaluation and the apparent unwillingness of school and youth athletic personnel to purchase the units suggested another application using Aeroqual equipment: installation of stationary monitors at volunteers' homes with a configuration that would allow the monitors to post to a central website.

After evaluation of the connectivity of the Series 500 monitors, GHASP decided to purchase a different model. The model selected, the series 930, was designed for installation in manufacturing facilities and connection to industrial automation control networks. It used the same sensor head as the series 500, but it lacked data-logging because it is intended for installation in a network where data is logged on a computer. GHASP purchased seven of the series 900 units for $1095 each.

During the period between the purchase of the series 500 and series 930, Aeroqual announced a new lower detection ozone sensor. This was called their "ultra-low" head, and all the 930s GHASP purchased came equipped with them. These heads could be scaled to 0.0 to 0.2 parts per million (ppm) ozone sensitivity. As a bonus for the large purchase, Aeroqual added a replacement ultra-low head to be used on one of the series 500 units.

The next step was to come up with a method for connecting the series 930 to the internet. The series 930 includes circuitry and software for an industry-standard communications protocol known as RS-485. This is essentially a two-wire implementation of Electronic Industry Alliance (EIA) standard serial communications. Many devices and adapters have been designed for RS-485, and GHASP began to evaluate those that acted as communications servers. One of these, the SimpleComTools, LLC, Com 1000 seemed especially promising. Unfortunately, after weeks of testing and even custom software design by SimpleComTools engineers, GHASP discovered that Aeroquals' implementation of RS-485 did not allow interoperability with off-the-shelf equipment such as the Com1000. This forced GHASP to explore a different method.

The series 930 also comes with industry-standard variable electrical current output. This is a 4 to 20 milliamp (mA) signal that is attenuated by the ozone sensitive semiconductor installed in the unit. GHASP located a standard industrial automation controller designed to measure and log a 4-20 mA output. This device, the Adam-6017 manufactured by Advantech Industrial Automation, could be configured to broadcast analogue data from the series 930 using another communications protocol known as "user datagram protocol" (UDP).

Selecting locations for the ozone monitors was based on analysis done by John Wilson of GHASP using mapping software. The krieging feature of this software was applied to 2005 regulatory ozone data for the Houston-Galveston area. The product was the map shown in Figure 5. This map suggested ozone "hotspots" in areas west and southwest of the central area of Houston. John Wilson's analysis has been confirmed numerous times, including recently by the TCEQ[9], by members of the 2000 Texas Air Quality Study (TEXAQS I)[10], and by the University of Houston's Institute for Multi-Dimensional Air Quality Studies (IMAQS)[11]. Compare John Wilson's map to one downloaded from a report on the University of Houston's modeling in Figure 6.[11]

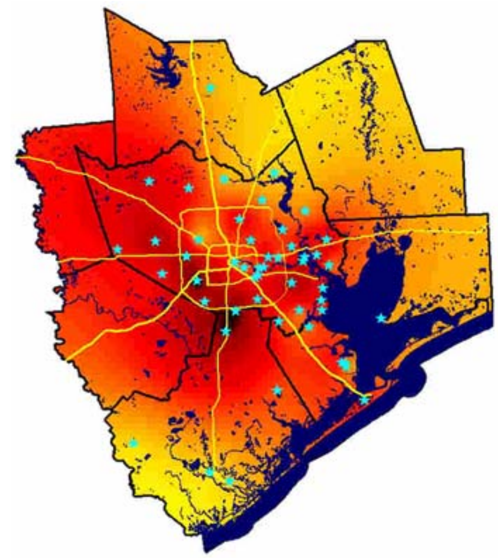


Figure 5. Krieging of 2005 Ozone Monitor Data in the Houston-Galveston Area

Based on John Wilson's analysis, GHASP began locating volunteers who could host ozone monitors in Fort Bend, Liberty and Waller Counties. GHASP then hired a web developer to create a website for the ozone data. This developer was hired with a contract which included deadlines for various project milestones. Concurrent to the start of his work, GHASP volunteers began meeting with volunteer monitor site hosts and installing the Aeroqual and Advantech units.


Figure 6. University of Houston IMAQS model results of Houston-Galveston ozone concentrations on 8/23/06.

Once the first site was brought online, a limitation of the communication protocol, UDP, was discovered. To save money on web hosting, GHASP uses what is called a "shared-server" by the web hosting industry. This means that the GHASP website resides on a fileserver that is shared by other customers of the web hosting firm. This necessitates a higher level of security for each website. Because of this higher security, the UDP packets coming from the Aeroqual equipment were blocked by the web hosting firm's firewall. The web hosting firm refused to change this, so GHASP had another problem to solve.

The solution involved configuring a file server at GHASP's offices that could accept the UDP packets, convert them to a different protocol, and then deliver them to the website using a safer protocol. GHASP decided to use the open-source operating system Linux because it can be obtained practically for free and because it can be run on older, less expensive hardware.

The web developer quickly designed an attractive and functional website. GHASP volunteers installed Aeroqual monitors in Sugarland, Hempstead and The Woodlands. A fourth was added to a volunteer's house in central Houston so that problems with the network could be conveniently troubleshot. Figure 7 summarizes the network.

After a couple of false starts, and issues with replacement of the ozone sensor heads, the GHASP website went live with the start of the 2008 ozone season. This is likely the first community-based, networked air quality monitoring system anywhere in the world. One can reach the site at http://www.ghasp.org/monitor.

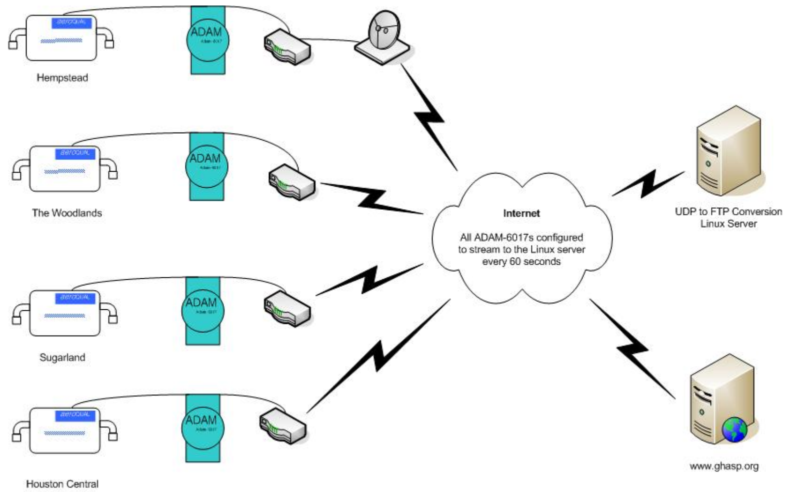



**Figure 7. GHASP Ozone Monitoring Network**

As soon as the network was brought online, the higher than expected ozone concentrations predicted by GHASP's mapping software were confirmed. These were tested by taking one of the handheld series 500 instruments out to the sites after it had been checked against the Texas Avenue regulatory monitor. Similar observations of higher than expected ozone concentrations at locations without regulatory monitors were made by Environmental Defense in 2003.[12]

The GHASP ozone monitor website has many features. These include allowing a user to download ozone concentration data from a specific site or to generate various reports on the GHASP website.

GHASP staff and volunteers continue to iron out problems with both the website and the ozone network. A number of issues remain, but GHASP staff and volunteers continue to work with the web developer and the manufacturers of the various components of the network on solutions.

**Particulate Project**

In May of 2006, GHASP made a press announcement that the Houston region had very likely exceeded the federal standard for 2.5 micron particulate matter ($PM_{2.5}$) for the first time.[13] At the time of the press release, the federal standard for $PM_{2.5}$ was a 24 hour average concentration of 65 micrograms per cubic meter ($\mu g/m^3$) and an annual average of no more than 15 $\mu g/m^3$.[14] A few months later, the 24 hour concentration average was tightened to 35 $\mu g/m^3$, but the annual average was retained.

GHASP's analysis of 2005 $PM_{2.5}$ data from the Clinton site indicated that, while the main $PM_{2.5}$ at the site was right at the 15 $\mu g/m^3$ limit, the backup monitor's data showed an annual average of 15.33 $\mu g/m^3$. This observation did not result in Houston's designation as a $PM_{2.5}$ non-attainment area, but it did spur greater scrutiny of the increase in local transportation, especially ship and tractor trailer, adjacent to the Clinton monitor.

A month or so prior to GHASP's announcement, the organization had purchased a device for measuring $PM_{2.5}$. This device, the Met-One Instruments E-BAM, is a portable beta-attenuation monitor that had been recommended by an air monitoring expert at Rice University, the US EPA and others.

Devices used to measure fine and ultra-fine particulate matter can cost well into six figures. At just over $10,000, the Met-One E-BAM was much more affordably priced, and GHASP decided to evaluate it in a manner similar to the evaluation of the ozone monitors. The city of Houston BAQC was again contacted and permission was granted to collocate it near the city's particulate monitors at the Clinton Drive site. A volunteer then installed it, and data collection began on May 7, 2006. Interestingly, a picture of GHASP's E-BAM (Figure 8.) was included in a report produced by an air pollution risk assessment task force assembled by Houston Mayor Bill White.[15]

Of the over 40 air quality monitors in the Houston area, only 10 measure particulate matter. All of these measure the finer 2.5 micron particulate matter. At each of these 10 sites, two methods are used to measure $PM_{2.5}$ pollution. The primary method, known at regulatory agencies as the “federal reference method” (FRM), takes an integrated sample over a six day interval. At the end of the interval, filters within the unit are removed and replaced with new filters. The used filters are carefully weighed and the material on them is speciated using analytical chemistry. $PM_{2.5}$ concentrations are then estimated based on statistical distributions of particles that are selected with the device’s inlet given the mass of material on the filter. The selective inlet is known as a “well impactor ninety-six” (WINS), and is designed to select only particles that are $PM_{2.5}$ or smaller.

**Figure 8. E-BAM installed at Clinton Drive. Picture from Mayor's Task Force Report on the Health Effects of Air Polution.**

The second method is known as ”tapered-element oscillating microbalance” (TEOM). It also has a selective inlet, in this case a “sharp cut”, or, at some sites, “very sharp cut”, cyclone. The TEOM is a continuous method that is based on empirical knowledge of the attenuation of an oscillating microbalance (or arm) by the masses of particulate matter that are able to pass through the cyclone. This “arm” sits in the path of the stream of cyclone selected particles that are drawn into the monitor during sampling. The TEOM is the device that the regulatory agencies use to give hourly $PM_{2.5}$ concentration estimates.

The TEOM and FRM methods are typically not well correlated,[16] especially at sites like the city of Houston’s Clinton Drive monitor. The TEOM generally produces $PM_{2.5}$ concentrations below the estimates produced by the gold-standard FRM. A number of reasons for this have been suggested. These include different inlet systems, different sampling flow rates, and, most important for the high humidity Houston region, different methods for handling sampled air moisture content. This last issue is extremely problematic for Houston area $PM_{2.5}$ monitoring because Houston air typically has higher humidity than other U.S. cities and the industry in Houston is a source for semi-volatile sulfates and nitrates.[17,18] A common strategy for removing air sample moisture content is to heat the sample during collection. Unfortunately, heating may alter the sample by boiling off volatile or semi-volatile aerosols in the sample and thereby reducing the total mass of collected particulate matter.

The Met-One E-BAM is designed with this strategy and it unfortunately did not perform well at the Clinton Drive site. The monitor ran continuously from May 7, 2006 until June 16, 2006 when its internal pump failed. The unit then had to be de-installed and shipped back to Met-One. Met-One repaired it, and it was returned to the Clinton site on July 23, 2006. It then ran continuously until October 14, 2006 when it was permanently de-installed. It was ultimately returned to the manufacturer for a discounted refund.

$PM_{2.5}$ concentration estimates generated using the E-BAM never correlated with the regulatory TEOM. During the evaluation period, a volunteer performed weekly downloads of the device. Linear regressions were performed on the data in comparison to the TEOM and Figure 9 is an example of the scatter of E-BAM obtained observations compared to those generated by the TEOM.

GHASP staff and volunteers spent a great deal of time in conversation with Met-One scientists and others at local universities including the UT-SPH. Attempts were made to identify correlations between the E-BAM to TEOM differences and a number of variables using analysis of variance statistical analysis. These variables included meteorological information such as wind speed and direction, ambient temperature and ambient relative humidity. Information such as concentrations of oxides of nitrogen was included but ultimately no driving variable to correlate E-BAM $PM_{2.5}$ concentration estimates with those generated by TEOM data could be identified. Recalculating the averaging interval to six hours increased the correlation between the two methods, but the E-BAM data still contained significant outliers.

The E-BAM has been used by a number of regulatory agencies including the US EPA. Although the nitrate/sulfate issue for $PM_{2.5}$ monitoring is well-known in the scientific and regulatory communities, this instrument had unfortunately never been tested in an urban environment with these interferences combined with high ambient humidity.

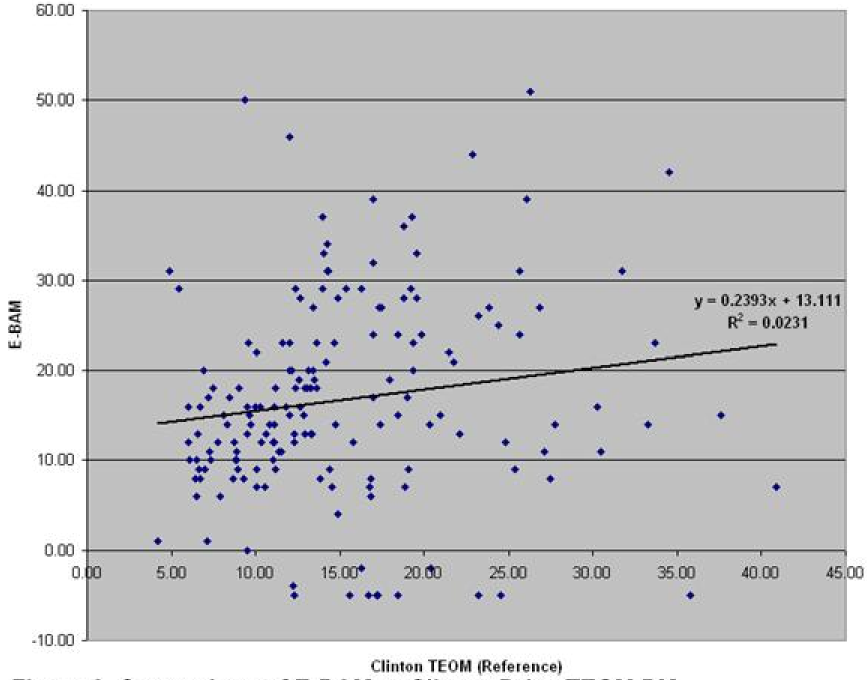



**Figure 9. Comparison of E-BAM to Clinton Drive TEOM $PM_{2.5}$ 08/19/06 – 08/26/06**

Following the evaluation of the E-BAM, the instrument was returned to the manufacturer for a refund minus restocking fees. The evaluation has contributed to GHASP personnel's understanding of the particulate situation in Houston. Selection of instruments for future evaluations should include some consideration of the lessons learned during this evaluation.

**Air Toxics**

While the target pollutants of the first two monitoring evaluations have enforceable concentration levels set by state and federal agencies, volatile organic compound air toxics currently do not. In the Texas, industrial releases of compounds in this category must be permitted by the TCEQ and the state uses so-called "effects screening levels" (ESLs) as guidelines for the permits. These ESLs have been widely criticized, however, and many Texas scientists and researchers believe that the levels are not protective of public health.

Public interest in TCEQ ESLs intensified in the Houston area following the publication of the Houston Chronicle's series *In Harms Way*[19] in January of 2005. This series was based on monitoring of airborne toxics in neighborhoods proximate to Houston's refining and petrochemical complex along the Houston Ship Channel. The series noted excessive levels of a number of compounds including benzene and 1,3-butadiene.

Following the release of the series, Mayor Bill White of Houston sought a response from the TCEQ. Dissatisfaction with the TCEQ's response spurred Mayor White's then on-going efforts to alter the permitting and enforcement relationship the city had with the TCEQ. Following the series, Mayor White formed a task force comprised of local air quality experts to evaluate the risk of airborne pollutants in Houston. This task force studied 179 chemicals known to be present in Houston air and identified twelve air pollutants as "definite risks" to public health.[15] The twelve included ozone and $PM_{2.5}$, diesel particulate matter, chlorine, hexavalent chromium, and seven organic compounds including benzene and 1,3-butadiene.

The Mayor's Task Force report was quickly followed by another study conducted by researchers at four local universities and funded by a local philanthropic foundation.[20] This study employed modeling estimates based on emissions data under the EPA's National-Scale Air Toxics Assessment (NATA). Four airborne hazardous contaminants, benzene, 1,3-butadiene, formaldehyde and diesel particulate matter, were identified as "of particular concern to the Houston region". While most of the inference in this study was based on data modeled from the EPA Toxics Release Inventory, it also included concentration estimates generated by local regulatory monitoring. The study noted that at least one site in the Houston area had a 24-hour average concentration of 1,3-butadiene of four parts per billion (ppb) which was 20 times the highest average in the urban area with the next highest annual average (Los Angeles with 0.2 ppb). This site, Milby Park, happens to be adjacent to densely populated residential areas, and is a popular location for youth soccer matches and other community outdoor activities. The report also noted that the highest 24-hour average concentration of this compound was almost 10 times (at 37.4 ppb) the alarming annual average. Ambient concentration estimates for benzene were an annual average of 1.7 ppb and a 24-hour average of 73.5 ppb. This paper was highly critical of the TCEQ's ESLs, and the apparent lack of rationality of these levels. For benzene, the TCEQ's ESL of 1 ppb represents a lifetime risk of cancer of 1 in 100,000. For 1,3-butadiene, the ESL is 5 ppb which represents a risk for cancer of 1 in 2660.[20]

Despite Mayor White's interest in these problems and his efforts to push the TCEQ to improve their record in the region, many local community groups feel compelled to address these problems from a grass-roots level. This has brought together residents from a broad spectrum of socioeconomic backgrounds who are interested in getting their industrial neighbors to comply with permit caps, upset and flaring rules and other regulatory instruments. Some of these, notably residents of the Shoreacres community which shares its western and southern boarders with very heavy petrochemical and refining operations, have begun funding community-based monitoring programs.

One of the most effective community-based monitoring techniques was invented in the mid 1990s by the lawyer who was profiled in the popular Hollywood movie *Erin Brokovich.* This technique was suggested by the lawyer,who fell ill following a refinery visit, but realized that he had no evidence of the pollution to which he was sure he was exposed. The technique is quite simply "grabbing" a sample of pollution by drawing an air sample into a Teflon-coated bag using a battery powered pump. The bag is protected by placing it in a plastic paint bucket. Citizens employing the technique are called "Bucket Brigades". The concept's simplicity belies its effectiveness in curtailing excessive industrial emissions to air. One group, Global Community Monitor, has traveled to virtually every continent to train residents of "fence-line" communities to use the technique.

A few Houston community-based air quality groups began forming bucket brigades in the late 1990s. They quickly discovered that the technique has significant limitations when deployed in the Houston area. Perhaps most problematic for small and under-funded community groups, the analysis of grab samples can be prohibitively expensive. For example, the Region 6 office of the EPA charges around $500 to analyze a bucket sample. Delivering the sample to the EPA laboratory is inconvenient and time consuming. Samples must be immediately delivered, and analysis frequently identifies no actionable levels, especially for highly reactive pollutants such as 1,3-butadiene which can have an atmospheric lifetime of only a few hours.[21] Another issue is that the TCEQ does not accept bucket samples as evidence against potential permit violators.[22] Finally, evaluation of bucket sampling under the EPA supported Houston/Galveston Citizen Air Monitoring Project and under the Seabrook Citizens Health Induced Air Monitoring Project demonstrated that bucket samples frequently have poor correlation with regulatory methods for air toxics sampling and analysis.[23]

Sampling and analysis of airborne toxics is challenging because levels even in polluted areas such as the Houston Ship Channel are low enough to be near or even below the detection limits of many analytical methods. For example, 2005 and 2006 data from the TCEQ's Milby automatic gas chromatograph (AutoGC) indicates an annual mean concentration of 1,3-butadiene of 1.41 parts per billion by volume (ppbv) but a median concentration of 0.19 ppbv. For benzene, these numbers are 0.41 and 0.2 ppbv respectively. For that period, method detection limits (MDLs) for 1,3-butadiene were 0.1 ppbv and for benzene were 0.07. Frequency analysis of the same 2005-2206 shows that for 1,3-butadiene 39% of observations were below the MDL as were 12.5% for benzene.

Analytical methods for this category of compounds often include some sort of concentration step. This usually means that sampling is conducted over a period of time that allows enough mass of the compound of interest to be accumulated on the sampler for accurate instrument detection. The mass, the sampling interval and the sampling rate are then used to calculate an average concentration value for the sampling interval. In the case of the AutoGC, this interval is one hour; canister sampling uses either one or twenty four hour intervals; adsorbent based methods such as sorbent tubes and organic vapor monitors typically have twenty four to seventy two hour intervals. While longer interval average concentrations are appropriate for most health effects inquiry, shorter interval estimates have certain advantages. These include rapid response to, and quantification of, concentration spikes.

Extraction of compounds from sorbent tubes, organic vapor monitors, or other absorbent/adsorbent devices creates other challenges for the analyst. Many techniques use sorbent materials and devices that must be discarded with each sampling which increases expenses. Some techniques also require solvents to extract the compounds of interest. Solvent extraction has many disadvantages including potential for hazardous exposure of laboratory personnel to solvent vapors, greater potential for contamination of samples during laboratory handling, and lower sensitivity than other techniques.[24] Thermal desorption offers many advantages and is becoming the technique of choice for extraction of toxics from sorbent materials. The main disadvantage of thermal desorption is that automated systems are prohibitively expensive, especially for community-based monitoring projects.

Other technologies exist that allow rapid, nearly real-time estimates of airborne toxics concentrations, but they have drawbacks. For example portable gas chromatograph/mass spectrometers (GC/MS) exist that give almost real-time estimates, but these cost well into the six figure range and may not detect at concentrations observed in the Houston area. So-called “open-path” technologies, including ultraviolet differential optical absorption (UV-DOAS), Fourier transform-infrared (FTIR), differential absorption light detection and ranging (LIDAR), Raman Spectroscopy, and tunable diode lasers (TDLs) can give rapid concentration estimates. All of these technologies are expensive in the same range as portable GC/MS, however, and most have detection limits for volatile organic compound toxics well above those found in community settings.[25] Similarly, solar occultation flux (SOF) is expensive and its detection limits are more appropriate for plume analysis.[26]

While evaluating air sampling and analysis techniques as a part of an internship for the city of Houston’s Bureau of Air Quality Control, a GHASP volunteer became aware of a technique in which the advantages of sorbent sampling are combined with very rapid analysis. This technique, known as “solid-phase microextraction” (SPME), is relatively new but is rapidly gaining acceptance among chemists, especially where sample extraction is laborious and expensive. It involves application of a polymer to an optical grade fiber to create a sampling device. The fiber is then installed inside the barrel of a laboratory syringe so that it can be exposed to a sample matrix by pushing it out of the barrel with the syringe plunger. This allows control of sampling by either extending the fiber into the matrix to begin sampling or retracting it into the barrel to cease sampling. Sampling durations are in the range of a few minutes depending on the compound of interest and the fiber coating used. Coatings are similar to stationary phases of chromatographic columns and include various amounts of polydimethylsiloxane, divinylbenzene, carboxen, carbowax, polyacrylate and combinations of these. Following sampling, the syringe barrel can be immediately inserted into a gas chromatograph’s injection port where the sample is thermally desorbed, and analysis can be completed in minutes. Polymers used to coat the fiber and are selected based on characteristics, such as polarity of the target compounds. According to product literature, fibers can be re-used for up to one hundred samples.

A GHASP volunteer is currently evaluating the SPME technique. Preliminary sampling and analysis of static, headspace samples of gas phase 1,3-butadiene and benzene have been very encouraging. Concentrations in the very low parts per billion have been successfully quantified in this matrix. Researchers already employing this technique have observed that sampling in air streams with velocities greater than 10 centimeters per second lower the sensitivity of the technique at least one magnitude. [27-32]

The main challenge to wider deployment of this technique for field sampling and analysis of a wide array of volatile organic compounds is designing a method for generating calibration curves. The current evaluation employs a dynamic air exposure chamber and construction of this system has been the most difficult and expensive part of the evaluation. Otherwise, the technique is relatively inexpensive, especially when older detector technologies such as flame or photo-ionization are employed. This bodes well for ultimately designing a method that is inexpensive and simple enough for deployment by a high school or community college chemistry or environmental science class.

**Conclusion**

Given the expense and difficulty, one may ask whether citizen-based monitoring for air pollution is really necessary. In this era of growing environmental awareness, citizens receive daily reports of new forms of environmental contamination. Fear of disease caused by pollution is a component of urban life and citizens want to know what risks are present in their communities. Unfortunately, confidence in regulatory entities is low. Histories of regulatory agencies are rife with examples of their willingness to allow public health to rank behind corporate profitability. Examples include the U.S. Public Health Service's role in what many consider the most catastrophic example of industrial pollution[33] to recent news that the TCEQ is blocking legislative inquiry into its connections to a well-known industrial polluter.[34]

Citizen-based monitoring initiatives instill confidence in participants. These initiatives arm citizens with evidence of otherwise hidden threats to human health. They increase awareness and understanding of pollution exposure. They increase citizens' ability to participate in the formulation of public policy. Despite the effort and expense, these initiatives should continue.

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