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U.S. EPA Region 6 Laboratory
Houston-Galveston Citizens' Air Monitoring Project
Document 001 - a Quality Assurance Project Plan

Approval Sheet

Approvals:

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D Houston Galveston Citizens' Air Monitoring Quality Assurance Project Plan (QAPP)

Background

This project is a cooperative effort by governmental agencies and citizens groups in the Houston area to collect and analyze air sampling using various sampling tools and defined quality assurance procedures which should yield data that could be useful in evaluating the tools. As an additional benefit, the project would provide some information on measured compounds and concentrations in the Houston area ambient air at specific locations and times.

The governmental agencies have been monitoring air according to their own regulatory processes. Various citizens' groups have been involved in the role of both collecting data and educating the public about the significance of air quality. Cooperative efforts of both groups have been done elsewhere and the results encourage the continuation of these projects with the goal of incorporating both field and laboratory quality control procedures, defining the capabilities of collection devices and sharing the results.

A **Purpose**

The purpose of this effort therefore is primarily the education all the participating parties and the general public about the usefulness, capabilities and limitations of the air sampling tools and media, and the role of quality control in scientific evaluation.

Although it is not the primary purpose, some tangible results of compounds concentrations at specific locations and times may be obtained. This could help with site selection for continued sampling and future monitoring. The determination of air quality is not a goal of this project, nor is it expected that any statement can be made in this regard at any time throughout its duration. Information can be obtained, however, on the toxicology, exposure and health effects of any compound as part of an education process. This could include compounds detected during these trials.

Citizens and agency personnel will meet on a regular basis and develop strategies for a cooperative effort. Subgroups of HGCAMP such as workgroups and committees will meet to discuss and define the means to implement this project successfully. From these meetings, methods, strategies and criteria will emerge and be incorporated into documents such as standard operating procedures (SOPs) for using the sampling tools, how to handle the information, protocols for training, quality control/quality assurance (QA/QC) and health and safety. These meetings will actually realize another purpose, the discovery of each others goals and expectations.

D The QAPP details that follow set quality goals for sample collection and analysis, training and results. Safety of the participants overrides all other considerations and is included.

Project Goals

The goals stated generally in the description are enumerated specifically below.

1. To evaluate the comparative results of the primary citizens' air sampling media, the Tedlar® bag, in a side-by-side comparison with one of the agency "standard" air sampling collection devices, the evacuated canister.
2. To compare the usefulness of the primary citizens air sampling tool, the "bucket" with an alternate device, the "suitcase." This project will use these two tools for collecting air samples into Tedlar® bags. These are both indirect aspiration devices utilizing a pressure differential to cause ambient air to be sampled without contact with oil or other possible contamination that might be encountered with direct pumping.

No side-by-side comparison of these two devices will be used initially in order to keep the project simple. There may be sufficient data collected to make a secondary comparison, each vs the canister, or to do a side-by-side comparison either in the lab, or later by the field samplers. However, at this time, the comparative evaluation of these "tools" will focus on ease of use, equipment integrity and adaptability to potential sampling situations.

3. To become acquainted with the quality assurance tools used in scientific evaluation. As part of the sampling, a field blank, field spike and field duplicate will be analyzed at a specific rate and these data will be evaluated separately as part of the evaluation process to show potential contamination problems, sample integrity and precision of the two media.

4. To obtain results of specific compounds at specific points in specific areas and to disseminate these results to the participants. These data will be made available for assessment of their toxicology effects and as indicators for further sampling efforts by HGCAMP or the agencies. These data will not be the sole basis for enforcement action of any kind.

5. To provide a venue for citizen and agency interaction, cooperative efforts of both and a mutual understanding of each other's expectations. To this end, the goals and the details of this QAPP may change as the project evolves.

Project Description

T It will be useful here to describe the participants and suggest some of the roles that they may undertake in accomplishing this project. This is not a rigid part of this QAPP and is only offered here to clarify who the "players" are and what they might do in accomplishing the Data Quality

Differences which are an important part of this QAPP and the project itself. The training especially will necessitate everyone’s participation as will the logistics of sample handling.

Project Organization and Management. Some of the participants in HGCAMP are given in the following table. This list is not meant to be comprehensive and is subject to change. It shows the current scope of participation.

Group or Agency	Classification	Description
Citizens League for Environmental Action Now (CLEAN) R	citizens’ group	A coalition of Houston citizens capable of sampling.
Texas Natural Resource Conservation Commission (TNRCC)	agency	The primary state Agency delegated to enforce the Clean Air Act and capable of analysis.
Mothers for Clean Air	citizens’ group	A coalition of Houston citizens capable of sampling.
Harris County Pollution Control District (HCPC) A	agency	The primary county Agency sub-delegated to enforce the Clean Air Act and to answer complaints.
Calcasieu League for Environmental Action Now	citizens’ group	advisory and contributors to instructions on “buckets.”
US Environmental Protection Agency	agency F	the author of the Clean Air Act and capable of analysis and equipment providers.
Subra Company	industry/company F	advisory/data correlation.
City of Houston Mayors Office and Bureau of Air Quality	agency	information on sampling sites, possible hubs and meeting locations.
Clean Air Clear Lake	citizens’ group	volunteer samplers from the Clear Lake area.
Texas Southern University	academic	volunteer samplers. T
UTMB Participants	academic	volunteer samplers from Galveston County and equipment providers

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Group or Agency	Classification	Description
Individuals	citizens	interested samplers.

The anticipated roles of the different groups will be dictated by commitment and resources. These roles are merely suggested and it is not the intention of this QAPP to assign them, but rather to provide a descriptive framework in which the logistics, sampling, equipment distribution, Chain-of-Custody and ultimately the analysis and Data Quality Objectives can be understood.

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The Citizens will provide input on site selection, and constitute the majority of the sample collectors. **Ultimately, the sampling site is entirely at the discretion of the sample collectors.** Sample collectors will mainly be drawn from the citizens groups or from the cadre of individual participants. In addition to co-location and synchronization, if required, of the sampling devices, the collectors (usually the citizens) would be asked to maintain certain records, participate in training and provide coordinators.

The citizens would also provide the “buckets,” the sampling device that is an integral part of the project as well as information on its use for training. The Tedlar bags require one of two types of sampling devices. One is the “**A**” which is owned by the citizens and another is a ten-liter sample device provided by the laboratory along with the Tedlar® bags (single use and disposable) and canisters (an accountable item and reused). The citizens must provide the instructions on the use of the “bucket” just as the agencies must provide instruction on their equipment.

Sample collectors are comprised of anyone within HGCAMP who participates in and is qualified to collect samples at one of several possible training sessions in which they are asked to demonstrate their proficiency in operating the sampling equipment and respond to questions about the project and sampling, including safety.

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Coordinators are individuals selected by the citizens groups collectively who will assist in site selection, delivery of equipment and media to the collectors and deliver samples to the laboratory. They may or may not collect samples depending upon their training as sample collectors.

Coordinators also may obtain information on site selection from citizen “sniffers” or complaints from citizens or as relayed from one of the agencies, and send out a collector to a site. Since the coordinator works with the collectors, sniffers and citizens and this role has been a traditional part of the citizens “bucket-collected sampling corps,” it is anticipated that the coordinator would come from the ranks of the citizens. A sniffer is a term used by the citizens to signify someone who normally does not possess a sampling device and is not necessarily trained to collect samples, but who may designate a probable sampling site.

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D Citizens may also provide a “hub,” a location at which samples may be gathered from the collectors, and from which samples may be shipped or delivered to the laboratory.

The citizen samplers will document certain atmospheric conditions such as temperature, humidity, wind directions, the time of sampling and site location and other information on a Chain-of-Custody initiated by the sample laboratory and issued with the sampling media.

Agencies. In general, TNRCC and HCPC can assist the citizens in site selection by providing information on emission sources or complaints. HCPC and the City can act as hubs or sample and equipment distribution centers and drop-off points between the lab and the sample collectors for samples, equipment, and collection media.

HCPC also will provide information on potential sampling sites and respond to citizen complaints. Any information they provide may be recorded on the Chain-of-Custody, particularly in the event of an episode such as a chemical spill or nearby plant upset.

The EPA laboratory will provide the bulk of the analysis and be assisted by TNRCC in its external quality assurance, that is the TNRCC laboratory will assist the EPA laboratory with its QC by providing challenge samples and a second or sequential analysis of the canisters on approximately a 5% basis. It will review the data. They may provide further information on the results provided the data is of good quality, amenable to their process of evaluating data and collected in canisters.

TNRCC has provided some of the protective cases for the canisters and, along with HCPC and some of the citizens, will help in the training for sample collection.

EPA will provide the proper number of spikes, field blanks and field duplicates based on the issuance records of the laboratory and the current number of samples processed.

HCPC, in addition to answering citizen complaints as they have always done, and providing information to assist in site selection, may also provide a hub, assist the citizens in site selection and may also provide some of the functions of a coordinator by delivery of samples to their hub as their resources may allow. On occasion that they may go to a sampling scene in answer to a citizen complaint. HCPC can assist with data review and may participate in canister analysis at a later date provided they have the equipment to do so.

EPA will participate in the training of its sample collection equipment and canisters.

TNRCC has the expertise and training in the proper collection of samples with the canister and can instruct on sampling strategies and provide training in site selection and safety.

EPA will analyze the samples and provide the results through the EPA’s Project Officer, who is

D the liaison for results between EPA and the Houston Citizens Air Monitoring Project. They will work with the TNRCC in analyzing challenge samples provided by the latter and split samples with TNRCC on a frequency determined by them (TNRCC) and according to their schedule.

EPA will provide the Tedlar™ bags which will be used once and discarded. A record will be kept of issuance both for inventory purposes and in the interest of fairness to assure equitable distribution of resources. A field blank, field spike or field duplicates in a Tedlar™ bag may also be issued 5% of the total sampling events.

R EPA will provide an alternate sampling medium consisting of a 6 liter silanized canisters equipped with a vacuum/pressure gauge, a dust cover and a three minute sampling device. A record will be kept of the issuance for accountability purposes due to the non-expendable nature of this device and because this item is government property and its permanent custody will be eventually returned to the laboratory. Some of the canisters will be issued as field blanks, field duplicates and field spikes. EPA will provide training in the use of this collection device according to the goals of the project.

EPA will provide the Chain-of-Custody seals, the Chain-of-Custody forms and will initiate the latter for field spikes, field blanks and field duplicates. This will consist of identifying the Tedlar™ bag(s) and canister(s) on the Chain-of-Custody at the time of issuance.

A TNRCC has already supplied protective boxes for the canisters and they will be reissued to the citizens with the canisters. EPA will also provide protective boxes for the Tedlar™ bags.

EPA will provide an alternate Tedlar™ bag sampling device, called a “suitcase” and provide training in its use.

F It will be the role of all the agencies to insure that the number of duplicates, field spikes, field blanks and duplicates are distributed evenly or according to what the Technical group determines are the correct number of each *vis a vis* the goal of tool evaluation. In this regard, it will also be the agencies’ role to provide the final results, QA/QC results and validate the data according to the methods and SOPs used by the respective agency, and make a determination of the reliability and usefulness of the data.

It will be the role of the laboratory to prepare the media, distribute to the citizens, instruct the citizens on the use of the EPA owned equipment, receive instructions on citizen owned equipment, revise this QAPP as needed, monitor conformance to the Data Quality Objectives (DQO) and prepare a Standard Operating Procedure for the methods, sampling, receiving, storage, reporting, QA/QC and data review and validation.

T The various parts of HGCAMP will be comprised of both agencies personnel and citizens.

D The Technical Workgroup is concerned mostly with the “front end,” how to get started, the means and methods of tools evaluation and sampling. This QAPP is a result of that workgroup.

The Information Workgroup is primarily concerned with sharing general information on available data, the measurement process, evaluation of monitoring results and how to use this information. These committees overlap to some extent in both participation and function and may be combined at a later date.

R The Training Subcommittee consists of individuals who meet and set up the training in order to accomplish the Deployment Objectives, described later in that section of this QAPP. They will be responsible for recommending the training regiment to the Technical Committee, conducting the training, writing the SOPs, instituting necessary revisions as dictated by the results, administering the qualifying tests and quiz, monitoring the feedback, administering the certificates and issuing the badges.

A Training is also a role required of everyone. The laboratory must be properly trained in the operation of the both the analytical equipment. The other agencies will provide challenge samples and do subsequent or second sampling analysis as part of the QA/QC part of this QAPP. The citizens must be properly trained on the use of its equipment and it is their role to receive this training before attempting any sampling. The laboratory must be properly trained on the uses of the citizen sampling equipment if and when it uses this equipment such as in house sample collection and comparisons.

Health and Safety

F Given the diverse backgrounds of the participants and the potential roles described above, not all of which may be within the participants range of experience, it is appropriate to describe early on the attention that should be given to health and safety considerations before proceeding further. The goals of this project are secondary to the well-being of each and every individual and it is the collective requirement of HGCAMP that this take top priority.

Sampling Safety. In undertaking this project, a primary concern is the safety of each individual. No individual is asked or expected to risk or endanger their health in order to collect samples as a part of this project. If at any time (an) individual(s) conducting sampling experience(s) any health effects, such as watering/burning eyes or burning sensation in the lungs, they are asked to put their own personal safety as the first priority over any sampling efforts.

T In many cases it is possible to minimize any potential exposure during downwind source sampling. The samplers can be prepared prior to getting out of the vehicle thus minimizing exposure to ambient air conditions. During sample collection (3-4 minutes) the individual may

Do not walk away from the sampling area if there is a concentrated odor or plume. Another option is to observe sampling from inside a nearby vehicle. After the sample has been collected, the samplers, sample media, and paperwork can be carried or loaded into a vehicle so that Tedlar™ bag recovery or sampling documentation can be done off-site shortly thereafter.

Individuals conducting sampling should also be aware of the types and uses of, personal protective equipment, which includes, dust masks, protective clothing, cartridge style respirators, supplied air respirators or breathing packs. For example, some citizens have noted that long-sleeved shirts and pants can be helpful in minimizing skin exposure. Additionally, in situations where dust masks provide some protection for particulate matter while respirators with appropriate cartridges may be appropriate for some of the organic and acidic compounds. Since neither dust masks or tight fitting cartridge respirators can remove all types of potential air pollutants, another possibility is lightweight supplied air samples. Individuals should also be aware of the advantages and risks associated with using personal protective equipment. For example, any type of tight fitting respirator or heavy supplied air system can place an increased burden on the cardiovascular system. In fact, if an individual has not been properly evaluated for wearing this type of protection equipment, properly fit tested with the actual mask or respirator, and does not have the correct or new cartridges the use of respirators is not recommended and can be hazardous to the user's health.

A sampler collectors are asked to obey all traffic regulations and not to park their cars in a traffic congested area. Observe caution when exiting vehicles and do not stop in the middle of roadways.

At the same time, do not park or walk on private property or otherwise trespass in order to collect a sample. It is better to collect samples at least in pairs. Avoid hostile behavior and confrontations. Since at least one sampler will be issued an ID card, with a telephone number to call in which his or her activities can be explained, reference to the card and a polite referral to the telephone number should be made at the very beginning of any challenge.

All precautions should be taken to avoid inhalation of hazardous air and prolonged exposures in potentially hazardous areas. For this reason, and for the reason given below in the description of memory effects, source level sampling such as close proximity to emission stacks, chemical spills or known hazardous waste sites, is not an appropriate sampling attempt, nor is trespassing on private property or dangerous confrontational situations.

Sampling Process Design

Site Selection. The sampling and who will sample has already been described above somewhat under roles. The critical elements require co-location and synchronization of two entities. Co-location means that the two entities are located as close to one another as possible without

D interfering in their mutual operation, and at the same height. Another critical element is the collection of samples likely to contain target compounds listed in the “Analytical Method Requirements” section below, or other compounds amenable to the analysis in the media being employed. Keeping in mind the safety consideration above and that the location of sampling sites is primarily at the discretion of the citizens, the following is offered as suggestions to help the citizen collect meaningful samples so that the Data Quality Objectives (described below) may be more easily met.

Procedures for Locating and Selecting Environmental Samples. Site selection and timing of ambient air sample collection will be at the discretion of citizens collecting the sample. Sample site constraints are that the sample be collected on public property within Harris or Galveston Counties and be representative of ambient air (and not a small, concentrated source such as a gas puddle or automobile tailpipe exhaust). Site selection can be based on odors, observed plumes, emissions inventory data, complaint databases, wind direction, and proximity of industry to neighborhood or public areas, among other factors.

A number of siting criteria documents exist such as CFR Part 58, Appendix D and E which provide information on how to properly select a sampling site. However, these documents are aimed at selecting fixed sites which are used to collect data representative of a general area over a long period of time (years). After a general area has been selected for sampling, some general hints for collecting representative short duration samples include:

- collect the sample upwind of any vehicular traffic if you are trying to characterize a source other than that of the roadway,
- do not collect the sample directly adjacent to (or directly downwind of) an automobile since you may end up sampling gas vapors and/or auto exhaust,
- do not handle any volatile organics prior to sample collection without thoroughly washing your hands (examples include putting gas in your car, polishing nails, removing fingernail polish, painting, using glues or varnishes, handling printer toner cartridges, or using liquid paper),
- do not allow water to enter the sampler since this may bias results or water soluble compounds low and cause instrument problems (sampling during rain or drizzle is usually not a good idea since this often acts as a natural scrubber to remove compounds from the ambient air),
- if possible it is preferable to collect the sample away from large obstructions (such as trees or buildings) since they can greatly affect wind direction and they sometimes bias measurements (high or low). A good rule of thumb is to try to sample at least 30 or more feet away from any such large obstacle, and
- do not connect any additional types of tubing to the sample inlet other than those provided and normally used since teflon, tygon, and some other materials are not acceptable in the inlet sample path for ambient level VOC sampling. (Note that there are relatively short sections of these types of tubing used in both the “bucket” and the “suitcase” and this should be considered a normal part of the

D tool evaluation. However, it is not necessary to add any additional tubing and it should not be done.

. Site selection will be at the discretion of the citizens. They may seek guidance from the agencies or from a collaborative input of the group based on historical or currently collected data. This is a citizen, a combined citizen and local agency, or a laboratory-local agency-citizen function. The critical element is that increasingly, samples should be collected where meaningful data exists as determined by history and currently generated results. That being said, please read the precaution in the next paragraph.

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Sampling. Sampling of the canisters would be a simple removal of the dust cover, opening the valve, closing the valve at the appropriate time to assure synchronization and replacement of the dust cover. For Tedlar® bag samples, the procedure for that particular sampling mechanism would be observed as defined by the entities employing using them, or by the laboratory for the suitcases. At this time no data is available on how the suitcases work. In fact, no suitcases are available. A detailed protocol will be developed and amended as needed describing the operation of both the individual unit and the co-collecting units. An abbreviated step-by-step procedure will be prepared on one page for use in training and for the sampler to take to the field.

A
Training. A critical part of the sample process design is the training of the sample collectors to insure that the Data Quality Objectives can be met

Logistics

Equipment Used for Sampling. The “buckets” will be provided by the citizens as they are relatively inexpensive to fabricate and are an historical part of the citizens’ sampling repertoire. The alternative indirect aspirating device for Tedlar® bags, the “suitcase,” the pumps to use with the “suitcases” and the canisters will be provided by the EPA. The Tedlar® bags, the boxes to hold them, the Chain-of-Custody forms and seals and some miscellaneous fittings, batteries and other related expendable supplies may also be provided by EPA as funds are available.

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Scheduling. Scheduling will be done by notifying the Sample Scheduling Coordinator at the EPA laboratory. An SOP for this already exists, which provides a telephone number, and will be available to those collecting the samples. In most cases, notification will be made before the actual collection, but it is realized that there are instances when promising sampling opportunities arise and, if the media are available, should be taken advantage of. This should not present a problem and the analyst will notify the sampling partners when there would be a delay such as vacation or breakdowns.

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Hubs. Initially, it was though a good idea to utilize hubs, or centers, where samples could be brought and stored for a short time and the equipment and/or sampling media and supplies could be distributed. In practice, this has not been the case for whatever reason. However, the use of hubs is perfectly acceptable as long as the sample Chain-of-Custody is completed showing the

Dtransfers and the non-expendable equipment exchange is recorded. Scheduling should still be done either by the hubs or if bringing the sample to the laboratory directly.

Data Quality Objectives (DQOs)

To collect enough data of known and acceptable quality to evaluate the canisters and bags as short duration sampling tools using a set (one each) of heterogeneous media (i.e. two different types of media) at the same time and at the same location. Field spikes, field blanks and duplicates (homogeneous) of both kinds of media will be provided on a 5% basis for co-location (also co-collection) for duplicates and these will be used to further evaluate the media in addition to any in-house studies, observations and the specific QA/QC specified under the analysis sections below.

An important aspect of insuring that the data from the analysis is appropriate for the intended use is to insure as much as possible the correct functioning of the sampling devices. The grab samplers, without the sintered inlet frits, have already been measured to insure that they obtain a proportional sample in the nominal 3 minute fill time. In order to insure a synchronous sampling, the "bucket" or suitcase should also fill a Tedlar® bag to no more than three-fourths of its capacity in that time (about 7.5 liters). This involves technique which will be built into the training and the SOPs but also should be verified by lab measurements. Thus, training will be an important part of determining that the Data Quality Objective is met from the sampling aspect. Only qualified samplers, trainees who have successfully complete the training course administered by the training committee, described earlier, will sample as part of this project. The laboratory has the right to reject, analyze, withhold data or exclude the results from the data base of any sample that has not been collected by a trained sampler, has not been co-locate or as not been co collected (if appropriate).

A more definitive control is the Chain-of-Custody and its correctness and completeness. Ultimately, the Chain-of-Custody and the verification observations of the condition of the bag by the analyst will be added to the aggregate data from each sampling event.

There will always be two entities involved in one sample collection event, either two Tedlar® bags, two canisters, one Tedlar bag® and one canister, a field blank and a sample of the same media or a field spike and a sample of the same media. The sample time will be approximately 3 minutes and the two entities are co-located and synchronously sampled in the case of a can and a bag, or duplicates of the same media, and co-located in the case of a sample and either a spike or blank of the same media. There are no other possibilities.

TThe method of sampling is to co-locate the two entities in such a way as to insure exposure to the same fraction of air that may have the same composition of analytes at the same time. This is all that is required for a sample that accompanies a field blank or field spike of the same media, that

Duplicates are co-located because only one entity is used for sampling. The other entity (the field blank or field spike) just sits there during the duration. Care must be taken to keep both entities together from the time they are picked up until the time they are delivered to the laboratory. This is called co-location.

For sampling duplicates of the same media, or duplicates of different media, the two sample containers must be co-located, but they also must be operated synchronously. That is, the start and stop of sampling must be as close to the same time as possible. Thus for Tedlar® bags, the two pumps must be started, the two valves must be opened and the valves closed after three minutes. For a Tedlar® bag and a canister, the two valves must be opened at the same time immediately after the pump is started on the Tedlar® bag and after three minutes the valve closed and the pump shut off. [Note, it seems that the pump should be started and the outer valve (on the “bucket” opened first and the before the valve on the bag is opened, but this instruction can be elucidated by those citizens who are familiar with the operation of the bucket and is one of the roles described below].

Both entities, when brought to the laboratory, will be stored together and analyzed on the same run to maximize their co-location.

A Sampling Equipment

Sampling Hardware.

1. The current project’s suggested media are 6-liter glass coated, or silanized, canisters with gauges capable of showing a range -30" of mercury to 30 psig. This vacuum/pressure gauge is merely to determine that the canisters have been supplied at the required vacuum (-25 " of Hg). Each canister will also have a manually operated valve which will be checked by the laboratory on an on-going basis for leaks. Each canister will be “certified” as clean before leaving the laboratory (see below under the analytical section to find out exactly what “certified” means) and will be equipped with a fritted “grab” sampler capable of a linear rate of inflow for at least 3 and a fast enough to nearly fill the canister in that period of time. Each canister will have a dust cover and a carrying case, the latter on loan from TNRCC.

None of the canisters and associated equipment is expendable and would be required to be returned to the laboratory.

2. 10-liter Tedlar® bags with 3/8" fitting and some fittings to be used in the connections to the “bucket” if they are available. They will also have protective boxes which can hold the collected sample and be sealed. These are semi-expendable as they can be used, but wear out in time and will then be replaced by the laboratory.

The lab will normally supply one Tedlar® bag for each canister. From time to time, on a 5% basis, the lab will also provide field blanks, field spikes and field duplicates in the form of

D canisters and protected in a manner similar to the sample canisters, or Tedlar® bag field spikes, field blanks or field duplicates. All field spikes and blanks would be at ambient pressure in order to simulate the conditions of sampling. Special directions for co-location (and co-collection in the case of field duplicates) will be provided at the time and are not a part of the training.

3. An alternate sampling device with fittings and a vacuum pump and stopwatch. The alternate sampling device, called a “suitcase,” is EPA property, has a property tag and is expected to be returned to the laboratory at the completion of the project.

The lab will also provide Chain-of-Custody forms, Chain-of-Custody seals and additional copies of the SOP as required.

Preservation and Holding Times. The sampling equipment is as described above, there is no preservation and the targeted holding time is 14 days although there is data in the laboratory to demonstrate that the list of analytes constituting the target list can be held for up to one month in the canister. No information is available for the Tedlar® bags and the determination of the holding time is really a part of the project. However, 72 hours has been suggested as a possible maximum holding time and every effort will be made to analyze the sample within this time. Once the samples are collected, the delivery to the laboratory, coordinator, hub or other transfer agent should be done as expeditiously as possible to avoid unduly long holding times.

Measurement and Data Acquisition

Analytical Method Requirements. It is proposed that the project use the current TO14A/TO15 Subset A 50 compound non-sulphur target list because the stable components (TO-14A list) last a year and the less stable components are in a separate container. The target list along with their last established detection and reporting limits is in the following table.

TO-14A/TO-15 Subset A Compounds	Standard Deviation	Minimum Detection Limit	Reporting Limits (undiluted)
dichlorodifluoromethane	0.02	0.08	0.5
1,2-dichloro-1,1,2,2-tetrafluoroethane	0.02	0.07	0.5
chloromethane	0.03	0.10	0.5
chloroethene	0.02	0.05	0.5
1,3-butadiene	0.04	0.13	0.5
bromomethane	0.03	0.09	0.5
chloroethane	0.02	0.06	0.5
vinyl bromide	0.06	0.17	0.5
acetonitrile	0.17	0.52	1.0
trichlorofluoromethane	0.04	0.11	0.5
1,1,2-trichloro-1,2,2-trifluoroethane	0.03	0.09	0.5
ethyl bromide	0.03	0.11	0.5
acrylonitrile	0.07	0.21	0.5

D O-15 Subset A Compounds	Standard Deviation	Minimum Detection Limit	Reporting Limits (undiluted)
cis-1,2-dichloroethene	0.04	0.13	0.5
allyl chloride	0.04	0.12	0.5
dichloromethane	0.03	0.10	0.5
vinyl acetate	0.04	0.13	0.5
hexane	0.05	0.17	0.5
methyl ethyl ketone	0.05	0.15	0.5
1,1-dichloroethane	0.03	0.11	0.5
1,1-dichloroethene	0.03	0.10	0.5
chloroform	0.03	0.10	0.5
1,1,1-trichloroethane	0.04	0.11	0.5
1,2-dichloroethane	0.03	0.10	0.5
carbon tetrachloride	0.03	0.11	0.5
benzene	0.04	0.14	0.5
2,2,4-trimethylpentane	0.03	0.10	0.5
trichloroethene	0.02	0.07	0.5
1,2-dichloropropane	0.03	0.09	0.5
methyl isobutyl ketone	0.03	0.08	0.5
cis-1,3-dichloropropene	0.03	0.11	0.5
trans-1,3-dichloropropene	0.04	0.13	0.5
toluene	0.04	0.14	0.5
1,1,2-trichloroethane	0.04	0.13	0.5
tetrachloroethene	0.04	0.14	0.5
1,2-dibromoethane	0.04	0.14	0.5
chlorobenzene	0.02	0.07	0.5
ethylbenzene	0.03	0.08	0.5
p/m-xylene	0.03	0.09	0.5
styrene	0.04	0.11	0.5
o-xylene	0.02	0.07	0.5
1,1,2,2-tetrachloroethane	0.03	0.10	0.5
1,3,5-trimethylbenzene	0.02	0.07	0.5
1,2,4-trimethylbenzene	0.06	0.18	0.5
1,3-dichlorobenzene	0.05	0.14	0.5
benzyl chloride	0.03	0.11	0.5
1,4-dichlorobenzene	0.03	0.09	0.5
1,2-dichlorobenzene	0.05	0.15	0.5
1,2,4-trichlorobenzene	0.15	0.48	0.5
hexachlorobutadiene	0.20	0.63	1.0

The duration of all compounds in a properly humidity silanized canister at 10% RH is 1 month. The nominal (a recommended target by the project) holding time is two weeks. However, all results would accompany the date and time of sample collection along with other information that accompanies the sample.

D Other compounds could be added if purchased neat and made up by static dilutions if requested by the Technical Workgroup. In this case, the duration of the 10 ppbv combined standard would have to be determined or the additional compounds evaluated.

The analytical methods TO-14A and TO-15 are published in the Compendium for Methods for the Analysis of Toxic Compounds in Air. These along with the laboratory, QA/QC, and other relevant SOPs in use and on file at the laboratory, including Instrument Specific Operating Procedures constitute the analytical method requirements of the project.

R **Detection and Reporting Limits for Target Compounds.** Refer to the table above. Normally the reporting limit will be 0.5 ppbv for most compounds except those whose MDL (the most recent minimum detection limits which is periodically determined, or updated with the most recent data at the same instrument settings) exceeds 0.5ppbv. In case the most recent MDL exceeds 0.5, a 0.5 ppbv or lower standard in a calibration curve whose relative standard deviation is <30%, or running a 0.5 ppbv standard in the analytical run and obtaining a response significantly above the noise level can validate the 0.5 ppbv lower detection limit. The inclusion of the low level standard is part of the TO-15 method, and the analysis of a low level standard during each run is part of the laboratory SOP both for validating low level responses and for ongoing determination accumulation of data for the detection limit determination.

A The reporting limit for a particular compound will be raised above the detection limit under certain conditions if

- a) instrument blank just preceding the sample showed the compound to be present at or above the detection limit, and there was no intervening sample to refute the presumption of contamination, or
- b) the certification representative for that collection media showed the presence of that compound at greater than 0.2 ppbv.

E In either case, the detection limit will be raised for that analysis and that compound to 10 times the amount shown in the instrument or certification blank, or to just above the level shown in the sample, whichever is lower.

The reporting limits may be raised uniformly for all compounds if a dilution is made or less sample withdrawn for the analysis or both. In these cases the detection limit is raised by the dilution factor or the factor determined by the amount of calibration standard withdrawn for calibrating the run divided by the amount of sample withdrawn. Such a case would be considered rare as the dilution necessitated by pressurizing the canister is compensated for by withdrawing a commensurately larger amount for analysis, and a dilution to avoid the interference or destruction caused by high concentrations should not be necessary with ambient samples.

D The upper quantitation limit is normally 25 ppbv, but occasionally 20 ppbv. In case a compound exceeds the upper calibration limit, a smaller portion will be reanalyzed until the concentration of the diluted compound in question falls below the upper quantitation limit. This does not affect the reporting limits and can be done **without physical dilution of either the canister or the Tedlar® bag**. Note that additional external dilutions are possible with the canister but are not suggested for the Tedlar® bag.

Memory Effects. The upper quantitation limit and the avoidance of source level sampling requires a critical analytical element of detecting and avoiding biased results because of memory effects, which is **R** moreover to subsequent analysis of high target results in one or more of the preceding analyses. Therefore, instrument blanks will be run after calibration and periodically throughout the run, especially after samples whose location indicates a high probability of a concentrated of compound(s). Otherwise an instrument blank will be run after every tenth sample. All samples whose results are even remotely suspected of being affected will be reanalyzed until subsequent samples after the high concentration event repeat themselves within the current relative deviation criteria (at the present time, its $\pm 10\%$ at a concentration near 10 ppbv).

Certification. Each canister and each Tedlar® bag would be certified prior to use by analyzing a representative from the batch. A batch could be as many as 10. In the case of the Tedlar® bag, it is one of a freshly opened container. **A** It is filled with the wash gas and analyzed. For canisters, it would be the canister farthest removed from the wash gas supply. It alone is filled with wash gas and analyzed. The wash gas is zero air or zero nitrogen. It is suggested that a target certification of <0.2 ppbv be the operative number. This may not be possible in some cases, especially with the Tedlar® bags. In this case, the targets and TICs will be recorded and the data collected from that container will be qualified.

A process of 2 cycles to 1000 mtorr and 1 cycle to 50 mtorr at 100 C will be used for the canisters and filling with wash gas between evacuation. **F** In any case, the final fill prior to evacuation would be analyzed for certification and additional cycles performed in order to reach the certification number unless the demand for canisters demands that they be sent out to the field and that the amount of residual contamination is not egregious, in which case the data will be qualified for the amount and type of contaminant.

As part of the evaluation of the reliability of Tedlar® bags (Project Description, above), a calibration curve could be performed using Tedlar® bags. The detection limit study could be repeated for Tedlar® bags and finally any known manufacturing contaminants (*e.g.* N,N - dimethylacetamide, phenol and possible chlorofluorocarbons) and any suspected contaminants (BTEX) would be examined both before and after the clean-up as part of the evaluation process. **T** At this time the Technical Workgroup has decided that pre-washing of the Tedlar® is not required and this will not be performed unless the individual or batch analysis uncovers some gross contamination from shipping or a manufacturing defect. At this point, the bags may be clean, discarded or returned to the manufacturer for replacement. A record of certification and

Data levels of any compound will be kept as part of the data package for the results of the sample that was collected in that particular media. These items are an auxiliary part of the program and suggested if time is available. (See the section on In House Studies below)

QC Procedures. A tune check is performed before any standards, samples or blanks are analyzed. A curve is prepared periodically and must meet the 30% RSD Acceptance criteria of the method before analysis is begun. Laboratory prepared standards normally require at least one day to equilibrate with the humidity and the walls of the container and will be re-prepared at designated intervals or as indicated by the Initial Calibration and/or Continuing Calibration results. The initial calibration curve is checked daily against a single point quantitation standard (10 ppbv proposed). **R**f this fails, and the cause is determined to be failing standards as determined by a repeat analysis and/or elimination of other possible causes, then a new standard and a new curve will be prepared.

A record of the curves and standard preparation is kept. New curves are validated against the initial performance of previous curves under the same instrument conditions and second source check standards. New standards are validated against second source prepared standards. Note, although a curve may be determined (optionally) with Tedlar® bags, the determining calibration curve and standard will be done with a qualifying standard obtained from a canister. In order to eliminate variables, it is proposed **A**t a new standard be prepared every 2 weeks on Friday (unless, of course, some untoward event has necessitated an unscheduled sample preparation), allowed to equilibrate over the week-end and analyzed on Monday. This suggestion is not made necessarily as a QA/QC instrument but as a practical consideration in sample scheduling

The method calls for an audit standard. The definition of an audit standard was a standard obtained from the reservoir kept and certified by EPA. These are no longer available. NIST certified standards are available from more than one source at an approximate cost of \$3200. Currently, fresh standards are on order from Matheson Tri Gas. Second source standards withdrawn from existing (some are technically expired) are prepared at the same frequency as the quantitation standards. After their concentration and **E**fficiency have been verified with a laboratory fortified blank, they will be used to perform laboratory fortified sample and laboratory fortified sample duplicate at a frequency of one *per* ten or one *per* batch, whichever is the most frequent, and establish a database with control and warning limits. Each day's run would consist of an instrument blank on which a BFB check is performed, a calibration standard check or a curve, whichever is required, a canister/autosampler blank, a laboratory fortified blank with audit or second source standard, field samples for analysis and/or canister/Tedlar bag cleaning certification samples and/or field spikes/field blank/field duplicates. Clean-out blanks and dilutions will be performed as required.

TAs mentioned under the roles above, the TNRCC lab in Austin has offered to analyze split standards and samples as is necessary to assure external QC, and to provide challenge samples with quantitative and qualitative unknowns on an periodic basis. An the US EPA Multimedia Permits and Planning Division for Region 6 will provide the laboratory with the next round robin

Duplicate sample from EPA's Research Triangle Park facility.

Laboratory duplicates will also be performed and control charts maintained for different concentration levels. Any co-collected (and, necessarily, collocated) duplicate samples with positive results will be evaluated for replicate precision according to TO-15 paragraph 11-3.2. and table 5.

One surrogate is used for a run. Additional surrogates are contemplated at this time and would be prepared and added with the internal standards. In the event that a dilution is required, a dilution surrogate is also proposed.

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In House QC Studies

These studies would be conducted at the laboratory and in conjunction with the sampling effort. They would be transparent to the balance of the HGCAMP effort, that is, they would require little or no extra work beyond sample collection, but the data would be available to all the partners. This is an additional and non-integral part of the project except those portions designed to validate non standard methods employed by the lab as a part of the study. There is no requirement as to when these additional studies should be done except as is necessary to complete those portions of the project that are required before the data is usable, for example, preparation of a Tedlar® bag spike as described and certification of Tedlar® bags described below. Here are a few scenarios which could supplement the data from the citizens sampling effort.

Validation of Any Non Standard Methods. The Tedlar® bag is one of two sampling media used by the sampler. Spiking a Tedlar® bag is a problematic issue because it is not a standard collection device. While spiking canisters is an easily performed procedure, some intra laboratory study will have to be performed before supplying this spiked Tedlar® bags to the sampler for co-location with the sample taking. Both canister and bag spikes are important to assess the potential impact on the representativeness of the data generated. It is especially important if the normal samples themselves yield few compounds. A method has already been tried using the dynamic diluter at low pressure. The contents of the bag were analyzed before sending to the field.

Preparation and Certification of Tedlar® Bags for Sample collection. At the present time, the SOP and training regimen require that the Tedlar® bags be unused. This precludes the possibility of purging the bags with zero nitrogen or zero air before issuing to the samplers. This presents a problem in certification since the Tedlar® bag frequently contains a residue, N, N - dimethylacetatamide which is detected in the chromatogram, and a contaminant, phenol, derivatives of the contaminant (phenyl acetate), CFCs and other hydrocarbons. The first in-house study should be directed toward finding a way of getting rid of most, if not all, of these interferences, and doing so in a manner which is not labor intensive nor costly.

In preparation for analyzing the representative batch in the certification process, a method has

D suggest itself. It consists of using the canister cleaner and three cycles of filling to approximately 3/4 capacity followed by evacuation with the rough pump. This may have to be done manually and care should be exercised so as not to over pressurize and rupture the bag, but it shows enough promise to be tried since data reporting and validation with Tedlar® bag collected samples is onerous and time consuming.

Limitations of In-House Studies. Practical limitations are the number of bags/canisters used in the project and the volume available to be tested. The first consideration depends only on the consensual experimental design. The canisters and Tedlar bags could be stored indefinitely; but the canisters simply would not be available for rotation.

R The second consideration requires some planning and possibly readjustment of the testing frequency as a function of the results. The Tedlar® bags are nominally ten liters and practically 6 liters when filled correctly. Since their pressure is constantly at equilibrium during sample withdrawal at analysis, theoretically the entire contents could be analyzed but practically only 4 liters is available. The sampling volume is set to 400 ml. This means a Tedlar® bag should be able to be accurately sampled $4000/400 = 10$ times. The canisters, on the other hand, have rigid walls and cannot equilibrate. The vacuum pump that withdraws the sample aliquot has such a slow rate at about 1/2 atmosphere that the mass flow controller sharply loses accuracy. That means that only 3 liters or about 7 tests would be available. Since one of the objectives of this project is to evaluate holding times, the frequency of sampling will have to be adjusted so no more than 7 tests are performed on the same collection medium. It is unlikely that more than 5 tests on any single comparison phase would be required.

Effect of Ambient Conditions and Permeability. The sampling protocol for the laboratory component of this study would include generating test atmospheres for collection and subsequent analysis. Samples could be collected into bags and canisters and those with “hits” could be analyzed at 1, 3, 7 and 14 days after the initial analysis. A group of three bags and three canister samples would be subjected to heat to determine storage effects. Other test batches (3 of each media) could be subjected to sunlight and commonly present ambient air compounds (such as ozone, CO₂, or NO_x) . In addition, some of these samples would be collected at low and others at high humidity. Test concentrations would approximate those expected in ambient air (5 ppbv or less). In the absence of (or in addition to) significant hits in the samples, laboratory spiked bags and canisters could also be used.

A test could also be conducted to determine if either sample media are prone to contamination when stored in an atmosphere containing target compounds. This test would be conducted in triplicate using clean, nitrogen filled test media and would be a test of the impermeability of the media.

Effect of Holding Times. Designated containers, bags and canisters, preferably including samples with positive results, would be stored and reanalyzed as necessary in order to satisfy any requirements for evaluating the holding times. Not only would this be a test of permeability but

Data on a test of stability of the compounds, including TICs if any, in the presence of the sample media. Also since the holding time only has relevance with respect to “hits” or positive results, only those samples as well as the field spikes could be evaluated for holding time and loss due to leakage, permeability, media catalyzed degradations or intermolecular interactions. Just as above, these trials could be augmented in the absence of (or in addition to) significant hits in the samples by the use of laboratory spiked bags and canisters.

Another method of evaluating the integrity of the media, or tools, is to positively challenge the blanks, spikes and previously analyzed samples in an atmosphere of known contaminant. The media could be repeatedly used up to 5 times to determine the effect. The design of both of these evaluations would be reconsidered, changed or discarded and (a) new evaluation(s) substituted at the discretion of the Technical Workgroup.

Equipment Evaluation. In conjunction with the Data Quality Objectives, the equipment has already been tested to insure an even flow rate in 3 minutes without overfilling the bag. This has been built into the SOPs and incorporated into the training. However, the hands-on experience has shown that this requires a certain technique and the variability of some of the sampling equipment causes variable fills with the bags. This is not a problem with under filling as long as sufficient sample was collected to perform the analysis and the sampling was consistent. However over filled bags are intrinsically inconsistently sampled (i.e. not sampled at a uniform fill rate) since the pumps used may have a decreased capacity to continue to evacuate the area surrounding the “bucket” or “suitcase”. This also has to do with tightness of the fittings and the how much the inlet valve to the Tedlar® bag is turned. The correct way to do this has already been incorporated into the SOPs directing the use of this equipment, but the difference between over filling and correctly filling is delicate and the entire procedure should be re-examined in the laboratory in the event that sample bags are too full.

Use of Other Sampling Media. Sorbent tubes, one liter canisters, 400 ml canisters or 1-liter Tedlar® bags have been mentioned by members of the group. They are, or can be made available at a future time; however, the decision of the Technical Workgroup at this time is to limit the project to 6-liter canisters, Tedlar bags and three minute sampling.

Data Validation and Usability

Data Reduction and Validation. The laboratory SOPs already in place in the laboratory will be used for data reduction and review. In addition, the review process will include the other agencies and citizens groups as requested.

Reconciliation of Results with Data Quality Objectives. This is applicable when and if the Technical Group establishes formal and specific DQOs other than the general objective, cited

D above Under Data Quantity Objectives, of obtaining usable information on co-collected, co-located sampling devices using heterogeneous media. Otherwise the data will be qualified on the basis of results, attendant QC/QA and sampler information.

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