

NYS DOH

Proposed VOC Air Sampling Plan (Second Round) – WTC

NYSDOH – DRAFT Version 5 10.23.01

Objectives:

1. To assess community exposure to specific VOCs (aldehydes, ketones, phenols, acrylates) inorganic acids and particulate matter (< 100 microns) that may be contributing to the eye, nose, throat irritation complaints in the community impacted by WTC.
2. To add additional information about the constituents of the smoke at the debris pile and to identify constituents that may be potential biomarkers of exposure for use in subsequent health investigations of either workers or residents in the WTC disaster.

Proposed Scope of Work

The plan is to sample at street levels and on the roof at the same three sites sampled for VOCs on Sept 28, 2001. In addition to the three sites used in September 28, 2001, we will collect samples in the smoke as near to its source as possible and at another location that is either further away from the WTC rubble than any of the original three sampling locations. The fourth location will be at the Stuyvesant School or at a location downwind of the WTC for the purpose of evaluating contaminant levels versus distance of the WTC disaster. The samples from these 4 locations will be collected concurrently. Sampling of the smoke as close to its source will be immediately after the concurrent sampling at the other locations. An overview of the plan follows:

1. Collect outdoor air samples at the same three sites (225 Rector Ave, 120 Broadway and 75 Park Place) used in the September 28, 2001 VOC sampling. Samples will be collected at roof-top and street level at these three locations. Preferred site selection criteria:
 - rooftop height likely to be most affected by smoke and steam plume from WTC from visual observation
 - represent areas both affected (downwind) and not-affected (upwind) by the smoke and steam plume
 - not located near (150') potential commercial sources of VOCs (e.g. dry cleaners, print shops, shoe-repair shops) or, if so located, such neighbors should be identified.
2. Collect samples (2-4 hour) in the smoke plume on the rubble pile.
3. Samples collected at two times: early morning (6-10AM) and late afternoon (6-10PM) at each site. To improve the sensitivity of the measurement some samples will be collected for a greater duration.
4. Samples will be collected and analyzed as specified in Table 1. The specific analytes for each sample method are listed in Appendix 1.

Table 1. Overview of Sampling Plan *

Analyte	Sample Duration	Location	Method	Sample Collection	Analysis	Detection Limit
1.*VOCs	2-4 hours	street, roof, source	TO-14	Summa canister	GC/MS	2-4 mcg/m ³
2. Aldehydes	2-4 hours	street, roof, source	TO-11	DNPH cartridge	HPLC	1-5 mcg/m ³
3.*Ketones	2-4 hours	street, roof, source	TO-14	Summa canister	GC/MS	2-4 mcg/m ³
4. Phenolics	2-4 hours	street, roof, source	TO_14	Summa canister	GC/MS	2-4 mcg/m ³
5.*Acrylates	2-4 hours	street, roof, source	TO-14	Summa canister	GC/MS	2-4 mcg/m ³
6. Inorganic acids	8-16 hours	roof, source	EPA IP-9	Denuder/filter	Chromatograph	1-2 mcg/m ³
7. Inorganic acids	2-4 hours	street, roof, source	NIOSH 7903	Adsorbent Cartridge	Chromatograph	1 mg/m ³
8. Semi-volatiles	8-16 hours	source only	PUF	Adsorbent cartridge	GC/MS	1-2 mcg/m ³
9. TSP particulates	2-4 hours	roof, source	light scatter	real-time	DataRam	?

* All of the sampling will be done at all four community locations except for the acids (number 6); this sampling will only be done at three community sites (including at least one downwind location) due to equipment limitations. Immediately after sampling in the community, samples with this equipment will also be collected from the source;

* These chemicals were evaluated in the September 28, 2001 sampling.

Logistics:

Equipment and logistic limitations make it necessary for us to do the sampling over a two day period. Sampling is proposed for October 29 and October 30 or some other time later in the week.

Day 1 will include identification and preparation of the four community sampling locations, at least one of which will be downwind of the WTC. That evening sampling will be done for analytes 1-5, 7 and 9 as listed in Table 1. The sampling for the analytes in items 6 and 8 of Table 1 will also be initiated and continued through the night into the next day until after the morning sampling event is completed. Additionally, because we only have three units to sample for the acids listed in item 6 analyte list number 6 (inorganic acid), we will collect samples at only one upwind location and at downwind locations. Similarly, we will only be able to do the same for the aldehyde sampling (analyte 2).

Day 2 will include the morning sampling at each location sampled the previous evening. Additionally, in the afternoon, sampling of the smoke from WTC disaster rubble as close to the rubble pile if not on it will be done for all of the analytes listed in Table 1. Where possible, these samples will be collected in duplicate.

Note: If equipment setup is not completed in time for the evening sampling on Day 1, then the evening sampling will be done at the end of Day 2.

Evaluation Criteria

Results from the air samples will be compared to typical urban (if available) background ranges to determine whether there are elevated or unusual levels of chemicals. Background ranges for many of the VOCs are obtained from two databases. The United States Environmental Protection Agency's Volatile Organic Compounds Database Update (EPA Database, March 1988) is a compilation of indoor and outdoor data from studies of homes and offices across the United States. The New York State Department of Health Database (NYSDOH Database, August 1997) is a summary of indoor and outdoor air sample results in control homes collected and analyzed by the NYSDOH from 1989 through 1996. These studies include sample locations where there were no known spills or unusual sources of VOCs. If available, the results will also be compared to data from EPA's BASE database (VOCs, aldehydes). Background data from the NYC asthma study (2000-2001) is available for aldehydes (rooftop lower Manhattan) and acidity. Also, data from the NYC asthma study is available for the gases, HONO, HNO₃, HCL, SO₂ and NH₃ from July 1999 to June 2000. Values for these constituents are also in the scientific literature.

All results will include an evaluation of how the results compare between the upwind, downwind and in the smoke samples. The upwind samples define background for the specific analyte on that day. The sample

Also, the results will be compared to acute, intermediate and/or chronic public health assessment comparison values for inhalation exposure. The choice of comparison value will depend on what the sampling site represents in the way of potentially exposed populations, environmental conditions and variability of the results.

Recommendations for the general public will be suggested based on the sampling results, public health comparison values, health endpoint, etc. Comparison values that are exceeded will be evaluated on a case-by-case basis with consideration being given to the sampling time, how representative is the sample, typical background levels, the strength of available toxicological information for the contaminant, and the estimated margins of exposure relative to exposure levels known to cause adverse health effects in animals or humans.

Sampling for semi-volatiles may provide data that is potentially useful in cohort studies including at least one proposed study of asthmatics. The purpose of this sampling is to see if there is a contaminant in the WTC fire smoke that could be used to identify a biomarker. The data will be evaluated by comparing downwind samples versus samples from upwind versus smoke leaving the rubble. The idea is to locate a semi-volatile compound that is unique or significantly increased in concentration compared to background. If such a compound is found, we will evaluate the significance of that compound by evaluating the finding to that in the published literature. If there is a particular semi-volatile that is a signature of the fire, this chemical or its metabolites may be something that can be measured in blood and or urine to indicate exposure and be useful in proposed epidemiologic studies.

The attached appendices in addition to showing the specific analytes provide more information on the specific to evaluate the resulting data.

Appendix 1. List of specific analytes for each sample method.**VOCs—Summa Canister**

3	CHLOROMETHANE	T62002	38	TRANS-1,3-DICHLOROPROPENE	T61502
4	VINYL CHLORIDE	T41002	39	ETHYLMETHACRYLATE	T71002
5	BROMOMETHANE	T61802	40	CYCLOHEPTANE	T54102
6	CHLOROETHANE	T61902	41	1,1,2-TRICHLOROETHANE	T51702
7	ETHYL ALCOHOL	T53102	42	TETRACHLOROETHENE	T41202
8	TRICHLOROFLUOROMETHANE	T61702	43	ETHYLCYCLOHEXANE	T54202
9	ISOPRENE	T53202	44	1,2-DIBROMOETHANE	T60402
10	1,1,2-TRICHLOROTRIFLUOROETHANE	T41802	45	n-NONANE	T53902
11	ACETONE	T42002	46	CHLOROBENZENE	T40902
12	1,1-DICHLOROETHENE	T50902	47	ETHYLBENZENE	T51002
13	METHYLENE CHLORIDE	T23802	48	M,P-XYLENE	T51302
14	METHYL-tert-BUTYL ETHER	T18502	49	O-XYLENE	T51402
15	n-HEXANE	T53602	50	STYRENE	T85402
16	1,1-DICHLOROETHANE	T51902	51	ALPHA-PINENE	T54302
17	2,4-DIMETHYLPENTANE	T53302	52	ISOPROPYLBENZENE	T85302
18	METHYL ETHYL KETONE	T17002	53	1,1,2,2-TETRACHLOROETHANE	T51802
19	CIS-1,2-DICHLOROETHENE	T87602	54	n-DECANE	T54002
20	CHLOROFORM	T39002	55	n-PROPYLBENZENE	T51102
21	2,3-DIMETHYLPENTANE	T53402	56	1,3,5-TRIMETHYLBENZENE	T85802
22	TETRAHYDROFURAN	T29802	57	tert-BUTYLBENZENE	T85602
23	CYCLOHEXANE	T20602	58	1,2,4-TRIMETHYLBENZENE	T85902
24	1,1,1-TRICHLOROETHANE	T23602	59	sec-BUTYLBENZENE	T86202
25	ISO-OCTANE	T53502	60	d-LIMONENE	T54402
26	CARBON TETRACHLORIDE	T36602	61	1,3-DICHLOROBENZENE	T49702
27	n-HEPTANE	T53702	62	1,2,3-TRIMETHYLBENZENE	T54702
28	1,2-DICHLOROETHANE	T50802	63	1,4-DICHLOROBENZENE	T44202
29	BENZENE	T34402	64	n-UNDECANE	T54502
30	TRICHLOROETHENE	T41102	65	n-BUTYLBENZENE	T86302
31	METHYLCYCLOHEXANE	T62402	66	1,2-DICHLOROBENZENE	T44102
32	1,2-DICHLOROPROPANE	T61302	67	n-DODECANE	T54602
33	METHYLMETHACRYLATE	T23502	68	1,2,4-TRICHLOROBENZENE	T44002
34	METHYL ISOBUTYL KETONE	T70602	69	HEXACHLORO-1,3-BUTADIENE	T52502
35	CIS-1,3-DICHLOROPROPENE	T61402	70	PHENOL	
			71	2-METHYLPHENOL	

This is a repeat of the September 28, 2001 testing. The resulting data will be similar and also compared to the September 28, 2001.

Analytes 70 and 71 (phenol and 2-methylphenol) were not measured in the September 28, 2001 samples. These two compounds are in the EPA database but are from source dominated sampling events and so should be higher than background. The EPA database in this case will be a benchmark, but a high benchmark. Phenol is in the EPA base database that evaluated outdoor at and indoor air in buildings across the country. This will provide background data.

Aldehydes

	ANALYTE
<u>1</u>	Formaldehyde
<u>2</u>	Acetaldehyde
<u>3</u>	Acrolein
<u>4</u>	Acetone
<u>5</u>	Propionaldehyde
<u>6</u>	Crotonaldehyde
<u>7</u>	Butyraldehyde
<u>8</u>	Benzaldehyde
<u>9</u>	Isovaleraldehyde
<u>10</u>	Valeraldehyde
<u>11</u>	O, M, and P – tolualdehyde
<u>12</u>	Hexaldehyde
<u>13</u>	2,5-dimethylbenzaldehyde

The Bronx Asthma study (Jan 1999-Nov 2000) included the above analytes using the same methodology. That dataset will provide a good reference for the aldehyde data. Additionally, the EPA database and the EPA base database have formaldehyde results. Aldehyde air levels will be evaluated with available health-based air comparison values for acute, intermediate and long-term exposure. Also, odor and irritancy values will be considered when available.

Acids

	ANALYTE
<u>1</u>	Hydrochloric acid (as per denuder system)
<u>2</u>	Sulfuric acid (as per denuder system)
<u>3</u>	PM 2.5 Acidity-pH of the filter (aerosol as per denuder system)
<u>4</u>	PM2.5 Sulfate on the filter (aerosol as per denuder system)
<u>5</u>	HONO
<u>6</u>	HNO3
<u>7</u>	Inorganic Acids (as per NIOSH Method 7903) Sulfuric, Nitric and Hydrochloric acids

The pH of the PM2.5 aerosol and the sulfate concentration of the aerosol were measured for the entire Bronx Asthma Study (Jan 1999 –Nov 2000) period. HCl, HONO, and HNO3 were measured during the Bronx Asthma Study from July 1999 to June 2000. The Bronx asthma study included sampling in Manhattan and these data will be used as a reference. NIOSH Method 7903 (sulfuric acid) has been used in monitoring the personnel working at the world trade disaster. These data will also be used as a reference. Most of the data from the NIOSH methodology has shown just trace amounts, which is probably because the detection limit for this method is high. Levels of acids in air will be evaluated with available health-based air comparison values for acute, intermediate and long-term exposure. Also, odor and irritancy values will be considered when available.

Semi-volatiles

	ANALYTE
<u>1</u>	Benzo (a) pyrene
<u>2</u>	Napthalene
<u>3</u>	Tentatively identified compounds

This analysis is being done for the purpose of objective number 2 and only on samples collected from the smoke. It is an exploratory analysis in an attempt to better characterize the smoke to provide information for possible use in future work. The sampling methodology (PUF cartridges) used in this measurement is used by other researchers who have published air testing results for semi-volatile organic compounds.

Particulate

	ANALYTE
<u>1.</u>	TSP (100 microns)

TSP has been measured for many years and data are available for comparison purposes. Also, values will be considered on irritancy.