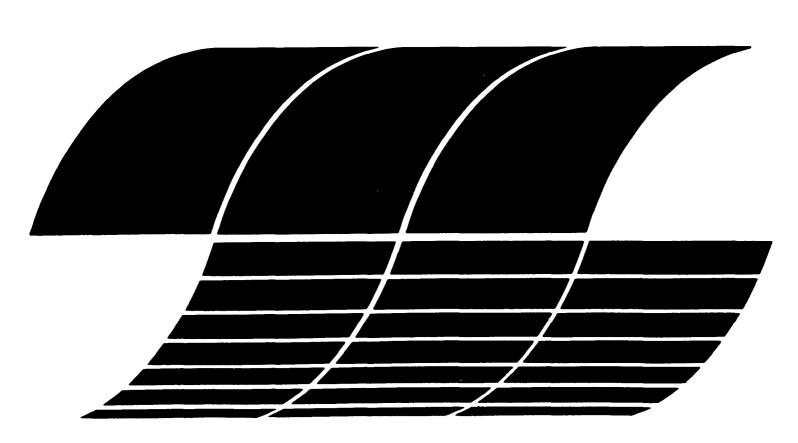
EPA-600/7-78-118 July 1978

Research and Development



Intercomparison of Samplers Used in the Determination of Aerosol Composition

Interagency Energy/Environment R&D Program Report



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INTERCOMPARISON OF SAMPLERS USED IN THE DETERMINATION OF AEROSOL COMPOSITION

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ABSTRACT

An intercomparison study was carried out to evaluate the performance of 11 different designs of aerosol samplers. The samplers were operated by participating scientific groups having recognized expertise in sampler development, operation, and the subsequent analysis of the samples they collected. The devices tested include hi-vol, TWO MASS, multiday, cyclone, CHAMP, streaker, stacked filter, and manual and automated dichotomous samplers. The samplers were operated simultaneously (on the roof of the Federal Building) in Charleston, West Virginia for eight consecutive days during May of 1977. The collection surfaces of each sampler were changed at least every 12 hours which enabled the intercomparison to be made for 16 sampling periods. Samples collected were analyzed by each participant for one or more of the pollutants for mass, nitrate, sulfur or sulfate, lead, and 8 other trace elements. The analysis methods used by the various participants included x-ray fluorescence, particle induced x-ray emission, atomic absorption, ion chromatography, colorimetry, beta gauge and gravimetric techniques.

Most of the samplers separated the aerosol into two fractions with 50 percent separation diameters ranging from 2.4 μm to 4.3 μm . The upper 50 percent cutoff diameter for the various samplers ranged from 14 μm to above 30 μm . Data were intercompared for the total, fine and coarse size fractions.

Best agreement among samplers was found for elements such as sulfur and lead that occurred primarily in the fine fraction.

The amount of total mass collected appeared to be strongly influenced by the upper 50 percent cutoff diameter of each sampler.

For the stacked filter samplers and the tandem filter samplers, the fine fraction appeared to be enriched with crustal elements such as Si, Ca, and Fe, which suggests that there are particle bounce errors.

Of all the samplers reporting results, the automated dichotomous sampler showed the greatest precision for the fine fraction species.

In the intercomparison study, total sulfur was measured by x-ray fluorescence, and sulfate was measured by ion chromatography and by wet chemical methods. The mean sulfur and sulfate concentrations were in agreement with the assumption that all of the sulfur is in the form of sulfate.

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ACKNOWLEDGMENTS

It is a pleasure to acknowledge the essential guidance provided by Mr. William Matthews, West Virginia Federal Buildings Manager, during the planning phase of this study. He was instrumental in seeing that additional electrical power was installed on the roof of the Federal Building in Charleston, WV. The cooperation and assistance rendered by Mr. Howard Stanley, Charleston Federal Building Foreman, and his crew allowed the study to proceed smoothly.

The continued support, creative suggestions, and encouragement offered by the Project Officers, Mr. Robert Stevens and Dr. Tom Dzubay, in the planning phase, during execution, and especially during the preparation of the final report is gratefully acknowledged. They were also helpful in all phases of the November, 1977 Workshop at which preliminary results of this study were presented.

Grateful appreciation is also extended to each of the intercomparison study participants who, through their creative criticisms, helped make this final report more comprehensive and complete.

Finally, it is a pleasure to acknowledge the Staff of the Director's Office Correspondence Center at Lawrence Livermore Laboratory who so cheerfully typed the many drafts and revisions required by a report of this magnitude.

INTRODUCTION

HISTORICAL PERSPECTIVE

One of the consequences that grew out of the environmental concerns of the 1960's was a demand for better air quality. For research scientists in this field this meant improving the measurement, characterization, and understanding of air pollutants both at their emission sources and in the ambient atmosphere. Consequently, more attention began to be focused on the performance of aerosol particulate samplers. Performance parameters examined more closely included sampler inlet designs, their flow rate capabilities, the particle size cutpoints employed, internal particle loss mechanisms, and types of collection substrates used, to name just a few. As a result of this attention, the development of both simple and sophisticated aerosol particulate samplers began to take place all across the country. Several conferences (1.2) helped focus on what had been accomplished as well as on what the needs were. By 1976 a great deal of air pollution information was being collected with the many different sampler designs, and results were being published in numerous journals. One of the questions that arose following the second conference (2) was how intercomparable are the results from different samplers? If the results did differ, was it by small percentages, by factors of 2, or did they differ by orders of magnitude? Were some pollutants easier to measure than others? Thus, it was suggested that a study be carried out which would begin to answer these and other questions.

OBJECTIVE

The objective of the study was to operate representative state-of-the-art aerosol particulate samplers simultaneously and side-by-side for an extended period and to compare the analytical results. This objective was achieved through a field study at which the samplers were operated by their developers or users in nearly the same manner as they are operated in typical air pollution research and/or monitoring programs. The samples collected were analyzed for selected pollutant concentrations by each participant using those analytical methods normally employed for the type of sample and pollutant collected.

SITE SELECTION

Several considerations entered into the selection of an appropriate site for the field study. Among the more important were that sufficient space, sufficient electrical power, and security for the samplers be provided. It was also desirable to conduct the study in an area where some pollutant information was available. The earlier results would give some indication of the

kind of pollutant concentrations to be expected. These considerations led to the selection of the Federal Building in downtown Charleston, West Virginia, as the site where the field study would be conducted.

This is a five story building through which there is access to a large, open roof area. It has the added bonus of a 24-hour security service. The earlier study (3) carried out in the Charleston area indicated that the month of May offered satisfactory weather conditions for the study. The field study was scheduled to begin at 8 am, Wednesday, May 11, 1977, and end at 8 am, Thursday, May 19, 1977. Sample collection was to be continuous throughout the study with collection substrates to be changed at least once every 12 hours. This 8-day duration led to sixteen 12-hour periods for which pollutant concentrations could be intercompared.

POLLUTANTS SPECIES SELECTED

There are a wide range of air pollutant species that could have been measured in such a study. Because the objective of the study was to intercompare results from as many different types of samplers as possible, the number of pollutant species selected was purposefully restricted.

Those pollutant results for which an intercomparison was believed to be meaningful were mass, nitrate, sulfur and sulfate, lead, and eight other trace elements to be selected after the field study was completed. Since the type of samplers brought to the study varied from simple to complex, the study was designed so that comparisons could be made for the total pollutant concentration reported; and also for fine and coarse fractions for samplers which collected particles according to aerodynamic size.

Following completion of the study eight trace elements were chosen. Three of these - silicon, calcium, and titanium - are representative of those elements found in the earth's crust. A fourth element, iron, is also found in this group, but may also be associated with local emission sources. These four elements tend to concentrate in the coarse or large particulate fraction, that is, in particles having aerodynamic sizes greater than 2.0 micrometers. Three other trace elements chosen were copper, zinc, and bromine. The last was chosen because of the well known bromine to lead ratio characteristic of automotive exhausts. The eighth trace element chosen was selenium, which usually occurs in very low concentrations. Its measurement becomes a challenging test of the various samplers and analytical methods used in the study.

PARTICIPANT SELECTION

Because of space restrictions atop the Federal Building in Charleston, only a limited number of samplers could be accommodated. This restriction plus the desirable option of replicate samplers limited the number of participants that could be invited to the study. Table 1 lists those participants invited to the field study and who brought samplers which were representative of those aerosol collection devices most widely used in research and monitoring programs.

TABLE 1. INTERCOMPARISON STUDY PARTICIPANTS

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and Dr. E. Macias: St. Louis. MO 63130

Environmental Sciences Research Laboratory, Dr. Thomas Dzubay

and R. K. Stevens: Environmental Protection Agency,

Research Triangle Park, NC 27711

Dr. Martin Hudson: Physics Department, Florida State University,

Tallahassee, FL 32306

Dr. Billy W. Loo: Lawrence Berkeley Laboratory, Berkeley, CA 94720

Dr. Peter Mueller: Environmental Research and Technology, Inc.,

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Dr. Charles Rodes: Environmental Monitoring & Support Laboratory,

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Dr. Roger Tanner and

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SAMPLER TYPES AND ARRANGEMENT

Table 2 lists those samplers brought to the study. Both a one page summary and detailed description of each type can be found in Appendix A. It is apparent that a number of duplicate samplers were brought. The well known high volume sampler was well represented at the study. Included were those with and without particle size inlet restrictions as used in the CHESS* study carried out in a number of communities by the Environmental Protection Agency (EPA). Of the 35 samplers brought to the study, 20 had the capability of collecting particles in two or more size fractions. Of these 15 reported size fraction results.

All of the samplers assembled on the roof of the Federal Building are shown in Figure 1. This view looks southeast toward downtown Charleston, WV.

^{*} Community Health and Environmental Surveillance Studies

The lower part of Fig. 1 includes a sketch of each sampler type. A number is is used to identify each sampler or group of samplers, while a capital letter is attached to only some of the samplers. This letter identification denotes those samplers reporting results which were intercompared and is useful in distinguishing between duplicate or triplicate samplers brought by the same participant. Sampler A is located approximately 9 meters from the eastern corner of the building while sample U is about 9 meters from the southern corner of the Federal Building. All of the samplers were located on a line approximately 1.5 meters from the southeast face of the building. All around the edge of the roof the side of the building continues upward 0.4 meter above the roof level.

Table 3 lists all of the samplers or groups assembled on the roof according to the numerical order shown on the sketch in Fig. 1. The last two columns list the sampler inlet height to the nearest centimeter, and the approximate spacing between sampler inlets. Inlet heights varied from a low of about 0.9 meters to a high of 1.75 meters. (This excludes the $\rm SO_2$ sampler inlets at 2.4 m. Its results were not part of the intercomparison study).

Table 4 lists the more important operating characteristics for those samplers whose reported results were intercompared. The alphabetical identification of the various samplers is used throughout this report both in the graphical presentations and in the tabular intercomparisons. There are several important points to be noted in this table. First, an examination of the column listing the fine cut points reveals that they vary between 2.5 and 4.3 micrometers. The first two stages of Sampler G, the Sierra Multiday Sampler, were added together before comparing its results with other samplers. Similarly, the column listing the inlet cutoff also shows a range of large particle sizes accepted by each sampler. These variations in cut-point sizes must be kept in mind when examining the results of the fine and coarse particulate fractions. The column listing the frequency of filter changes shows that for some samplers, two to four sub-period totals had to be added together to obtain the desired 12-hour pollutant concentrations. Florida State University employs an analytical technique which is capable of analyzing their linear streaker filters to within ± 30 minutes.

The filter substrates used in the automated dichotomous samplers - C, L, and S - were changed automatically every 6 hours. These samplers also employed a flow control mechanism which shut the samplers down in the event the flow rate dropped below a prescribed tolerance. On several occasions at night the particulate loading was sufficiently heavy to cause shut down very near the end of the first 6 hour period. In these instances the following 6 hours of data were not obtained.

TABLE 2. SAMPLER TYPES BROUGHT TO THE STUDY

 Type of Sampler P	articipan	t Inst.	# Units at study	Results reported for
Diffusion Battery Sampler	Tanner	BNL	1	(b)
High Volume Sampler:	Tanner	BNL	1	1
High Volume Samplers:	Rodes	EPA	2	1 ^{c)}
High Volume Sampler:	Burton	EPA	1	1
Champ (with size cuts)	Burton	EPA	2	2
Dichotomous Samplers - ERC.	Rodes	EPA	2	1 ^c)
Dichotomous Samplers - Manual	Dzubay	EPA	2	2
Dichotomous Samplers - Automated	Loo	LBL	4	3 _d)
Linear Streaker	Hudson	FSU	4	₂ e)
Batelle Impactors	Hudson	FSU	4	(e)
Tandem Filter Units	Dzubay	EPA	2	2
Stacked Filter Units	Cahill	UCD	2	₂ f)
Sierra Multiday	Cahill	UCD	1	1
Cyclone (1 w & 1 w/o size cut)	Mueller	ERT	2	2
Two Mass	Delumyea	WU	4	1
Sulfur dioxide experiment	Loo	LBL	4	(g)

a) See Appendix A for a detailed description of each sampler type.

b) Results were reported but were not intercompared, and are not included in the tables of Appendix C.

c) Data were taken with both samplers for only half of the study.

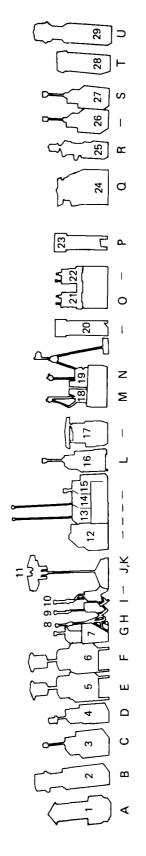
d) The fourth sampler was included in case spare parts were needed for the other three.

e) All four operated throughout the study. Results available from FSU.

f) A third total filter unit was operated throughout the study with no sizing. Only one filter change was made after four days, hence its results could not be intercompared.

g) These samplers were not part of the intercomparision study.





A photograph of the 39 different samplers assembled on the roof of the Federal Building by 9 invited participants. The profile sketch provides a key to sampler identification. The sampler numbering is from Table 3 and the alphabetical coding from Table 4. Figure 1.

TABLE 3. SAMPLER TYPES, INLET HEIGHTS AND SPACINGS

	ler Type	Investigator	<pre>Inlet Height(cm)</pre>	Spacing(cm)
1.ª	Hi-Vol and Diffusion	(Tanner-BNL)	135 & 114	
2.	Champ + Size Fractionator	(Burton-EPA)	160	91
3.	Auto Dichotomous	(Loo-LBL)	160	69
4.	Manual Dichotomous	(Dzubay-EPA)	132	81
5.	Cyclone-total	(Muller-ERT)	175	71
6.	Cyclone-fine	(Muller-ERT)	175	71
7.	Sierra Multiday	(Cahill-UCD)	140	20
8.	Total Filter Unit-1 stage	(Cahill-UCD)	137	30
9.	Stacked Filter Unit-2 stages	(Cahill-UCD)	140	28
10.	Stacked Filter Unit-3 stages	(Cahill-UCD)	140	√ 81
11.	4-Batelle Impactors 6 stages	(Hudson-FSU)	165	v 01
	4-Linear Streakers	(Hudson-FSU)	185	140
12.	Sulfur Dioxide Analyzer	(Loo-LBL)	114	√ 0
13.	ERC Sampler, w/o MgO	(Loo-LBL)	238	36
14.	ERC Sampler, w MgO	(Loo-LBL)	238	36
15.	ERC Sampler w/o MgO	(Loo-LBL)	107	76
16.	Auto Dichotomous	(Loo-LBL)	160	71
17.	2-Two Mass Samplers	(Delumyea-WU)	89	84
18.	Stacked Filter Unit	(Dzubay-EPA)	157	56
19.	Stacked Filter Unit	(Dzubay-EPA)	157	124
20.	Hi-Vol	(Rodes-EPA)	112	74
21.	ERC Virtual Impactor	(Rodes-EPA)	124	56
22.	ERC Virtual Impactor	(Rodes-EPA)	124	89
23.	Hi-Vol	(Rodes-EPA)	112	132
24.	Two Mass + Beta Gauge	(Delumyea-WU)	114	91
25.	Manual Dichotomous	(Dzubay-EPA)	132	71
26.	Auto Dichotomous	(not working)	157	58
27.	Auto Dichotomous	(Loo-LBL)	157	79
28.	Hi-Vol	(Burton-EPA)	112	64
29.	Champ + Size Fractionator	(Burton-EPA)	157	V 1

^{29.} Champ + Size Fractionator (Burton-EPA) 157

These numbers are used in Figure 1 to identify the sampler groups.

TABLE 4. SAMPLER TYPE VS. OPERATING CHARACTERISTICS & POLLUTANTS REPORTED

Sai	mpler Type	Investig and La		Fine Cut ^{a)} Points µm	Inlet ^{a)} Cutoff µm	Flow ^{a)} Rate (!/m)	Filter ^{a)} Change (hrs)	Pol M a s	lut N O 3	ant: S 0 4	s Rep sul fur	L e	ted trace ^b ele- ments
A	Hi-Vol	Tanner	BNL	-	large	700	12		N	S			
В	Champ												
	+ Size Cut	Burton	EPA	3.5	∿ 26	1130	12	М	N	S			
С	Auto Dicho-												
	tomous	Loo	LBL	2.4	∿ 25	50	6	М			s	L	te
D	Manua1			•									
	Dichotomous	Dzubay	EPA	3.5	14	14	12	M		S	s	L	te
E	ERT - Total	Mueller	ERT	-	∿ 15	100	3	M	N	S			
F	ERT - Fine	Mueller	- ERT	2.5	-	100	3	М	N	S			
G	Sierra			0.78									
	Multiday	Cahill	UCD	4.3	< 20	24	12				s	L	te
Н	Total Filter												
	1 stage	Cahill	UCD	-	< 20	24	12				s	Ł	te
I	Stacked Filter												
	2 stages	Cahill	UCD	2.6	< 20	5	12				s	L	te
J	Linear Streaker	Hudson	FSU	-	∿ 15	0.35	contin	uous			s	L	te
K	Linear Streaker	Hudson	FSU	-	∿ 15	0.50	contin	uous			s	L	te
L	Auto Dicho-												
	tomous	Loo	LBL	2.4	∿ 25	50	6	M			s	L	te
M	Tandem Filter	Dzubay	EPA	3.5	c)	7.2	12				s	L	te
N	Tanden Filter	Dzubay	EPA	3.5	c)	5.9	12				S	L	te
0	ERC Dichotomous	Rodes	EPA	3.5	\sim 20	14	12	M		S		L	
P	Hi-Vol	Rodes	EPA	-	large	1415	12	M		S			
Q	Two-Mass	Delumy	ea WU	3.5	c)	16.7	3	M			s		
R	Manual												
	Dichotomous	Dzubay	EPA	3.5	14	14	12	M	N	S	S	L	te
S	Auto Dicho-												
	tomous	Loo	EPA	2.4	∿ 25	50	6	М			s	L	te
T	Hi-Vol	Burton	EPA	-	large	1130	12	М	N	S			
U	Champ												
	+ Size Cut	Burton	EPA	3.5	√ 26	1130	12	M	N	S			

a) See Appendix A for a more detailed discussion of these sampler types and their

c) Not measured

operating characteristics.

Trace element means that silicon, calcium, titanium, iron, copper, zinc, bromine, and selenium were usually reported when they could be detected.

CONCLUSIONS

An intercomparison study was carried out to evaluate the performance of 11 different designs of aerosol samplers. The devices tested include hi-vol, TWO MASS, cyclone, CHAMP, streaker, stacked filter, and manual and automated dichotomous samplers. The samplers were operated simultaneously on the roof of the Federal Building in Charleston, West Virginia for eight consecutive days during May of 1977. The collection surfaces of each sampler were changed at least every 12 hours which enabled the intercomparison to be made for 16 sampling periods. The collected samples were returned to the laboratory of each participant and analyzed for mass, nitrate, sulfur or sulfate, lead, and 8 other elements.

Most of the samplers separated the aerosol into two fractions with 50 percent separation diameters ranging from 2.4 μm to 4.3 μm . The upper 50 percent cutoff diameter for the various samplers ranged from 14 μm to above 30 μm . Results were intercompared for the total, fine and coarse size fractions. Elements found most abundantly in the fine fraction included S, Zn, Cu, Br, and Pb; elements found most abundantly in the coarse fraction included Si, Ca, Ti, and Fe. The total mass was equally distributed between both size fractions.

Best agreements among samplers was found for elements that occurred primarily in the fine fraction. For lead the standard deviation of the results from all of the samplers were 17% and 11% for the total and fine fractions respectively. The standard deviations for sulfur were 15% and 11% for the total and fine fractions respectively. In computing the standard deviation for sulfur, the results associated with the TWO MASS sampler were excluded. For that sampler the results were lower than the mean by a factor of about 3.

The amount of total mass collected appeared to be strongly influenced by the upper 50 percent cutoff diameter of each sampler. The amounts of Si, Ca, Ti, and Fe collected in the coarse fraction were similarly affected by the inlet. The hi-vol sampler, which had the largest upper cutoff diameter, collected about 50% more mass than the manual dichotomous sampler, which had the lowest upper diameter (14 μ m).

For the stacked filter samplers and the tandem filter samplers, the fine fraction was enriched in crustal elements such as Si, Ca, and Fe. This indicates that there are particle bounce errors for such samplers.

Of all the samplers reporting results the automatic dichotomous sampler

showed the greatest precision for the fine fraction species. Three automated dichotomous samplers when compared pairwise yielded an average agreement of 1.8%, 1.8% and 3.3% for sulfur, lead, and mass in the fine fraction, respectively. For the total fraction, the agreement between pairs averaged 2%, 3%, 7% and 12% for sulfur, lead, mass and iron, respectively.

In the intercomparison study, total sulfur was measured by x-ray fluorescence, and sulfate was measured by ion chromatography and by wet chemical methods. The mean sulfur and sulfate concentrations were in agreement with the assumption that all of the sulfur is in the form of sulfate. The nitrate results showed the greatest differences among samplers, and no simple explanation for the differences was found.

RECOMMENDATIONS

This sampler intercomparison study was the first side-by-side field test of a large number of representative state-of-the-art aerosol samplers. It was successful in that it demonstrated for those samplers brought to the study that particulate mass and selected pollutant concentrations can be determined with reasonable accuracy. In fact, for lead, sulfur, and zinc concentrations in the fine fraction, all reported results were within 10% of a mean value. On the other hand nitrate concentrations were not well determined in this study for reasons that remain unclear at this time.

Among those who participated in this study, it was unanimous that the field study was well worthwhile, and it was a general consensous that a similar study should be held again at some future date. With such a future study as a possibility and based on the experiences gained in the present study a number of recommendations can be advanced which may help insure that any future study will be even more successful.

The flow rate of all samples at any future study should be checked periodically (e.g., at least twice a day). More importantly all flow rates ought to be cross-checked with a single flow rate meter so that all sampler flow rates at the study are tied relatively to a single calibration device.

All samplers brought to a future study should have nearly the same inlet restrictions and preferably axially symmetric inlets. Similarly, the cut point used to define the fine particle fraction for all samplers at such a study should be very nearly the same.

Samplers used to evaluate the possibility of any inhomogeneity in the sampled air should be run side-by-side both prior to and following the study for periods approximately 1/4 the duration of the study (i.e., two days before and two days after in an 8-day study).

One or more separate studies should be held soon and devoted to a determination of those factors that influence the determination of nitrate concentrations.

Following completion of the study, analytical technique quality control samples should be mailed to all participants and all participants required to report concentrations in ng/cm² for at least three selected pollutants. The method of appealing to independent referee analysts for quality control was successful in this study.

All samplers deployed at any future study should guarantee that they do not exhaust any pollutant which can bias another samplers results. This may require additional filtration of the exhausts of some samplers.

The spacing between samplers at any future study should average 1 meter.

All participants should be required to field and report results for at least duplicate samplers. Also, no samplers should be allowed to take up space or electrical power which do not report results.

As was the case in this study, some form of security is desirable to prevent access to the samplers by the general public.

Multi-redundant fusing of the electrical power was well worth the planning and additional investment required. A number of samplers at this study blew fuses at various times, but none was responsible for the shut down of any other sampler.

Although no rain fell during this study, any future study should plan for this eventuality.

FIELD STUDY CONDITIONS

AIR HOMOGENITY SAMPLERS AND QUALITY CONTROL SAMPLES

The aerosol samplers were assembled on the roof of the five story Federal Building in Charleston, WV along the southeast face of the building. Since the objective of the field study was to intercompare the pollutant concentrations obtained by samplers that were not located at the same point, it was necessary to test the possibility that the air sampled might not be homogeneous. Interaction between wind and the roof penthouse structures might create non-uniform wind streams. To monitor this possibility, three Lawrence Berkeley Laboratory (LBL) designed automated dichotomous samplers were operated near both ends and near the middle of the linear array of samplers. A detailed discussion of the results is presented in Section 6.

In general duplicate samplers brought by a single participant were not set up side by side. However, an attempt was made to "pair-up" samplers which were similar in operating or design principle. Two samplers might be operated side by side, but were brought to the study by different participants. Some types of samplers were more effectively operated in clusters.

In planning the study it was recognized that the concentrations reported by the various participants would be different. How much of any reported differences are due to sampler performances and how much to the different analytical methods used to analyze the samples, should be resolved if possible. The method chosen to resolve these two for this study was based, in part, on the fact that most of the participants would report trace element concentrations determined from an x-ray emission technique. The method chosen was as follows.

From one of the automated dichotomous samplers operated at the field study, a set of fine particulate fraction samples were selected. This set was analyzed by two referee analysts who were not participants in the study. Both referee analysts used energy dispersive x-ray fluoresence analysis to determine the trace element concentrations in ng/cm² of filter area. They sent their results to the study director and from the combined data, concentration values in ng/cm² were adopted for each trace element and sample in the set. Then, 3 samples were selected from the set and mailed to each of 8 participants (24 samples-total). X-ray fluorescence analysis carried out before and after extremely vigorous shake tests on the entire set of samples demonstrated that no particle losses would occur as a result of mailing. Each participant then determined selected trace element concentrations in ng/cm² for his three samples and reported these results to the study director. Their

results were compared with the adopted values from the referee analysts. Agreement between the two would suggest that the analytical method was not a source of any reported pollutant concentration differences. Results for each participants analytical quality control samples can be found in Section 6.

FIELD STUDY PRECAUTIONS AND PROCEDURES

The roof of the Federal Building was of a standard tar and gravel construction. Since the filter substrates used in most of the samplers required changing every 12 hours, a great deal of traffic would occur on this roof surface. To reduce the potential for creating large particles, certain precautions and procedures were adopted. A plywood walkway was laid down on the roof all along and in front (NW) of the samplers. A narrow walkway leading from the roof entrance/exit to the samplers was also laid down. Almost all participant traffic on the roof used these walkways. The roof also contained 3 rest rooms vent stacks and 2 water drains in the vicinity of the samplers. The presence of $\rm H_2S$ gas was clearly noted from these stacks (most serious in the former), hence they were vented away from the immediate sampling area using 6.1 m lengths of tlexible plastic pipe. The 3 rest room stacks were vented at the top of the 1st level penthouse (3.35 m) and the water drains were vented at roof level 4 m NW of the sampler array.

Filter substrates were changed at least every 12 hours, at 8 am and 8 pm. Each participant was responsible for the operation of his own sampler, including the changing and storage of new or used filter substrates. At other times traffic on the roof was discouraged. Except for one TV news interview, there was no public traffic on the roof throughout the study. At the end of the study each participant was responsible for the disassembly and removal of his samplers.

Electrical power for all of the samplers was distributed via 12 circuits each with an individual 20 amp circuit breaker. Each of these circuits terminated in a 4-plex electrical outlet into which were plugged one or two individually fused (at 15 amps) 6-circuit multi-outlet modules. Individual sampler power cords were plugged into one of the six circuits which were also separately fused at an appropriate current rating for the particular sampler connected. In the event one sampler drew too much current, this multi-redundant fusing isolated and protected each sampler from all others.

METEOROLOGICAL CONDITIONS

Meteorological conditions were satisfactory during the entire study; however, no rain was recorded during any of the sixteen 12-hour periods. Fig. 2 shows the hourly temperature variations recorded at the Charleston Airport located approximately two miles northeast of the Federal Building. Morning temperatures varied from a low of 3°C (37°F) on the first day of the study to 17°C (63°F) on the last day of the study, while the daytime maximum readings varied from 20°C (68°F) to 31°C (87°F). Since these data were obtained above the valley floor, actual temperatures atop the Federal Building may have been several degrees higher.

The relatively humidity as recorded hourly at the Charleston Airport

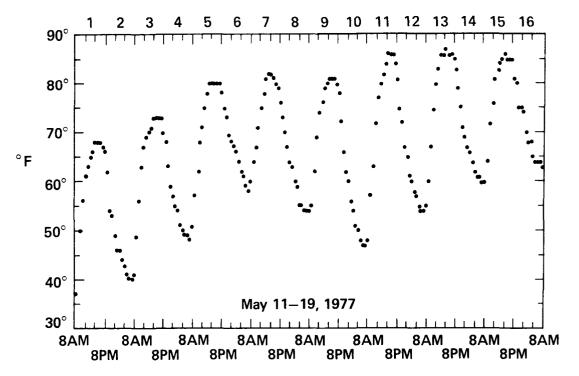


Figure 2. Hourly temperatures recorded at the U.S. Weather Station, Charleston Metropolitan Airport, throughout the intercomparison study.

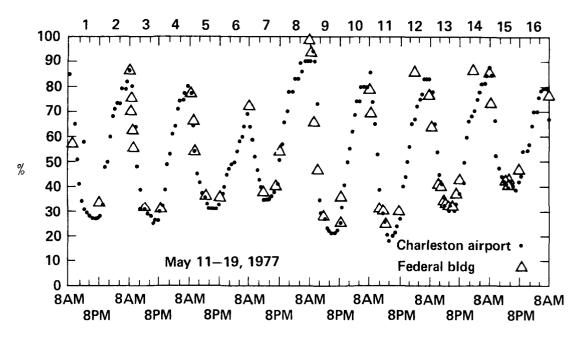
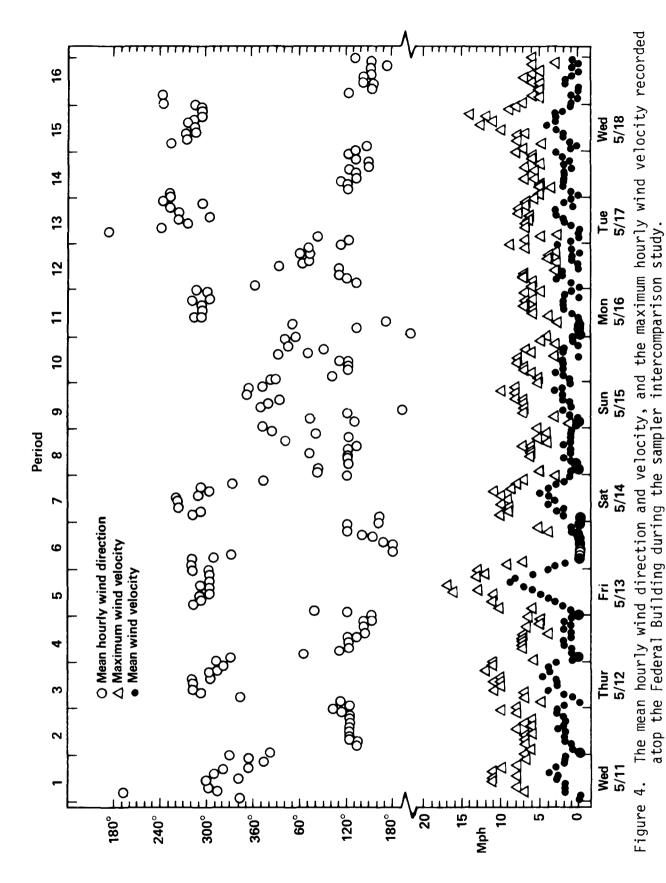
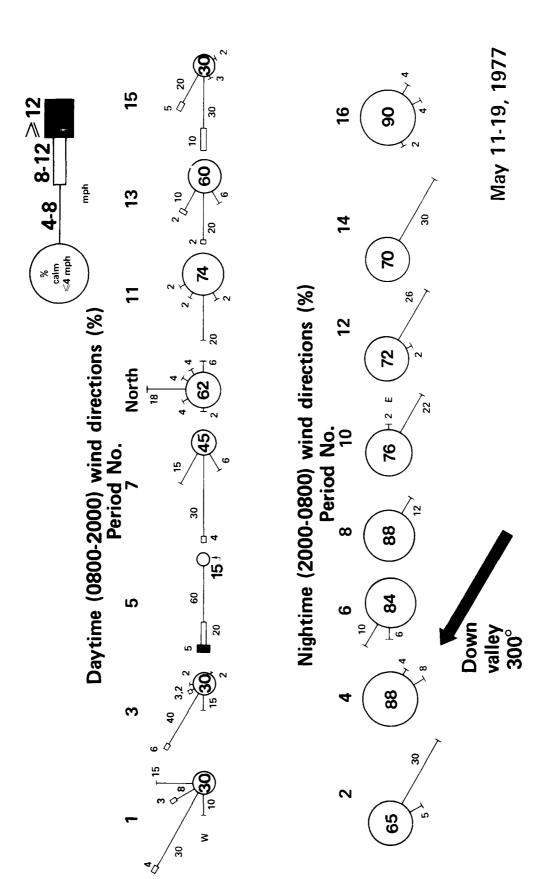


Figure 3. The relative humidity recorded hourly at the U.S. Weather Station, Charleston Airport, and occasionally on the roof of the Federal Building, downtown Charleston.

varied from 18 to 91%, while that recorded intermittently atop the Federal Building showed variations from 24 to 98%. Even though these ranges are different, it appears that the daily cycle of minimum humidity near 4 pm and maximum near 8 am are sufficiently well represented by the hourly Airport data. These data can be used to evaluate any humidity induced chemical effects that may have occurred in the filter substrates. The hourly readings are shown in Fig. 3.

The wind speed and direction (as recorded by an anemometer, wind vane, and strip chart recorders atop the Federal Building) showed a diurnal pattern. The daytime wind direction averaged about $300^{\circ}\pm45^{\circ}$, while the nightime wind direction was $120^{\circ}\pm15^{\circ}$. During four of the study periods (2,4,14,16) the winds came nearly directly into the southeast face of the building. After the study, the wind vane strip chart recording was examined and wind directions were analyzed for every 15 minutes throughout the study. From this analysis, hourly directional averages were obtained and plotted. The results are shown in the top section of Fig. 4. Using the anemometer strip chart recording the approximate mean wind velocity sustained during each hour was estimated and also the maximum wind velocity recorded during each hour was noted. These data are plotted in the lower portion of Fig. 4. Wind rose patterns are shown in Fig. 5. The odd periods (daytime) are grouped together at the top, while the even periods (night) are grouped at the bottom. These wind rose data clearly show the diurnal wind pattern typical of the Kanawha Valley in the spring.





The wind speed and direction results recorded atop the Federal Building shown as wind roses. Figure 5.

MATHEMATICAL TREATMENT OF RESULTS

CALCULATION OF A MEAN CONCENTRATION

Table 4 listed 21 samplers that reported pollutant concentrations which could be intercompared. Concentrations were reported in micrograms per cubic meter for the mass fractions, and in nanograms per cubic meter for all other pollutants. Since no sampler brought to the study was to be regarded as the standard of comparison, the reported pollutant concentrations from all samplers were assigned equal weights. Thus, a mean concentration can be calculated for each of the 16 periods, for the 13 different pollutants, and for the total, fine, and coarse particulate fractions. Only one participant reported results for coarse nitrate, while thirteen participants reported total lead concentrations.

Since all samplers were accorded equal weight, the calculation of a mean concentration can be regarded as a "composite sampler" concentration. However, there are three effects which can bias the calculated mean concentrations.

First, any sampler can potentially malfunction with the result that less than 16 concentrations values are reported. The remaining values may or may not distort the composite sampler concentration and a priori there is no way to judge which samplers should be included or excluded. Another reason for unreported results might be that the pollutant could not be detected because of poor analytical sensitivity or insufficient amounts collected. Thus, not-detected is not synonymous with zero concentration.

Second, in any large data set there always exists the possibility of outliers. These values may appear "bad" because of sampling errors, analytical technique calibration errors, sampler malfunction, or errors in transcribing results. Also an actual measured value may be quite reasonable, but is identified as an outlier by any statistical tests, because all other values reported happen to be nearly identical. Thus, statistical tests for outlying values should not be applied indiscriminately, but can be used to identify unusual values in very large data sets.

Third, in calculating a composite concentration, the mean value may be biased by duplicate or triplicate samplers if the reported concentrations from these additional samplers all lie to one side of the mean. Thus, mean concentrations can be calculated from <u>all</u> samplers reporting results, or from only <u>one</u> sampler of each type. The influence of these three factors (1) fewer than <u>16</u> periods of results reported, (2) outlying values, and (3) multi-sampler

bias must be considered in calculating a mean. After defining the equations from which the mean composite concentration is derived, each of the three factors will be discussed.

The mean concentration for any period can be calculated from the simple expression

$$Z_{j} = \frac{1}{n} \sum_{i=1}^{n} C_{ij} , \qquad (1)$$

where C_{ij} is the concentration reported by the i^{th} sampler for the j^{th} period, n is the number of sampler result sets used, and j is the period number (j = 1, 2,....16). The standard deviation associated with Z_j is calculated from

$$S_{zj} = \left[\frac{1}{n-1} \left(\sum_{j=1}^{n} C_{j}^{2} - n Z_{j}^{2} \right) \right]^{\frac{1}{2}}$$
 (2)

There will be 16 Z-mean concentrations for the 39 pollutant size fractions reported (13 pollutants \times 3 size fractions).

Fewer Than 8 Results

Because of a number of reasons including sampler malfunction, non-detectable pollutant concentrations, and others, some participants reported fewer than the total of 16 periods expected. Since there is no way to decide a priori which results are "bad" or "good" or for what reasons, the decision was arbitrarily made to eliminate from the mean concentration calculation any result set containing fewer than 8 of the 16 period results for any given pollutant size fraction. Applying this criterion, there were only 4 result sets eliminated out of 139 reported for the total particulate fractions, 4 out of 111 for the small fraction, and 5 out of 100 for the large fraction. Seven of these were because of low to non-detectable pollutant concentrations, leaving only 6 of 350 (< 2%) result sets rejected because of fewer than 8 periods reported.

Outliers

Almost always in large data sets, values can be found which fall well outside the expected statistical spread in the mean. For whatever reasons these values appear "bad", two major decisions are required. First, should a statistical test for outliers be applied and if so which one? Second, if outliers are found, should they be eliminated from the mean indiscriminately, or should some subjective judgement be employed? This is not simply rhetoric since the definition of an outlying value depends on the breadth of the distribution deemed acceptable. If the probability for rejecting an observation is made sufficiently small enough, all values can be made to be acceptable.

Two different statistical tests were used to identify outliers. One is the well-known Dixon criterion (4); and the second, the Grubbs-criterion as developed by Tietjen and Moore (5) for the detection of multiple outliers. The latter is a multi-pass or cylical test in which means are calculated,

outliers identified, the mean value recomputed, addditional outliers sought, and etc. The number of cycles and the statistical breath to the mean distribution depend on the number of observations. Application of this statistical test resulted in many values being identified as "outliers" – too many it seemed. Although it appears to be a very sophisticated test, the number of observation sets (result sets) obtained in this study was too few for most of the pollutant species reported. The Dixon criterion when used in the single pass mode is much more conservative, i.e., fewer outliers identified. The Dixon criterion was used with α arbitrarily set equal to 4%. This is the probability assumed in rejecting an observation that really belongs in the group. Any values falling more than 2% high or 2% low will be rejected. The equations which define the Dixon criterion as applied to this study's results can be found in Appendix B.

The Dixon criterion was applied to all result sets submitted. Immediately, punch card errors and recording errors were spotted. Several participants submitted results for the wrong pollutant, or results in ng/cm² instead of ng/m³. These were quickly identified by the outlier criteria. Another participant had 9 of 16 results identified as outliers. Since only 7 of the 16 periods results remained, their results were eliminated from the mean composite calculation. This was the only data set eliminated by the outlier test.

Table 5 lists all those sampler-period results which were identified as outliers by the Dixon criterion. Most of these outlying values can be understood or explained. For example, the selenium concentrations lie near the threshold of detectability, hence wide flucuations are expected. The zinc values occasionally clustered very tightly, allowing even a reasonable value to appear as an outlier. The copper excursions were due to local sources (copper from pump motors), and the excursions observed in certain crustal elements were probably real. The outlying small nitrate values also could be explained (see Section 6). In effect, then, except for the Q-sampler's small sulfur results, which were generally low by a factor of 3, all of the outliers identified were allowed to remain in the calculation of the mean.

Multiple Sampler Bias

There is a potential problem due to some participants having duplicate samplers and others having only a single sampler. If one or more sets of duplicate samplers lie well to one side of a calculated mean, the mean would be biased. To examine this posssibility an alternative mean concentration can be calculated by averaging results from only one sampler of each type. Clearly, the latter mean is defined by a sub-set of the samplers defining the former mean. Statistically, one expects the difference between these two means to show a positive or negative bias if the additional duplicate samplers are high or low. Since the number of samplers contributing to the the subset mean is less than or equal to the full set, the standard deviation in the subset mean is usually greater. Defining the full set of sampler means as Z and the subset sampler means as X, the quantities (Z-X) and ($S_{\rm X}$ - $S_{\rm Z}$) can be calculated and compared.

Table 6 shows the results of 592 mean comparisons. Almost as many mean pollutant concentrations decreased as increased when the duplicate samplers

were eliminated. As expected S_{x} is on the average, larger than S_{z} . Therefore, there is no strong evidence that including duplicate and triplicate sampler results biases the composite Z-means. In general, samplers N and R were lower than the composite mean by about the same amount that samplers C and S were higher, hence these four samplers offset each other and reduced the influence of other duplicate samplers.

TABLE 5. OUTLIERS ACCORDING TO DIXON CRITERION ($\alpha = 4\%$)

Total	Sampler-Period	Small	Sampler-Period	Large	Sampler-Period
s0 ₄	_{P-13} a)	N03	F-3,5,8,14	Mass	$0-8,10^{a}$
S	K-7 b)	S	Q-4-7,9,12-15 c)	Ti	J-15 d)
Si	_{J-9} d)	Si	I-9,12 d)	Fe	N-8
Fe	N-8	Ti	M-12;I-8,12	Cu	_{D-2,9} e)
Cu	_{D-9} e)	Zn	N-8; S-3	Zn	R-13
Zn	N-8	Se	M-9,11,16; N-8 f)	Se	_{M-2} f)
Se	M-2,9,11,14 f)				
Pb	J-9; K-9 b)				

- a) EPA (Rodes) Hi-Vol Sampler. Reason for high value unknown.
- b) FSU Linear Streaker. Apparently an artifact of the averaging process.
- c) These data were low because of an unresolved analytical error.
- d) Crustal elements. Incorrect subtraction of blank values.
- e) Occasional high values of copper due to local sources, see Section 6.
- f) Because selenium concentrations were at the threshold of detectability, these values cannot be considered outliers.

RATIO TO MEANS

Once a composite mean has been defined for each pollutant specie and sampling period, it is very useful to normalize all reported concentrations to these composite sampler mean concentrations. This results in a table in which all of the entries are near 1.0. This has numerous advantages. Among them are

- (1) Deviations from the mean are more easily observed and can be quickly converted to approximate percentage differences.
- (2) Average ratios for all 16-periods for each sampler can be calculated independent of day to day changes in concentrations. A relative measure of a sampler's overall accuracy (how far from 1.0 which is equivalent to the mean concentration) is shown by this average; and

an indication of a sampler's precision may be shown by the standard deviation in the 16-period average ratio.

- (3) Appropriate graphs of these average ratios vs samplers reporting allow sampler to sampler comparisons.
- (4) Multiple graphs of the type described in (3) allow pollutant to pollutant comparisons independent of their actual aerosol concentration differences (which may be orders of magnitude).

These advantages will become evident upon a detailed examination of the results presented in Section 6.

TABLE 6. MEAN CONCENTRATION CHANGES VS NUMBER OF SAMPLERS AVERAGED

Quantity		Change		Totals b)
	+	0 a)	-	
(Z-X)	263	77	252	592
$(S_x - S_z)$	344	59	189	592

a) No change is defined as less than a 1% change in the Z-mean or standard deviation, S_{τ} , compared to the X-mean or S_{τ} .

b) A total of $6\overline{2}4$ period-pollutant-means can be calculated (16 pds x 13 pollutants x 3 size fractions). Since only one sampler reported results for large NO₃ and one sampler remained in the X-group for large sulfate, only 592 comparisons were made.

REGRESSION ANALYSIS

Regression analyses were performed between the results from every pair of samplers, and between each sampler and the composite Z-mean. If a linear mathematical relationship is assumed to exist between two variables (sampler concentrations), then we can write

$$y = a + bx , (3)$$

where y is the dependent variable, and x is the independent variable (the Z-mean, for example). Since in this study both x and y are pollutant concentrations in $\mu g/m^3$ or ng/m^3 , the intercept, a, will also be in these units. Standard equations exist for calculating ea, the error in a. Similarly, the slope, b, and its error, ϵ_b , can also be calculated. The equations for these calculations are given in Appendix B. The extent to which artifacts exist between any two pairs of samplers, will be indicated by the extent to which a \pm ϵ_a does not overlap 0, and any consistent bias between any two samplers by the extent to which b \pm ϵ_b does not overlap 1.0. A measure of one samplers precision relative to another is given by 100 ϵ_b/b in percent. Another

form of this precision is given by the root mean square deviation concentration of the y-sampler from the regression fit y = a + bx. It is useful to see this value for all samplers compared to the composite sampler. Finally, it is useful to examine the extent to which the variables y and x are correlated. This is revealed by the correlation coefficient. In this study all samplers attempted to measure the same pollutant concentration, hence their correlation with the composite mean will usually be near 1.0. However, whenever sampler malfunctions occurred and/or few results were reported, the reported results will correlate poorly with the composite mean. The equations used to calculate all of these quantities are given in Appendix B.

SAMPLER RESULT TABLES

The complete set of results from the study is given in Appendix C. Concentration values were reported for 13 different pollutant species in 3 size fractions, the total, the small or fine, and the large or coarse particulate fraction (39 Tables). The sulfur concentration results were multiplied by 3 and combined with the sulfate results to give 3 additional tables. Figure 6 illustrates a portion of one of the 42 tables (small sulfur).

The top most grouping lists the reported concentrations in appropriate units as a function of period (1 through 16) of the study. The alphabetical sampler identification letter is that of Table 4. A dash means no value reported and a concentration value preceded by a minus sign indicates an outlier value according to the Dixon Criterion (α = 4%). The composite sampler concentration or Z-mean is listed next along with its standard deviation. Any sampler excluded is noted parenthetically, and as discussed above, all outlier values are included in the Z-mean (except for sampler Q, small sulfur). The X-mean and its standard deviation exclude selected duplicate samplers. Those included in this calculation are shown in parentheses.

The next grouping lists all sampler concentrations normalized to the composite Z-mean concentrations. Most of these entries generally lie near 1.0. To the far right, the 16 period average ratio, its standard deviation, and the coefficient of variation (percent error) are shown. An asterisk preceding any tabular values indicates that the participants reported error for that period allows his value to overlap the Z-mean (1.0). If a participant's value deviates far from 1.0 yet still has an asterisk, this indicates a rather large error; while values close to 1.0 without asterisks may suggest a small error. Below this grouping appears the mean ratios which by definition are always 1.0. However, its standard deviation reflects how tightly clustered all of the reported results are as a function of period. Note that the 16-period average standard deviation multiplied by the average pollutant concentration yields the error given to the far right of the top most grouping.

The lower grouping tabulates results of the regression analysis of each sampler vs the composite sampler (Z-mean). The quantities listed left to right are the intercept and its error in either μg or ng/m^3 , the slope and its error, the root mean square deviation in concentration units, and the correlation coefficient.

Appendix C of this report contains only the regression analysis results

1	INTERCOMPARISON ST	TUDY C PE	RIODS 1-16, MAY	11-18 1977.	
RESULTS PERIOD	1 2	3 4	11 12 13	14 15	16 AVG SD
D EPA DZUBAY MDS-A M EPA DZUBAY TF-M N EPA DZUBAY TF-P R EPA DZUBAY MDS-S C LBL LOO DICOT L LBL LOO DICOT S LBL LOO DICOT G UCD CAHILL SMDAY I UCD CAHILL SFU Q STL DEL/EO ZMASS Z MEAN(WITHOUT Q) STANDARD DEVIATION	5009 3572 3894 4951 3170 3443 4297 3040 3707 5336	+ 4182 6L 3 3684 552 7 3373 5742 - 4123 6572 9 3945 6430 4 - 6448 0 3800 5570 1 3481 7557 0 -970 -1430 4 3691 6157	5571 8475 3468 8617 . 514 - 75 - 725 3 6950 -1155 -2090 7650 7809	- 8951 9298 6606 - 8612 - 9234 9532 10125 9851 9998 9577 10146 9314 7375 -1390 -1920 9514 9131 226 959	- D 8687 M - N - R 9019 C 8969 L 9094 S - G 5833 I 3130 O
X MEAN(D,M,L,G,I) STANDARD DEVIATION	4592 2990 3674 601 512 507			9488 8733 315 1081	7830 1735
RATIO TO Z PERIOD	1 2 3	3 4 5	6 7	14 15	16 AVG SD CV
M EPA DZUBAY TF-M N EPA DZUBAY TF-P R EPA DZUBAY MDS-S C LBL LOO DICOT L LBL LOO DICOT S LBL LOO DICOT	0.90 *0.98 *1.00 1.12 1.12 1.13 1.16 *1.10 1.19 1.15 *0.91 0.81 0.79 0.79 0.87 *0.94 0.40 0.39 0.34	5 1.13 *0.98 2 *1.00 0.90 0 0.91 0.93 - 1.12 *1.07 5 *1.07 *1.04 5 - *1.05 9 *1.03 *0.90 4 *0.94 1.23 4 0.26 0.23	*1.03 *1.01 0.88 *0.98 0. 0.91 *0.96 0. *1.08 *1.08 *1.03 *1.07 *1.04 *0.92 1. *0.95 *0.95 *1. 0.15 0.16 0.	9 - 0.94 91 - 1.01 - 1.11 - 1.10 - 1 .11 31 *0	- D 0.92 0.08 9 *1.04 M 1.02 0.06 6 - N 0.95 0.05 5 - R 0.94 0.03 4 *1.08 C 1.09 0.03 3 *1.08 L 1.09 0.03 3 *1.09 5 1.09 0.05 5 - G 0.94 0.15 16 0.70 I 0.95 0.13 14 0.38 Q 0.29 0.14 47
REGRESSION VS Z D EPA DZUBAY MDS-A M EPA DZUBAY TF-M N EPA DZUBAY TF-P R EPA DZUBAY MDS-S C LBL LOO DICOT L LBL LOO DICOT S LBL LOO DICOT G UCD CAHILL SMDAY I UCD CAHILL SFU O STI DEL/ED 2MASS	INTERCEPT ERR -219.166 396.7 387.016 195.0 62.634 207.5 -95.827 167.4 266.537 189.1 195.124 114.0 325.002 196.5 -1002.408 731.9 449.415 610.2	721 0.963 029 0.944 018 0.934 055 0.962 94 1.040 091 1.051 095 1.023 034 1.170	0.070 530 0.031 284 0.036 281 0.029 227 0.029 240 0.018 166 0.031 270 0.139 880	DEV. COR.COB 1.327 0.9 1.104 0.9 1.747 0.9 1.354 0.9 1.356 0.9 1.201 0.9 1.438 0.9 1.238 0.9 1.555 0.9	972 993 991 995 996 998 995

Figure 6. A portion of one of the tables listing results for the pollutant small sulfur. Complete results for all pollutants can be found in Appendix C. See text for an explanation of the entries.

of each sampler with the composite sampler. Regression analysis results on all pairs of samplers are available from the study director, the EPA project officers, or any of the participants.

SELECTED RESULTS AND DISCUSSION

PRECAUTIONS IN INTERPRETING RESULTS.

The objective of the study was to evaluate sampler performance by intercomparing the reported concentrations of selected pollutant species as measured by the samplers. The measured concentrations contain many factors which influence their magnitude. Before presenting the results, it is worthwhile examining some factors that can influence the concentration values obtained.

In Section 1, Table 4, the various sampler performance parameters were presented. Among the more prominent differences were sampler flow rates, inlet designs, particle size cut-points, and collection substrates. Those samplers which had cylindrically symmetric inlet designs should be insensitive to wind direction, but not necessarily wind speed. Samplers with such inlets will accept particles up to some limiting aerodynamic size. Others which do not have cylindrically symmetric inlets will be wind direction dependent. In comparing total pollutant specie concentrations, the maximum size particles accepted may influence the final concentrations obtained.

Some of the samplers brought to the study separated the incoming air particles into two or more size fractions. In comparing results from these samplers, the particle size distribution will influence the results obtained. A sampler having a fine particle cut-point of 2.5 micrometers cannot obtain the same concentration as one having a 3.5 micrometer cut-point, all other factors being equal. In comparing results for large particle sulfur, for example, a sampler having a cut-point of 2.5 micrometers may record significantly more large particle sulfur than one having a cutpoint of 4.3 micrometers particularly if very little sulfur is associated with particles having diameters greater than 3.0 micrometers. Also some filter substrate materials, particularly fiberglass, will allow the formation of stable SO_4 ions from SO_2 gas which passes through them. This adds some mass and causes an artificial increase in the SO_4 concentration.

Another important factor is the analytical technique, its sensitivity, accuracy, and precision. Supposedly all analytical techniques used are calibrated as carefully as possible. But different calibrations can result even for identical instruments if two different "standards" are used. Thus, even analytical technique calibrations can lead to differences as large as 5%, and possibly 10% depending on the technique.

Clearly, sampler flow rates, cut-points, and analytical techniques can lead to differences in reported concentrations. Other important parameters

that may cause differences are the extent of particle bounce-off from sampler walls, sticky vs non-sticky substrates, different methods employed in the initial calibration of a sampler flow rate and cut points, different methods of monitoring sampler flow rates at the field study, screened or unscreened inlets, and possible inhomogeneity in the air actually sampled. These are just a few of the sampler parameters which can lead to differences in the final results. Some of the differences may be explained and removed, other parameters will be unknown and the differences they cause in the results not removable. Therefore, the reader is urged to consider very carefully those factors which can contribute to observed differences, before drawing conclusions about a samplers relatively "good" or "bad" performance.

POLLUTANT CONCENTRATION VS PERIOD

Pollutant concentrations were reported for each 12 hour period in $\mu g/m^3$ for all mass fractions and in ng/m³ for all other pollutants. Table 7 lists the 16 period pollutant concentration averages and standard deviations for all thirteen species measured. For the total fraction, maximum and minimum values and their standard deviations observed during the 16 periods are also given. For the small and large fractions, only the 16-period averages and standard deviations are tabulated. The sum of the latter two averages is not always equivalent to the total average because some sampler types measured the total fraction, but not either sub-fraction. An inspection of the results shows that large particulate crustal elements have the largest standard deviations. On the other hand, those elements typically found in the small particulate fraction are somewhat better measured even though their absolute concentration is less.

Not all of the various pollutant species measured behaved in the same manner throughout the study. Figure 7 shows several selected pollutant specie composite sampler concentrations (the Z-means) as a function of half day periods for the total and small fractions. The error bars shown represent standard deviations. The slightly displaced squares indicate the small or fine fraction (< 3.0 \pm 0.5 μ m) Z-mean concentrations. From Table 4 it was clear that there was a wide range in particle sizes selected by the sampler inlets (as well as the fine particle cut-points), hence part of the spread in the standard deviations is due to variable size particles accepted by the different sampler inlet designs and cutpoints. The standard deviations in the crustal elements, silicon, calcium, titanium, and iron, show the greatest variation; mass shows somewhat less variation. Pollutants typically concentrated in the fine fraction show the smallest standard deviations.

Throughout Figure 7 the odd periods represent daytime collections (0800 - 2000 hrs) while the even periods represent nighttime collections (2000 - 0800 hrs). Except for sulfur the lowest pollutant concentrations were recorded during period 9. Note that the silicon and iron concentrations track each other closely, and mass behaves similarly to the crustals, but is not identical. The zinc concentrations were approximately constant except for two large excursions during periods 2 and 4. Lead concentrations peaked Friday and Saturday nights, periods 6 and 8. Sulfur slowly increases as the study progressed except for the 24 hour dip beginning Sunday at 0800. Visibility was good during the beginning of the study, but deteriorated steadily ending in

TABLE 7. 16-PERIOD POLLUTANT CONCENTRATION AVERAGES FROM ALL SAMPLERS REPORTING RESULTS FOR MAY 11-19, 1977

	Total	Fraction	Small Fraction	Large Fraction	
Pollutant	Av g	Max & Min Values Recorded	Avg	Av g	
Mass g/m ³	104 <u>+</u> 18*	146 <u>+</u> 23 47 <u>+</u> 6	55 <u>+</u> 13	43 ± 15	
Nitrate ng/m ³	1880 <u>+</u> 1000	2860 <u>+</u> 2400 860 <u>+</u> 450	1020 ± 760	1090 ± 500	
Sulfate ng/m³	19350 ± 3000	30600 ± 3800 6420 ± 2360	18200 ± 3000	930 ± 400	
Sulfyr ng/m	6640 <u>+</u> 1000	10800 ± 970 1935 ± 400	5870 <u>+</u> 630	574 <u>+</u> 240	
Siligon ng/m	9950 <u>+</u> 3650	17600 ± 7200 4000 ± 2100	1140 ± 520	7680 ± 3300	
Calcium ng/m ³	2500 ± 900	4200 ± 1500 730 ± 350	300 ± 160	2230 ± 1000	
Titagium ng/m	250 <u>+</u> 90	400 ± 100 88 ± 46	44 <u>+</u> 29	210 <u>+</u> 100	
Iron ng/m ³	1750 <u>+</u> 500	2400 ± 670 730 ± 240	350 ± 150	1400 <u>+</u> 600	
Copper ng/m ³	88 ± 40	400 ± 70 24 ± 12	80 ± 30	17 <u>+</u> 9	
Zinc ₃ ng/m	116 <u>+</u> 22	283 ± 41 62 ± 14	76 <u>+</u> 13	40 <u>+</u> 13	
Selegium ng/m	10 ± 3	27 ± 4 3 ± 1	9 <u>+</u> 3	1 <u>±</u> 1	
Bromine ng/m ³	236 <u>+</u> 59	489 ± 126 65 ± 19	190 ± 48	64 <u>+</u> 23	
Lead ₃ ng/m³	1070 <u>+</u> 180	1660 ± 260 326 ± 93	820 <u>+</u> 90	220 <u>+</u> 90	

^{*} Standard deviations

an air stagnation alert (throughout the southeastern mountain states) that began 36 hours before the end of the study.

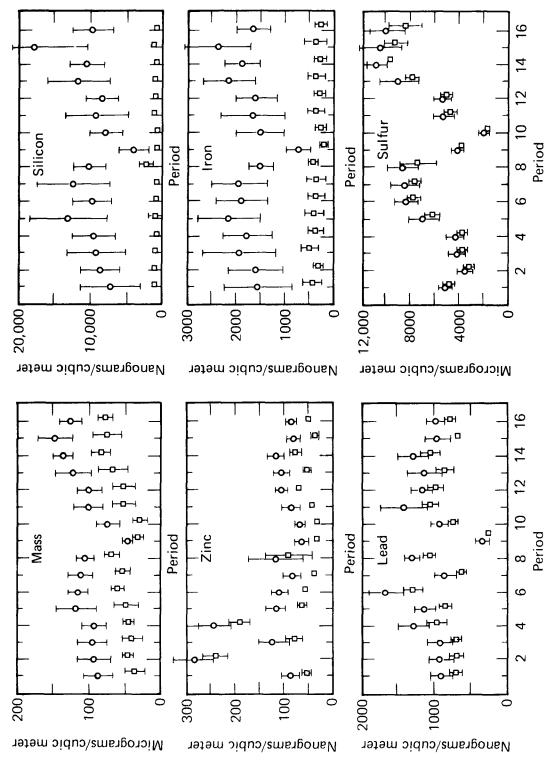
Typically, the small mass fraction constituted about half of the total mass collected; while small silicon and iron constitute only 11 and 20% of their totals, respectively. About 80% of the sulfur and lead are found in the small fraction, while zinc is almost equally distributed 60/40% in the small/large fraction. All of the results from which these plots were made can be found in the complete tabulation of the total, small and large fraction results in Appendix C.

AIR HOMOGENEITY

As mentioned in Section 1 all samplers were arranged in a linear array 1.5 meters from the southeast face of the building. Sampler A was located about 9 meters southwest of the eastern corner of the roof, and sampler U about 9 meters from the southern corner of the building. Two CHAMP samplers, B and U, were duplicates and collected both large and small fractions; samplers C, L and S were the automated dichotomous samplers (ADS); and samplers D and R were the manual dichotomous samplers (MDS). Note that samplers B, C, and D were adjacent while R, S, and U were nearly adjacent. The former group was toward the eastern end; the latter group toward the southern end. Sampler L was located nearly centrally. The three automated dichotomous samplers C, L, and S were brought to the study and used to evaluate the homogeneity of the air sampled on the roof (see Section 4, page 13).

One method of evaluating any possible inhomogeneity in the air sampled is to ratio concentration results from pairs of duplicate samplers. This can be done for selected pollutant species, say mass and the crustal elements in one group, and man-made elements in a second group. Table 8 lists the ratio of pollutant concentrations as obtained from 4 pairs of samplers for three size fractions and two pollutant groups. Ratios obtained from the two ADS pairs for the crustals pollutants in the total and large fraction suggest that about 20% more crustals are collected at the south end relative to the east end. However, the MDS and CHAMP sampler pairs do not observe this dispersion. For the small particulate fraction in either pollutant group there is no disper-The MDS samplers suggest a reverse dispersion for the fine particle crustal elements at the east end. For pollutant group B (anthropogenic trace elements) there really is no strong evidence for any south to east dispersion. In retrospect it would have been useful to have operated the ADS samplers side by side before or after the study to verify that they would yield identical results. However, such tests were not carried out.

Results obtained for wind velocity and direction, which were monitored atop the Federal Building, indicated a strong diurnal wind pattern. Winds were predominantly from $300^{\circ}\pm45^{\circ}$ during the day, while at night they were from $120^{\circ}\pm15^{\circ}$. If the south to east dispersion were caused by the roof penthouses one might expect it to disappear or reverse as the winds changed directions from night to day. Ratios similar to those in Table 8 were obtained for the same pairs of samplers, only grouped according to odd and even periods, and mean values obtained. There was no significant statistical evidence for any diurnal variation of the dispersion. That is, the ADS sampler



Sixteen 12-hour mean concentrations of all samplers reporting results for total (circles) and small (boxes) particle size fractions for the pollutants mass, Si, Zn, Fe, Pb, and S. Figure 7.

showed the south to east dispersion consistently for pollutant group A, total and large fractions, night or day; while the MDS did not. The observed dispersion, then, appears to be independent of any micrometeorological wind streams associated with the penthouses or roof.

TABLE 8. POSSIBLE SOUTH TO EAST DISPERSION IN THE AIR SAMPLED

Pol	lutant	a) Sam	pler Identif	ication and Ra	itios
Gro	up	S/C ADS	S/L ADS	R/D MDS	U/B CHAMP
Total Fraction		1.19 ± .05 b) 1.06 ± .05	1.08 ± .02 1.04 ± .05	0.99 ± .05 0.97 ± .12	0.98 c)
Large Fraction	A B	1.22 ± .01 1.10 ± .08	1.08 ± .02 1.02 ± .08	1.04 ± .05 0.97 ± .09	1.05 ^{c)}
Small Fraction		1.00 ± .05 1.03 ± .05	0.98 ± .04 1.04 ± .06	0.74 ± .06 6 0.98 ± .08	e) _{0.96} c)

a) Pollutant Group A contains mass, silicon, calcium, titanium, iron, i.e., the crustal elements. Pollutant Group B contains the anthropogenic elements sulfur, zinc, bromine, and lead.

b) Standard deviation.

ANALYTICAL TECHNIQUE QUALITY CONTROL SAMPLES

From one of the automated dichotomous samplers operated by LBL, a set of 30 fine fraction samples was selected. These samples were analyzed by two referee analysts (Robert Giauque of LBL and Norman Bonner of LLL) for Ca, Ti, Fe, Cu, Zn, Se, Br, and Pb. Silicon was not determined because of significant particle size corrections that must be applied for the soft silicon x-ray. Agreement between the results from the two referee analysts was good. Regression analyses were peformed on the two sets of data and the results are tabulated in Table 9. In two past intercomparison studies (6,7) in which these two referee analysts have participated the LLL values were also observed to be 5% or so lower than the LBL values. Thus, for this study adopted concentration results were used which were essentially mean values of the reported referee results.

c) Only mass was determined by the CHAMP samplers.

d) Excludes the large zinc fraction ratio (0.73).

e) Excludes the small mass ratio (1.04).

TABLE 9. REGRESSION ANALYSIS FITS OF REFEREE ANALYSTS RESULTS

Element	LLL = $(B \pm \epsilon_b)LBL + (A \pm \epsilon_A)$	No. Values LLL/LBL
Ca	0.915 ± 0.071 66.2 ± 25.9	30/30
Ti	0.933 ± 0.114 8.2 ± 7.7	29/23
Fe	1.003 ± 0.026 -12.0 ± 15.0	30/30
Cu	0.986 ± 0.012 -4.6 ± 4.9	29/30
Zn	0.937 ± 0.007 9.2 ± 2.1	30/30
Se	0.887 ± 0.018 1.2 ± 0.7	28/28
Br	1.063 ± 0.020 -6.3 ± 9.2	30/30
Pb	0.935 ± 0.014 8.9 ± 36.2	30/30
Mean Slop	e 0.957 ± 0.056	

Sulfur was analyzed on all 30 samples by one of the participants (Loo) and on 6 samples by one of the referee analysts (Giauque). Before the sulfur measurements could be performed by the referee the six filter samples had to be cut down to 2.54 cm diameter circles. Since the sulfur analyses were performed after the samples were cut, there was a possibility that material may have been lost as a result of the cutting process in which case the sulfur data would be biased. Five of the six filter samples were analyzed for sulfur, and then reanalyzed at LLL for the 8 trace elements previously measured. The sixth sample was rendered unmeasurable in trying to cut it. Table 10 shows the results for the LLL reanalysis. Sample 80721 may have been contaminated somehow by a copper-zinc source because the values were unquestionably different afterwards. The selenium concentration on sample 80730 was very low (large error). Otherwise there is excellent agreement before and after cutting. There is evidence that the bromine concentration changed and additional evidence for its loss with time is discussed below. There was excellent agreement between Loo's 5-sulfur results and the LBL referee values, hence Loo's sulfur values were used as reference values for the remaining 24 samples.

TABLE 10. RATIO OF XRF RESULTS FOR CUT TO UNCUT FILTER SAMPLES

Cut Sample Concentrations (ng/cm ²) by XRFA Uncut Sample Mean Concentrations (ng/cm ²) by XRFA										
Sample Number	Ca	Ti	Fe	Cu	Zn	Se	Br	Pb		
80721	1.053 ±.167 ^a)	N.D.	0.959 ±.163	1.809 ±.177	1.368 ±.191	N.D.	0.814 ±.203	0.935 ±.142		
80724	0.966 ±.126	0.903 ±.169	0.897 ±.125	1.092 ±.201	0.879 ±.201	0.861 ±.150	0.819 ±.120	0.933 ±.142		
80725	1.062 ±.131	1.288 ±.264	1.125 ±.138	1.081 ±.159	1.023 ±.191	1.000 ±.264	0.912 ±.159	1.052 ±.141		
80730	1.000 ±.168	0.630 ±.226	1.126 ±.157	1.051 ±.150	1.026 ±.145	0.571 ±.566	0.945 ±.157	1.036 ±.141		
80734	0.993 ±.157	1.188 ±.223	0.943 ±.151			N.D.		0.896 ±.141	GRAND MEAN terror/# samples	
MEAN	1.015 ±.041	1.002 ±.297	1.010 ±.108	1.223 ±.394	1.074 ±.208	0.811 ±.219	0.873 ±.066	0.970 ±.069	1.003 ±.209/34	
	WITHOU	т[] і	Entries	1.028 ±.068	0.976 ±.084	0.931 ±.098			0.979 ±.123/31	

a) Standard deviation

Eight sets of three samples each were mailed to the remaining participants. Some of the participants did not make trace element concentration measurements on their own samples, so were not required to measure them on the reference samples. The results for all elements except silicon are shown in Table 11. Except for the Washington University group these results eliminate the analytical technique as a source for any large (> 10%) differences in reported pollutant concentrations. The bromine values appear to be unstable with time and will be discussed more completely below.

TABLE 11. PARTICIPANT RESULTS FROM ANALYTICAL TECHNIQUE QUALITY CONTROL SAMPLES

	S	Ca	Ti	Fe	Cu	Zn	Se	Br	Pb	Mean
Cahill a) UCD (3)	1.01 ±.07	1.41 b) ±.26	1.04 ±.43	1.01 ±.06	0.90 ±.01	1.14 ±.05	0.93 ±.06	0.91 ±.05	0.92 ±.03	0.98 c) ±.08
Dzubay EPA (3)	0.93 ±.04	0.89 ±.06	1.14 ±.13	0.96 ±.05	1.04 ±.13	0.95 ±.06	0.96 ±.14	0.92 ±.05	0.93 ±.02	0.97 ±.08
Loo (30) ^d LBL	0.98 ^{d)} ±.04	1.27 ±.13	1.33 ±.19	0.98 ±.05	1.02 ±.07	1.10 ±.06	0.87 ±.14	1.16 ^{e)} ±.06	1.03 ±.02	1.08 ±.15
Hudson FSU (3)	0.89 ±.05	1.06 ±.16	1.01 ±.05	0.94 ±.04	1.33 ±.44	1.12 ±.20	(f)	0.92 ±.07	0.84 ±.05	1.01 ±.16
Rodes EPA (2)	1.06 ±.16	~		-	-	-	~	-	1.03 ±.02	-
Tanner BNL (3)	0.84 ±.12									
Delumyea WU (3)	0.76 ±.15									

Burton (EPA) and Mueller (ERT) did not report trace element concentrations.

AVERAGE SAMPLER RATIOS VS SAMPLER TYPE

Each sampler's 12-hour pollutant concentration was normalized to the Z-means to yield ratios near 1.0. These ratios can be averaged for all the periods to obtain an average sampler ratio for the duration of the study. For example, if the high volume sampler consistently collects more total mass than the composite sampler Z-mean, its mean ratio for the entire 16 periods would be greater than 1.0. Another sampler with a more restrictive inlet would have a ratio less than 1.0. An examination of these mean ratios can show systematic trends, illustrate consistent differences between sampler

a) The number of reference samples measured is given in parenthesis.

b) The filters were temporarily exposed to a known source of calcium contamination (cement dust).

c) Mean value calculated without including calcium.

d) All 30 reference samples were originally from one of the automated dichotomous samplers. Only five could be compared with the referee results.

e) These bromine values were obtained early, then divided by the referees' results which were obtained later after an apparent bromine loss. See the Bromine Loss discussion below.

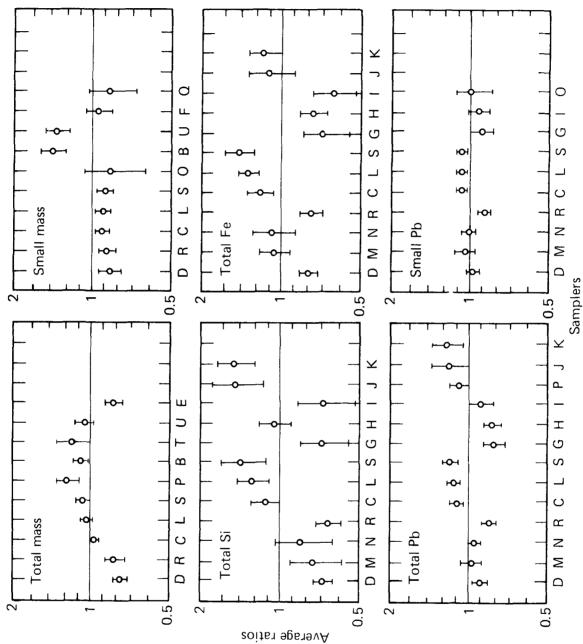
f) Selenium concentrations were to small to be accurately measured by PIXE.

types, and even give an indication of the accuracies and precisions for groups of samplers brought to the study by an individual participant.

Figure 8 shows results for a composite of four selected pollutant species. The 16-period average ratios are plotted as a function of sampler type. The abscissa lists the sampler identification number (see Table 4). The samplers are grouped by participants and arranged within each group in an east to south direction. The top two plots display those samplers reporting total and small mass. Some participants reported both. The two ordinary Hi-Vol samplers P and T report the highest relative mass, undoubtedly because of their ability to collect larger sized particles (unrestricted inlet size). These two samplers report 50% more total mass than the two manual dichotomous samplers, D and R. The CHAMP samplers, B and U, with inlet restrictions report 15% less mass than P and T. Sampler E, the cyclone unit, also reports relatively lower total mass. For small mass, all of the samplers excluding B and U report an average mean sampler ratio of 0.89 \pm 0.03 vs 1.36 \pm 0.03 for B and U, a factor of 1.56 times as much mass. This is a large difference and suggests that more than a single sampler performance parameter is responsible. Sampler O (Rodes manual dichotomous reports more variability than do samplers D or R (Dzubay manual dichotomous). Sampler O is an older model.

The middle set of plots display all of the sampler results for total silicon and iron. Note the much larger scatter in these two elements compared to total mass, the larger standard deviations, and the same patterns for groups of samplers for the two elements. Sampler H is anomalously high only for silicon, not for iron (or calcium or titanium). The systematic increase shown by samplers C, L and S - east to south is the same 20% air inhomogeneity discussed above, but it is not evidenced by the ratio of samplers R to D, or U to B (total and small mass). The two tandem filter samplers M and N also record more iron (and titanium and calcium) than silicon, relative to D and R. These two tandem filter samplers operate in a similar manner to the UCD stack filter sampler, I, but record relatively more iron than silicon.

The two lower plots display the behavior of the mean sampler ratios for total and small lead. The tight clustering of the small lead results and the generally smaller standard deviations for both is immediately apparent. Note the lack of statistically significant evidence in samplers C, L and S for the south to east air inhomogeneity. As discussed above the crustal elements exhibited such an inhomogeneity in these samplers, but the fine particles, e.g. sulfur, lead, and zinc, did not. Once again, the pattern of certain groups of samplers high, others low, is repeated. Thus, a given participant has reproducible results regardless of which kind or type of sampler he operates, but apparently there are real group to group calibration differences. For example, LBL (samplers C, L, and S) reported 10% more lead in the analytical technique control samplers (Table 11) than did EPA (Dzubay-samplers D, M, N, and R) or UCD (samplers G. H and I). If an appropriate correction is made to their small lead average ratios averages there is even better agreement in the overall results. However, how does one correct for the fact that the fine particle cut-points of samplers C, L, S, and I are about 2.5 micrometers, versus 3.5 micrometers or greater for samplers D, M, N, R and G? The former should record less small lead, not the same, unless there are yet other compensating



The average ratio vs sampler type. Each sampler reported concentration results for up to 16 periods. Each reported result was normalized to the Z-mean and averaged over the number of results reported to yield the ratios and standard deviations shown here. Figure 8.

factors. For total lead concentrations inlet particle size restriction differences may be invoked to explain any remaining differences. Sampler 0, which operates on the same principle and has the same flow rate as D and R, is less precise. It also shows a larger variation for small mass than did D and R.

Figure 8 is an example of the kind of comparison that can be drawn for the pollutant species measured at the intercomparison study. The foregoing discussion points out some of the striking differences, and in several cases, advances possible explanations. Other comparisons of sampler average ratios will be discussed below.

PAIRWISE PRECISION OF SAMPLERS

There were 6 participants who brought two or more samplers of one type to the field study. Of these 4 reported results that could be intercompared. Since one participant brought triplicates and another, two different duplicates, 7 sets of samplers can be pairwise compared. One measure of the precision of one sampler 'ersus another is contained in the error on the slope of the linear regression fit to the results from both samplers. Since a regression analysis was performed on all pairs of samplers, the data are available. In the expressions

$$y = a + bx \text{ or } x = c + dy \tag{4}$$

the percent error or precision, P, is given by

$$P = 100 e_b/b = 100 e_d/d$$
 (5)

where ϵ is the error in the slope b or d. Note that, in general, b \neq d, nor does ϵ_b = ϵ_d , unless the correlation coefficient and both slopes are nearly exactly equal to 1.0.

Table 12 lists the precisions of the 7 pairs of samplers for selected pollutant species in the three size fractions. Of course, not all of the samplers were able to measure each of the size fractions hence the blank entries. For example, samplers J and K measured only the total fractions. The best precisions were obtained on fine sulfur and lead as was suggested by the standard deviations shown in Figs. 8 and 9. For these two pollutants, the automated dichotomous samplers obtained excellent precision or reproducability (1.4 to 2.3%). When the good to excellent precision obtained by the manual and automated dichotomous samplers for the fine particulate fraction is compared to results for the large fraction, there is a suggestion that large particulates are not as easy or reproducible to collect. In addition, it appears that the automated dichotomous sampler, S, did not behave as uniformly as did C or L. Perhaps there are variable amounts of particle bounce off or other loss mechanisms associated with large particles in dichotomous samplers; or differences between sampler inlet designs.

Appendix C contains all of the reported results for all pollutants, participants, and periods. However, the only linear regression analysis results included are those for each sampler versus the composite sampler (Z-mean).

Detailed regression analysis results for all pairs of samplers can be obtained from the study director, one of the EPA project officers, on any of the participants.

TABLE 12. PAIRWISE INTERCOMPARISON OF SAMPLER PRECISIONS (%)

Frac- tion	Pollu- tant	Burton ^{a)} B vs U		Dzubay ^{c)} D v s R				
_	MASS	6.2		10.6	4.6	8.9	8.3	
T O T A	SULFUR		7.3	5.9	1.5	1.8	2.3	5.7
A	IRON		14.3	8.2	9.0	15.6	11.8	12.6
L	LEAD		5.7	5.1	1.7	2.7	2.8	11.2
S	MASS	4.8		7.0	2.5	3.4	4.1	
M A	SULFUR		5.0	6.1	1.5	1.9	1.9	
L	LEAD		5.3	3.3	1.7	1.4	2.3	
L	MASS	15.2		18.5	8.0	13.1	11.0	
L A R G E	IRON		13.1	9.3	9.2	17.8	11.8	
	ZINC		14.5		8.0	30.0	14.2	

a) The CHAMP sampler with inlet size restrictions and one size cut.

SULFUR-SULFATE COMPARISONS

Recently it has been shown (8) that sulfate concentrations can be obtained by determining the elemental sulfur concentration and multiplying by three. Figure 9 shows an intercomparison of the sulfur and sulfate concentrations as reported by the various participants. The sulfur concentrations were multiplied by three, combined with the sulfate results, and a combined Z-mean concentration determined. Then, the normalized ratios were calculated for each period, and regression analyses were performed on the combined result set. These results are included in Appendix C. The 16-period average sample

b) The tandem filter units; however, different substrates were used.

c) The manual dichotomous samplers.

d) The automated dichotomous samplers.

e) The linear streaker samplers, one with 0.4 μ nucleopore, the other with 0.2 μ nucleopore substrate filters.

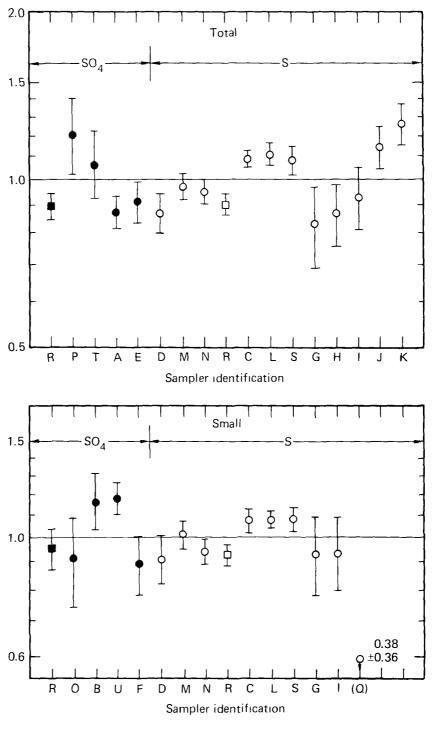


Figure 9. 16-Period average sampler ratios for sulfur and sulfate combined. It was assumed that the determined elemental sulfur concentration times 3 is equivalent to determined sulfate concentration. Only one sampler, R, reported both. Participant using sampler Q reported results which were low.

ratios are plotted vs sampler type for total and small sulfate-sulfur. Filled symbols represent sulfate, open symbols sulfur. Only one participant (Dzubay-EPA) measured both for the same sampler (R). It is assigned a square symbol versus circles for all other samplers.

Sulfur occurs predominantly in the small fraction; and comparison with the small lead results shown in Figure 8 reveals the same samplers are relatively high and low. Samplers C, L, and S suggest no south to east inhomogeneity for small sulfur. Dzubay's group (D, M, N, and R) and the UCD group (G, H, and I) report on an average 10% lower concentrations than the LBL group. However for sulfur, Table 11 indicates that there is not a 10% difference in the analytical technique quality control results for these three groups as there was for lead. Sampler G (the Sierra Multiday - UCD, fine cut point $\leq 4,3~\mu\text{m}$) reports only 5% as much sulfur as does sampler I (stacked filter unit, UCD, fine cut point $\leq 2.6~\mu\text{m}$) in the large (coarse) particles. Yet for total sulfur the former two groups are lower than the LBL values by about 18%. Therefore, from the total sulfur and lead results there appears to be at least a 10% difference between what samplers D, M, N, R, G, H, and I collect and what C, L, and S collect. Samplers J and K, the linear streakers, also report relatively more sulfur.

For the total sulfate results, the two EPA Hi-Volume samplers, P and T, are 28% higher than the average of the three remaining samplers R, A, and E. (Note that sampler A is a Hi-Volume sampler, which used phosphoric acid treated filters.) Similarly for small sulfate, the two samplers, B and U are 28% higher than the average of the three remaining samplers R, O, and F. This 28% increase in both the total and fine fraction results may be due to artifact formation (9) of SO_4 from SO_2 by the fiberglass filters used in samplers P, T, B, and U. The standard deviations in the sulfate determinations do not appear to be as good as those for total and small sulfur (\pm 12% for SO_4 vs \pm 8% for S). If the sulfate to sulfur ratio is calculated from the total and small concentration results instead of assuming it to be 3.0, the 16-period means are 3.03 ± 0.34 for total sulfate to sulfur, and 3.11 ± 0.23 for the small fraction. Thus the assumption of obtaining sulfate concentrations from elemental sulfur results multiplied by three, is supported by results obtained in this intercomparison study.

NITRATE RESULTS

An inspection of the reported results in Appendix C for total or small nitrate concentrations reveals a number of strange variations in reported concentrations. For total nitrate the sampler pairs R and T showed higher nitrate concentrations relative to themselves during the day (odd periods) than at night (even periods). The samplers A and E relative to themselves showed the opposite pattern, that is, higher nitrate concentrations at night.

Nitrate concentrations in the small fraction were measured by samplers R, B, U, and F; coarse nitrate was measured by only sampler R. Samplers E and F operate similarly except for fine particle cutpoint. No diurnal pattern similar to that recorded for the total fraction was evident for those samplers reporting small nitrate. Except for periods 1, 14, and 16, sampler R reported nitrate concentrations below their detectability limit of 50 ng/m³, compared

to concentrations of nearly 4000 ng/m^3 reported by sampler F for periods 3 and 8.

There are two hypotheses which may explain the wide disparity of nitrate results. The results varied by a factor of 4 to 9 for total nitrate concentrations and up to two orders of magnitude for the fine fraction nitrate concentrations. Neither hypothesis invokes problems with nitrate determination after collection and extraction since all investigators determined nitrate by either a reduction-colorimetric technique or by ion chromatography. Cross-checks by both methods of the same extract from samples derived from sampler A yielded roughly equivalent results: mean (IC $[NO_3^-]/colorimetric [NO_3^-]$) = 1.03 \pm 0.57.

One hypothesis is that the differences in nitrate levels reported are due to the presence of nitric acid vapor and/or NO_2 in the sampled air, which was collected with varying efficiency depending on the filter material used, and analyzed as nitrate. Based on the work of Spicer (10) on nitric acid collection efficiency one would predict total nitrate values for the reporting samplers (R, T, A, and E) which increased in the order R (Teflon) \leq A (acid-treated quartz) < E (Teflon-coated glass) < T (glass fiber). The actual order was R < T < A < E and it is necessary to introduce other explanations for the observed nitrate concentration order.

A second explanation is that already-collected nitrate-containing particles may be impacted by acidic sulfate particles resulting in the topochemical reaction

$$HSO_4^- + NO_3^- \rightarrow HNO_3^{\uparrow} + SO_4^{2-}$$
 (4)

releasing nitrate from those filter materials which, by reason of surface neutrality do not adsorb nitric acid vapor. This might explain why, for example, the total nitrate values of sampler A sometimes are close to those of sampler R (periods 7, 13; acidic sulfate present) while at other times sampler A values approximate those of sampler E (periods 4 and 6). But this hypothesis does not explain the relatively low results of sampler T. Thus, results from this study would suggest that further extensive laboratory and field studies are required before credible nitrate concentrations can be quoted for ambient aerosols.

PARTICLE BOUNCE

Recently, John et al (11) described tests on the filtration of solid particles by Nuclepore filters in which evidence for the phenomenon of particle bounce was presented for tandem or stacked filter units. The mechanism for this phenomenon is pictured as solid particles nominally in the coarse fraction rebounding from the filter surface, being re-entrained in the flow, penetrating the filter, and being collected as part of the fine fraction. By contrast liquid particles stick to the filter surface inihibiting the bounce phenomenon. Thus, the collection efficiency assumed for the coarse or fine fraction may become dependent on the physical state of the aerosol particles collected, and possibly on the substrate used.

Results were reported by two groups that used either Tandem Filters (TF) or Stacked Filter Units (SFU). These two samplers operate similarly; however, their fine cut points were different, 3.5 μ m for the TF and 2.6 μ m for the SFU. Nevertheless, some evidence for the bounce of coarse particles into the fine fraction can be found for these samplers if a comparison is drawn with other samplers having similar fine cut points. The manual dichotomous samplers had a 3.5 μ m fine cut point, while the automated dichotomous samplers had a 2.4 μ m fine cut point. By ratioing the results reported for one sampler to another for pollutants found predominently in the fine fraction, e.g., Zn, Pb, and S; and then for those found primarily in the coarse fraction, e.g., Si, Ca, and Fe, a relative measure of bounce into the fine fraction can be obtained. Table 13 lists the ratios of 16-period averages from just the small fraction results for selected samplers. For example, samplers M and N obtained 16-period average ratios of 1.13 and 1.03 respectively for Zn (see results, page 132, Appendix C), while D and R obtained 0.99 and 0.88, respectively. Ratioing the sum of (M + N) to (D + R) yields the ratio of 1.16 shown for Zn.

TABLE 13. COARSE PARTICLE BOUNCE INTO THE FINE FRACTION

Selected Sampler Ratios of 16-Period Average Small Fraction Results

	Element_				Element				
	Zn	Pb	S		Si	Ca	Fe		
% in Small Fraction ^a	57	77	90	Mean Fine	11	12	20	Mean Coarse	Mean C Mean F
M+N ^b) D+R	1.16	1.11	1.06	1.11 ±.05	1.45	2.53	2.10	2.03 ±.54	1.83
3(I) ^{c)} C+L+S	0.88	0.86	0.87	0.87 <u>+</u> .01	2.54	1.70	1.44	1.89 ±.57	2.17
The coarse particle content in the fine fraction for the tandem or stacked filter samplers relative to the manual or automated dichotomous samplers appears to be about 2.								2.00 ±.17	

a) From Table 14 (page 48).

Column 5 in Table 13 gives the mean ratio for three of the elements characteristically found in the fine fraction, while column 9 gives the mean ratio for three elements characteristic of the crustal fraction. It appears that tandem filters M and N obtain 11% more fine pollutant concentration than D and R, the manual dichotomous samplers while the stacked filter unit obtains 13%

b) M and N are the Tandem Filter Samplers (Dzubay) and D and R are the Manual Dichotomous Samplers (Dzubay). The 16-period average ratios for individual samplers and particular pollutants can be found in Appendix C.

c) I is the Stacked Filter Unit (Cahill) and C, L, and S are the Automated Dichotomous Samplers (Loo).

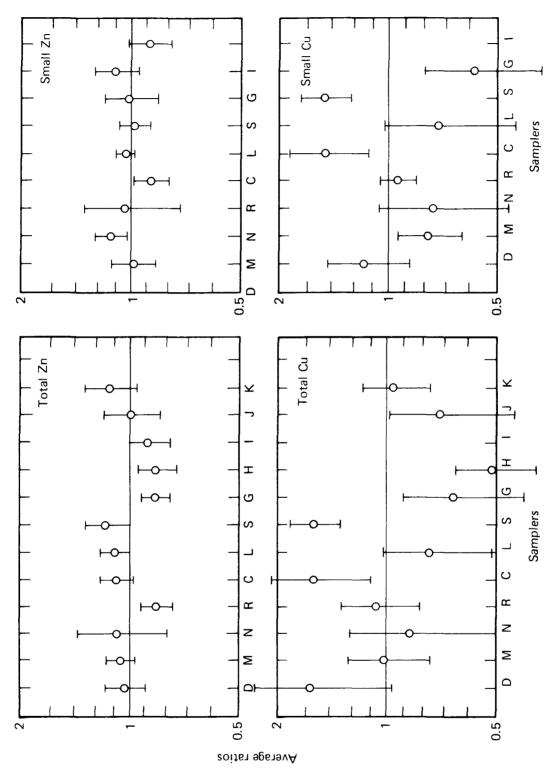
less than the automated dichotomous sampler. The small percentage differences for Zn, Pb, and S are <u>not</u> the focus of the particle bounce question. Continuing, column 9 shows that M and N record twice as much Si, Ca, and Fe as do samplers D and R, while sampler I records almost twice as much as samplers C, L, or S. Finally, if the mean coarse results are ratioed to the mean fine results (last column), any sampler bias or normalization differences are removed. The average mean ratio shown in the bottom section of Table 13 indicates that there is about twice as much coarse particle content in the fine fraction for the tandem and stacked filter units relative to the manual and automated dichotomous samplers. Once again, the very excellent agreement in pollutant concentrations obtained by all of the sampler types at the study for fine lead, sulfur, and zinc would indicate that the crustal particle increases in the fine fraction observed for the tandem and stacked filter units can be attributed to particle bounce from the coarse filter onto the fine filter.

There is also some evidence for particle bounce in another sampler that collects particles by inertial impaction. The CHAMP sampler uses a 26 μm cutoff inlet, a glass fiber filter covered impaction stage and backup filters designed to collect particles in the 0-3.5 μm and 3.5-26 μm ranges. Compared with other samplers the CHAMP sampler collected more mass in the fine fraction and relatively less mass in the coarse fraction. This is consistent with a particle bounce phenomenon that has been observed in previous field studies when dry surfaces were used as impaction plates (12). Because of the bounce problem, overestimation of the crustal materials in the fine fraction can occur depending on the sampler type, and any attempt to measure the acidity of the fine particle fraction would be compromised due to the presence of alkaline crustal elements.

LOCAL SOURCES OF COPPER

Thirty nine samplers were assembled on the roof of the Federal Building within approximately 18 meters. This is an average of one-half meter separation between samplers, much closer together than samplers would normally operate in monitoring programs. Precautions were taken to vent the exhaust of selected samplers over the edge of the roof if they were suspected of causing problems. Several participants claimed filtered exhausts. In spite of the precautions taken there appears to have been several localized sources of copper, probably from winding dust generated in several sampler pump motors.

Copper and zinc are neighboring elements in the periodic chart (Z = 29 and 30, respectively) and their mean concentrations throughout the study were comparable (90 \pm 40 and 120 \pm 20 ng/m 2 - totals, and about 80 ng/m 2 each—small). Their respective K x-rays are not considered soft and are easy to excite via the several x-ray fluorescence analysis techniques used to obtain the concentrations from the collected particulate matter. Thus, they would appear to be excellent monitors of each other if one assumes their behavior as aerosols are similar. As has already been mentioned in the previous sections, the zinc pollutant levels were, along with sulfur and lead, among the most consistently and accurately measured. This is illustrated by the two graphs shown in the top half of Figure 10. These plots show the 16 period average ratios for total and small zinc obtained by all those samplers reporting trace elements. The standard deviations on the total fraction are



be accurately determined; while copper concentrations show large fluctuations. This was probably due to nearby high-volume sampler pump motor exhausts which caused localized copper 'hot' spots for samplers D, C, and S. The zinc concentrations appear to show large fluctuations. This 16-Period average sampler ratios for zinc and copper. Figure 10.

comparable to those for the small fraction (indicating that even the large zinc particles were well behaved).

These two graphs are to be compared to the lower half of Figure 10 which shows similar results for copper. Note that samplers M, N, and L report approximately equivalent concentrations for total and small, zinc and copper. These samplers are centrally located. Samplers C and S report twice as much small and large copper as L, while the nearly adjacent samplers D and R report less than twice as much as M and N. This decrease in recorded concentration towards the center suggests the outer samplers A and/or B, and T and/or U all CHAMP or high volume samplers - may be responsible for the localized copper source. These samplers have the highest flow rates. Two additional high volume samplers were in permanent operation by the West Virginia Air Pollution Board about 2 meters to the southwest of sampler U. This makes a total of 3 high volume samplers to the southwest of sampler S, and only one to the northeast of sampler C, yet the concentrations recorded by S and C are nearly the This suggests a rapid decrease in localized concentrations levels with distance. Note also that sampler D was 0.7 m inwards and adjacent to C. while R was 1.3 m inwards and NOT adjacent to S (see Table 3). Since no trace element concentration levels were evaluated for any of the CHAMP or high volume filter samples, it is not known whether these samplers can induct their own emissions. This can probably happen, but will be dependent on meteorological conditions.

There also appeared to be a strong local source of copper and its concentrations were highest during some of the even periods (2000-0800 hrs). From the diurnal wind patterns this places the source southeast of the Federal Building. For periods 2, 4, 12, 14, and 16 mean copper concentrations varied from 80 to 400 ng/m³ and averaged 200 ng/m³. The other three even periods averaged 38 \pm 6 ng/m³; while all odd periods except 13 and 15 averaged 28 \pm 6 ng/m³ (13 and 15 averaged 54 \pm 6 ng/m³). Eliminating all results from the five high concentration even periods, and calculating an average concentration value for samplers (D, C, and S) less samplers (M, N, R, L, G, H, J, and K) yields 32 ng/m³ additional total copper collected by samplers D, C, and S. Almost 95% of the total copper seen during periods 2, 4, 12, 14, and 16 was contained in the small fraction (\leq 3.5 μ m); whereas only about 60% of the pump motor copper is contained in the small fraction.

BROMINE LOSS

Thirty fine particulate samples were selected from one of the automated dichotomous samples. These particulate samples were collected on teflon filter substrates having 1 μm pore sizes and were used as analytical technique quality control samples. Results obtained by the participants were presented above. It was mentioned that a possible bromine loss with time may have occurred on these substrates. This evidence comes from four measurements. First, the original measurement of bromine concentration on all 30 samples by Loo when normalized to the lead concentrations gave 1.19 \pm 0.10. Second, the LLL value obtained for Br to Pb one month later gave 1.14 \pm 0.03. Two months later 5 of the 30 samples when remeasured after cutting gave 1.02 \pm 0.10 for the Br to Pb ratio. Finally, six months after Loo's original measurement, he remeasured 2 of the 24 samples that were mailed out and obtained 1.00 \pm 0.03

for the relative bromine to lead concentration. In this last measurement Loo also observed a 12% loss of chlorine. Thus, it appears that fine fraction lead bromochloride deposited on teflon filter substrates may require two to six months to stabilize after deposition.

DIURNAL VARIATIONS IN POLLUTANT CONCENTRATIONS

Because of the regular and dramatic wind shifts of nearly 180° at approximately 9 am and 9 pm each day, it is worthwhile examining the reported pollutant concentrations for any day/night variations in the size fraction concentrations. These variations are easily obtained from the composite sampler concentrations or Z-means for the totals and two size fractions reported. Odd periods correspond to daylight hour collections (0800-2000 hrs); while even periods correspond to predominantly nighttime collections (2000-0800 hrs).

Table 14 lists the percentage of selected pollutants found in either the small or large fraction. The tabular entries are recorded in percent. The second column lists the 16-period average percent of pollutant concentration measured in the small fraction, exceptions as footnoted. The results under column three indicate that perhaps as much as 12% more small fraction mass is collected at night as during the day. The crustal elements are definitely concentrated in the large fraction, and only a suggestion of any diurnal variation is found. Note that the sum of the small and large fractions for the silicon and titanium percentages do not total to 100%. This bias is introduced by samplers which report only total trace elements. sources of copper were discussed earlier. Selenium is not entered in this table. Its concentrations were very low, were concentrated 88% in the small fraction, and showed no diurnal variation. During periods 13 and 11 selenium concentrations increased to 2 and 3-times the typical concentrations of 10ng/m³ observed. Zinc also showed three excursions above normal during periods 2, 4, and 8. Otherwise about 60% of it is found in the small fraction. Bromine and lead are two well known pollutants associated with the internal combustion engine. They show evidence of a diurnal variation. The recorded bromine concentration did increase to about twice the average observed concentrations during period 2, indicating a local non-automotive source. There appears to be 20% more bromine collected at night. One possible explanation is that the lack of sunlight allows more bromine to remain in particulate form, while during the day more of it is converted to a gaseous form.

Period 8 and 9 appear to yield anomalous Z-mean ratios for all of the crustal elements. These two periods were also the least normal in terms of the typical diurnal wind patterns (see Figures 4 and 5); and period 9 was unusual because the wind was nearly calm and shifted constantly (see Fig. 5).

TABLE 14. PERCENT OF POLLUTANT IN THE SMALL OR LARGE FRACTION

Pollutant	% in Small Fraction	% in Small or Large Fraction Day, Night, Fraction ^a)	Comments
Mass	51 ± 7 ^{b)}	48 ± 6 , 54 ± 8 , small ^b)	Pd. 8/9 high, 67% small
s + so ₄	90 ± 3	No diurnal effect	Pd. 8/9 normal
Silicon	11 ± 3^{b}	76 ± 5, 84 ± 3, large ^{b)}	Pd. 8/9 low, 57%-large
Calcium	12 ± 2 ^{b)}	87 ± 2, 93 ± 4, large ^{b)}	Pd. 9 low, 68%-large
Titanium	17 ± 2 ^{b)}	86 ± 6, 89 ± 2, large ^{b)}	Pd. 8/9 low, 72%-large
Iron	$20 \pm 3b$	77 ± 3, 84 ± 3, large ^{b)}	Pd. 8/9 low, 68%-large
Copper	See discussion	on local sources of coppe	r, page 44
Zinc	57 <u>+</u> 7 ^{c)}	55 ± 7, 60 ± 7, small	Pd. 8/9 normal
Bromine	79 ± 9 ^{d)}	72 ± 7, 86 ± 3, small	20% more Br at night
Lead	77 <u>+</u> 4	74 ± 2, 79 ± 3, small	Pd. 8/9 normal
Br/Pb	20 ± 4 ^d)	18 ± 3, 23 ± 3, small	

a) The plus or minus value is the standard deviation. Small or Large refers to the percentage of either the small or large fraction (Z-mean) found relative to the total (Z-mean).

b) Periods (Pd.) 8 and 9 were omitted from calculations because of anomalous percentages and unusual meteorology (see text).

c) Periods 2, 4, and 8 were omitted from the calculation. During these periods 87, 79 and 79% respectively, of the total zinc was recorded in the small fraction. A local source of zinc probably caused the dramatic increase in zinc concentrations recorded during these periods.

d) Periods 2 and 10 were omitted from the calculation. The bromine concentration increased dramatically during period 2. The bromine to lead ratios went to 61 and 33%, respectively, for periods 2 and 10.

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APPENDIX A

SAMPLER AND ANALYTICAL TECHNIQUE SUMMARIES

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PARTICIPANT: Robert M. Burton

INSTITUTION: U.S. EPA, Health Effects Research Laboratory

SAMPLER TYPE: CHAMP Particulate Fractionator

OPERATING CHARACTERISTICS:

FLOW RATE: 1130 \(\ell / m \)

PARTICLE SIZE CUTPOINTS: 26 μ m (upper cut-off)

3.5 μ m (lower cut-off)

COLLECTION SUBSTRATE: 12-inch diameter Glass Fiber,

Gelman Type A $(3.5-26 \mu m)$ 8-inch by 10-inch Glass Fiber,

Gelman Type A $(0-3.5 \mu m)$

METHOD OF FLOW CALIBRATION AND MAINTENANCE:

1. Sierra Calibration Orifice Model 330.

2. Sierra High Volume constant Flow Controller model 310, with measured stability of .03 cubic meters/minute.

ALL SPECIFIC POLLUTANT SPECIES MEASURED:

- 1. Mass $(0-3.5 \mu m)$.
- 2. Mass $(3.5-26 \mu m)$.
- 3. Suspended Nitrates $(0-3.5 \mu m)$.
- 4. Suspended Sulfates $(0-3.5 \mu m)$.

- 1. Mass (0-3.5 $\mu\text{m})$ and (3.5-26 $\mu\text{m})$ Mettler Digital Balance (.01 mg sensitivity).
- 2. Suspended Nitrates $(0-3.5~\mu\text{m})$ Filter strip reflux with distilled water, copper-cadmium reduction, sulfanilamide reaction.
- 3. Suspended Sulfates $(0-3.5 \, \mu\text{m})$ Filter strip reflux with distalled water, water soluble sulfate then measured by the methylthymol blue (MTB) method.

PARTICIPANT: Robert M. Burton

INSTITUTION: U.S. EPA, Health Effects Research Laboratory

SAMPLER TYPE: CHAMP Flow Controlled High Volume Sampler

OPERATING CHARACTERISTICS:

FLOW RATE: 1130 ℓ/m

PARTICLE SIZE CUTPOINTS: none

COLLECTION SUBSTRATE: 8-inch by 10-inch Glass Fiber,

Gelman Type A

METHOD OF FLOW CALIBRATION AND MAINTENANCE:

1. Sierra Calibration Orifice, Model 330.

2. Sierra High Volume Constant Flow Controller Model 310, with measured stability of .03 cubic meters/minute.

ALL SPECIFIC POLLUTANT SPECIES MEASURED: (including those not intercompared)

- 1. Total Mass
- 2. Total Suspended Nitrates
- 3. Total Suspended Sulfates

- 1. Mass Mettler Digital Balance (.01 mg sensitivity).
- 2. Suspended Nitrates Filter strip reflux with distilled water, copper-cadmium reduction, sulfanilamide reaction.
- 3. Suspended Sulfates Filter strip reflux with distilled water, water soluble sulfate then measured by the methylthymol blue (MTB) method.

PARTICIPANT: Thomas A. Cahill, + Air Quality Group, Crocker Nuclear Lab.

INSTITUTION: University of California, Davis 95616

SAMPLER TYPE: Sierra Multiday Impactor

OPERATING CHARACTERISTICS:

j

FLOW RATE (in liters/m): 24 liters/min

PARTICLE SIZE CUTPOINTS: Stage 1 - 4.3 microns - less than 20 microns*

Stage 2 - 0.78 microns - 4.3 microns Stage 3 - 0.01 microns - 0.78 microns

COLLECTION SUBSTRATE: Mylar type S, with about 60 micrograms/cm²

Apiezon L coatings; filter - 0.4 micron

Nuclepore

METHOD OF FLOW CALIBRATION AND MAINTENANCE:

Rotometer in instrument; orifice $(0.5" H_20)$ on intake, (interm.) cal. by 9 litre Collins

Spriometer

No flow control (early unit borrowed for test)

Mean change in flow - 5.7%; Estim. error, $\pm 2\%$

ALL SPECIFIC POLLUTANT SPECIES MEASURED: (including those not intercompared)

1. Routinely included in output: Na,Mg,Al,Si,P,S,Cl,K,Ca,Ti,V,Cr,Mn,Fe Co,Ni,Cu,Zn,Ge,Ga,As,Se,Br,Rb,Sr,Zr,Mo,Ba,Pt,Au,Hg,Pb

2. All other elements heavier than sodium - x-ray lines recorded, with energy and intensity, for manual reduction. Second analysis with higher gain to cover Ca - Rare earths.

- 1. PIXE 18 MeV alphas (2 detector gains)
- 2. XRF secondary fluorescers and filters

^{*}Intake calibrated for 20 micron cut point (approximate); 60 mesh stainless steel screen added since that time has reduced the cut point.

PARTICIPANT: Thomas A. Cahill, + Air Quality Group, Crocker Nuclear Lab.

INSTITUTION: University of California, Davis 95616

SAMPLER TYPE: Stacked Filter Unit

OPERATING CHARACTERISTICS:

FLOW RATE (in liters/m): 5 liters/min

PARTICLE SIZE CUTPOINTS: Coarse stage - 2.6 microns - less than 20

microns*

Fine stage - 0.01 microns - 2.6 microns

COLLECTION SUBSTRATE: Coarse stage - 8 micron Nuclepore Filter

Fine stage - 0.4 micron Nuclepore Filter

METHOD OF FLOW CALIBRATION AND MAINTENANCE:

Orifice meter intermittantly placed over intake, calibrated by 9 litre Collins Spirometer

Passive flow control through a 10:1 ballasting orifice at pump.

Mean change in flow - 9%; Estim. error, ± 2%

ALL SPECIFIC POLLUTANT SPECIES MEASURED: (including those not intercompared)

- Routinely included in output: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Ga, As, Se, Br, Rb, Sr, Zr, Mo, Ba, Pt, Au, Hg, Pb
- 2. All other elements heavier than sodium x-ray lines recorded, with energy and intensity, for manual reduction. Second analysis done during this test for Ca through rare earths.
- 3. Mass, coarse and fine

- 1. PIXE 18 MeV alphas (2 detector gains)
- 2. XRF secondary fluorescers and filters
- 3. Mettler blance

^{*}Intake calibrated for 20 micron cut point (approximate); 60 mesh stainless steel screen added since that time has reduced the cut point.

PARTICIPANT: Thomas A. Cahill, + Air Quality Group, Crocker Nuclear Lab.

INSTITUTION: University of California, Davis 95616

SAMPLER TYPE: Total Filter Unit

OPERATING CHARACTERISTICS:

FLOW RATE (in liters/m): 24 liters/min

PARTICLE SIZE CUTPOINTS: None; intake, less than 20 microns*

COLLECTION SUBSTRATE: Gelman GA4 Filters (NOTE: Results obtained at

Charleston low by 8% due to incorrect filter

area used.)

METHOD OF FLOW CALIBRATION AND MAINTENANCE:

Orifice meter imtermittantly placed over intake, directly calibrated by a 9 litre

Collins Spirometer

Passive flow control through a 2:1 ballasting

orifice at pump.

Mean change in flow - 1%; Estim. error, ± 1%

ALL SPECIFIC POLLUTANT SPECIES MEASURED: (including those not intercompared)

Routinely included in output: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Ga, As, Se, Br, Rb, Sr, Zr, Mo, Ba, Pt, Au, Hg, Pb

2. All other elements heavier than sodium - x-ray lines recorded, with energy and intensity, for manual reduction. Second analysis done during this test for Ca through rare earths.

3. Mass

- 1. PIXE 18 MeV alphas (2 detector gains)
- 2. XRF secondary fluorescers and filters
- 3. Mettler blance

^{*}Intake calibrated for 20 micron cut point (approximate); 60 mesh stainless steel screen added since that time has reduced the cut point.

SUMMARY OF SAMPLING AND ANALYSIS METHOD

PARTICIPANT: Richard Delumyea & Ed Macias

INSTITUTION: Washington University

SAMPLER TYPE: TWOMASS two stage sequential tape sampler

OPERATING CHARACTERISTICS:

FLOW RATE (in liters/m): 12 to 18 ℓ/m

PARTICLE SIZE CUTPOINTS: $3.5 \mu m$

COLLECTION SUBSTRATE: Glass fiber with celluose backing

METHOD OF FLOW CALIBRATION AND MAINTENANCE:

See long write-up, page 74

SPECIFIC POLLUTANT SPECIES MEASURED:

Mass, Sulfur

PARTICIPANT: T. Dzubay, et al

INSTITUTION: US EPA

SAMPLER TYPE: Two manual Dichotomous, Samplers D and R

OPERATING CHARACTERISTICS:

FLOW RATE (in liters/m): 14 l/m

PARTICLE SIZE CUTPOINTS: 3.5 μ m (14 μ m upper cut-off)

COLLECTION SUBSTRATE: Sampler D: asymmetric teflon (1-10 μ m)

Sampler R: $1 \mu m$ (FALP) Fluoropore

METHOD OF FLOW CALIBRATION AND MAINTENANCE:

Sampler D: Differential pressure regulator on pump exhaust

Sampler R: Sierra Series 250 servo system

ALL SPECIFIC POLLUTANT SPECIES MEASURED: (including those not intercompared)

Sampler D: mass and all elements detected by XRF

Sampler R: mass, SO₄, NO₃, S, Pb, and other trace elements detected

by XRF

ANALYTICAL TECHNIQUE(S) USED:

Gravimetric, XRF, Ion chromatograph

PARTICIPANT: T. Dzubay, et al

INSTITUTION: US EPA

SAMPLER TYPE: Two Tandem Filter Samplers, M and N

OPERATING CHARACTERISTICS:

FLOW RATE (in liters/m): 7.2 \(\ell / m \)

PARTICLE SIZE CUTPOINTS: 3.5 µm

COLLECTION SUBSTRATE: Sampler M: 9.6 \(\mu \) Nucleopore (coarse)/

0.4 µm Nucleopore (fine

Sampler N: 9.6 µm Nucleopore (coarse)/

Assymetric Teflon (fine

METHOD OF FLOW CALIBRATION AND MAINTENANCE:

Sierra flow servo system

ALL SPECIFIC POLLUTANT SPECIES MEASURED: (including those not intercompared)

All elements detected by XRF

ANALYTICAL TECHNIQUE(S) USED:

XRF

PARTICIPANT: G. Martin Hudson, Physics Department

Alistair C. D. Leslie, Oceanography Department

INSTITUTION: Florida State University

SAMPLER TYPE: Linear Streaker Samplers

OPERATING CHARACTERISTICS:

Streaker #1 Streaker #2

FLOW RATE (in liters/m): $0.5 \ell/m$ $0.35 \ell/m$

PARTICLE SIZE CUTPOINTS: Total filter Total filter

COLLECTION SUBSTRATE: 0.4 μ nuclepore 0.2 μ nuclepore

METHOD OF FLOW CALIBRATION AND MAINTENANCE:

Calibrated TYLAN model FC 260 Mass Flow Controllers. Field checks made with rotometers.

ALL SPECIFIC POLLUTANT SPECIES MEASURED: (including those not intercompared)

Particulate, elemental: Al, Si, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Br, Rb, Sr, Mo, Ag, Cd, Sn, Sb, I, Cs, Ce, Au, Hq, Pb, Bi

ANALYTICAL TECHNIQUE(S) USED:

PIXE (proton induce x-ray emission) calibrated to commercially prepared standards good to \pm 5%.

SUMMARY OF SAMPLING AND ANALYSIS METHOD

PARTICIPANT: Billy W. Loo

INSTITUTION: Lawrence Berkeley Lab, Univ. of California

SAMPLER TYPE: 3 Automated Dichotomous Air Samplers: C, L, and S

OPERATING CHARACTERISTICS:

SAMPLING FLOW RATE: 50 g/m

PARTICLE SIZE CUTPOINTS: 2.4 µm

COLLECTION SUBSTRATE: 0.1 μ m pore size teflon membrane filter

mounted on 5 x 5 cm plastic frames

METHOD OF FLOW CALIBRATION AND MAINTENANCE:

The Dwyer RMC-103-SSV and Metheson #603 rotometers were used for field calibration. They were cross-checked with laboratory dry and wet test meters.

An automated flow controller consisting of pressure sensors and water driven micrometer valves maintains the flow to within 1% of present values.

SPECIFIC POLLUTANT SPECIES MEASURED:

Total mass, Si, S, Ca, Ti, Fe Cu, Zn, Se, Br, and Pb

ANALYTICAL TECHNIQUE(S) USED:

Beta gauge, Energy dispersion x-ray fluorescence analysis, secondary exciters.

PARTICIPANT: Peter K. Mueller

INSTITUTION: Environmental Research & Technology, Inc.

SAMPLER TYPE: Sequential Filter Samplers: E and F

OPERATING CHARACTERISTICS:

FLOW RATE (in liters/m): 100 l/m

PARTICLE SIZE CUTPOINTS: Sampler E: About 15 m at inlet

Sampler F: $2.5 \mu m$

COLLECTION SUBSTRATE: 47 mm dia. Teflon-coated glass fiber,

(Pallfelx TX40HI20)

METHOD OF FLOW CALIBRATION AND MAINTENANCE:

Calibrated orifice used for field calibration.

Flow monitored by continuous chart recording of vacuum upstream pump.

ALL SPECIFIC POLLUTANT SPECIES MEASURED: (including those not intercompared)

Total mass, SO_4 , NO_3

Small mass, SO_4 , NO_3

ANALYTICAL TECHNIQUE(S) USED:

Mass: Gravimetry

 SO_4 , NO_3 : Ion chromatography

PARTICIPANT: Charles E. Rodes

INSTITUTION: EPA/EMSL

SAMPLER TYPE: EMSL Dichotomous

OPERATING CHARACTERISTICS:

FLOW RATE (in liters/m): 14 l/min

PARTICLE SIZE CUTPOINTS: Inlet 20 μ m, cutpoint 3.5 μ m

COLLECTION SUBSTRATE: Fluropore 37 mm

METHOD OF FLOW CALIBRATION AND MAINTENANCE:

Flow Calibration using mass flow meters.

Flow maintained by restrictor valves.

ALL SPECIFIC POLLUTANT SPECIES MEASURED: (including those not intercompared)

TSP, Pb, SO_4

ANALYTICAL TECHNIQUE(S) USED:

TSP gravimetric

Pb Atomic Absorption (flameless)

 SO_4 Ion Chromatograph

PARTICIPANT: Charles E. Rodes

INSTITUTION: EPA/EMSL

SAMPLER TYPE: Hi-Vol

OPERATING CHARACTERISTICS:

FLOW RATE (in liters/m): 1415 \(\ell / m \)

PARTICLE SIZE CUTPOINTS: "Total Suspended Particulates" (TSP)

COLLECTION SUBSTRATE: Glass Fiber 8 x 10 inch

METHOD OF FLOW CALIBRATION AND MAINTENANCE:

Flow Calibration using orifice meter.

Flow maintained by mass flow controller.

ALL SPECIFIC POLLUTANT SPECIES MEASURED: (including those not intercompared)

TSP, Pb, $SO_{4}^{=}$

ANALYTICAL TECHNIQUE(S) USED:

TSP: gravimetric

Pb: Atomic Absorption

 SO_4 : Methyl Thymol Blue

SAMPLING AND ANALYSIS METHOD SUMMARY

PARTICIPANT: Roger L. Tanner, Leonard Newman

INSTITUTION: Brookhaven National Laboratory

SAMPLER TYPE: Diffusion Sampler

OPERATING CHARACTERISTICS:

FLOW RATE (in liters/m): DBO: 10.6 \(\ell/min; \) DB1: 16.8 \(\ell/m \)

DB2: 13.8 l/min.

PARTICLE SIZE CUTPOINTS: DBO: 0 to ca 5 μ m; DB1: 0.03 μ m to ca 5 μ m;

DB2: $0.12 \, \mu \text{m}$ to ca $5 \, \mu \text{m}$.

COLLECTION SUBSTRATE: Phosphoric acid-treated Pallflex GAO tissue

quartz.

METHOD OF FLOW CALIBRATION AND MAINTENANCE:

Flows were calibrated with open Matheson rotometer tubes in series with and upstream from the 47 mm filter holders. The flow variations in calibrations before and after the Intercomparison averaged 11% for the 3 sample sets.

ALL SPECIFIC POLLUTANT SPECIES MEASURED: (including those not intercompared)

- 1. Sulfate
- 2. Nitrate
- 3. Strong acid
- 4. Ammonium
- 5. Sulfuric acid

ANALYTICAL TECHNIQUE(S) USED:

- 1. Extraction into pH 4 aqueous solution and determination by ion chromatogrphy.
- Hydrazine reduction and colorimetry.
- 3. Gran titration with correction for pH 4 leach solution.
- 4. Indophenol colorimetry.
- 5. Benzaldehyde extraction and determination by flash volatilization-FPD or by ion chromatography.

SAMPLING AND ANALYSIS METHOD SUMMARY

PARTICIPANT: Roger L. Tanner, Leonard Newman

INSTITUTION: Brookhaven National Laboratory

SAMPLER TYPE: Staplex HiVol with 5-in circular filter pack in conventional

HiVol enclosure.

OPERATING CHARACTERISTICS:

FLOW RATE (in liters/m): 700 \(\ell / m \)

PARTICLE SIZE CUTPOINTS: 0 to ca 20 μ m

COLLECTION SUBSTRATE: Phosphoric acid-treated Pallflex GAO tissue

quartz for aerosol collection. K_2CO_3 , glycerol-impregnated cellulose (S & S 2W, 2

sheets) for SO₂ collection.

METHOD OF FLOW CALIBRATION AND MAINTENANCE:

Magnetohelic gauge measured with filter pack in place with unexposed filters; checked for repeatability with representative exposed filter packs after study. The average reduction in flow during sampling was 1.1 m³/hr (3%) with average flow used for concentration calculations.

ALL SPECIFIC POLLUTANT SPECIES MEASURED: (including those not intercompared)

- 1. Sulfur dioxide
- 2. Sulfate
- 3. Nitrate
- 4. Strong acid
- 5. Ammonium
- 6. Sulfuric acid

ANALYTICAL TECHNIQUE(S) USED:

- Filter pack, extraction into peroxide solution, determination as sulfate by trubidimetry or ion chromatography.
- 1. Extraction into pH 4 aqueous solution and determination by ion chromatogrphy, or extraction into 10⁻²N HCl with determination by Methylthymol Blue colorimetry.
- 2. Hydrazine reduction and colorimetry.
- Gran titration with correction for pH 4 leach solution.
- 4. Indophenol colorimetry.
- 5. Benzaldehyde extraction and determination by flash volatilization-FPD or ion chromatography.

CHAMP AND HIGH VOLUME SAMPLERS

Robert Burton Health Effects Research Laboratory Environmental Protection Agency Research Triangle Park, NC 27711

EQUIPMENT DESCRIPTION

Two CHAMP RSP samplers and one flow-controlled high volume sampler were sent to Charleston, W. Va., to participate in an intercomparison study of particulate analyzers. The CHAMP RSP sampler divides the particulate matter into two collected groups, 3.5-26 microns and 0-3.5 microns.

Particles greater than 26 microns in diameter are excluded by the aero-dynamic construction of the analyzer. Particulate matter in the 3.5 to 26 micron region is impacted on a 12-inch diameter filter utilizing a single stage Andersen impactor plate. Particles smaller than 3.5 microns are collected on a standard 8 X 10 inch hi volume filter. The Andersen impactor is adapted to fit between the after filter and the base section of the fractionator itself. All filter media are of glass fiber construction.

The third sampler was a standard hi volume sampler, which collects all particulate matter smaller than 100 microns. All samplers used Sierra Flow controllers operating on General Metal's Model 2000H motor assemblies to maintain a constant 1.13 m 3 /min (40 cfm) flow. The hi volume sampler is described in detail in Volume 36, No. 228 of the Federal Register.

SAMPLER CALIBRATION

All devices were calibrated using a standard sierra orifice calibrated at the factory and verified by our laboratory Rootsmeter. The calibration curve of the orifice is: $Q = 1.4054 \ (\Delta P)^{1/2}$ where ΔP is the pressure difference in inches of water as measured across the orifice. Q is then corrected using the following equation to 760 mm Hg and 25°C (298°K):

 Q_S = (Pa/Ta) $^{1/2}$ (3.156)Q where Q_S is the standard flow, Pa is the barometric pressure in mm HG, and Ta is the ambient temperature in degrees Kelvin.

The orifice was placed on top of the Andersen head without the RSP top hat and a calibration curve was drawn using clean filters for the Andersen and hi volume heads which are assembled in series. Various flows were obtained by

changing the speed of the hi vol motor with a variac to simulate different loadings on the filters. A curve was obtained for each sampler. For field operations a small rotameter was attached to the bottom of each hi vol and calibrated simultaneously with the orifice. The rotameters facilitated taking field flow measurement, although both rotameter and orifice readings were recorded for this study. After the response equations were determined for each device the flow controllers were then set to obtain 1.13 m /min (40 cfm) flow. The flow obtained during the study show little variation from this 1.13 setting, varying only from 1.17 to 1.11 m /min. Keep in mind, however, that only stop and start flows were recorded during operation and actual flows during sampling may vary but should have been kept within the above tolerances with properly operating flow controllers.

ANALYSIS

The glass fiber filters were conditioned at 40% relative humidity and 25°C for 24 hours. They were then numbered and weighed to the nearest 0.1 mg. Upon return from the field they were again equilibrated at the previous conditions and weighed. Total suspended particulate (TSP) and respirable suspended particulate (RSP) were then determined for the appropriate samplers. The weight of the collected particulate matter was divided by the total volume of air sampled to obtain TSP and RSP concentrations in $\mu\text{g/m}^3$. The sample volumes were calculated using the following equation:

$$V = \frac{Qi + Qf}{2} \quad T \qquad \qquad \text{where } Qi = initial flow - 3m^3/min \\ Qf = final flow - m^3/min \\ T = total sampling_3 time - min \\ V = air volume - m^3$$

After the particulate concentrations were determined, the filters were then sent to Stewart Laboratories in Knoxville, Tenn. for SO_4^- and NO_3^- analysis. The SO_4^- analysis was performed using the methylthymol blue (MTB) method while the NO_3 analysis utilized a copper-cadmium reduction column and NEDA dye. The concentrations were expressed as $\mu g/m^3$ of each ion.

Our program does not routinely analyze for lead. For specific lead samples, Tom Dzubay would perform our lead analysis. Since his section also participated in this study, no lead analyses were performed on these filters.

Further detailed explanation of these methods can be found in EPA publication 600/1-76-011, Community Health Environmental Surveillance Studies Air Pollution Monitoring Handbook: Manual Methods.

SIERRA MULTIDAY AND STACKED FILTER UNITS

T. A. Cahill Crocker Nuclear Laboratory and the Department of Physics University of California, Davis, CA 95616

The Davis Air Quality Group, working in conjunction with the California Air Resources Board, the Research Applied to the National Needs Division of the National Science Foundation, and the U.S. Energy Research and Development Agency, had developed and modified techniques for collecting and analyzing atmosperic particulates. Monitoring of aerosols in California (1) by size and elemental composition for the California Air Resources Board (CARB), began in January, 1973, using a Lundgren-type rotating drum impactor (2), modified for this program, and since marketed as the Environmental Research Corporation, and later, Sierra Instruments Corporation, Multiday Impactor. Quantitative operation of this device was achieved through use of quasi-monolayer depositions on coated surfaces in the two impaction stages, and non-hygroscopic, surface-deposition filter media for the backup filter. Normal integration period was 24 hours. Approximately 5000 station-days of data in three size fractions, 20 μ m to 3.6 μ m, 3.6 μ m to 0.65 μ m, and 0.65 to 0.01 μ m, have been accumulated in this program. The major aims of the program are in characterization of aerosol components, the identification of aerosol sources, study of transport, transformations, and sinks, identification of sources of gaseous pollutants measured by the ARB monitoring network, and effects of aerosols and gases upon visibility.

Elemental analysis of samples collected in this program occurs after transport of samples to Davis, with contamination and loss effects summarized in the Table. Analysis occurs primarily via particle induced x-ray emission (PIXE) (3,4) with significant support through energy-dispersive x-ray fluorescence (XRF) and ion scattering analysis (ISA). Smaller numbers of analyses are done using a scanning electron microscope and an electron microprobe with wave-length-dispersive XRF capabilities. Total number of elemental values to date in the monitoring program exceed 500,000. The system has participated in numerous interlaboratory comparisons (5), in addition to a massive (6000 analyses/year) internal program of analytical validation.

The need to perform diurnal and spatial profiles that have some size information and full gravimetric and elemental analysis compatibility has led to development of low cost, portable stacked filter units (SFU's) (6) following a suggestion of K. R. Spurney et al.(7) These units are designed to deliver a quasi-respirable separation of aerosols, with a 50% cut point and shape as close as possible to that occurring between the nasal-pharangeal and tracheo-pulmonary compartments of the human respiratory tract. Evaluations of this

device are given in the SFU table for a two stage device designed to operate at 5 /min.

In an attempt to upgrade the information delivered by the large number of Hi-Vol samplers operated by state and local agencies in California, the SFU has been evaluated as a continuous monitoring device. The SFU would operate on a 7 day integration period, avoiding the statistical problems inherent in a 1 day in 6 Hi-Vol mode, while delivering respirable and non-respirable size cuts in samples suitable for gravimetric and full elemental analysis. Lower flows are used, $2\ell/\min$, and on occasion, especially when visibility problems exist, a third stage is added to mimic the cut points of the multiday.

For the sampler intercomparison study, a Multiday impactor and a stacked filter unit will be used. The impactor will use 0.6 mg/cm² mylar, coated with 0.065 mg/cm² Apiezon type L grease, as impaction surfaces, and 0.4 micron Nuclepore filter for the afterfilter. The stacked filter unit will use 8 micron and 0.4 micron filters. Flow for both units will be set by a spirometer-calibrated orifice meter on the intake. Analysis will be by both PIXE and XRF, with elements aluminum and heavier quoted either as observed values or upper limits of elements not observed. Calibration of the analysis systems will be via gravimetric thin element standards, and total accuracy will be within \pm 10% absolute when statistical precision is adequate.

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Summary of Sample Collection Evaluations

MULTIDAY IMPACTOR

1.	Large particle cut-off (50%) (intake)	$D_p = 20 \mu m$, variable w. wind speed*
2.	First stage cut-off (50%)	$D_p = 4.3 \ \mu m, \pm 0.4 \ \mu m$
3.	Second stage cut-off (50%)	$D_p = 0.78 \ \mu m, \pm 0.05 \ \mu m$
4.	Impaction collection efficiency	(97 <u>+</u> 3)%
5.	Filter capture efficiency a) laboratory aerosols b) ambient aerosols	(96±2)% (99±3)%
6.	Sizing errors due to non- optimum ollection a) coarse collected on filter (soils) b) fine collected on coarse (Pb, S aerosols)	< 1% < 1%
7.	Summary of sizing:	Stage 1 (coarse) < 20 μm to 4.3 μm Stage 2 (intermediate) 4.3 μm to 0.78 μm Stage 3 (fine) 0.78 μm to 0.01 μm
8.	Flow calibration	Rotometer - continuous Orifice and meter on Intake (0 to 1" H ₂ 0 (Intermittent; Spirometer calibrated)
9.	Total unit efficiency (fine particles)	(93±3)% (4 X 5a) [correction <u>not</u> applied to the Charleston data]

Summary of Sample Transport and Handling Corrections

١.	Contamination in Handling	$ \widetilde{<}$ 15 ng/m $_3^3$ Si, $<$ 10 ng/m 3 Al, K; 6 ng/m 3 others < 2% of Si value at most locations
2.	Loss of particles during transport	less for other elements < 2%

3. Loss of material during storage << 10%

^{*}Addition of a 60 mesh screen has lowered this cut.

Summary of Sample Collection Evaluations

U.C. Davis Stacked Filter Unit at 5 1/min (2 stage)

1. Large particle cut-off (50%) (intake)

 $D_n = 20 \mu m$, variable w. wind speed*

2. Coarse stage cut-off (50%)

 $D_p = 2.6 \mu m \pm 0.5 \mu m$, quasi-respirable shape

3. Filter collection efficiency

a) laboratory aerosols b) ambient aerosols

(96<u>+</u>2)% (99±3)%

Sizing errors due to nonoptimum collection

> a) coarse particulates on fine stage (soils)

< 6%

b) fine particulates on coarse stage (Pb, idling auto)

< 2.5%

5. Summary of sizing: Coarse $< 20 \, \mu m$ to 2.6 μm 2.6 µm to 0.01 µm

Shape quasi-respirable, 20 1/min

nasopharynx

Flow calibration

Orifice and meter on Intake (0 to 1"

(Intermittent; Spirometer calibrated)

7. Total unit efficiency

 $(96\pm2)\%$ (4a)

[correction not applied to the Charleston test]

Summary of Sample Transport and Handling Corrections

1. Contamination in Handling

 \approx 15 ng/m 3 Si, <10 ng/m 3 Al, K; < 6 ng/m 3 others

< 2% of Si value at most locations less for other elements

2. Loss of particles during

transport

< 2%

3. Loss of material during storage

<< 10%

^{*}Addition of a 60 mesh screen has lowered this cut.

Summary of Analytical Corrections and Uncertainties

- Statistical uncertainty in peak counts variable 2. Uncertainty in gravimetric standards ± 5% + 2% 3. Integration of Ion beam Ion beam attenuation < 5% Electronic corrections, accuracy ± 5% Peak integration and background + 7%, (variable) uncertainties + 5% Thus, reproducibility system uncertainty +10% 7. Loss of volatile elements (beam + < 5% vacuum)
- 8. Particle Size Corrections

	Stage #1	Stage #2	Filter Stage
Na	2.49	1.32	< 10%
Mg	1.96	1.22	II
ΑĨ	1.68	1.16	11
Si	1.49	1.12	и
Р	1.37	1.09	11
S	1.26	1.07	и
C1	1.31	<10%	11
K	1.12	<10%	11
thers	<10%	<10%	и

9. Loading Corrections (for 120 μ g/m³ aerosol)

_	Stage #1	Stage #2	Filter Stage
Na	< 10%	1.70	1.22
Mg	tt.	1.39	1.11
ΑĨ	ŧI	1.23	1.07
Si	и	1.14	1.04
others	11	<10%	<10%

Uncertainty in particle size and loading corrections are estimated at \pm 20% for most ambient aerosols, although, especially for the particle size corrections, worse cases are common. These corrections thus increase the total error for the four lightest elements.

REFERENCE (Sierra Multiday)

"Monitoring California's Aerosols by Size and Elemental Composition", R. G. Flocchini, T. A. Cahill, D. J. Shadoan, S. J. Lange, R. A. Eldred, P. J. Feeney, G. W. Wolfe, D. C. Simmeroth, and J. K. Suder, Env. Sci. and Technology 10, 76 (1976).

REFERENCE (Stacked Filter Units)

"Analysis of Respirable Fractions in Atmospheric Particulates via Sequential Filtration", T. A. Cahill, L. L. Ashbaugh, J. B. Barone, R. A. Eldred, P. J. Feeney, R. G. Flocchini, C. Goodart, D. J. Shadoan, and G. W. Wolfe, J. Air Pollution Control Assoc. 27, 675 (1977)

TWO MASS SAMPLER

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INTRODUCTION

As part of an EPA/DOE sponsored Sampler Intercomparison Field Study, TWOMASS tape samplers were installed on the roof of the Federal Building in downtown Charleston, West Virginia and run from May 11 through May 19, 1977. One TWOMASS sampler ccllected 6 hr samples at a nominal flow rate of 12 ℓ pm and another collected 3 hr samples at a nominal flow rate of 18 ℓ pm. The 3 hr sampler was equipped with a beta-attenuation mass monitor system which provided a continuous record of coarse (>3.5 μ m) and fine (<3.5 μ m) particle concentration.

The purpose of the study was to compare results obtained from various sampling and analytical procedures. The sulfur content of the samples was determined by flash vaporization followed by flame photometric detection (FV-FPD). The sampling system was designed for high time resolution (30-120 min). For this study three hour samples were collected. Since the reporting time for all intercomparison data was set at 12 hour intervals, four 3-hr samples were added to give the required information. In cases where one 3-hr sample was not available, the remaining three were averages. If more than one sample was missing during a twelve hour period, no results were reported.

ANALYTICAL METHODS AND PROCEDURES

Sampler

Atomospheric aerosol samples were collected in two size ranges with a TWOMASS automated two-stage sequential filter sampler. The flow system separated particles into two size fractions. Coarse particles (diam > 3 μ m) were impacted on a glass fiber filter with cellulose backing. Fine particles were collected on the same type of high efficiency-low mass density filter. The flow rate through the TWO MASS was set at 12 or 18 ℓ /min using a GAST rotary vane pump.

Beta Attenuation Mass Monitor

Both the impaction and filtration heads of one TWOMASS were fitted with independent sources (Carbon-14) and detector systems (solid state ruggedized silicon surface-barrier type). After electronic amplification and filtration

the output signals were sent through counters to a programmable calculator. Mass was calculated using the equation

$$\Delta M = \frac{A}{\Delta t f \mu_m} \ell n (I_0/I)$$

where ΔM is the mass concentration, A the spot area, f is the flow rate, μ_{m} the mass attenuation coefficient, t the time counting interval, I_{0} the count rate of the previous interval and I the count rate of the current interval. The beta intensity transmitted through the filter paper was measured as the particulates were being deposited; mass concentrations were obtained at the end of each 10-min counting period. Tapes were automatically advanced at three hour intervals.

Particulate Sulfur Analysis

Water soluble particulate sulfur in the fine particle samples from the TWOMASS instrument was determined using a flash vaporization-flame photometric detection method. The sulfur analyzing system consisted of a flash vaporization vessel, flame photometric detector (Meloy SA-160), electronic integrator, and a strip chart recorded. The sample vaporization was performed by capacitor discharge across a tungsten boat, resulting in resistance heating to 1100°C. Vaporized gaseous decomposition products of sulfur compounds were carried to the flame photometric detector by a stream of clean, charcoal filtered air at a flow rate of 2 cm³/sec. The linearized output was registered on the strip chart recorder and the peak area integrated by an electronic integrator.

To the filter deposits, 0.5 to 1 ml double distilled deionized water was added and utrasonically disintegrated at 25°C for 10 minutes. Sample standard solutions were transferred with a 5 $\mu\ell$ microsyringe to the tungsten boat and heated at 60°C for 30 seconds until dry. The residue was then vaporized by capacitor discharge.

This technique was calibrated using solutions of sulfuric acid, ammonium sulfate and bisulfate, zinc- and zinc-ammonium sulfate in the range 0.16-34 $\mu g/ml$ of sulfur. [Husar et al, Anal. Chem., 47, 2062 (1975)]. A 5 $\mu \ell$ sample of distilled deionized water gave a signal equivalent to 0.3 \pm 0.05 ng sulfur, corresponding to a solution concentration of 0.06 $\mu g/ml$. This value was a factor of five lower than the measured sulfur content of filter blank extract.

MANUAL DICHOTOMOUS AND SERIES FILTER RESPIRABLE SAMPLERS

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AEROSOL SAMPLING DEVICES

For our participation in the sampler intercomparison conducted in Charleston, West Virginia between May 11 and May 19, 1977, four size fractionating aerosol samplers were used. Two were manual dichotomous samplers (1) (MDS-S and MDS-A), and two were tandem filter respirable samplers (2) (TF-M and TF-P). Table 1 summarizes the characteristics of each sampler and the filter media that were used.

The manual dichotomous samplers use a virtual impactor designed to separately collect fine and coarse particles with a 50% separation diameter occurring at $3.5~\mu m$. The upper 50% cutoff occurs at $14~\mu m$ and is due partly to losses in the virtual impactor but is mainly due to the use of a sampling inlet designed to sample particles with an efficiency that is independent of wind speed and also to reject giant, nonrespirable particles.(3)

The tandem filter sampler consists of a large pore sized Nuclepore filter followed by a highly efficient filter. This sampler seprately collects the coarse and fine particle fractions on the two filters.(2,4,5) For the flow rates and filters shown in Table 1, the cutpoint occurs at 3.5 μm for liquid particles.(2,4) Although there are no particle losses for this fractionator, the size separation is not quantitative because of tendency for dry, solid particles to bounce through the first filter.(6) The upper 50% cutoff of the inlet is estimated to occur at about 20 μm .

Flow rates were checked using a Sierra Model 541* portable mass flow meter at the beginning and end of each sampling interval. Such measurements were made while the samplers were running and required about one minute per

^{*}Mention of commercial products or company names does not constitute endorsement by the U.S. Environmental Protection Agency.

sampler. The calibration of the protable flow meter was checked daily against a dry test meter at flow rates of 6 and 14 liters per minute. After the first 4 days of sampling the jets in the virtual impactor were inspected and cleaned.

CALCULATION OF CONCENTRATIONS

In determining the sampled volumes, the mean of the initial and final flow rates was used. Samples were rejected if the final flow rates differed by more than 15% from the nominal values indicated in Table 1. (See page 78.)

For each dichotomous sampler there is a small flow of air through the coarse particle filter, and a proportionally small amount of fine particle mass is collected on the coarse particle filter. To correct for this effect, particle concentrations in the two size ranges were determined from the equations:

$$C_f = M_f/(tF_f)$$
 $C_c = [M_c - (M_f F_c/F_f)]/[t(F_f + F_c)].$

where C_f and C_c = the atmopheric concentrations of the fine and coarse particle fractions, respectively in $\mu g/m^3$ M_f and M_c = the masses collected on the fine and coarse particle filters, respectively in μg F_f and F_c = the flow rates through the fine and coarse particle filters, respectively in m^3/m in the sampling time in minutes.

MASS ANALYSIS

The masses of the aerosol deposits were determined gravimetrically using a Perkin Elmer Ad-2 electrobalance that was located in the laboratory at Research Triangle Park, N.C. The electrobalance was operated on the 100 mg scale, and the weighing precision was 10 μ g. At the beginning of each daily series of weighings, the span of the electrobalance was adjusted for correct response to a standard 100 mg weight. The zero of the electrobalance was checked before the weighing of each filter and was adjusted whenever a nonzero reading occurred. To eliminate any electrostatic charges on the filters, they were held for a few seconds within 1 cm of a Po radioactive source (500 μ Ci) before weighing. A second similar radioactive source was positioned inside the balance enclosure. The relative humidity in the balance room was between 35 and 45% for all weighings. To equilibrate the filters after sampling, the petri dishes containing the filters were stored in the balance room for a least 24 hours with the covers partly open.

ELEMENTAL ANALYSIS

Elemental analysis of samples by x-ray fluorescence spectroscopy was carried out with an energy dispersive unit. (7) The detector is a Si(Li) diode with a resolution of 208 eV for Mn-55 K x-rays. This spectrometer (a pulsed x-ray tube design) excites the sample by characteristic x-rays from a selected set of secondary fluorescers. Elements with atomic numbers 13 through 20 are

TABLE A.1. SAMPLER AND FILTER MEDIA DESCRIPTIONS USED IN THE INTERCOMPARISON STUDY.

Sampler Type	Description	Upper 50% cutoff dia.	Flow rate l/min	Depo Area . cm	Filter Media
Dichotomous (MDS-S)	Two stage virtual impacto having 50% cut point at 3.5 µm. The flow rates through the fine and coar filters is 13.6 and 0.4 liters/min respectively a is maintained using a Sierra Series 250 mass flosensor and pump servosyst	measured se nd	14	6.7	Teflon membrane having lum pores bonded to a polyethylene net (FALP Fluoropore from Millipore Corp.)
Dichotomous (MDS-A)	Same as MDS-S except that the constant flow rate is maintained using a constant differential pressure controller on the pump exhaust.	14 μm measured	14	6.7	Teflon membrane having assymetric pores (lµm/10 µm) oriented so that particles are collected on the l µm side (P137PL25 Ghia Corp.)
Tandem Filter (TF-M)	Two filters operated in series with a sampling velocity of 15 cm/sec. maintained using a Sierra (Kurtz) servosystem.	20 µm estimate		8.0	Coarse: Nucle- pore having 9.6 µm dia. pores (N137PE2 Ghia Corp.) Fine: Nuclepore having 0.4µm dia. pores (N040 Poly 101 Ghia Corp.)
Tandem Filter (TF-P)	Same as TF-M	20 µm estimat	5.9 ed	6.7	Coarse: 9.6 µm Nuclepore (N137- PE1, Ghia Corp.) Fine: Teflon, same as used for sampler MDS-A above.

analyzed using a titanium fluorescer; elements with atomic number between 22 and 38 plus Pb and Hg are analyzed using a molybenum fluorescer; elements Cd, Sn, Sb and Ba are analyzed with a samarium fluorescer.

Spectral analysis was carried out with a linear least squares fitting program which uses a library of single element spectra as the fitting functions. These spectra were acquired by the spectrometer under analysis conditions. A blank filter spectrum is used for the background and is included in the library.(8) The spectrometer is calibrated for copper and sulfur using a well characterized thin copper film standard and thin laboratory generated deposits of 0.3 μm copper sulfate particles.(8) Evaporated metal film standards obtained from Micromatter Co. (Seattle, Washington) were used for lead and other elements.(8)

To correct for attenuation of sulfur x-rays in the fine particle fraction, a very slight correction (1 to 10%) was made in proportion to the amount of mass collected.(8) For the coarse particle fraction, the attenuation correction factors for Si, S, K, Ti, Fe, Cu, Zn, Se, Br, and Pb, used were 0.48, 0.78, 0.87, 0.94, 0.94, 0.95, 0.98, 0.99, and 1.00 respectively.(9) Descriptions of the analysis procedure are described in more detail by Stevens et al.(8)

ANALYSIS OF IONIC SPECIES

The samples from MDS-S were analyzed for sulfate and nitrate using ion exchange chromatography. Extraction, the initial step in the analysis was accomplished by placing each sample in a Nalgene polypropylene bottle (30 ml volume) containing 20 ml of 5 x 10^{-5} N perchloric acid extraction solution. The extraction vessel was capped and put in a sonic bath for 20 minutes. A study using x-ray fluorescence techniques has shown this procedure extracts 99% of the sulfur from the fine fraction and 95% of the sulfur from the coarse fraction.

After extraction, sulfate and nitrate were determined using a Dionex Model 14 Ion Chromatograph (IC). The samples were spiked with a base (.003M NaHCO $_3$ + 0.0005M Na $_2$ CO $_3$) so that the range 10 $^-$ M to 10 $^-$ M was spanned. Retention times and peak areas were obtained using standards (10 $^-$) to 10 $^-$ M of (NH $_4$) $_2$ SO $_4$ and NaNO $_3$), and a calibration curve was drawn. Analysis of sulfate data showed that the minimum detectable level was 10 $^-$ neq/ml and that sulfate concentrations were determined to within \pm 10%.

The minimum detectable level for nitrate was 5×10^{-2} neq/ml, and the concentrations were determined to within \pm 155. For the 12 hour samples collected with a 14 l/min flow rate, the detection limits expressed in units of atmospheric concentrations were $10^{-2} \, \mu \text{g/m}^3$ and $7 \times 10^{-3} \, \mu \text{g/m}^3$ for sulfate and nitrate, respectively. A more detailed description of the extraction and analysis procedures is given by Stevens et al.(8)

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LINEAR STREAKER SAMPLERS

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LINEAR STREAKER SAMPLERS

The Florida State Elemental Analysis Group working with the Environmental Protection Agency, the National Science Foundation, the Florida Sulfur Oxide Study Board, and numerous international groups in Europe, Asia, Africa, and South America has developed a complete air particulate monitoring system. The heart of this system is the linear streaker.(1)

During the Charleston study four streakers were deployed, but data were reported for only two of the samplers. These devices filter continuously collecting particulate over a small area of 2 mm x 5 mm. An orifice is moved by a synchronous motor-screw drive across the filter surface at a rate of 1 mm per hour to produce a 5 mm wide, 168 mm long strip sample in a time of one week. Analysis of the filter is limited to a width of 2 mm which yields pollutant data equivalent to 84 time averaged 2 hour samples. For the purpose of the intercomparison study 6 two hour samples were averaged to give the 12 hour samples reported. Polycarbonate nuclepore filters of 0.4 μ m and 0.2 μ m pore size were used depending on the flow rate desired. The Nuclepore filter itself may be used to limit the flow, or a flow control device may be connected in series. Flows of one liter per minute or less produce satisfactory loadings for PIXE analysis of elements $Z \geq 13$. Regularly measured are Al, Si, S, Cl, K, Ca, Fe, Zn, Br, and Pb; and less often Ti, V, Cu, Ni, Sn and As. The streaker samples are also well suited for PESA(2) (proton elastic scattering analysis) which gives trace element information in the range 1 < Z < 20.

The streaker is a simple reliable, and flexible sampler, which is also highly portable and inexpensive. This has led to its reliable use in the Amazon basin, in the Namib desert, and in the Indian Ocean. Over 100,000 elemental data points have been generated in one year with a time resolution needed to compare with meteorological data. The linear streaker is a total filter device. Its main disadvantage is that it does not give two size fractions. This will be remedied by the circular streaker(3) which will soon be network tested. The linear streaker's intake is vertically upward, and electron microscope pictures of filters indicate an upper size limit of 15 μ m for particles collected. The Nuclepore filter is mounted on an aluminum frame which can be quickly inserted and removed from the streaker.

The streaker filters frames require no preparation before being placed in a specially designed vacuum chamber(3) where the filters are irradiated with 5 MeV protons from FSU's super-FN Tandem Van de Graaff. (A small vertical Van de Graaff dedicated to PIXE analysis is planned for operation in 1979 and will allow the production of 10 data points a year). The x-rays generated are detected using an energy dispersive Si(Li) detector purchased from Nuclear Semiconductor, which has a resolution of about 170 eV FWHM for the iron K x-ray (6.4 keV). The detector signals are processed using Nuclear Semiconductor electronics which include an amplifier, a pulse pile up rejector, a low level discriminator, and live time counter. Processed signals are fed into a Northern Scientific ADC which is Camac interfaced to an EMR 6130 on-line computer. At the end of each run the data is written on magnetic tape for off-line analysis. The PIXE technique is well understood(4) and the Elemental Analysis Group has taken part in numerous intercomparison studies.(5,6)

A sophisticated FORTRAN code REX(7) is used to fit the x-ray spectra. This code carefully models the spectra obtained. It contains information relevant to elemental x-ray line shapes, the Bremsstrahlung background, the silicon absorption edge, x-ray production cross sections, self absorption and attenuation, and other parameters. Absolute calibration is made from standards produced by Micro-Matter, Inc. and checked by PESA.(2)

During this experiment flow rates were maintained using a Mass Flow Controller TYLAN Model FC 260. The precision of this device was confirmed before and after the experiment using a spirometer and a factory calibrated variable area flowmeter (Matheson Model 601).

As a side experiment two other linear streakers were run. One was uncontrolled at 0.8 ℓ/m and one had a prefilter of 8 μm pore size. Modified Battelle cascade impactors were used as well with 4 hour sampling periods. These impactors have size cuts > 4, 4-2, 1-0.5, 0.5-0.25 and < 0.25 m, respectively. Mylar impaction surfaces and 0.4 μm Nuclepore afterfilters were employed. Petroleum jelly was used to coat the impaction surface except for the last impaction stage which was coated with parafin. Flow rates of the impactors were controlled by a critical flow orifice and were measured with a calibrated variable area flowmeter. Additional results from these samplers will be reported in a separate publication at a later date.

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AUTOMATED DICHOTOMOUS SAMPLERS

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QUALITY ASSURANCE MEASURES

Sampling |

- 1. Flow calibrations performed in the field.
- 2. Automated flow controller in the sampler maintains the preset flow rate.
- 3. Fault sensors continuously check for filter loading, proper filter transport and vacuum seals.
- 4. Flow calibrations checked upon completion of study.

Analysis

- 1. Checked calibration and XRF spectrometer gain setting.
- 2. Checked helium level during XRF analysis.
- 3. Calibrate beta-gauge every hour.
- 4. Check and correct for long term beta-gauge response.
- 5. All samples measured twice for both total mass and elemental composition which checks for precision and any obvious error.

DETAILED ANALYTICAL METHODS AND PROCEDURES

Mass Measurement

A beta gauge consisting of a Pm¹⁴⁷ source and a cooled Si detector was used. The areal mass of all filters was measured twice prior and subsequent to to field sampling. The measured beta intensity I was related to the sample thickness X in $\mu g/cm^2$ by I = I_0e^{-mX} where I_0 and μ were constants derived from a leastsquare fit to five calibration standards. These standards were gravimetrically weighted polycarbonate films of thicknesses 1034.6, 1511.9, 1970.6, 2552.2 and 2931.0 prg/cm². The counting times used for calibration and routine measurement were 100 and 30 sec. respectively. About 4 x 10° counts were accumulated within 30 sec. for a sample of 1 mg/cm². For a mean aerosol concentration of 107 $\mu g/cm²$ the mean reproducibility was 4.7 $\mu g/cm²$. A correction factor for long term systematic changes of 12.5 $\mu g/cm²$ was determined from the remeasurement of 25 unexposed filters.

XRF Measurements

An XRF spectrometer including a pulsed x-ray source, cooled anti-coincidence guard-ring Si(Li) detector and fluorescent targets of Ti, Mo and Sm were used for elemental analysis. The x-ray calibration factors were determined using a series of thin-film standards which closely replicate the membrane filter samples. These standards are either uniform evaporation deposits of single element whose mass has been determined gravimetrically or multiple element standards in which the elemental concentration ratios are accurately known. For example the sulfur calibration was obtained by measuring specimens of 0.3 μm Cu SO_4 5H_2O aerosols deposited on the surface of 0.1 μm pore size nucleopore filters. In this case evaporated deposits were used as primary standards. This calibration was cross-checked with that determined from a series of relative standards, namely K_2SO_4 , K_2Cr_2O and Cu-Cr mixed aerosol standards. The agreement was within 1%.

The x-ray attenuations due to the size of the particles were corrected using the method described by Dzubay and Nelson (Adv. in X-ray Anal. 18, 619, 1975). The values employed are listed as follows:

Element	Fine Particles	Coarse Particles
Si	0.93 ± 0.07	0.48 ± 0.15
Š	0.97 ± 0.03	0.64 ± 0.22
Ca	0.99 ± 0.01	0.81 ± 0.13
Ti	-	0.87 ± 0.10
Fe		0.94 ± 0.05
Cu		0.94 ± 0.06
Zn		0.95 + 0.05

Due to the flow division within the virtual impactor, the reported values on size segregated samples have an implicit 5% interference of fine particle on the coarse particle fraction. This effect, of course, disperses when the two size fractions are summed. The only case where it may introduce any significant error is where the particles are found predominantly in fine particles and where the coarse particle size attenuation correction is large. This was the case with S and the attenuation corrections were applied after making the 5% fine particle interference correction.

CYCLONE SEQUENTIAL FILTER SAMPLERS

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The samplers used in the aerosol sampler intercomparison controlled in Charleston, West Virginia between May 11 and May 19, 1977, were per Model 5200 Sequential Filter Samplers. The sampling head consists of a 5 cm I.D. by 50 cm long tube topped by a cylindrical shroud. The purpose of the shroud is to render the entry of large particles into the sampler relatively insensitive to changes in wind speed. The conical covering prevents entry of rain. Wire screens are located over the top and the bottom of the shroud to prevent entry of insects into the duct.

One of the samplers, F, was equipped with a cyclone preseparator located within the shroud. The Unico 240 cyclone used was calibrated for particle removal by Eisenbud and Kneip (1975). Based on their results, the 50 percent collection efficiency size for unit density spheres varied from 2.0 to 2.7 μm diameter as the flow rate varied over the range from 100 to 150 $\ell\,pm$. The sampler equipped with the cyclone collected only particles smaller than these sizes. The second sampler did not have a preseparator and collected particles smaller than approximately 15 μm diameter.

Sampled air passes through the inlet duct to the cylindrical chamber containing position for 13 filter holders. The circular arrangement of the filters subjects each to similar flow patterns. Air is never sampled through the thirteenth position; a filter is placed in this position to assess the effects of particle deposition when sampling is not occurring.

The filter holders are connected to a common pump through a system of solenoid valves. The valves are actuated by timers to allow sampling of the twelve filters in succession. The sampling times are programable for periods from 5 minutes to 24 hours by means of a 24-hour time switch. A sampling sequence can be programmed to start at any time within seven days after set-up. The deviation of the actual starting time from the programmed time is 30 minutes or less.

Flow rates are monitored continuously by means of a vacuum recorder connected upstream of the pump. The recorder is calibrated for flow rate.

The samplers accommodate open-face 47 mm diameter filter holders. The filter holders are equipped with quick-disconnect type fittings to allow easy installation and removal. Filters were shipped to and from the field in fil-

XRF Measurements

An XRF spectrometer including a pulsed x-ray source, cooled anti-coincidence guard-ring Si(Li) detector and fluorescent targets of Ti, Mo and Sm were used for elemental analysis. The x-ray calibration factors were determined using a series of thin-film standards which closely replicate the membrane filter samples. These standards are either uniform evaporation deposits of single element whose mass has been determined gravimetrically or multiple element standards in which the elemental concentration ratios are accurately known. For example the sulfur calibration was obtained by measuring specimens of 0.3 μm Cu $SO_4{}^{\circ}SH_2O$ aerosols deposited on the surface of 0.1 μm pore size nucleopore filters. In this case evaporated deposits were used as primary standards. This calibration was cross-checked with that determined from a stries of relative standards, namely K_2SO_4 , K_2Cr_2O and Cu-Cr mixed aerosol standards. The agreement was within 1%.

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Element	Fine Particles	Coarse Particles
Si	0.93 + 0.07	0.48 ± 0.15
S	0.97 ± 0.03	0.64 ± 0.22
Ca	0.99 ± 0.01	0.81 ± 0.13
Ti	_	0.87 ± 0.10
Fe		0.94 ± 0.05
Cu		0.94 ± 0.06
Zn		0.95 + 0.05

Due to the flow division within the virtual impactor, the reported values on size segregated samples have an implicit 5% interference of fine particle on the coarse particle fraction. This effect, of course, disperses when the two size fractions are summed. The only case where it may introduce any significant error is where the particles are found predominantly in fine particles and where the coarse particle size attenuation correction is large. This was the case with S and the attenuation corrections were applied after making the 5% fine particle interference correction.

CYCLONE SEQUENTIAL FILTER SAMPLERS

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The samplers used in the aerosol sampler intercomparison conducted in Charleston, West Virginia between May 11 and May 19, 1977, were ERT Model 5200 Sequential Filter Samplers. The sampling head consists of a 5 cm I.D. by 50 cm long tube topped by a cylindrical shroud. The purpose of the shroud is to render the entry of large particles into the sampler relatively insensitive to changes in wind speed. The conical covering prevents entry of rain. Wire screens are located over the top and the bottom of the shroud to prevent entry of insects into the duct.

One of the samplers, F, was equipped with a cyclone preseparator located within the shroud. The Unico 240 cyclone used was calibrated for particle removal by Eisenbud and Kneip (1975). Based on their results, the 50 percent collection efficiency size for unit density spheres varied from 2.0 to 2.7 μm diameter as the flow rate varied over the range from 100 to 150 $\ell\,pm$. The sampler equipped with the cyclone collected only particles smaller than these sizes. The second sampler did not have a preseparator and collected particles smaller than approximately 15 μm diameter.

Sampled air passes through the inlet duct to the cylindrical chamber containing position for 13 filter holders. The circular arrangement of the filters subjects each to similar flow patterns. Air is never sampled through the thirteenth position; a filter is placed in this position to assess the effects of particle deposition when sampling is not occurring.

The filter holders are connected to a common pump through a system of solenoid valves. The valves are actuated by timers to allow sampling of the twelve filters in succession. The sampling times are programable for periods from 5 minutes to 24 hours by means of a 24-hour time switch. A sampling sequence can be programmed to start at any time within seven days after set-up. The deviation of the actual starting time from the programmed time is 30 minutes or less.

Flow rates are monitored continuously by means of a vacuum recorder connected upstream of the pump. The recorder is calibrated for flow rate.

The samplers accommodate open-face 47 mm diameter filter holders. The filter holders are equipped with quick-disconnect type fittings to allow easy installation and removal. Filters were shipped to and from the field in fil-

ter holders to eliminate the need for filter handling at the sites. A protective plastic cap is placed over the filter holder during shipment and handling.

The vacuum recorders in the samplers were calibrated three times during the program: on 10, 15, and 19 May 1977. Calibrations were performed with dry test meter attached at the sampler inlet. The cyclone preseparator was removed from the RSP sampler and the dry gas meter was connected in its place. Various types and combinations of filters were installed in the sampler to produce various flow rates for the calibration. The calibration was performed by cycling the sampler through these filters and recording the readings of the dry gas meter and the vacuum recorder. In the case of the TSP sampler which did not have a cyclone, the cylindrical chamber from the RSP sampler was installed for the calibration.

The results of the first and second and the second and third calibrations for each sampler were taken together and linear least-squares fits to each set of two calibrations were made. The calibration curve from the first set was used for reducing the data from the 11-14 May sampling; that from the second set was used for the 15-19 May sampling data.

CALCULATIONS OF CONCENTRATIONS

To calculate the volume of air sampled during each 3-hour sampling interval, the initial and final flow rates were averaged and multiplied by the time elasped during the interval.

The quantity of anionic material on each filter was determined as the product of the concentration of the anion in the extracted solution times any dilution factor times the reciprocal of the fraction of the filter which was extracted. These products, in nanograms, for four 3-hour intervals were added and the sum was divided by the sum of the volumes of air sampled during the four intervals to yield the average concentration of the anion in air, in ng m⁻³, for each 12-hour reporting period.

FILTER MEDIUM

Particulate samples were collected on 47 mm diameter Teflon-impregnated glass fiber disks with the designation TX40HI20 manufactured by Pallflex Products Corp. to ERT specifications. This choice was based on the following considerations:

- The filter medium must retain particles efficiently while transmitting gases.
- Flow rates achievable using the filters in the Sequential Filter Samplers must be sufficient to allow collection of adequate material for analysis by the methods chosen.
- The filters must have sufficient mechanical strength for easy handling.

The first consideration, transmission of gases, eliminated ordinary glass fiber filters, because filters of this type have been shown to interact strongly with sulfur dioxide and other acid gases such as nitrogen oxides leading to erroneously high measurements of sulfates and nitrates. Membrane filters were

eliminated by the second consideration because of their high flow resistance. The remaining types of filters to be considered were quartz fiber filters and the Teflon-impregnated glass fiber filters. Evaluation of the quartz fiber filters indicated they were too fragile to handle without significant loss of filter material.

GRAVIMETRIC ANALYSIS

Weighings were performed with a Cahn Model 4700 Automatic Electro-balance. Static charges were removed from the balances and from filters with Po^{210} ionization units located inside the weighing chambers in the balances.

Filters were equilibrated for a minimum of 24 hours in the balance room prior to weighing. The room was maintained between 23 and 25°C and at a relative humidity below 50 percent. Unexposed filters were equilibrated in the containers with the lid open in which they were received from the manufacturer. Exposed filters remained in the shipping containers with the lid open and the protective caps in place during equilibration.

Filters were inspected visually for defects prior to weighing. Unexposed filters showing defects were discarded.

The balance was operated at a full-scale range of 2000 μ g with a resolution of 10 μ g. Calibration was performed with Class M weights.

ANION ANALYSIS

Nitrate and sulfate were determined from a single extract by the technique developed by Small and co-workers (1975). This technique is called ion chromatography (IC).

A quarter of the filter was placed in a numbered borosilicate culture tube which had been previously cleaned and conditioned with eluent buffer, and 10 ml of buffer were added by means of a Repipet liquid dispenser. The tube was then capped and shaken ultrasonically or minutes in a Bransonic 32 ultrasonic cleaner. Because standing waves may exist at some points in the cleaner, the tubes were moved continuously during the extraction process.

Stock solutions of standard were prepared by dissolving analytical grade reagents in distilled deionized water and storing them in the refrigerator. Standard mixtures of NO_3 and SO_4 were prepared in eluent buffer daily. All solutions were allowed to equilibrate at the instrument room conditions before analysis.

A Model 10 ion chromatograph (Dionex Corp., Palo Alto, CA) was used for the analysis of the anions. For maximum resolution of the ions of interest, the instrument was operated at a pump speed of 2 ml/min. The eluent buffer was 0.001M Na_2Co_3 and 0.003M $NaHCo_3$ prepared in distilled deionized water having a conductivity of less than 0.1 μ mho/cm. All samples were run at the 10 μ mho full-scale setting.

A disposable syringe was used to load the solution into the sample loop.

Each sample was individually filtered in-line with a 0.2 μm pore size membrane filter during the sample-loading step in order to prevent contamination of the column with insoluble matter. Injections of the samples were spaced by fifteen minutes to allow complete elution of all anions.

For each ionic species, the peak height was measured from the defined baseline of initial to final inflection.

Calibration curves were prepared from a plot of peak height in inches versus concentration in $\mu g/ml$. The linear regression for each curve was used to reduce the data.

HIGH VOLUME AND DICHOTOMOUS SAMPLERS

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INTRODUCTION

The Environmental Monitoring and Support Laboratory (EMSL) of EPA will participate in the Aerosol Sampler Comparison Study by operating 2 high-volume (hi-vol) samplers and 2 EMSL dichotomous samplers. EMSL will be responsible for all aspects of our portion of the study including: (1) equipment and personnel transportation, (2) set-up and take-down, (3) operation during the 8 day period and (4) analysis for selected parameters.

SAMPLING DEVICES AND FILTER SUBSTRATES

The hi-vols used will conform to the standard Federal Register (1) requirements with the addition of constant mass flow controllers and Dixon flow recorders. The hi-vols will be operated at 1.42 sm 3 /min (50 SCFM) using acid washed 200 x 250 cm (8 x 10 in.) glass fiber filters.

The EMSL dichotomous samplers have the standard "Coarse" and "Fine" channels with a 3.5 um cutpoint and an inlet cut-off of $\sim 20~\mu m$. These samplers also include a separate "Total" channel which collects aerosols $\stackrel{<}{\sim} 20~\mu m$. Flow control is maintained by critical flow valves with rotameters on all 3 channels. The sampler utilizes 37 mm Fluoropore Teflon filters with a polyethylene backing. These filters are backed with a 37 mm cellulose pad and placed in circular holders which fit holders in the respective sampler channels.

OUALITY CONTROL

The samplers will be checked for flow calibration only. All samplers will be calibrated initially in RTP using a Rootsmeter® as the traceable standard. After the samplers are set up in the field, transfer flow standards will be used to audit check the flowrate initially and in the middle of the study. A standard audit orifice also calibrated using the Rootsmeter® is used to check the hi-vols. A 300 mm rotameter calibrated in the lab against a dray-test meter is used to audit check the "Total" and "Fine" dichotomous channels. The "Coarse" channel is checked with a calibrated mass flowmeter. At the conclusion of the study all samplers will be recalibrated with the audit flow devices.

During sample collection a change in flowrate from the beginning to the end of a sampling period (12 hrs) of \pm 15% is allowable. Flow changes greater than this would invalidate the respective sample.

In order to obtain reproducibility information 2 samplers of each type will be operated simultaneously for 8 sample periods (4 days). After these comparison tests the samplers will be operated alternately to obtain only one sample of each type per time period.

ANALYSES

The primary measurements will be gravimetric mass using a 5-place balance, with subsequent analyses for sulfate (SO_4) by the MTB method and lead (Pb) by atomic absorption. Mass measurements will be made on all fiters. Two measurements - SO_4 and Pb - will be performed on all samples collected except the duplicate dichotomous samples. The wet chemistry and mass analyses will be performed by the Analytical Chemistry Branch of EMSL.

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HIGH VOLUME AND DIFFUSION SAMPLER

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The samplers used in this study are a conventional Staplex High Volume sampler sampling at about 0.9 m³/min and a diffusion sampler sampling through three 47 mm filters at a total flow rate of about 2.5 m³/hr. The Hi-Vol sampler samples all particles less than about 20 μ m in diameter. All three diffusion-processed samples were taken through an entrance tube that excluded most particles larger than about 5 μ m in diameter: Sample DBO samples all remaining size ranges of particles; particles smaller than about 0.04 μ m are removed by diffusion from sample DB1, particles smaller than about 0.1 μ m are removed from sample DB2.

Samples from both the Staplex HiVol and the diffusion sampler were collected on phosphoric acid-treated quartz filters (1) (Pall Corp., Putnam, Conn., Type GAO). This filter material is prepared as follows: the filter as received is ignited overnight at 750°C to remove binder material; filter is then washed then treated with hot (80°C) phosphoric acid; following a rinse to remove excess $\rm H_3PO_4$, filter is reignited to 750°C. A post-ignition rinse in Ph 5 HCl removes excess $\rm P_2O_5$ and following drying at 100°C, the filter is ready for use. The HiVol sampler was also used to collect an SO_2 sample during each period on two $\rm K_2CO_3$, glycero-impregnated cellulose filters in series with the quartz prefilter.

The HiVol sampler was mounted in a conventional HiVol enclosure protected from precipitation and could be operated under any precipitation conditions. The diffusion-sampling pump was placed in a protective box but in the absence of an enclosed shed, no protection was used with the diffusion battery and filter holders; although no diffusion sampling during heavy rain conditions could be conducted, these conditions were not encountered during the study.

The HiVol sampler has been calibrated with the filter pack in place using a magnetohelic guage. Decreses in flow during 12 hr sampling were checked out after the experiment and found to be less than 1 cfm, insignificantly low to require measurement for each sample. The diffusion sampler has been calibrated using unrestricted Matheson rotameter tubes in series upstream from the three 47 mm filter holders, (i.e., in line at ambient pressure). This calibration was assumed to hold constant for 47 mm quartz filters from the same batch of treated quartz. The calibration was checked after the experiment for constancy; changes of only a few % were observed

and the average of flows before and after the Intercomparison were used for sample volume calculations.

Each 4-in diameter, HiVol quartz particulate filter was quartered with one filter quarter sequentially extracted by benzaldehyde and isopropanol and the extract contents analyzed for $\rm H_2SO_4$ and bisulfate, respectively, by the flash volatilization-FPD techique (3). A second quarter was extracted into pH 4 aqueous solution and soluble strong acid determined by Gran titration (1), ammonium and nitrate ions by Autoanalyzer colorimetric techniques (1), and soluble sulfate determined by ion chromatography (4) and also by Methylthymol Blue colorimetry (5). The reamining quarters were saved for replicate determinations as needed or for cross checks of sulfur content by the reduction-sliver-110 technique (2). The SO₂ was determined in the two $\rm K_2CO_3$, glycerol-impregnated cellulose backup filters by extraction into aqueous peroxide with determination as sulfate by ion chromatographic or turbidimetric Autoanalyzer techniques.

The diffusion-processed samples, collected on 47 mm treated quartz filters, were bisected. One half was analyzed for soluble strong H , NH $_4$, SO $_4^-$ and NO $_3^-$ by the methods described above; the second half was sequentially extracted by benzaldehyde for determination of H $_2$ SO $_4$ and also by the techniques described above.

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APPENDIX B

OUTLIER AND REGRESSION ANALYSIS EQUATIONS

OUTLIER TEST

The Dixon criterion is a statistical test applied to any set of n observation, where $n \geq 3$. Its objective is to identify an observation, which to within a chosen probability, does not belong to the other (n-1) observations. These do not include observations where there is a known cause for its deviation. Otherwise when the deviation is larger than one can reasonably expect, this should serve as a stimulus to discover what happened. If it appears that nothing happened then the results in this intercomparison study were left as is; however, the outlying values were flagged for all to see.

Let n be defined as the number of real non-zero sampler concentrations reported for a given period of the intercomparison study. Four coefficients are defined by each periods result set; however, only one coefficient will apply. Its use and definition depend on the number of results for that period, and whether the suspected observation lies at the low or high end. If the observations are ordered from 1 to n, where the first value, X_1 , is the lowest concentration reported and X_n is the greatest, then the four coefficients are defined as follows depending on n.

$$\begin{array}{lllll} r_1: & 3 \leq n \leq 7 \\ r_2: & 8 \leq n \leq 10 \\ r_3: & 11 \leq n \leq 13 \\ r_4: & 14 \leq n \leq 25 \end{array} \tag{B-1}$$

If result X_n is suspect, then

If the result X_1 is suspect, then

The r_j coefficients are calculated and compared to tabulated coefficients $r(1-\alpha/2)$, where α is defined as the probability assumed in rejecting a re-

sult that really belongs in the group. For the intercomparison study α was defined as 4%, thus any value greater than 2% high or less than 2% low would be defined as an outlier.

The calculated r_i Coefficients are compared to standard tables, a portion of which is given in Table B-1. Although α was chosen as 4%, if α is chosen smaller the coefficients will become larger and the likelihood of rejection decreases.

TABLE 8-1. CRITERIA FOR REJECTION OF OUTLYING OBSERVATIONS

		Upper	r Perce	ntiles			Upper 1	ercen	tiles
Coeffi-	# of	$\alpha = 10$	$\alpha = 4$	$\alpha = 2$	Coeffi-	# of —	α=10	$\alpha = 4$	α =2
cient	Observ.	•95	•98	.99	<u>ci</u> ent	Observ.	0.95	0.98	0.99
	3	.941	.976	.988		11	.576	.638	.679
	4	.765	.846	.889	r_3	12	.546	.605	.642
r_1	5	.642	.729	.780		13	.521	.578	.615
	6	.560	.644	.698		14	.546	.602	.641
	7	.507	.586	.637		15	.525	. 579	.616
	8	.554	.631	.683	r_4	16	.507	.559	.595
r_2	9	.512	.587	.635	т.	17	.490	.542	.517
<u>-</u>	10	.477	.551	. 597	_	•	:	:	•

More detailed information on the Dixon criterion can be found in <u>Experimental Statistics</u>, a National Bureau of Standards Handbook 91, Chapter 17, by M. G. Natrella, issued August 1, 1963, reprinted October 1966, with corrections.

REGRESSION ANALYSIS

Assume that the pollutant concentration results obtained for sampler Y are linearly correlated with those obtained for sampler X. Let j be the period number (j = 1, 2, 3, ..., 16). Then for any sampler Y we can write

$$y = a + bx (B-13)$$

The intercept, a, will be given by

$$a = \frac{1}{n} \left[\Sigma Y - \frac{SXY}{SXX} \Sigma X \right]$$
 (B-14)

and

$$b = \frac{SXY}{SXX} = \frac{\Sigma XY - \frac{1}{n}\Sigma X \Sigma Y}{\Sigma X^2 - \frac{1}{n}(\Sigma X)^2}$$
(B-15)

and n is defined as the number of <u>paired</u> X_jY_j values (≤ 16). Note that when regression analysis is performed between any sampler and the composite Z-means there will always be $16\ Z_j$ values, but not necessarily $16\ \underline{paired}\ Y_jZ_j$ values.

Similarly, when regression analysis is performed between any two samplers X_jY_j , the number of paired values will define n. The errors ε_a and ε_b can also be calculated using

$$\epsilon_{a} = \left\{ \frac{1}{n-2} \left[\Sigma Y^{2} - \frac{1}{n} \left(\Sigma Y \right)^{2} - \frac{\left(SXY \right)^{2}}{SXX} \right] \left[\frac{1}{n} + \frac{\left(\overline{X} \right)^{2}}{SXX} \right] \right\}^{\frac{1}{2}}$$
(B-16)

where

$$\overline{X} = \frac{1}{n} \Sigma X_j$$
 and $\overline{Y} = \frac{1}{n} \Sigma Y_j$

$$\epsilon_{b} = \left\{ \frac{1}{n-2} \frac{1}{SXX} \left[\Sigma Y^{2} - \frac{1}{n} (\Sigma y)^{2} = \frac{SXY}{SXX} \right] \right\}^{\frac{1}{2}}$$
(B-17)

The root mean square residual, r, of the fit is one measure of how well the two samplers define a linear relationship. The results from two samplers may tightly define their mutual slope, b, in which case r is small. However, if two samplers report widely fluctuating values, then r will be large. If all samplers are compared to the composite sampler, then an intercomparison of their respective r's is a measure of their relative precisions (assuming that b is approximately 1.0). The root mean square residual concentration for sampler Y relative to sampler X is defined by

$$r = \left[\frac{1}{m} \sum_{j=1}^{m} (Y_j - \hat{Y})^2\right]^{\frac{1}{2}} \text{ in ng/m}^3 \text{ (or } \mu g/m^3) ,$$
 (B-18)

where there are m concentration results for sampler Y_j and \hat{Y} is given by (B-13). Finally, it is useful to examine how well the two samplers X and Y are correlated, i.e., how linearly related there concentrations are. The correlation coefficient is given by

$$(bXY \cdot bYX)^{\frac{1}{2}} = (\frac{SXY}{SXX} \frac{SYX}{SYY})^{\frac{1}{2}}$$
(B-19)

SXY was given in (B-15) and SYX is obtained by interchanging X and Y in that expression.

The intercept and its error, the slope and its error, the root mean square deviation in μg or ng/m^3 , and the correlation coefficient are listed in Appendix C for each sampler that reported results for any pollutant fraction or total concentration.

More detailed information on linear regression analysis of two variables can be found in Experimental Statistics, a National Bureau of Standards Handbook 91, Chapter 5, by M. G. Natrella, issued August 1, 1963, reprinted October 1966, with corrections.

APPENDIX C

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Mass .	•	•	•	•		•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	101
Nitrate		•	•	•		•	•	•	•		•	•	•	•	•	•	•	•	•	•	104
Sulfate	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	107
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Calcium	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	119
Titanium	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	122
Iron .	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	125
Copper	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	128
Zinc .	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	131
Selenium	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	133
Bromine	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	136
Lead .									•	•		•									139

POLLUTANT RESULTS ARE GROUPED TOTAL, SMALL, & LARGE WITH THE FOLLOWING ORDER: MASS, NO3, SO4, S, S+SO4, & TRACE ELEMENTS-SI, CA, TI, FE, CU, ZN, SE, BR, & PB.

TOTAL: REPORTED TOTAL CONCENTRATIONS OR SUM OF ALL FINE & COARSE FRACTION RESULTS

SMALL: USUALLY THE FINE FRACTION(S); CUT POINTS WILL VARY WITH SAMPLER TYPE: SMALL MEANS ABOUT 3.0 + OR - 0.5 MICROMETERS AND SMALLER

LARGE: THE COARSE FRACTION; INLET RESTRICTIONS AND FINE CUT POINTS VARY ALSO. LARGE MEANS ABOUT 3.0 + OR -0.5 MICROMETERS AND GREATER, UP TO THE INLET CUTOFF

MASS RESULTS & ERRORS(NOT SHOWN) ARE PUNCHED IN TENTHS OF MICROGRAMS/CUBIC METER BUT ROUNDED OFF IN THE TABLES. ALL OTHER RESULTS ARE LISTED IN NANOGRAMS/CUBIC M

SAMPLER DEFINITIONS

DICOT= AUTOMATED DICHOTOMOUS SAMPLERS (3-C, L, & S) FROM LBL-LOO

DICOT= AN ERC DICHOTOMOUS SAMPLER (1 - 0) FROM EPA-RODES

HIVOL = HIGH VOLUME SAMPLERS (3: A FROM BNL-TANNER & P/T FROM EPA-RODES/BURTON)

LS = LINEAR STREAKER SAMPLERS (2 - J & K) FROM FLA.ST.UNIV.- HUDSON

MDS = MANUAL DICHOTOMOUS SAMPLERS (2 - D & R) FROM EPA-DZUBAY

RSP = CHAMP SAMPLERS(2-B&U) FROM EPA-BURTON; CYCLONE SAMPLER(1-F) FROM MUELLER

SMDAY = SIERRA MULTIDAY SAMPLER (1 - G) 3-STAGES UNIV.CA.DAVIS-CAHILL

SFU = STACKED FILTER UNIT () - 1) 2-STAGES FROM UNIV.CA.DAVIS-CAHILL

TTLF = TOTAL FILTER UNIT (1 - H) 1-STAGE FROM UNIV.CA.DAVIS-CAHILL

TSP = CYCLONE SAMPLER (1 - E) FROM ERT-MUELLER

2MASS= TWO MASS SAMPLER (1 - Q) FROM WASH.UNIV., ST.LOUIS-DELUMYEA/MACIAS

FOR EACH POLLUTANT, THE FIRST RESULT TABLE LISTS THE REPORTED CONCENTRATIONS AS A FUNCTION OF PERIOD, EACH 12 HOURS LONG, AND LISTED FROM COLUMNS 1 THROUGH 16.

EACH SAMPLER IS ASSIGNED AN ALPHABETICAL INDEX ACCORDING TO ITS SPATIAL LOCATION AT THE FIELD STUDY. SEE FIGURE 1 AND TABLE 4 IN THE FEXT FOR MORE INFORMATION.

A DASH - ENTERED IN THE TABLE INDICATES NO VALUE REPORTED FOR THAT SAMPLER & PD. OUTLIER VALUES ARE DENOTED BY A -(NEG) SIGN BUT ARE INCLUDED IN MEAN CALCULATION

THE Z-MEAN INCLUDES ALL SAMPLER RESULTS & OUTLIERS EXCEPT THOSE IN PARENTHESIS.

THE X-MEAN INCLUDES ONLY THOSE SAMPLER RESULTS NOTED IN PARENTHESIS-NO DUPLICATE

THE SECOND TABLE LISTS RATIOS OF REPORTED RESULTS TO THE APPROPRIATE Z-MEANS. THE LAST 3 COLUMNS LIST THE 16-PERIOD AVERAGE RATIOS, THEIR STANDARD DEVIATIONS, AND THE PERCENT ERROR ASSOCIATED WITH THAT STD.DEV.(COEFFICIENT OF VARIATION)

AN ASTERISK BY ENTRIES IN THIS TABLE INDICATE THAT A PARTICIPANTS REPORTED ERROR FOR THAT PERIOD ALLOWS HIS RESULT TO OVERLAP 1.0 OR THE Z-MEAN CONCENTRATION.

NOTE THAT THE STANDARD DEVIATIONS VS PD. IN THE MEAN RATIOS INDICATE THE DEGREE OF SCATTER IN THE REPORTED CONCENTRATIONS FOR THAT PARTICULAR PERIOD & POLLUTANT

THE LAST TABLE LISTS THE RESULTS OF A LINEAR REGRESSION ANALYSIS OF EACH SAMPLER WITH THE Z-MEAN. LEFT TO RIGHT ARE THE INTERCEPT, ITS ERROR; THE SLOPE, ITS ERROR; THE ROOT MEAN SQUARE DEVIATION IN CONC. UNITS; AND THE CORRELATION COEFFICIENT.

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	SD		973		so cv	0.23 35 0.37 53 0.33 27 0.24 16		
	AVG		1880		AVG	0.64 0.68 1.24 1.52	1.00	
	9.	2020 R 685 T 3570 A 3990 E	2566 1514	2748 1799	16	0.79 R 0.27 T 1.39 A 1.56 E	1.00	
. 22	15	1750 634 970 2640	1499 893	1415	15	1.17 0.42 0.65 1.76	1.00	
NANOGRAMS/CUBIC METER; PERIODS 1-16, MAY 11-18 1977	<u> </u>	1530 604 3150 3190	2119	2315 1482	<u>*</u>	0 72 0 29 1.49	1.00	
ΜΑ	13	1070 753 980 2150	1238 622	1294	13	0.86 0.61 0.79 1.74	1.00	
91-16	12	530 839 2430 2040	1460 918	1770 829	12	0.36 0.58 1.67 1.40	1.00	
2ER 10DS	Ξ	730 1030 1070 1850	1170	1317	Ξ	0.62 0.88 •0.91 1.58	1.00	
TER; F	01	470 1531 1270 970	1060	1257	10	44.0 1.20 50.00	1.00	.COEFF. 0.647 0.148 0.864 0.942
MBIC ME	σ	460 777 - 1350	862 451	504 4901	σ	0.53 0.90 -	1.00 0.52	COR.
RAMS/CL	æ	593 593 4120 5590	2861 2390	3434 2568	œ	0.40 0.21 1.44 1.95	1.00 0.84	RMS.DEV. 436.355 629.071 585.282 436.978
NANOGE	٢	2180 1550 2130 3600	2365 872	2427 1057	٢	*0.92 0.66 0.90 1.52	1.00	
NO3 :	ø	1250 1014 4290 4380	2734 1852	3228 1918	9	0.46 0.37 1.57 1.60	1.00	ERROR 0.177 0.255 0.262 0.179
	ß	1810 2365 2740 3340	2564 643	2815 492	S	0.71 0.92 •1.07	1.00	SLOPE 0.561 0.142 1.623
UDY OF TOTAL	£	710 1089 3290 3020	2027 1316	2466 1200	J	0.35 0.54 1.62 1	1.00	
JN STU	M	1360 2187 3120	2222 881	2654 660	м	0.61 *0.98 1.40	1.00	ERROR 349.713 504.164 532.221 354.334
MPAR I S(ſŮ	925 925 2480 2240	1624 856	1882 837	N	0 52 0.61 0.57 *0.98 1 53 1.40 1.38	1.00 0.53	
INTERCOMPARISON ST	-	1270 2267 1610	1716 507	1939 465	~	0.74 1.32 *0.94	1.00	INTERCEPT 141.429 910 096 -680.118 -378.121
Ξ	PER100	MDS-S HIVOL HIVOL TSP	ERS) AT10N	AT 10N	PFR10D	MDS-S HIVOL HIVOL TSP	ERS) ATION	MDS-S H1VOL H1VOL TSP
	u.	DZUBAY BURTON TANNER MULLER	Z MEAN(ALL SAMPLERS) STANDARD DEVIATION	EAN(T,A,E) STANDARD DEVIATION		DZUBAY BURTON TANNER MULLER	MEAN(ALL SAMPLERS) STANDARD DEVIATION	
	LTS	EPA DZ EPA BU BNL TA	AN (ALL TANDAR	X MEAN(T,A,E) STANDARD D	RAT10 TO Z	EPA DZ EPA BU BNL TA ERT MU	AN (ALL TANDAR	REGRESSION VS Z R EPA DZUBAY T EPA BURTON A BNL TANNER E ERT MULLER
<u></u>	RESULTS	и н о	Z ME	X NE	RATI	$\alpha \vdash \alpha \cap \alpha$	Ā S	REGR TEGR E B E

					> C	35 43 34 22		
	SD		761		SD	0.18 0.24 0.20 0.42		
	AVG		1015		AVG	0.50 0.56 0.58 1.86	1 00 6.75	
	16	760 R 356 B 357 U 2660 F	1124	1509 1628	91	0.68 R 0.32 B 0.32 U 2.37 F	1.00	
1977.	15	<50 405 315 1170	630	743 605	15	<0.08 0.64 0.50 1.86	1.00	
11-18	<u>+</u>	550 441 611 -2220	1091 982	1416	<u>+</u>	0.50 0.40 0.56 2.04	0.90	
. MAY	13	<50 442 429 970	614 309	700 383	13	<o.08 0.72 0.70 1.58</o.08 	1.00	
5 1-16	12	<50 545 435 1380	787 517	899 908	12	(0.06 0.69 0.55 1.75	1.00 0.66	
PER 1 0D9	=	<50 671 418 1240	776 421	829 581		(0.06 · 0.86 · 0.54 · 1.60	1.00	
TER; F	10	<50 700 796 770	755 50	783 18	10	0.93 0.93 1.05	1.00	COEFF. 0. 0.476 0.593 0.906
1810 18	on .	<50 699 556 900	718	728 243	თ	.0.07 .0.97 0.77	1.00	00 .
NANOGRAMS/CUBIC METER; PERIODS 1-16, MAY 11-18 1977.	80	<50 369 355 355	1541 2043	2128 2507	80	0.03 c 0.24 0 0.23 c 2.53 c	1.00	RMS.DEV 0. 229.402 208.002 413.356
NANOGE	7	<50 277 360 1440 -	692 649	900 764	7	0.40 0.40 0.52 2.08	1.00	ERROR RI 0. 0.159 6 0.144 6
. 503	ø	<50 315 501 2510	1109	1506	ω	0.05 0.28 0.45 2.26	1.00	щ о о о о о о о о о о о о о о о о о о о
INTERCOMPARISON STUDY OF SMALL NO3;	ß	<50 862 849 -1750	1154 516	1300	ഗ	60.04 0.75 0.75 1.52	1.00	SLOPE 0. 0.321 0.397 2.282
0Y OF	ŧ	<50 273 538 2180	997 1033	1359	£	(0.05 0.27 0.54 2.19	1.00	
ON STU	M	<50 1184 1162 -3770	2039 1499	2466 1844	M	0.02 0.58 0.57 1.85	1.00	ERROR 0. 170.831 154.894 307.818
MPAR1S	ď	<50 355 430 2180	986	1305	ũ	0.33 <0.05 <0.05 0.60 0.36 0.58 0.80 0.44 0.57 1.60 2.21 1.85	1.00	
NTERCO	-	400 740 978 1960	1226 647	1469 694		0.33 0.60 0.80 1.60	1.00	INTERCEPT 0. 213.792 165.610 -379.402
=	PER10D	MDS-S CHAMP CHAMP RSP	ATION	ATION	PER10D	MDS-S CHAMP CHAMP RSP	ATION	MDS-S CHAMP CHAMP RSP
	a.	DZUBAY BURTON BURTON MULLER	Z MEAN(WITHOUT R) STANDARD DEVIATION	EAN(U,F) STANDARD DEVIATION		DZUBAY BURTON BURTON MULLER	MEAN(WITHOUT R) STANDARD DEVIATION	
	2		V CW I T	ACU, FINDAR	10 2	_	V CWIT	SSION TO A BUILLIAN
~	RESUL TS	R EPA B EPA U EPA F ERT	Z MEAN STA	X MEAN(U,F) STANDARC	RAT10 T0	R EPA B EPA U EPA F ERT	MEAN STA	REGRESSION VS Z R EPA DZUBAY B EPA BURTON U EPA BURTON F ERT MULLER

	SO		0		S	0		
	AVG	~	1089		AVG	٦ . 00	1.30	
	16	1260 R	1750 1260 0 0	. 0	16	• 1.00	1.00	
1977.	15	1750		1 0	15	•1.00	1.00	
11-18	Ţ	980	980	1 0	<u>+</u>	*1.00 *1.00 *1.00 *1.00 *1.00 *1.00 *1.00 *1.00 *1.00 *1.00 *1.00 *1.00 *1.00 *1.00 *1.00 *0.00 *1.00	1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00	
∀A	13	1070	1070	1 0	13	•1.00	1.00	
5 1-16	12	530	530	1 0	12	•1 00	1.00	
PER 10D	110 11	730	730	i O	Ξ	•1.00	1.00	
ETER:	10	470	470	1 0	10	•1.00	1.00	COEFF.
INTERCOMPARISON STUDY OF LARGE NO3 ; NANOGRAMS/CUBIC METER; PERIODS 1-16, MAY 11-18 1977.	on	460	460	· 0	6	•1.00	1.00	ERROR RMS.DEV. COR.COEFF 0. 0. 1.000
RAMS/C	80	1140	1140	. 0	80	•1.00	1.00	MS.DEV 0.
NANOG	7	2180	1810 1250 2180 1140 0 0 0 0	10	7	•1.00	1.00 1.00 0. 0.	ROR R
NO3 :	Φ	1810 1250	1250	1 0	Ð	•1.00	1.00	E.9
LARGE	ī	1810	1810	+ 0	IJ	•1.00	1.00	SLOPE 1.000
DY OF	Ŧ	710	710	10	±	*1.00	1.00	Œ
ON STU	М	1360	1360	1 0	٣	•1.00	1.00	ERROR 0.
MPARIS	C	850	850 0	10	ď	*1.00	1.00 1.00 0. 0.	EPT
NTERCO		870	870 0	1 0	-	•1.00	1.00 0.	INTERCEPT 0.
-	PER10D	MDS-S	PLERS)	/1AT10N	PER 100	MDS-S	PLERS)	Z MDS-S
_	RESUL TS	R EPA DZUBAY MDS-S	Z MEAN(ALL SAMPLERS) STANDARD DEVIATION	X MEAN() STANDARD DEVIATION	RAT10 TO Z	R EPA DZUBAY MDS-S *1.00 *1.00	MEAN(ALL SAMPLERS) STANDARD DEVIATION	REGRESSION VS Z R EPA DZUBAY MDS-S

					>	010		
	SD		3011		SD (09 12 09 04		
	AVG		19344 3		AVG	0 90 1.21 1.07 0.88 0.92	1.00 0.16	
	16	27930 R 30900 P 28800 T 26000 A 26900 E	28106 1885	28150 2173	91	•0.99 R 1.10 P •1.03 T •0.93 A	1 00 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	
1977.	5	28600 34900 25700 23900 28200	28260 4176	28175 4818	15	1.01 1.24 0.91 0.85	1 00 0 15	
11-18	<u>*</u>	29100 33100 34150 25800 29300	30290 3367	30588 3811	<u>+</u>	0 96 1.09 1.13 0 85	1.00	
. MAY	13	3500 24080 7800-30900 8200 25200 4800 23600 6600 25000	25756 2950	26175 3229	13	0.94 1.20 •0.98 •0.92	1.00	
NANOGRAMS/CUBIC METER: PERIODS 1-16, MAY	12	13500 17800- 18200 14800 16600	16180 1998	15850 1526	12	0.83 1.10 1.13 •0.92	1 00 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	
PER 100	Ξ	14750 18700 16500 13000 14400	15470 2194	15650 2491	Ξ	0.95 1.21 1.07 0.84 0.93	1.00	
ETER;	10	4470 9600 8290 5040 4700	642 0 2360	6908 2417	10	0.70 1.50 1.29 0.79	1.00	COR.COEFF. 0.994 0.983 0.994 0.991
UB1C F	σ	11000 17700 14890 -	13273 3724	14030 4167	o	0.83 1.33 1.12 -	1 00 0.28	J - M
RAMS/C	60	24000 27900 25960 -	25953 1950	2 693 0 1372	ω	0.93 1.08 •1.00	1.00	RMS DEV 872.124 1408.431 1510.943 743.091
NANOG	7	22330 25200 23330 20200 22800	52775 1804	22883 2063	7	0.98 1.11 •1.02 0.89	1.00	ERROR F 0.032 0.051 0.055 1.029 0.029
. +05	9	21440 27300 25480 21800 23400	23884 2488	24495 2401	G	0.90 1.14 1.07 •0.91	1.00	# 6 6 6 6 6
TOTAL	ស	17820 22100 20540 16400 16700	18712 2500	18935 2829	S	0.95 1.18 1.10 0.88	0.13	SLOPE 1 069 1.019 0.957 0.893 1.064
UDY OF	t	11100 15600 15250 12300 13200	13490 1921	14088 1594	#	0.82 1.16 1.13 •0.91	1.00	77 7 7 7 1 1 2 1 2 1 2 1 2 1 2 1 2 1 2 1
ON STU	M	11670 16400 13080 11300	13113	13593 2588	M	0.89 1.25 •1.00 0.86	1.00	ERROR 651.527 1052.180 1128.762 587.006
MPAR19	a	12910 10230 11670 17600 19000 16400 13650 15360 13080 13500 11500 11300	14415 13418 13113 2147 3695 2322	14917 14215 13593 2325 3738 2588	Ŋ		1 00 0.28	
INTERCOMPARISON ST	-	MDS-S 12910 10230 11670 HIVOL 17600 19000 16400 HIVOL 13650 15360 13080 HIVOL 13500 11500 11300 TSP - 11000 -	14415			0.90 1.22 •0.95 •0.95	1.00	-2876.984 3072.122 1754.886 -152.720
	PER 10D	MDS-S HIVOL HIVOL TSP	ERS)	IATION	PER 100	MDS-S HIVOL HIVOL TSP	ERS)	MDS-S HIVOL HIVOL HIVOL TSP
	-	DZUBAY RODES BURTON TANNER MULLER	Z MEAN(ALL SAMPLERS) STANDARD DEVIATION	X MEAN(P,T,A,E) STANDARD DEVIATION		DZUBAY RODES BURTON TANNER MULLER	MEAN(ALL SAMPLERS) STANDARD DEVIATION	REGRESSION VS Z R EPA DZUBAY P EPA RODES T EPA BURTON A BNL TANNER E ERT MULLER
	.15	0 w w - 2	ANCAL	AN (P.	RAT10 10 Z		AN (AL I	SRESSION EPA DI EPA R(EPA B(EPA BL
	RESUL 15	R EPA T EPA A BNL ERI	Z MEJ	X ME.	RATIC	R EPA T EPA T EPA BNL E ERT	ME.4 S1	REGRESS R EPA P EPA T EPA A BNL

				>	8 C D D E		
SD		93		SD C			
9				9/		91	
¥	ar o m o h	1819		Á	0.0 0 0 0	0.0	
16	26868 27730 28646 28998 25000	27448 1600	27243 2043	9	0.98 1.01 1.04 1.06	1.00	
15	27707 25260 29437 29695 24800	27380 2283	26585 2703	15	1.01 0.92 1.08 1.08 0.91	1.00	
<u>+</u>	28599 32713 32438 25400	29788 3476	28919 4977	<u>±</u>	0.96 1.10 1.09 0.85	1.00	
13				13	0.94 0.93 1.12 1.15 0.86	1.00	
12	15820 15820 14400 17081	14657 1804		12	0.87 *1.08 *0.98 1.17 0.91	1.00 0.12	
=	13776 11600 16442 15434 12000	13850 2105	13011	=	• 0.99 0.84 1.19 1.11	1.00	
10	3799 4550 7887 6787 4200	5445	5179 1404	10	0.70 •0.84 1.45 1.25	1.00	COR.COEFF. 0.991 0.970 0.987 0.993
on	10493 10710 11977 13026 7800	10801 1965	10512 2619	on	0.97 •0.99 1.11 1.21 0.72	1.00	COR.
80	22975 23230 26935 26899 13700	22748 5406	21276 6813	œ	1.01 1.02 1.18 1.18 0.60	1.00 0.24	1069.188 1882.892 1259.845 993.405
7	21758 21170 22933 27662 22800	23265 2565	23877 3377	7	0.94 0.91 •0.99 1.19	1.00	ERROR R 0.037 1 0.071 1 0.043 1 0.034
φ	20915 21970 26343 27159 24600	24197 2705	24576 2595	O	0.86 0.91 1.09 1.12	1.00	<u>п</u>
ប	17139 16330 22256 22222 16700	18929 3035	18417 3300	J.	0.91 0.86 1.18 1.17 0.88	1.00	SLOPE 0.994 1.031 1.008 1.059 0.891
ŧ	11478 4800 13816 14815 10600	11102 3913	10072 5028	ŧ	1.03 0.43 1.24 1.33	1.00	
М	10795 8250 13649 12829 10100	11125 2162	10393 2304	м	0.97 0.74 1.23 1.15 0.91	1.00	ERROR 721.269 1331.718 849.885 670.146 1504.520
N		11827 2144	11640	ď	0.83 *0.99 1.22 1.14 0.82	1.00	
-	12379 11600 14985 14643 14600	13641 1540	13614 1745	-	0.91 0.85 1.10 1.07	1.00	-929.696 -921.2.424 1956.156 1466.196
PER10D	MDS-S DICOT CHAMP CHAMP RSP	LERS)		PERIOD	MDS-S DICOT CHAMP CHAMP RSP	LERS) I AT I ON	MDS-S DICOT CHAMP CHAMP RSP
•	DZUBAY RODES BURTON BURTON MULLER	LL SAMPI ARD DEV	ARD DEV	2	DZUBAY RODES BURTON BURTON MULLER	LL SAMPI ARD DEV	REGRESSION VS Z R EPA DZUBAY O EPA RODES B EPA BURTON U EPA BURTON F ERI MULLER
บนรร		EAN (A	EAN (C	10 10		EAN (A STAND	SRESSI EPA EPA EPA EPA
RESI	0.000 Dr	Σ ν	×	RAT	α O @ ⊃ r	Σ ΄΄	
	3 4 5 6 7 8 9 10 11 12 13 14 15 16 AVG	DZUBAY MDS-S 12379 9773 10795 11478 17139 20915 21758 22975 10493 3799 13776 12686 23468 28599 27707 26868 R R R R R R R R R R R R R R R R R R	DZUBAY MDS-S 12379 9773 10795 11478 17139 20915 21758 22975 10493 3799 13776 12686 23468 28599 27707 26868 R POLES DICOT 11600 1720 8250 4900 16330 21970 21170 23230 10710 4550 11600 15820 23200 - 25260 27730 0 BURTON CHAMP 14985 14441 13649 13816 22252 27159 27662 26899 13026 6787 15434 17081 28650 32438 29695 28998 U MULLER RSP 14600 9700 10100 10600 16700 22800 13700 7800 12000 13300 21600 25400 25900 F POLOT 1102 18929 24197 23265 25748 10801 5405 1102 18929 24197 23265 5406 1965 1791 2105 1102 18929 27197 23565 5406 1965 1791 2105 1102 18929 27197 23565 5406 1965 1791 2105 1102 18929 27197 23565 5406 1965 1791 2105 1804 2105 2718 2418 2418 2418 2418 2418 2418 2418 24	DZUBAY MDS-S 12379 9773 10795 11478 17139 20915 21758 22937 10797 1600 1500 1500 22930 1770 25830 1770 1600 1500 23200 1770 26808 R POLL SAMPLERS) 1460 970 1170 1000 1000 1000 1000 1000 1000	Marie Mari	Fertion Fert	Ferrior Ferr

SD		405		SD CV	0.33 39 0.33 28		
AVG		928		AVG	0.84 0. 1.16 0.	1.00	
16	1060 R 1030 O	1045 21	1030	16	0.91 *1.01 R 0.84 0.33 *1.09 *0.99 0 1.16 0.33	1.00 0.02	
15	988 1070	979 129	1070	15	• 16.0	1.00	
Ŧ	490 2320	1405 1294	2320 0	<u>*</u>	0.35	1.00	
13	609 1880	1245 899	1880	13	0.49	1.00	
12	570 1310	9+0 523	1310	12	0.61	1.00	
Ξ	975 1440	1208 329	1440	=	0.53 0.81 1.47 *1.19	1.00	
01	667 1840	1254 829	1840	10	0.53	1.00	COEFF. 0.412 0.956
6	506	353 216	200	б	1.43	1.00	. COR. 6 6
80	1017	1309 412	1600	œ	0.51 0.78 1.43 1.49 *1.22 *0.57	1.00 1.00 0.69 0.32	RMS.DEV. COR.COEFF 191.696 0.412 191.696 0.956
7	571 1670	1121 777	1670	7	0.51	1.00	ERROR R 0.145 0.145
9	527 690	609 115	690	9	0.87	0.19	E.R.
ស	682 1070	876 274	1070	Ŋ	0.78 0.87 *1.22 *1.13	1.00	SLOPE 0.245 1.755
Ŧ	629 1350	990 510	1350	ŧ	0.64 •1.36	1.00	
М	875 530	703 244	530	M	1.25	1.00	ERROR 142.678 142.678
ď	453 200	327 179	200	ณ	1.39	1.00 1.00 1.00 0.12 0.55 0.35	
	532 450	491 58	450	-	1.08		INTERCEPT MDS-S 463.515 DICOT -463.515
PER 10D	MDS-S DICOT	LERS) I AT I ON	1 A T 1 ON	PER 1 00	MDS-S DICOT	ERS)	
	EPA DZUBAY EPA RODES	Z MEAN(ALL SAMPLERS) STANDARD DEVIATION	EAN(O) STANDARD DEVIATION		EPA DZUBAY MDS-S 1.08 1.39 1.25 EPA RODES DICOT *0.92 *0.61 *0.75	MEAN(ALL SAMPLERS) STANDARD DEVIATION	REGRESSION VS Z INTERCEPT R EPA DZUBAY MDS-S 463.515 O EPA RODES DICOT -463.515
RESULTS	EPA D	EAN (AL STANDAI	X MEAN(O) STANDA	RAT10 TO Z	EPA D	EAN (AL I S FANDAI	RESSION EPA D. EPA R(
RES	αo	Σ.	Σ *´	RAT	α O	Σ *΄	REGI R t

INTERCOMPARISON STUDY OF LARGE SO4 ; NANOGRAMS/CUBIC METER; PERIODS 1-16, MAY 11-18 1977.

		0, 111 0, 11	•			_
1977	15	9160 9040 9610 9610 11033 11013 11013 7851 13235	10453 1798 10149 2283	51	0 88 0 0 97 1 0 92 1 0 92 1 0 92 1 0 92 1 0 92 1 0 93 1 2 1 1 2 1 1 31	1 00 17 0 17
11-18	ž	10020 100587 10974 10620 9513 10306 11933	10798 967 10932 1074	Ţ	0.93 1.02 1.03	00 0 0 0 0 1
¥ ≻	13	8220 8040 8480 7680 9345 9538 7174 7174 7644 11064	8915 1566 9080 1760	13	**************************************	00 · - 0
9:-1	12	5000 5000 6102 6106 6106 6106 7465 5748 5748	5346 636 5467 745	12	**************************************	1.00 0.12
ER 1005	:	5240 4880 4820 6054 5957 - 3584 4980 4982 4982 4982 5971	5316 901 5291 1202	Ξ	- 0.99 - 0.99 - 0.97 - 0.94 - 0.94 - 0.94	0.17
TER; F	10	- 1750 1860 1820 2158 2234 2250 1578 1578 1934 2502	1935 395 1928 271	10	. 80.00 	1.00 0.20 COEFF 0.993 0.995 0.995 0.995 0.995 0.995 0.995 0.995 0.995 0.995 0.995
BIC ME	σ	3680 3840 3650 4540 4528 4540 4528 4540 4540 4540 4541 4560 4541 8650	4107 493 4126 615	σ	0.99	00 COR
NANOGRAMS/CUBIC METER; PERIODS 1-16,	00	7950 7380 - 9620 6919 8874	8605 1276 9704 807	Φ	0 92 0.86 0.86 1.12 0 80 1.12	1.00 1 0 15 0 345.0EV 345.384 343.608 203.568 203.568 203.568 204.168 305.120 305.120 914.8938 914.8938 914.8938
NANOGE	7	7660 7870 7880 7560 8954 8956 8968 8968 7555 7555 7555 71509 71509	8438 1199 8420 1504	7	0.93 0.93 0.93 0.90 1.06 1.06 1.05 0.93 1.18	00 1
 v	9	- 8370 7120 71330 90052 9072 8592 7183 7183 7764 8699	8320 977 8707 1039	ω	0.86 0.88 0.88 0.88 0.10 0.10 0.096 0.096	ERROR 0.12 0.03 0.033 0.033 0.023 0.023 0.023 0.031 0.031 0.031
	Ŋ	5870 6380 6040 6040 7313 7206 7206 5577 5582 6582 8309 9725 1	6943 1279 7141 1563	ъ	0.95 0.95 0.95 0.95 0.95 0.95 0.95 0.95	1 00 0 . 18 SLOPE 0 .922 0 .916 0 .913 0 .973 0 .973 0 .973 0 .973 0 .973 0 .973 1 . 063 1 . 196 1 . 196
)Y OF 1	.	3300 4550 4280 3690 4819 4685 - 3819 3847 3847 3836 4620	4322 763 4381 983	<i>±</i>	0.76 0.99 0.85 0.85 1.12 1.08 0.88 0.88	0.18
INTERCOMPARISON STUDY OF TOTAL	M	- 4300 3960 4130 5174 5145 6145 7243 3724	4187 724 4041 932	M	0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.0	ERROR 285 986 252 792 262 792 263 794 265 655 267 655 267 655 267 655 267 655 267 655 268 612 268 612
1PAR I S	u	3060 3930 3730 3350 +283 14382 2503 3120 	3479 641 3345 736	'n	0 88 1 13 1 13 1 1.23 1 1.23 1 1.23 0 .40 0 .85	00
VTERCO	-	+830 5230 5280 +540 +540 - 5969 5869 - 5027 +579	5166 538 5152 607	-	*0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0.10 0 1 0.10 0.1 10 0.10 0.1 147.906 147.906 147.906 1735.796.496 735.798.496 735.798.496 735.798.496 735.798.496 735.798.496 735.798.496 735.798.496
Ξ	PER 100	MDS-A TF-P TF-P MDS-S DICOT DICOT SMDAY TTLF SFU LS 2	ERS) ATION K)	PER I OD	MDS-A TF-P TF-P MDS-S DICOT DICOT SMDAY TTLF SFU	MDS-A TF-M MDS-A TF-M MDS-S DICOT DICOT SMDAY TILF SFU LS 2
	a.	DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO CAHILL CAHILL CAHILL HUDSON	MEANCALL SAMPLERS) STANDARD DEVIATION MEANCO,M.L.G.I.K) STANDARD DEVIATION	_	DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO CAHILL CAHILL CAHILL CAHILL CAHILL CAHILL CAHILL	SAMPL DEVI US Z DBAY DBAY DBAY DBAY DBAY DBAY DBAY DBAY
	(O	E E C C C C C C C C C C C C C C C C C C	YOAR YOAR	70 Z	H T C C C C C C C C C C C C C C C C C C	VOAR VOAR VOAR VOAR VOAR VOAR VOAR VOAR
	RESUL TS	EPA EPA EPA EPA LEBL LEBL UCD UCD UCD	MEANCALL STANDAR MEANCD, M STANDAR	RAT10 TO	EPA EPA EPA EPA EPA EPA EPA EPA EPA EPA	MEANIALL OPESSION OPESSION CEPA D21 CEP
-	RES	σεχαυινοι-υχ	ΕΣ	RAT	O E Z Œ O L O O I - 7 Y	κοΣΣΚΟΊΝΟΙ-JΑ Σ

SD CV 0.05 6 0.07 7 0.06 6 0.09 4 0.05 5 0.09 8 0.13 16 0.13 16 0.10 12 0.09 8

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9580 M - N - N - C 10097 C 10109 S 10109 S 9307 H 7042 I 11709 J 11517 K

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AVG

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	SD		626	SC	0.08 0.05 0.03 0.03 0.03 0.13 0.13		
	AVG		5869	AVG	0.92 0.92 0.95 0.95 0.94 0.94 0.95 0.95 0.95	1.00	
	16	8687 M 8687 M - N - N - R 90119 C 8969 L 9094 S - G 5833 1	8320 1399 7830 1735	16	1.04 M 1.04 M 1.08 C 1.08 C 1.09 S 0.70 1	1.00	
1977.	15	8951 8612 9234 10125 9998 10146 7375	9131 959 8733 1081	15	*0.98 0.94 0.94 1.001 1.10 1.11 0.81	1.00	
11-18	<u>±</u>	9298 - - 9532 9851 9877 - 9314	9514 226 9488 315	<u>#</u>	.0.98 .1.00 .1.01 .1.01 .0.98	1.00	
MA∀	13	7912 7586 7764 7362 8475 8617 - 6950	7809 591 7766 694	13	*0.97 *0.99 0.94 *1.09 *1.10	1.00	
5 1-16.	13	4336 4695 4525 4683 5571 5468 5514 5433	5028 514 4983 560	12	0.86	1 00 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	
PER I ODS	1.1	4542 4998 4411 4368 5225 5150 5261 3560 4473	4665 552 4545 622		*0.97 1.07 0.94 1.12 1.12 1.13 0.76 *0.96	1.00 0.12	
ETER; 1	10	1506 1642 1495 1601 1795 1819 1825 1580 1744	1667 132 1658 125	10	0.90 0.09 0.09 0.09 0.09 0.09 0.09 0.09	1.00	.00EFF. 0.993 0.991 0.995 0.996 0.998 0.995 0.923
JBIC M	m	3541 3813 3413 3499 4131 4100 3987 3470 3801 -860	3751 280 3745 251	on	0.94 0.91 0.91 0.93 0.93 1.09 1.06 1.00 1.00 1.00	1.00	COR
NANOGRAMS/CUBIC METER;	60	5449 6804 6678 - - 9600 8148	7336 1586 7732 2106	ω	0.93	1.00	RMS. DEV. 283. 327 284. 104 281. 747 227. 354 240. 356 166. 201 270. 438 880. 238 890. 555
NANOGE	7	7367 7661 7426 7284 8186 8172 8119 7000 7225	7604 451 7485 453	7	.0.97 .0.98 .0.98 .1.08 .1.08 .1.08 .0.92 .0.92	1.00	ERROR RI 0.070 0.035 0.035 0.029 0.029 0.018 0.031 0.031 0.037
 s	φ	7901 6709 6938 8287 8270 7859 7970	7650 603 7851 423	ω	1.03 0.88 0.98 0.91 0.95 0.95	1.00	
SMALL 9	ľ	5548 6019 5529 5743 6572 6430 6448 5570	6157 670 6225 829	Ŋ	0.90	1.00	SLOPE 0.963 0.944 0.934 0.962 1.040 1.051 1.023 1.170 0.866
PF	÷	2943 4182 3584 3373 4123 3945 - 3800 3481	3691 416 3670 479	ŧ	1.13 1.100 0.91 1.12 1.03 1.03 0.26	1.00	
NO STUDY	m	3737 3894 3443 3707 - 4309 4274 2940 3491	3724 451 3674 507	M	1.00 0.92 1.00 1.15 0.79 0.34	1.00	ERROR 396.721 195.029 207.518 167.455 189.194 114.091 196.595 731.934 610.244
MPAR I SC	N	2568 3572 3170 3040 - 3518 3693 2500 2693	3107 458 2990 512	a	0.86 • 1.15 • 0.98 • 1.13 1.13 1.19 0.81 0.87	1.00	
INTERCOMPARISON	-	4562 5009 4951 4297 5336 5308 5244 4310 3769	4754 548 4592 601	-	*1.05 *1.04 0.90 1.12 1.12 *0.91 0.79	1.00	INTERCEPT -219.166 387.016 62.634 -95.827 266.537 195.124 325.002 419.415
=	PER I OD	MDS-A TF-P MDS-S DICOT DICOT DICOT SMDAY SFU	Q) /1AT10N /1) /1AT10N	PER 100	MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY SFU ZMASS	Q) (IAT10N	MDS-A TF-M TF-P MDS-S DICOT DICOT DICOT SMDAY SFU
		DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO CAHILL CAHILL CAHILL	MEAN(WITHOUT Q) STANDARD DEVIATION MEAN(D.M.L.G.I) STANDARD DEVIATION	Z 0	DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO CAHILL CAHILL CAHILL DEL/ED	MEAN(WITHOUT Q) STANDARD DEVIATION	ION VS Z DZUBAY DZUBAY DZUBAY LOO LOO LOO CAHILL CAHILL
-	RESUL TS	EPA N EPA R EPA C C LBP C LBP C C C C C C C C C C C C C C C C C C C	Z MEAN(I STANI X MEAN(I STANI	RATIO TO	TO EPA R EPA C LBL C LBL C LBL C UCD O UCD	MEANO	REGRESSION VS D EPA DZUBAN N EPA DZUBAN N EPA DZUBAN C LBL LOO L LBL LOO S LBL LOO S LBL COO G UCD CAHILL I UCD CAHILL OCT CAHILL

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	SD		237	SD	0.15 0.34 0.11 0.14 0.14 0.02		
	AVG		574	AVG	0.58 0.62 1.14 0.62 1.35 1.47 1.47 0.03	1.00	
	16	424 D 896 M 1072 N 537 R 1078 C 1148 L 1015 S	922 289 919 357	16	0.46 • 0.97 M • 1.16 N • 1.7 C • 1.10 C • 1.10 C • 1.31 I	1.00	
1977.	15	212 438 1655 374 908 989 867 -	740 466 529 328	15	0.29 0.59 2.24 0.51 1.23 1.34 1.17	1.00	
	<u>*</u>	716 1000 484 1055 1123 1043	916 230 944 208	<u>+</u>	•0.78 •1.09 0.53 1.15 1.23 1.14	1.00	
MAY 11-18	13	307 450 714 319 870 921 -	611 253 593 271	13	0.50 0.74 11.17 0.52 1.42 1.51	1.00	
1-16,	12	257 299 546 192 531 638	397 171 377 176	12	.0.65 .0.75 .1.38 .0.48 1.34 1.61	1.00	
NANOGRAMS/CUBIC METER; PERIODS 1-16.	Ξ	240 469 450 799 807 23	F 29 227 485 291		0.45 0.89 0.85 1.51 1.53 0.04	1.00	
TER; P	10	113 363 219 363 415 425	298 123 239 157	10	0.38 • 1.22 • • 0.73 • 1.22 1.39 1.43	1.00	COEFF. 0.547 0.935 0.866 0.964 0.969 0.949
BIC ME	6	139 26 231 156 797 440 361	255 143 223 180	თ	0.55 0.10 0.091 0.61 1.56 1.73 1.42	1.00 0.56	COR.
AMS/CU	80	1148 701 8	881 236 794 0	œ	.30	1.00	RMS. DEV. 74. 998 80. 428 80. 428 226. 894 72. 863 63. 244 53. 250 71. 126 0.
NANOGR	7	290 212 447 280 768 749	515 239 470 267	7	0.56 0.41 0.54 ·0 0.54 ·0 1.49 1.45 1.45 1.45	1.00	u .
	ø	- 470 637 385 775 802 733 18	615 164 591 183	9	- 0.76 *1.04 * *0.63 1.26 1.31 1.19 0.03	1.00	ERROR 0.135 0.115 0.290 0.093 0.090 0.074 0.103 0.240
ARGE S	ហ	327 362 507 293 741 776 738 4	534 198 499 205	Ŋ	0.61 0.68 0.95 0.95 1.38 0.01	1.00	SLOPE 0.249 1.072 1.472 0.603 1.057 0.933 0.
UDY OF LARGE	£	356 367 601 319 696 740 26	491 182 455 190	Ŧ	0.73 0.65 0.65 1.42 1.51 0.05 0.72	1.00	
ST	٣	393 518 427 - 865 871 233	551 262 497 329	M	0.71 0.94 0.98 0.78 1.55 1.58 0.04	1.00	ERROR 76.598 65.619 175.854 56.473 54.417 43.445 62.598 0.
PAR I SC	۵	391 360 559 316 - 765 689	477 196 443 222	ď	.0.82 .0.76 .1.17 .0.66 .1.45 .1.45	1.00	
INTERCOMPARISON	-	267 228 329 239 - 661 625	450 241 490 291	-	0 59 • 0.49 • 0.49 • 0.73 • 0.53 • 0.53 • 1.47 1.39	1.00 0.54	101 ERCEPT 162 . 482 -222 . 130 -170 . 241 9 . 778 159 . 077 206 . 966 205 . 820 0
	PER10D	MDS-A TF-H TF-P MDS-S DICOT DICOT SMDAY SFU	6) IATION IATION	PER10D	MDS-A TF-M TF-P MDS-S UICOT DICOT SMDAY SFU	3) IAT I ON	MDS-A TF-M TF-P TF-P MDS-S DICOT DICOT SMDAY SFU
	-	DZUBAY DZUBAY DZUBAY UZUBAY LOO LOO CAHILL	MEANGWITHOUT G) STANDARD DEVIATION MEANG,M,L,I) STANDARD DEVIATION	7	DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO CAHILL	MEAN(WITHOUT G) STANDARD DEVIATION	ON VS Z DZUBAY DZUBAY DZUBAY LOO LOO CAHILL
	.15		ANCHI ANDA (NCD.)			ANCHI	10
-	RESULTS	EPAN EPAN EPAN EPAN EPAN EPAN EPAN EPAN	Z MEA ST ST ST	RATIO TO	EPA R EPA PA C C C C C C C C C C C C C C C C C	ME.	REGRESS EPA T EPA C C LBL C LBL C LBL C UCD

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60000000000000 AVG 00 KOMPLOEZKUJNO-O26205 3269 9 26868 27730 28646 28998 25000 26001 27057 26907 27282 2759 2390 25366 4091 03 00 00 00 00 00 00 36 36 36 00 ------25260 29437 29695 24800 26853 25818 25818 25836 27702 30375 30438 5760 27388 2563 26**36**4 2782 00 22.1 0.98 27942 29096 ; 2278 28599 32713 32438 25400 -27894 28596 29553 28731 28645 ± 98 - 0 24076 0.98 0.95 0.50 0.50 0.95 0.97 23468 23200 28650 28650 23736 22758 22758 222086 25425 25625 20850 6270 23806 2668 1.00 15142 12686 15820 14400 17081 14085 14089 16713 16404 14920 16299 1500 0.85 0.85 0.94 11 13776 11600 11600 11600 11600 11600 11904 11904 11904 11904 11904 11904 11904 11904 11904 11908 119 13400 13944 0.99 0.93 1.11 0.11 1.11 0.94 0.95 0.95 0.77 0.96 0.35 0.35 METER: 3799 4550 7887 7887 7887 4200 4200 4451 84803 5385 5457 54740 3390 5051 809 5160 0.74 0.088 1.53 1.53 1.53 0.087 0.087 0.097 1.06 0.087 0.092 0.092 0.092 0.092 0.092 0.092 0.092 0.092 0.092 0.092 0.092 0.093 0.003 992 992 993 993 993 994 996 997 997 997 0.992 0.992 0.992 0.993 0.993 0.993 0.993 0.993 0.993 0.993 0.993 0.993 0.993 0.993 0.993 0.993 NANOGRAMS/CUBIC 10493 10710 13026 7200 7200 10623 11439 10497 12300 11961 11403 2580 0.95 0.97 1.17 0.70 0.96 1.18 1.18 1.18 1.18 1.18 1.18 1.18 1.18 1.18 1.19 1.10 11091 1294 10964 1556 90 5. COR ~ 0 22975 23230 26935 26899 13700 16347 20412 28800 22378 22237 5971 093 095 200 200 200 200 114 114 200 200 200 889 - 980 - 980 - -----21758 21170 225933 22600 22101 22101 22983 22578 21558 21515 215000 21675 1790 22988 2203 ERROR 0 035 0 039 0 053 0 073 0 073 0 035 0 034 0 054 0 035 0 035 SO4: 20915 21970 2463 2460 2460 2460 2481 29814 2481 23577 23577 2357 23429 2178 23992 00--- -00:----00 - 0 17139 22256 22256 22226 16644 16644 16587 17229 19716 19344 18635 ; 2318 18578 2581 00 5.1 00PE 324 053 031 031 038 955 955 955 004 006 002 840 SMALL - 0 11478 4800 13816 14815 10600 8829 12546 11052 11052 11052 11053 11400 2940 11085 10.43 0.43 11.25 11.34 0.09 0.09 0.10 0.10 0.10 0.10 0.10 0.26 8 8 Ь - 0 INTERCOMPARISON STUDY 10795 13649 12869 10100 111682 11682 11682 11682 11682 11682 11682 11721 11721 12927 12822 8820 10473 3810 10787 11154 1620 97 77 77 74 115 115 115 115 115 34 34 5.5 673 (1484 1024 1024 1526 1526 1526 1548 580 643 655 580 655 156 150 655 1903 00--0--0---00 - 0 9773 11720 11720 13500 9700 8004 10716 9510 2060 9972 2071 0.95 1.40 1.40 1.40 0.94 0.09 0.89 0.89 0.89 0.89 0.79 0.79 0.79 0.89 0.79 90 INTERCEPT
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15	888 1070 636 1314 1314 1324 2724 2967 2967 2601	1972 6 1339 1 1483 6 183 1	15	0.45 0.54 0.54 0.63 0.57 0.57 1.38 1.38 1.38 1.00 1.00 0.68 0.68
ž	490 2320 2148 3000 1452 3165 3369 3129	2450 958 2703 569	<u>*</u>	0.20 0.95 0.59 1.28 1.28 1.28 1.28 0.39
13	609 1880 921 1350 2:42 957 2610 2763	1702 775 1799 705	13	1.00 1.53 1.00 1.00 1.00 1.00 1.00 1.00
12	570 1310 771 8871 1638 576 1593 1914	1135 435 1167 463	12	00.51 00.51 00.51 00.51 1.40 1.40 00.51 1.60 00.51 00.
	975 1440 720 1407 1350 2397 2421 69	1492 615 1452 713	Ξ	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
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σ	1017 1600 3444 2103 	2109 909 1991 553	80	0.48 1.63 • 1.00
7	571 1670 870 836 1341 840 2364 2364 2364 2745 7757	1461 707 1461 704	7	0.39 0.104 0.044 0.044 0.58 0.58 1.58 1.00 1.00 1.00 1.57 1.5
Ø	527 690 1410 1911 1155 2325 2406 2199 2199	1570 693 1502 704	Ø	
ľΩ	682 1070 981 1086 1521 873 2223 2328 2328 2214 1587	1457 614 1410 565	Ŋ	0.47 •0.73 •0.75 •1.04 0.60 1.53 1.00 0.10 0.42 0.07 0.0
#	629 1350 1068 1101 1803 957 2088 2220 2220 78	1365 548 1361 495	<i>±</i>	0.46 0.40 0.40 0.70
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_	532 450 801 801 1987 717 1983 1875	1160 1733 1266 1882	-	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
PER 100	MDS-S DICOT MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY SFU	6) VIATION VIATION	PER10D	MDS-S DICOT MDS-S DICOT DICOT DICOT SMDAY SFU 6) VIATION VIATION TF-M MDS-S DICOT MDS-A TF-M MDS-S DICOT MDS-S DICOT MDS-S SMDAY SFU SFU SFU SFU SFU SFU SFU SFU SFU SFU
	DZUBAY RODES DZUBAY UZUBAY DZUBAY DZUBAY LOO LOO CAHILL CAHILL	MEAN(WITHOUT G) STANDARD DEVIATION MEAN(ODMLG!) STANDARD DEVIATION	2	EPA DZUBAY MDS-S EPA RODES DICOT EPA DZUBAY MPS-A EPA DZUBAY TF-M EPA DZUBAY TF-P EPA DZUBAY TF-P EPA DZUBAY TF-P EPA DZUBAY HDS-S LBL LOO DICOT LBL LOO DICOT LBL LOO DICOT UCD CAHILL SMDAY UCD CAHILL SFU MEAN (MITHOUT G) STANDARD DEVIATION GRESSION VS Z EPA DZUBAY MDS-S EPA DZUBAY MDS-S EPA DZUBAY TF-M EPA DZUBAY MDS-S LBL LOO DICOT LBL LOO DICOT LBL LOO DICOT LBL LOO DICOT UCD CAHILL SFU
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	SD		520	SD	0.24 0.28 0.26 0.18 0.13 0.13 0.33		
	AVG		1144	AVG	0.94 1.04 1.27 0.65 0.63 0.65 1.47	1.00	
	16	1211 D 712 M 1081 N 723 R 497 C 492 L 507 S	730 275 758 315	16	*0.98 M *0.98 M *0.99 R *0.68 C 0.68 C 0.67 C 0.69 C 0.69 C 0.69 C 0.69 C	1.00	
1977.	15	1320 2208 2088 733 819 797 787	1390 716 1673 743	15	1.59 1.50 0.53 0.59 0.57 0.57	1.00 0.52	
MAY 11-18	<u>±</u>	720 1227 743 667 666 656	831 245 843 261	Ť	0.87 1.48 •0.89 0.80 0.79	1.00	
	13	1269 1215 1758 699 882 848 - -	1232 475 1322 461	13	*0.93 *0.99 1.43 0.57 0.72 0.69	1.00	
91-19	12	1001 843 1059 828 793 701	1037 457 1146 607	12	0.97 0.81 0.80 0.76 0.68 0.68	1.00	
PER 1005	Ξ	1286 1736 1603 917 934 967 978 1270 2309	1333 473 1514 523	1.1	1.30 1.30 1.20 0.70 0.73 0.73	1.00	
NANOGRAMS/CUBIC METER; PERIODS 1-16.	10	756 616 860 448 416 427 430 1370	797 501 1003 589	10	0.77 0.77 1.08 0.56 0.54 0.54 0.54	1.00	COR.COEFF. 0.750 0.754 0.824 0.800 0.706 0.757 0.757 0.718 0.857
JBIC ME	σ	782 539 869 496 749 729 703 1220	917 513 1088 654	6	0.85 0.59 0.54 0.82 0.80 0.77 1.33	1.00	00 00 00 00 00 00 00 00 00 00 00 00 00
RAMS/CI	80	1622 1749 1539 - - 3670 3360	2388 1037 2884 1104	œ	0.68 0.73 0.64 - - 1.54	1.00	7MS.DEV. 269.122 307.438 177.353 135.986 140.403 160.356 384.022
NANOGE	7	676 1397 1517 294 454 462 464 1540	894 519 1064 470	7	0.76 1.56 1.70 0.33 0.51 0.52 1.39	1.00	ERROR R. 0.132 0.350 0.205 0.118 0.191 0.192 0.215 0.295 0.291 0.291 0.291 0.291 0.291 0.386 0.386
: 15	9	853 1205 667 478 480 465 2040	958 573 1213 688	9	.0.89 1.26 0.70 0.50 0.50 0.49 22.13	1.00	
SMALL 9	ιΩ	842 1270 1749 446 514 518 474 1490 3258	1173 921 1476 1065	ស	*1.08 *1.09 0.38 0.38 0.44 0.40 0.40 2.78	1.00	SLOPE 0.520 1.832 0.573 0.591 0.604 0.761 1.402
UDY OF S	±	782 893 1149 737 545 550 - 1760 1455	984 438 1088 502	t	0.80 10.91 1.17 1.17 0.55 0.55 0.56 1.79	1.00	
51	M	1181 1405 1309 706 - 913 797 1250 1833	1174 367 1316 339	M	*1.01 *1.12 0.60 0.78 0.68 *1.06	1.00	ERROR 163.924 377.476 246.987 142.480 199.756 196.932 231.569 353.108
1PAR1S	٥	1271 1172 1374 1070 - 1047 1870 11110	1250 274 1294 332	N	*0.94 *1.10 0.85 0.84 0.87 1.50 *0.89	1.00 0.22	
INTERCOMPARISON	-	1031 1359 1879 748 925 839 1750	1208 419 1240 327	-	0.85 1.56 0.62 0.77 0.69 1.45	1.00	1NTERCEPT 460.916 -814.294 749.156 60.839 27.643 -106.150 -59.102 54.117 389.221
ā	PER 10D	MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY SFU	LERS) TATION 1)	PER 10D	MDS-A IF-M MDS-S DICOT DICOT SMDAY SFU	SAMPLERS) DEVIATION	MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY SFU
		DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO LOO CAHILL CAHILL	MEAN(ALL SAMPLERS) STANDARD DEVIATION MEAN(D,M,L,G,I) STANJARD DEVIATION	2 (DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO CAHILL CAHILL	EAN(ALL SAMPLERS) STANDARD DEVIATION	ION VS Z DZUBAY DZUBAY DZUBAY LOO LOO CAHILL
-	RESULTS	EPA	Z MEAN () STANE X MEAN () STANE	RAT10 TO	M EPA EPA R EPA C LBL C LBL C LBC G UCD	MEAN(ALL STANDARD	REGRESSION VS D EPA DZUBAY N EPA DZUBAY N EPA DZUBAY C LBL LOO L LBL LOO S LBL LOO S LBL COO G UCD CAHILL I UCD CAHILL

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	SD	3283		S	.06 .20 .27 .10 .21 .21 .28 .28		
	AVG	E 9797		AVG	0.77 0.80 0.88 0.75 1.39 1.53 1.68 0.67	1.00	
	16	5847 0 5183 M 7191 N 5554 R 10348 C 111435 L 11706 S 7759 1	7556 2807	91	0.72 D 0.64 M 0.68 R 0.68 R 1.27 C 1.41 L 1.44 S - 6	1.00	
1977.	15	m - m + 0 ~ m - m +	5123 10909 6813	15	*0.84 *0.93 *0.84 1.32 1.40	1.00	
11-18	<u>+</u>	- 7110 7955 5975 10136 11378 12452 - 9057		<u>+</u>	-0.78 *0.87 0.65 *1.11 1.24 1.36	1.00 0.25	
NANOGRAMS/CUBIC METER; PERIODS 1-16, MAY 11-18	13	6158 7320 7857 6048 12920 13428 13428 13428	3260 8208 3533	13	0.72 *0.86 *0.92 0.71 1.58 1.58	1.00	
91-18	12	5137 5772 6651 4641 10356 10514 2330	2681 6338 2887	51	.0.77 .0.86 .0.99 0.69 1.54 1.57	0.40	
2ER1009	Ξ	2800 2130 6332 12064 12613 3978 4938	4279 6082 4441	:	0.33 0.33 1.88 1.97	1.00	
ETER; 1	10	5309 8066 5556 7732 10373 11135 3408 2498	3112 5397 3518	10	*0.79 *0.79 *0.82 1.14 1.53 1.65 0.50	1.00	.COEFF. 0.981 0.848 0.922 0.928 0.924 0.924 0.924
JB1C ME	σ	1320 1347 1347 1837 2277 2277 3480 4017 1740 1079	1056 1856 946	თ	0.61 0.62 0.62 0.62 1.38 1.61 1.61 1.86 0.50	1.00	COR
RAMS/CL	æ	7453 4828 - - 6225 6046	1074 6136 127	ω	. 1.21 . 0.79 . 1.01	1.00	RMS. DEV. 484.373 1329.3373 1685.445 1685.445 1194.810 1149.926 1153.463 1133.320
NANOGF	7	7292 7877 8372 7319 2242 3322 5478 6221 7230	3303 8388 2822	7	.0.77 .0.83 .0.88 .0.77 1.29 1.41 1.63 0.66	1.00	_
: 15	9	7790 7808 5515 11207 11798 11798 12149 12149 12149 18393	3169 7228 3392	9	0.95 0.95 0.67 1.37 1.44 0.54	00.1	ERROR 0.057 0.195 0.195 0.084 0.176 0.131 0.217
	ស	7628 9767 - 6641 13355 13378 15964 5590 5857	3989 8444 3225	ľ	.0.78 .1.00 68 1.37 1.37 1.63 0.57	1.00	SLOPE 0.820 1.072 1.034 0.743 1.206 1.140 1.211 0.502 0.463
UDY OF LARGE	÷		2813 7364 2910	±	1.50 1.50 1.50 1.50 1.58 1.58	1.00	
ST	М		5939 5939 3800	M	*0.81 *0.82 *0.82 *0.82 *0.65 *0.54	1.00	ERROR 474.498 1476.522 1532.234 667.713 1468.358 1062.408 1813.536 1322.193
1PAR I SC	ď		3057 6698 2791	N	0.71 •1.10 •1.10 • 0.64 • 1.52 • 1.58 0.58	1.00	
INTERCOMPARISON	-	5267 2806 1694 4539 - 10953 1 13332 1 2512	4505 5385 3912	-	*0.90 0.48 *0.77 - 1.87 2.27	1.00	INTERCEPT -372.738 -1847.693 -1005.701 15.335 1355.206 2765.691 3326.841 1065.548
Ξ.	PER100	∢ ₤ ६ ഗ ⊢ ⊢ ≻	IATION	PER 10D	MDS-A TF-M TF-M TF-M DICOT DICOT DICOT SMDAY SFU	ERS)	MDS-A TF-M - TF-P - MDS-S DICOT DICOT SMDAY SFU
	ш	DZUBAY MDS-DZUBAY TF-DZUBAY TF-DZUBAY MDS-LOO DICO CAHILL SMDA CAHILL SFU	STANDARD DEVIATION MEAN(D,M,L,G,I) STANDARD DEVIATION	Z F	DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO COMILL CAHILL	MEAN(ALL SAMPLERS) STANDARD DEVIATION	REGRESSION VS Z D EPA DZUBAY M EPA DZUBAY N EPA DZUBAY R EPA DZUBAY C LBL LOO C LBL LOO S LBL LOO G UCD CAHILL I UCD CAHILL
	LTS	EPA DZ; EPA DZI EPA DZI EPA DZI LBL LOC LBL LOC UCD CAH UCD CAH	TANDA TANDA	RAT10 T0	EPA D EPA D EPA D LBL L LBL L LBL L LBL L UCD C	AN (AL TANDA	RESSIO EPA D EPA D EPA D EPA D LBL L LBL L LBL L LBL C
-	RESULTS	A GOSTONSED A GOSTONE	× Æ	RATI	D E S E O N C O	Σ M	R R R B B B B B B B B B B B B B B B B B

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1977	15	2220 2900 2180 3558 3712 3570 2199 1555 3298	2868 177 2718 1006	51	101-2-4-101-2-4-101-2-4-101-2-4-101-2-4-4-101-2-4-4-101-2-4-4-101-2-4-4-101-2-4-4-101-2-4-4-4-4-4-4-4-4-4-4-4-4-4-4-4-4-4-4-
11-18	<u>*</u>	2250 2400 1560 2766 3282 3523 1330 2082 2084	2327 695 2410 589	ž	0 97 0 103 0 65 0 65 1 1.5 1 1.5 1 00 0 88 0 88 0 88 0 87 0 88 0 88
AA	13	1990 2860 3000 1940 3992 4134 4134 2017 2017 3165 3270	2833 838 2863 893	13	0.70 0.70 0.10 0.10 0.10 0.10 0.10 0.10
1-16	51	1560 2210 2310 1460 3240 1714 1125 2022	2108 656 2077 721	57	
PER 1005	Ξ	- 1950 2030 3976 4164 - 1346 1421 1638 2900	2398 1056 2428 1163	11	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
ETER; F	10	2340 2580 1640 2337 3144 2601 1150 11630 2100 25100	2006 666 1835 897	01	1.29 1.29 1.157 1.57 1.57 1.57 1.57 0.50 0.50 0.50 0.50 0.50 0.50 0.50 0
JBIC M	m	160 590 590 590 784 937 1028 159 159 1654 856	731 355 628 216	σ	63 88 88 88 88 88 88 88 88 88 88 88 88 88
NANOGRAMS/CUBIC METER; PERIODS 1-16, MAY 11-18	00	2350 1746 1776 1776	1798 468 1946 351	α	1 35 0 1 35 0 1 35 0 1 1 31 0 1 0 0 1 0 0 1 0 0 1 0 0 1 0 0 2 0 99 0 2 0 99 0 2 0 99 0 2 0 99 1 3 1 1 0 3 1 1 0 3 1 1 0 4 1 8 8 6 7 3 1 1 0 4 1 8 8 6 7 4 1 8 8 8 8 7 4 1 8 8 8 8 7 4 1 8 8 8 7 4 1 8 8 8 7 4 1 8 8 8 8 7 4 1 8 8 8 7 4 1 8 8 8 8 7 4 1 8 8 8 7 6 1 8 8 7 8 1 8 8 8 7 8 1 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8
NANOGI	7	2570 3560 3660 2470 4129 4595 5398 2151 2708 4592 4592	3536 1074 3307 985	7	22 - 1 01 53 0 - 1 04 54 0 1 07 55 0 0.66 57 0 0.77 57 0 0.77 58 0 0.66 58 0 0.66 59 0 0.66 50 0 1 00 50 0 0 0 0 50 0 0 50 0 0 0 50
 •	9	2980 2980 3480 3480 3480 11848 11848 11831 11809 2463	2705 919 2668 938	9	0.688 0.688 0.677 0.009 0.677 0.009 0.009 0.009 0.009 0.009 0.009 0.009 0.009 0.009 0.009 0.009 0.009 0.009 0.009
	ហ	2970 +520 - 2780 5793 5725 6453 2194 2298 2587 2587 5459	4177 1491 3830 1420	ιΩ	0 71 0 67 1 28 1 58 0 62 1 31 1 29 1 29 1 29 1 29 1 29 1 29 1 29 1 2
۲ 9	+	1790 3250 2900 1670 3924 4115 - - - - - - - - - - - - - - - - - -	2670 901 2710 1011	#	24
N STUD	м	3150 3170 2220 2220 - 4080 1426 2795 1499	3004 1406 2539 1300	m	-1 05 -1 05 -1 06 -1 136 -1 189 -1 18
PAR150	C)	1490 2650 2510 1320 3243 3638 1670 1570 1369	2135 893 2064 835	5	70 1 - 1 - 2 - 4 - 4 - 4 - 4 - 4 - 4 - 4 - 4 - 4
NTERCOMPARISON STUDY OF TOTAL	-	1850 1550 1510 1510 1510 1510 1510	2318 1215 2237 1041	-	0.81 0 0 68 1 0 0 65 1 0 0 65 1 0 0 65 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
z	PER100	MDS-A TF-P MDS-S DICOT DICOT SMDAY TTLF SFU ES .2		PER 10D	-
		DZUBAY DZUBAY DZUBAY DZUBAY OZUBAY OZ	MEANCALL SAMPLERS) STANDARD DEVIATION MEANID.M.L.G.I.K) STANDARD DEVIATION	Z	EPA DZUBAY TF-H EPA DZUBAY TF-H EPA DZUBAY TF-H EPA DZUBAY HOS-S LBL LOO DICOT LBL LOO DICOT UCD CAHILL STD FSJ HUDSON LS FFA HUDSON LS FEA DZUBAY TF-P EPA DZUBAY TF-P UCD CAHILL SMDAY UCD CAHILL SMDAY UCD CAHILL SMDAY UCD CAHILL SMDAY
	ESULTS	EPA EPA EPA EPA LBL LBL UCD UCD UCD UCD FSU	MEAN(ALL STANDARE MEAN(D,M,	AT10 T0	EPA EPA EPA EPA LBL LBL UCD UCD UCD FSU FSU EPA EPA EPA EPA EPA EPA EPA EPA EPA EPA

	SO		158	SD	0.16 0.25 0.05 0.09 0.09 0.09 0.27		
	۵۸¢		305	AVG	0.81 1.84 1.63 0.56 0.60 0.61 0.51 1.31	1.00 0.52	
	16	248 D 328 M 304 N 123 R 137 C 146 L 123 S - G	197 84 222 83	16	1.26 U 1.57 N 0.63 R 0.70 C 0.63 S 0.63 S	1.00	
1977.	15	296 588 508 188 149 163	306 168 350 183	15	0.97 1.92 1.66 0.62 0.49 0.53	1.00	
MAY 11-18	<u>*</u>	331 349 124 149 155 145	211 94 238 88	7.	1.57 1.65 0.59 0.71 0.69	1.00	
	13	307 599 616 170 204 203	354 187 372 168	13	0.87 1.69 1.74 0.48 0.58 0.57	1.00	
1-16,	12	211 435 415 172 188 166 -	263 115 267 118	12	0.80 1.65 1.58 0.65 0.72 0.63	1.00	
ER 1 005	=	279 783 683 178 193 193 212 313	352 224 380 232	1.1	0.79 2.23 1.94 0.51 0.55 0.60 0.89	1.00	
NANOGRAMS/CUBIC METER; PERIODS	10	218 518 419 162 143 146 344 280	264 137 301 1 ¹ 2	10	0.83 1.96 1.59 0.61 0.54 0.55 0.54	1.00 0.52	COEFF. 0.747 0.951 0.888 0.911 0.882 0.815 0.815
BIC ME	თ	126 236 227 98 112 107 84 244	158 65 180 62	σ	0.80 1.50 1.44 0.62 0.71 0.68 0.53	1.00	COR.
AMS/CU	00	215 - 101 177 - 177 + 194	341 137 375 144	ω	0.63 1.18 0.52 	1.00	RMS.DEV. 33.822 60.192 82.577 14.472 14.266 20.760 20.705 89.523
NANOGR	7	262 730 686 207 186 200 180 452	350 219 378 219	7	0.75 2.09 1.96 0.59 0.53 0.51 0.51	1.00	č
: V	ဖ	- 554 461 195 180 197 171 571	324 174 397 193	ω	1.71 1.42 0.60 0.56 0.61 0.53 1.76	1.00	ERROR 0.127 0.214 0.051 0.053 0.053 0.074 0.076 0.389
	ഹ	300 878 892 220 208 202 191 545	444 288 497 263	ហ	0.68 2.01 0.50 0.47 0.45 0.43 1.23	1.00	SLOPE 0.493 2.377 2.102 0.421 0.331 0.374 0.862
STUDY OF SMALL	£	228 570 439 167 185 197 - 497	326 157 363 165	£	0.70 1.75 1.35 0.51 0.51 0.61	00.1	
	m	283 792 641 214 246 196 360 347	385 216 406 221	М	0.74 2.06 1.67 0.56 0.56 0.51	1.00	ERROR 40.290 66.442 90.926 15.936 16.330 22.915 23.483 128.214
1PAR I SC	ru,	211 457 391 143 205 199 406 241	282 118 304 119	u	0.75 1.62 1.39 0.51 0.73 0.71	1.00	
INTERCOMPARISON		228 703 643 162 159 174 325 288	317 211 343 210	-	0.72 2.22 2.03 0.51 0.50 0.53 0.53	1.00	INTERCEPT 91.035 -151.457 -135.349 40.567 73.316 65.877 53.932 136.120 -30.842
-	PER 10D	MDS-A TF-P TF-P MDS-S DICOT DICOT SMDAY SFU	PLERS) //ATION //1	PER100	MDS-A TF-P TF-P MDS-S DICOT DICOT SMDAY	SAMPLERS)) DEVIATION	MDS-A TF-M TF-P MDS-S DICOT DICOT DICOT SMDAY
		DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO CAHILL CAHILL	MEAN(ALL SAMPLERS) STANDARD DEVIATION MEAN(D,M,L,G,I) STANDARD DEVIATION	2 0	DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO CAHILL CAHILL	EAN(ALL SAMPLERS) STANDARD DEVIATION	REGRESSION VS 2 DEPA DZUBAY MEPA DZUBAY NEPA DZUBAY REPA DZUBAY CLBL LOO LLBL LOO SLBL LOO SLBL LOO GUCD CAHILL I UCD CAHILL
	RESULTS	6 S S C C R R R P A A B C C C C C C C C C C C C C C C C C	Z MEAN(STAN X MEAN()	RAT10 T0	OSCRNAO OSCREPA CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	MEAN (ALL STANDARD	REGRESS REPA REPA CLBL LBL LBL CUDD

				>	7 255 255 113 117 117 24		
	SD		993	20	.05 .09 .09 .21 .29 .29 .29		
	AVG		2232	AVG	0.70 0 0.89 0 0.91 0 0.71 0 1.39 0 1.57 0 1.68 0	1.00	
	16	1358 D 1610 M 2009 N 1319 R 2515 C 2921 L 2929 S - 6	2051 660 1909 694	16	0.66 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	1.00	
1977.	15	1924 2396 1990 3369 3563 3507	2563 930 2226 1215	15	0.75 - *0.94 *0.78 1.31 1.39 1.37	1.00	
MAY 11-18	<u>*</u>	1922 2058 1437 2617 3127 3378	2342 716 2301 716	<u>*</u>	*0.82 *0.88 0.61 1.12 1.34 1.44	1.00	
	13	1682 2265 2386 1671 3788 3931 -	2436 983 2390 1063	13	0.68 •0.91 •0.96 0.67 1.58 1.58	1.00	
NANOGRAMS/CUBIC METER; PERIODS 1-16	12	1346 1776 1895 1286 3001 3674	2021 956 1992 1150	12	*0.67 *0.88 *0.94 0.64 1.49 1.49 1.82	1.00	
PER 100	Ξ	1163 828 1854 3783 3971 1043	1993 1326 1871 1404		0.58 0.42 0.42 1.90 1.90 1.99 0.52	1.00	
ETER;	10	- 1821 2058 1476 2194 2998 2458 806	1817 788 1587 1065	10	*1.00 *1.13 0.81 1.21 1.65 1.35 0.44	1.00	COEFF. 0.986 0.913 0.796 0.930 0.923 0.967 0.642
JB1C ₹	σ	331 359 359 398 372 830 944 330	498 250 423 230	60	0.66 0.72 0.80 1.35 1.67 1.89 0.66	1.00	
RAMS/CI	æ	2038 1262 - - 1856	1630 376 1609 349	80	1.25 0.77 -	1.00	RMS.DEV. 111.030 346.803 346.803 190.208 477.125 374.139 672.880 338.740
NANOG	7	2306 2936 2974 2265 3943 4395 5218 1699	3122 1154 2739 1012	7	0.74 •0.91 •0.95 0.73 1.26 1.41 1.67 0.54	1.00	ERROR R 0.045 0.136 0.136 0.072 0.189 0.145 0.154 0.154
. .	9	- 2735 2515 1634 3300 3763 3962 1277	2591 1037 2330 1147	Q	*1.06 *0.97 0.63 1.27 1.45 1.53 0.49	1.00	A
LARGE	ហ	2671 3640 - 2559 5085 5123 6262 1649	3627 1683 3022 1396	J.	0.74 -1.00 - 0.71 1.40 1.41 1.73 0.46	1.00	SLOPE 0.756 1.049 0.681 1.322 1.257 1.695 0.365
UDY OF	ŧ	1563 2677 2459 1503 3739 3918 	2355 1037 2228 1095	t	0.66 *1.14 *1.04 0.64 1.59 1.66 0.77	1.00	
ST	M	2355 2527 2003 2003 3834 5494 1066	2633 1569 2102 1296	M	*0.89 *0.89 *0.96 0.76 0.76 2.09 0.41	1.00	ERROR 107.871 319.013 451.644 167.134 455.011 343.923 641.340 364.035
INTERCOMPARISON	CJ	1278 2197 2119 1175 1175 3038 3439 1164	1942 913 1761 838	6	0.66 *1.13 *1.09 0.61 1.77 0.60 0.58	1.00	
NTERC(-	1644 1344 906 1350 1350 - 3555 4508 4508	2046 1405 1890 1140	-	0.80 0.66 0.44 0.66 1.74 2.20 -	1.00 0.69	INTERCEPT -107.809 -313.112 -97.891 52.768 141.423 652.945 -61.516 460.189
_	PER I OD	MDS-A TF-P TF-P MDS-S DICOT DICOT SMDAY SFU	LERS) TATION 1) TATION	PER I 00	MDS-A TF-P TF-P MDS-S DICOT DICOT SMDAY SFU	SAMPLERS) DEVIATION	MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY SFU
		DZUBAY DZUBAY DZUBAY UZUBAY LOO LOO CAHILL CAHILL	MEAN(ALL SAMPLERS) STANDARD DEVIATION MEAN(D,M,L,G,I) STANDARD DEVIATION	2	DZUBAY DZUBAY DZUBAY LOO LOO LOO CAHILL CAHILL	(1)	ON VS Z DZUBAY DZUBAY DZUBAY LOO LOO LOO CAHILL
	RESULTS	EPA EPA EPA EPA LBL LBL UCD UCD	MEAN (A STAND MEAN (D STAND	RATIO TO	EPA EPA EPA EPA EPA CCD CCD	MEAN (ALL STANDARI	REGRESSION VS D EPA DZUBAN M EPA DZUBAN N EPA DZUBAN R EPA DZUBAN C LBL LOO L LBL LOO S LBL LOO S LBL LOO G UCD CAHILL I UCD CAHILL
	쮼	O E Z K O I O O -	N X	Ŗ	O # Z & O L O O		A O E S & O T N O -

	S		06	SD C	0.22 0.03 0.03 0.03 0.03 0.03 0.03 0.03		
	AVG		246	AVG	0.82 1.03 1.03 1.27 1.55 1.55 0.67 1.25	1.00	
	9	2552 D 231 M 2556 N 2556 N 1933 R 297 C 3339 L 333 S 120 H 1	237 72 239 75	16	**************************************	1.00	
. 778	ភ	379 411 388 449 482 480 - 251 197 471	401 103 391 140	15	• 0.94 • 0.97 • 0.97 • 1.20 •	1.00	
MAY 11-18 1977	7	286 258 258 381 381 464 163 325 325 325 325 325 325 325 325 325 32	284 293 84	ž	- 1.01 - 0.91 0.77 0.77 1.13 1.63 1.63 0.64 0.85	1.00	
	13	265 347 347 347 222 404 431 431 191 281 281 369	307 84 321 94	13	. 1.13 . 1.13 . 1.13 . 1.40 . 1.40	1.00	
91-16	12	255 190 155 330 332 322 170 240 156 218	219 67 237 62	12	0.69 •0.87 •0.71 1.51 1.51 1.47 •0.78 •0.71 •0.71	1.00	
2ER 1009	Ξ	186 90 241 441 153 153 153 350	244 121 254 135	=	. 0.37 . 0.37 . 0.37 . 0.37 . 0.54 . 0.63 . 0.63 . 0.63	1.00	
NANOGRAMS/CUBIC METER; PERIODS 1-16,	0	- 197 268 268 220 309 309 322 95 171 189 156	208 71 202 76	0	. 0.95 . 0.96 . 1.96 . 1.95 . 0.91 . 0.91 . 0.91	1.00	COR. COEFF. 0.961 0.897 0.727 0.913 0.904 0.865 0.904 0.867 0.087
æic æ	6	24 23 23 24 24 24 24 25 26 26 26 26 26 26 26 26 26 26 26 26 26	88 4 88	o	*0.23 *0.28 *0.83 *1.08 *1.08 *1.08 *1.53 *1.53 *1.53	1.00	COR
RAMS/CI	00	267 166 166 160 178 139 217	<u>8</u> 8 8 8	80	*0.92 *0.92 0.71 0.71 1.20	1.00	RMS. DEV. 26 830 45.387 67.254 27.179 46.297 37.851 30.276 21.172 50.148 46.183 36.966
NANOG	7	198 289 284 299 352 397 135 145 145 303	263 268 84 84	7	20.00 0.00 0.00 0.00 0.00 0.00 0.00 0.0	1.00	ERROR RI 0.111 0.236 0.267 0.106 0.191 0.153 0.236 0.082 0.082 0.253
	ဖ	- 273 297 171 308 333 346 121 148 1182 175	239 81 236 84	9	- 1.20 - 2.20 - 2.20 - 2.20 - 2.20 - 2.30 - 2.30 - 2.30 - 3.30 - 3.00 -	1.00	W
INTERCOMPARISON STUDY OF TOTAL TI	'n	273 442 213 393 379 456 123 213 284 350	295 119 282 135	ις.	- 1.50 - 1.50 - 1.50 1.54 1.54 0.45 0.41	1.00	SLOPE 1.097 1.0655 1.020 0.887 1.151 1.151 1.152 0.285 0.034 1.107
of	ŧ	222 338 280 192 356 386 188 189 121 121	253 88 265 103	*	0.88 1.33 1.11 0.76 1.40 1.52 1.52 0.74 0.78 0.78	1.00 0.35	
N STU	M	300 242 242 254 254 254 381 120 120 141 148	270 151 237 154	M	11.11 10.90 1.14.1 1.14.1 1.186 1.186 1.186 1.19	1.00	ERROR 29.270 57.785 67.119 67.119 39.476 61.196 40.440 20.957 66.099 47.130
PAR15	N	294 294 294 294 186 186 150 150 135 135 135	246 101 234 101	6	0.87 1.20 0.76 0.76 1.65 1.65 0.61	1.00	EPT 3900 3900 172 179 172 179 172 178 193 183 183 183 183 183 183 183 183 183 18
MTERCO	-	192 162 95 172 172 382 149 153	203 97 207 77	-	0.95 0.90 0.47 0.085 0.95 1.57 1.88 1.88	1.00	INTERCEPT -58 800 -137 890 -8.179 -15 172 31.590 63.959 78.020 64.015 165.833 -43.787
=	PERIOD	MDS-A TF-H TF-H MDS-S DICOT DICOT SMDAY TTLF SFU LS .2	MEANCALL SAMPLERS) STANDARD DEVIATION MEANCD.M.L.G.I.K) STANDARD DEVIATION	PERIOD	MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY TTLF SFU LS .2	EAN(ALL SAMPLERS) STANDARD DEVIATION	HDS-A TF-H TF-P HDS-S DICOT DICOT DICOT SMOAY TTLF SFU LS .2
		DZUBAY DZUBAY DZUBAY DZUBAY COO CONTICL CAHILL CAHILL CAHILL CAHILL CAHILL CAHILL HUDSON HUDSON	MEANIALL SAMPLERS) STANDARD DEVIATION MEANID,M.L.G.I.K) STANDARD DEVIATION	2	DZUBAY DZUBAY DZUBAY DZUBAY COO COO CONTICL CAHILL CAHILL CAHILL CAHILL HUDSON HUDSON	MEAN(ALL SAMPLERS) STANDARD DEVIATIO	ION VS Z DZUBAY DZUBAY DZUBAY LOO LOO CAHILL CAHILL CAHILL HUDSON HUDSON
_	RESUL TS	EPA EPA EPA EPA EPA EPA EPA EPA EPA EPA	Z MEAN(A STAND X MEAN(D STAND	RAT10 10	EPA EPA EPA EPA EPA EPA EPA EPA EPA EPA	MEANCA	REGRESSION VS D EPA DZUBAN N EPA DZUBAN N EPA DZUBAN N EPA DZUBAN N EPA DZUBAN C LBL LOO C LBL LOO S LBL LOO S LBL LOO I LOC CAHILL I UCD CAHILL UCD CAHILL J FSU HUDSON K FSU HUDSON
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EPA DYUBAY TF-P 1.45 0. 0.40 0. 0.05 0. 0.05 0. 0.05 </td <td>EPA EPA</td> <td>_</td> <td>1.25</td> <td></td> <td></td> <td>. 55</td> <td></td> <td>, 9.</td> <td>11</td> <td>SS .</td> <td></td> <td>1.00</td> <td>L 7</td> <td>0.74</td> <td>. 70</td> <td></td> <td></td> <td></td> <td>0 ~</td> <td>.55 .59</td> <td>00</td>	EPA EPA	_	1.25			. 55		, 9.	11	SS .		1.00	L 7	0.74	. 70				0 ~	.55 .59	00
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DICOT 0.73 *1.14 *0.93 *0.87 0.75 0.79 0.70 - *1.25 0.50 0.56 0.72 0.81 *1.08 0.52 0.69 1.08 0.52 0.50 0.56 0.72 0.81 *1.09 0.52 0.69 1.09 0.70 0.50 0.70 0.50 0.70 0.50 0.70 0.50 0.70 0.50 0.70 0.50 0.70 0.50 0.70 0.50 0.70 0.50 0.70 0.50 0.70 0.50 0.70 0.50 0.70 0.50 0.70 0.50 0.70 0.50 0.70 0.50 0.70 0.7	ЕВ	DICOT	0.70			.80		74.	0.56			0.69	0.52	0.76	. 65				0	.31	
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MDS-A 0.618 24.043 0.942 0.523 23.752 0. TF-M -5.169 18.069 1.642 0.405 18.538 0. TF-P 3.963 24.666 0.504 0.548 25.403 0. MDS-S 7.268 8.958 0.251 0.199 9.286 0. DICOT 18.253 5.398 0.244 0.122 5.387 0. DICOT 11.608 7.694 0.496 0.172 7.894 0. DICOT 10.458 9.300 0.477 0.222 8.633 0. SMDAY -54.261 54.394 2.550 1.247 53.002 0. SFU 35.849 63.916 0.947 1.377 43.086 0.	STANDARD	DEVIATION	0.45	0.54		99		.45	.13	0.91	1.01	0.80	<u> </u>	0.99	•	0.21	•	0 20			
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EPA DZUBAY TF-M -5.169 18.069 1.642 0.405 18.538 0. EPA DZUBAY TF-P 3.963 24.666 0.504 0.548 25.403 0. EPA DZUBAY MDS-S 7.268 8.958 0.651 0.199 9.266 0. LBL LOO DICOT 18.253 5.398 0.244 0.122 5.387 0. LBL LOO DICOT 11.608 7.694 0.496 0.172 7.894 0. UCD DICOT 10.458 9.300 0.477 0.222 8.633 0. UCD CAHILL SMDAY -54.261 54.394 2.550 1.247 53.002 0 UCD CAHILL SFU 35.849 63.916 0.947 1.377 43.086 0	EPA				24.043		546.	0.5		23.752		•									
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DZUBAY MDS-S 7.268 8.958 0.551 0.199 9.226 0. LOO D1C0T 18.253 5.398 0.244 0.122 5.387 0. LOO D1C0T 11.608 7.694 0.496 0.172 7.894 0. LOO D1C0T 10.458 9.300 0.477 0.222 8.633 0. CAHILL SMDAY -54.261 54.394 2.550 1.247 53.002 0 CAHILL SFU 35.849 63.916 0.947 1.377 43.086 0					54.666		.504	0.5		25.403		•									
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LOO DICOT 10.458 9.300 0.477 0.222 8.633 0. CAHILL SMDAY -54.261 54.394 2.550 1.247 53.002 0 CAHILL SFU 35.849 53.916 0.947 1.377 43.086 0.		D1C0T			7.694	0	.496	0.1		7.894		•									
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			35.		63.916		.947			43.086		•									

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	AVG	2 -	AVG	0.90 1.05 0.83 0.83 1.35 1.51 1.64 0.50	0 B - C
	16	170 D 159 M 157 R 157 R 277 C 310 S 10 S 10 S 10 S 10 S 10 S 10 S 10 S	16	0.82 O 0.76 M 0.75 M 0.	0 0 1
1977.	15	328 3339 334 421 450 447 447 173 343 343 126	15		0.37
1-18	<u> </u>	264 210 183 284 340 363 363 141 141 141 160	<u>+</u>		6 E
₩A	13	200 261 294 198 371 330 138 138 265 94 247	13	0.76 *0.99 *1.11 0.75 1.40 1.47	S &
1-16,	12	214 214 192 123 296 290 290 290 190 81	51		0 M 0 + 0
ER 1005	Ξ	95 89 215 372 405 61 115 115 174 174	Ξ		0.71
NANOGRAMS/CUBIC METER; PERIODS 1-16, MAY 11-18	10	145 259 155 195 195 195 195 198 198 198 199	0.1		.COEFF. 0.47 0.970 0.672 0.878 0.893 0.893 0.862
JB1C 1€	თ	254 73 73 73 73 73 74 74 74 74 74 74 74 74 74 74 74 74 74	თ		CO ROO
RAMS/CL	00	235 126 126 57 120 57 74 74	œ		RMS.DEV. 20.132 45.637 66.626 28.348 47.845 37.028 37.028 37.028 37.028
NANOGE	7	193 224 224 184 274 370 102 143 85 85 85	7		CERROR RI 0.092 0.252 0.287 0.119 0.239 0.138
:	9	203 257 150 281 304 320 92 130 217 86	ø	1 + 00 00 00 00 00 00	A 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
ARGE	ស	217 350 182 364 350 431 100 87 260 131 128	ស		0.50 0.50 SLOPE 1.034 1.454 0.939 0.817 1.196 1.196 1.178 1.218
UDY OF LARGE	ŧ	262 283 156 321 321 33 30 107 107	ŧ	*0.91 1.21 1.30 0.72 1.48 1.61 -	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
ST	M	224 220 209 333 458 95 55 137 175	M	. 0.997 . 0.997 . 0.95 . 1.46 . 2.02 . 0.41	ERROR 20.895 53.451 61.959 26.108 49.865 36.882 35.882 53.845 53.845
MPAR1S	N	237 2955 172 172 333 360 90 95 104 104	N		68 0.48 ERCEPT 47.643 19.409 -0.335 32.793 68.482 84.743 44.198
INTERCOMPARISON	-	142 90 37 143 290 355 113 113 114 114	-		1.00 1.00 1.00 0.68 0.10 1.00 1.00 1.00 1.00 1.00 1.00 1.0
ī	PER 100	MDS-A TF-P TF-P MDS-S DICOT DICOT SMDAY SFU SFU (1ATION	PER100	MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY SFU	MDS-A TF-P MDS-S DICOT DICOT SMDAY
	ý	EPA DZUBAY MDS-A EPA DZUBAY TF-M EPA DZUBAY TF-P EPA DZUBAY MDS-S LBL LOO DICOT LBL LOO DICOT LBL LOO DICOT UCD CAHILL SMDAY UCD CAHILL SMDAY UCD CAHILL SFU MEAN(ALL SAMPLERS) STANDARD DEVIATION STANDARD DEVIATION	10 2	DZUBAY DZUBAY DZUBAY LOO LOO LOO CAHILL CAHILL	REGRESSION VS Z D EPA DZUBAY MDS-A M EPA DZUBAY TF-M N EPA DZUBAY TF-M N EPA DZUBAY TF-P R EPA DZUBAY
_	RESUL TS	EPA R EPA C C LBL C LBL C LBL C C C C C C C C C C C C C C C C C C C	RATIO TO		STAN STAN STAN SEPA C LBL C LBL

_		=	INTERCOMPARISON STUDY OF TOTAL FE	1PAR I SC	N STUE	7 OF 1	OTAL F	••	NANOGR	NANOGRAMS/CUBIC METER; PERIODS 1-16, MAY 11-18 1977	BIC ME	TER: PI	:R100S	1-16,	MAY	1-18	. 776				
RESULTS	v	PER 10D	-	N	٣	#	ល	g	7	₩.	6	10	Ξ	51	13	<u>*</u>	15	9	AVG	SD	
EPA EPA C C LOR C C LOR C C LOR C C LOR C C C C C C C C C C C C C C C C C C C	EPA DZUBAY NOS- EPA DZUBAY TF- EPA DZUBAY TF- EPA DZUBAY NDS- LBL LOO DICO LBL LOO DICO LBL LOO DICO LBL LOO DICO LBL LOO DICO CAHILL SMOA UCD CAHILL SMOA UCD CAHILL STOA UCD	MDS-A TF-P MDS-S DICOT DICOT SMDAY S	1380 1150 1200 1200 2350 2908 1004 1004 1561	2060 2030 2030 1110 2456 1091 1159 1159 1024	2090 2170 1610 2469 3356 1111 1111 1111 1111 1111 1111 1111	1410 2190 1980 1210 2400 2533 - 1519 1515 1613 2244	1640 2630 2532 2532 2536 3053 1375 1375 1275 2699 2823	2290 2160 1410 2335 2517 2604 11225 1112 1112 1112 1112 1112 1112 11	1520 2050 2170 - 1500 2155 2155 2792 1097 1360 1205 2501 2513	-2010 1290 1590 1316 1316 1392 1379 1557	700 620 570 770 1024 1024 490 1937 1237	1690 2090 1300 1635 2254 901 1189 735 1466 1236	1310 1050 1510 2480 2617 1083 1003 1073 2483	1270 1910 1910 1910 1980 2206 2206 2206 1467 1469 1715	1530 2170 2340 1420 2685 2880 - - 1881 1484 2401 2814	- 1850 2040 1400 2338 2500 2500 1402 1539 1799 1799	2020 2550 1980 2637 2755 2755 2855 1758 1026 3059 3141	1390 0 1460 M 1790 N 1250 R 1913 C 2172 L 2178 S - 6 1271 H 1271 H 1781 1 1744 K	7471	29	
STANDA X MEAN(D. STANDA RATIO TO	STANDARD DEVIATION MEAN(D,M.L.G,I.K) STANDARD DEVIATION TO 70 Z	IATION I,K) IATION PERIOD	696 1557 568	572 1519 556 2	775 1655 740 3	509 1819 589 4	653 2047 692 5	536 1817 628 5	578 1802 615	248 1499 93		506 1345 585 10	673 1713 117		546 2160 650	369 1927 331		343 1617 349 16	AVG	SD CV	
EPA EPA EPA EPA EPA EPA EPA EPA EPA EPA	DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO CAHILL CAHILL CAHILL CAHILL CAHILL CAHILL CAHILL	MBS-A TF-M TF-P MBS-S D1C01 D1C01 D1C01 SMDAY SFU LS 2 LS 4	0.83 0.94 0.77 0.77 1.51 1.86 0.64	0.78 1.29 1.27 0.70 0.70 1.37 1.54 0.05	1.08 1.12 0.83 1.74 1.74 0.58	0.79 1.11 1.15 1.35 1.42 1.42 - 0.85 0.95 0.95 1.26	0.76 0.70 - 1.17 1.17 1.41 0.53 0.81 1.25	1 2 3 4 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	0.78 1.16 1.17 1.11 1.25 1.44 0.57 0.62 1.30	1.34 1.86 1.08 1.03 1.09 1.04	0.68 0.96 0.85 0.09 1.06 1.41 1.41 0.68 0.69	1.12 1.38 1.38 1.43 1.43 1.43 1.49 0.79 0.79	0.78 0.63 0.90 11.49 11.57 0.65 0.66 11.25	0.80 1.06 • 0.68 0.68 1.38 1.38 1.38 0.59 • 0.92 • 0.92 • 0.92 • 0.92	0.71 1.09 0.66 0.66 1.25 1.30 - - 0.69 0.69	- 0.98 - 1.06 - 1.24 - 1.33 - 0.74 - 0.95 - 0.95	0.85 - 1.07 0.83 0.83 1.11 1.20 1.20 - 1.20 1.32 •	0.84 D 0.88 M 0.75 R 0.75 R 1.15 R 1.15 C 1.	79 0 79 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0.06 8 0.15 14 0.07 10 0.07 10 0.14 12 0.15 21 0.15 21 0.09 12 0.03 20 0.23 21	
MEANN STAN STAN BEPAN C LBR C LBR C LBR C LBR C LBR C UCD C	##EANIALL SAMPLERS] STANDARD DEVIATION SPECSION VS 2 EPA DZUBAY HTF-M EPA DZUBAY TF-M	MDS-A TF-P MDS-S DICOT DICOT DICOT SMDAY TTLF SFU SFU ELS F	INTERCEPT - 34.674 - 230.956 - 73.757 956 - 107.011 107.011 162.945 945 - 108.297 - 108.297 - 108.297 - 173.240	9 9	ERROR 138-113 348-113 348-113 348-115 168-876 317-160 4415-166 168-876 317-160 4415-166 199-166 275-969	. 29	1 00 0.30 SLOPE 0.811 1.200 1.145 1.145 0.508 0.508 0.425 1.454	ERROR 0.29 0.37 0.199 0.174 0.174 0.174 0.174 0.174 0.174 0.174 0.174 0.174 0.174 0.174 0.174 0.175 0.		1.00 1.00 1.00 0.33 0.33 0.33 0.33 0.33	0.33 CON CON CON CON CON CON CON CON CON CON	·	0.40	0.27	0 0 	0.20	0.28	0.21	0.30		

	_	_	CV	0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.0
	SD	158	SD	0.13 0.13 0.06 0.06 0.06 0.06 0.06 0.06
	AVG	356	AVG	0.89 1.78 1.58 0.70 0.65 0.65 1.08 0.92 0.92
	9	350 D 474 M 415 N 188 R 171 C 177 L 165 S 211 1 269 125 333 136	16	1.30 D 1.76 M 1.54 N 1.56 M 1.54 N 1.56 M 1.
1977.	15	356 787 704 258 263 207 211 211 390 390 229 229 431	15	0.91 0.91 0.66 0.67 0.57 0.53 0.53 0.53 0.53
MAY 11-18	<u>+</u>	217 191 194 198 198 285 285 128 310	<u>±</u>	- 1.69 1.61 1.61 0.67 0.68 0.70 0.70 0.70 0.70 0.70 0.70 0.70 0.7
	13	361 625 674 219 242 237 368 389 188 398 163	13	0.93 1.73 1.73 1.73 1.73 0.56 0.56 0.67 0.48
1-16,	12	282 431 232 223 223 191 - - 291 302 106	12	0.93 1.43 1.43 1.43 0.63 0.96 0.35
NANOGRAMS/CUBIC METER; PERIODS 1-16.	=	310 740 621 230 226 225 238 386 355 370 188	Ξ	9.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00
TER; F	10	238 486 416 203 148 154 161 161 231 233 122 263 122 122	10	0.90 1.85 1.58 0.77 0.56 0.59 1.00 1.00 0.46 0.93 0.93 0.917 0.93 0.93 0.93 0.93 0.93 0.93
JBIC ME	თ	175 372 321 154 153 153 197 216 216 211 81	o	0.83 0.74 0.74 0.74 0.74 0.74 0.74 0.74 0.74
AMS/CL	æ	354 314 314 631 487 465 131 491	00	0.76 0.68 0.68 0.68 1.36 • 1.05 •1 1.00 1 0.28 0 37.154 56.204 84.549 22.909 17.112 23.689
NANOGE	7	289 722 698 230 210 213 217 264 360 356 206 206	7	25 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5
٠٠ ليا لا	ω	652 532 279 215 232 217 489 303 365 169 189	ω	- 0.8 1.46 1.5 0.54 0.6 0.54 0.6 0.64 0.6 0.68 0.6 0.68 0.6 0.46 0.6 0.46 0.7 0.70 0.75 0.0084 0.0084 0.0084
SMALL F	Ŋ	315 740 733 264 235 239 250 413 423 423 423 426	Ŋ	0.79 1.83 0.66 0.59 0.60 0.60 1.00 0.51 2.07 1.08 0.51 0.640 0.640 0.640 0.683
UDY OF S	±	306 606 521 253 238 241 477 313 369 144	±	
S	М	454 866 712 385 382 362 431 437 504 184 189	M	0.90 1.72 1.41 0.76 0.76 0.86 0.87 0.87 0.87 0.36 0.36 1.00
INTERCOMPARISON	വ	294 511 441 235 217 223 369 233 315 113 120	വ	93 66 66 69 71 71 71 74 36
TERCON	-	366 810 751 304 293 308 373 417 417 456 200		0.84 0.1.86 1.1.72 1.1.72 1.0.0.59 0.0.69 0.0.86 1.0.0 1.00 1.00 1.0.46 0.1.3331 20.263 20.26
-	PER I OD	BAY MDS-A BAY TF-P BAY TF-P BAY MDS-S DICOT DICOT ILL SMDAY ILL SFU SAMPLERS) DEVIATION L.G.1)	PER 10D	
	_		7	EPA DZUBAY MDS-A EPA DZUBAY TF-M EPA DZUBAY TF-P EPA DZUBAY TF-P EPA DZUBAY MDS-S LBL LOO DICOT LBL LOO DICOT UCD CAHILL SMDAY UCD CAHILL SFU RESSION VS Z EPA DZUBAY MDS-A EPA DZUBAY TF-M EPA DZUBAY MDS-A EPA DZUBAY UCD CAHILL SMDAY UCD CAHILL SMDAY UCD CAHILL SFU
	RESULTS	EPA DZI EPA DZI EPA DZI EPA DZI LBL LOG LBL LOG UCD CAN UCD CAN UCD CAN MEAN(ALL STANDARG	RAT10 TO	EPA DZUBAY EPA DZUBAY EPA DZUBAY EPA DZUBAY LBL LOO LBL LOO UCD CAHILL UCD CAHILL UCD CAHILL STANDARD DE EPA DZUBAY EPA D
-	RE	DEXKONQ- V X	R.	OESKOINO - ACESKOINO -

	SD		601	SO	0.06 0.21 3 0.29 3 0.11 1 0.22 1 0.18 1 0.28 1 0.14 6		
	AVG		1331	AVG	0.77 0.87 0.95 0.79 1.36 1.51 1.67 0.59	1.00	
	16	1044 D 985 M 1376 N 1059 R 1742 C 1995 L 2013 S	1416 438 1284 477	16	0.74 0.70 M 0.70 M 0.93 N 1.23 C 1.41 L 1.42 S 0.78 S 0.78 S 0.78 S	1.00	
1977.	15	1661 1849 1719 2414 2548 2644 -	1927 693 1620 949	7	0.86 0.89 1.25 1.37 1.37	1.00	
MAY 11-18	<u>+</u>	- 1374 1576 1182 1810 2144 23302 -	1669 433 1601 472	<u>*</u>	0.82 0.95 0.71 1.29 1.38	1.00	
	13	1170 1549 1663 1201 2443 2563 -	1672 604 1600 671	13	0.70 0.93 0.72 0.72 1.46 1.53	1.00	
1-16,	12	984 1237 1478 849 1983 2020	1315 539 1223 583	12	0.75 0.94 1.12 0.65 1.51 1.54	1.00	
PER 10DS		574 432 1281 2254 2392 - 697	1193 817 1095 867	Ξ	0.48 0.36 1.07 1.89 2.01 - 0.58 0.58	1.00	
ETER; F	10	- 1196 1669 1095 1487 2009 2093 570	1328 599 1070 700	10	0.90 1.26 0.82 1.51 1.51 1.58 0.43	1.00	COR. COEFF. 0.968 0.831 0.873 0.871 0.798 0.798 0.543
JB1C ME	თ	314 319 299 413 517 738 869 328	464 220 396 192	თ	0.68 0.69 0.64 0.89 1.33 1.59 1.87	1.00	COR
NANOGRAMS/CUBIC METER;	60	-1474 974 974 -	1068 272 912 9	ω	1.38 0.91 0.86 0.85	1.00 0.26	RMS.DEV. 259.880 344.794 152.454 292.824 216.263 359.384
NANOGE	7	1235 1334 1469 - 1269 1945 2213 2575 833	1524 600 1292 562	7	0.08 0.09 0.09 0.09 1.78 0.09 0.05 0.05	1.00	ERROR RP 0.076 0.230 0.276 0.118 0.240 0.173 0.300 0.154
FE .	Q	1640 1623 1134 2120 2285 2387 736	1592 649 1368 736	ဖ	1.03 0.71 1.33 1.44 1.50 0.46	1.00	W 0 0 0 0 0 0 0 0
LARGE F	ß	1323 1891 - 1256 2297 2297 2803 956	1710 715 1464 618	ស	0.77 1.11 0.74 1.34 1.34 1.64 0.56	1.00	SLOPE 0.838 1.192 1.192 1.142 1.142 1.192 0.394 0.114
STUDY OF 1	±	1105 1588 1464 960 2162 2292 2292 1042	1414 574 1346 616	£	0.78 1.12 0.68 1.53 1.62 0.74	1.00	
	M	1228 1454 1225 1225 2087 2994 680	1454 852 1127 709	M	0.84 0.84 0.84 1.44 2.06 0.47	1.00	ERROR 110.273 324, 095 388, 208 168, 438 354, 726 250, 927 439, 063 208, 362 244, 331
4PAR1S(N	948 1549 1589 877 - 1964 2233 722	1334 579 1195 540	CJ	0.71 1.16 1.19 0.66 0.66 1.47 1.67 0.54	1.00	
INTERCOMPAR! SON	-	1012 653 395 891 - 2060 2600	1174 829 1084 676	-	0.86 0.34 0.76 1.75 2.21	1.00	1NTERCEPT -89.030 -416.830 -230.279 100.328 300.208 540.858 629.590 233.377
Ξ	PER I OD	MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY SFU	VLERS) //AT10N //1	PERIOD	MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY SFU	LERS)	MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY SFU
		DZUBAY DZUBAY DZUBAY UZUBAY UZUBAY LOO LOO CAHILL CAHILL	MEAN(ALL SAMPLERS) STANDARD DEVIATION MEAN(D,M,L,G,I) STANDARD DEVIATION	Z 0.	DZUBAY DZUBAY DZUBAY LOO LOO CAHILL CAHILL	MEAN(ALL SAMPLERS) STANDARD DEVIATION	REGRESSION VS Z D EPA DZUBAY M EPA DZUBAY N EPA DZUBAY C LBL LOO L LBL LOO L LBL LOO S LBL LOO S LBL LOO G UCD CAHILL I UCD CAHILL
_	RESULTS	T EPA C LBL C LBL C LBL C CBL C CBL	Z MEAN(STAN X MEAN(RATIO TO	EPAA EPAA C C C C C C C C C C C C C C C C C C	MEAN (STAN	REGRESS REPA N EPA C LBL L LBL S LBL O UCD

CV 88 31 14 116 116 128 23

		-	INTERCOMPARISON STUDY OF TOTAL CU	1PAR I SC	ON STUE	70 ≻	TOTAL	 ?:	NANOGE	NANOGRAMS/CUBIC METER; PERIODS 1-16, MAY 11-18	SIC ME	ER; PE	R100S	1-16,	H¥		1977.				
SULTS		PER100	-	ď	M	±	ū	ဖ	7	8	o	01	Ξ	15	13	<u>*</u>	15	91	AVG	SD	
	DZUBAY	MDS-A	39	172	1	381	52	1	59	1	- 38	•	1	18	= 1	' '	29	125 0			
₩ 6 6 7	DZUBAY		3 2	¥ ;	8 6	444	29	ት 5	<u>بر</u> م	י ע	ล =	% <u>~</u>	ي د	- 123 - 25 - 25 - 25 - 25 - 25 - 25 - 25 - 25	, g	275 275	, 68				
	DZUGAT		, d	2 2	g g	386	T.	53	36	8 8	. 82	33	36	151	26	115	ą				
	00	DICOT	} '	;	'	469	ţ	102	Į,	1	Į Į	99	9	223	76	305	9				
	8		20	115	30	19	52	£	17	1	0	<u>*</u>	18	155	ģ	265	30				
	007		φ	150	ē.	4	57	83	26	1	33	52	ı	1	ŧ	311	62				
	CAHILL		1	82	<u>-</u>	359	<u>+</u>	19	=	32	17	55	58	•	ı	t	1				
	CAHILL	TTLF	=	57	Ξ	275	16	56	=	92	13	16	œ	109	31	180	10	T			
CO	CAHILL		1	6	t	345	26	6	25	1	ı	1	ı į	120	1	12	١ ,				
FSU	NOSON	ر د د	•	1	1	340	9	<u>-</u>	=	33	17	30	5	167	† †	583	9	7 : G :			
FSU	HUDSON		1	1	1	519	¥	₹	23	38	ති	m	ις.	B6 (63	5	90	co ×			
MEANCH	MEAN (M) THOUT 1)	1	28	611	ů,	396	36	₩.	30	e t	30	31	ς,	162	90	243	9	æ	88	0,	
STAND	STANDARD DEVIATION	1AT 10N	15	35	15	69	8	53	<u></u>	5	25	18	17	36	23	65	22	33			
MEANCO	MEAN (D. M.L.G.K)	ŵ	30	124	ب 1	ţ Ç	37	3.	29	37	35	23	52	167	69	257	÷	79			
STAND	STANDARD DEVIATION	1A110N	0.7	36	00	62	20	Ξ	6	a	36	7	D	31	23	39	18	31			
AT10 TO	2	PER 10D	-	N	m	£	2	9	7	Ф	o	10	Ξ	15	13	<u> </u>	ī.	16	AVG	S	<u>ک</u>
	DZUBAY	MDS-A	. 39	1 45	i	96 0		1	- 0	1				<u>+</u>	#6	1	1.30	1 48 D	1 62	0.66	o
	DZUBAY				83	1.12	171	÷0	1 13			0.85			•0.95	98 0	1	Σ	1.01		ľ.
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3	CAHILL	111.	0 33			0.69		0 00	9.5	9				9 6))	r -	9 0		- 4
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GRESSI	Z SV NO		INTERCEPT	Ы	ERROR		SLOPE	3	_	RMS.DEV	COR	COEFF.									
EPA	EPA DZUBAY	MDS-A	9	931	9 362		6.8 0	0	+90 O	21.739		979									
EPA	DZUBAY	¥ L	æ (880	7.383		1.047	0 0	0.053	20 544		286. 0									
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	1 00 GA	5001	949	0 0	10.11		150		770	16.522		5 6									
	3 6	D100	1.61	192	3 147		1.102		123	980 6		997									
	007	DICOT	15.330	330	4.547		1 219	0	0.050	10.467		365									
	CAHILL	SMDAY	-11.5	929	3.684		956.0	0.0	751	9.495		. 997									
	CAHILL	TTLF	9-	72.3	1.665		0 730	0.0	313	4.982		966									
	CAHILL	SFU	0.		0		ė.	ö		0.											
	HUDSON	LS 2	101-	413	8 409		978	0	0.059	22.638	<u>.</u>	186									
FSU	HUDSON	12	-50 (176	1.0		1 332	0	32	12.154		987									

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AVG	- 0 0 L L C M Z Z D	80	AVG	M 0.79 M 0.77 N 0.77 R 0.95 C 1 50 L 0.74 S 1.51 G 0.58	0.190.0
16	86 1 51 1 72 1 101 52 1 113 51 51 113 51 51 51 51 51 51 51 51 51 51 51 51 51	75 25 63 20	16	1.14 0.68 0.70 0.70 1.34 1.34 1.50	0.34
15	29 33 33 47 47 50	38 11 28 5	15	0.76 0.87 1.36 6.87 1.23 0.60	1.00
: <u>±</u>	- 200 206 192 287 253 289 -	238 44 227 37	<u>+</u>	0.84 0.87 0.81 1.21 1.22 1.22	0.100.19
13	53 31 43 62 38 79	49 17 43 9	13	1.08 0.76 0.63 0.88 1.27 1.27	1.00
12	154 115 122 138 200 145 183	151 31 138 20	5	*1.02 0.76 0.81 0.91 1.32 *0.95 1.21	1.00 0.21
=	24 19 20 70 44 11	23 15 18 5	Ξ	*1.04 0.82 0.22 0.87 1.99 0.48 1.90	1.00 0.64
0.1	29 17 12 23 23 9 39 16	25 16 18 8	10	1.16 0.68 0.48 0.92 2.20 0.36 1.56	1.00 0.62 COEFF. 0.994 0.995 0.996 0.997 0.998
6	42 9 11 18 18 35 7 28 17	2. 13 19 16	6	2.01 0.43 0.53 0.86 1.68 0.34 1.34	1.00 0.51 . COR.
80	68 42 52 52 - 7	17 17 18 18 29	80	1.44	I.00 I 0.37 C RMS.DEV. 10.412 14.203 9.155 8.267 11.337 8.413 6.786
7	28 20 24 24 12 41 41 35	22 12 16 10	7	1.27 *0.91 0.55 1.09 1.55 0.55 1.86 1.86	1.00 0.55 ROR 030 037 024 021 022 022
- 6	268 268 388 82 18 63	339 25 21 6	9	0.72 0.67 0.63 0.98 2.11 0.45 0.44	0.63 0.63 0.0 0.0 0.0 0.0
. C	23 24 18 29 30 30 18 11 11	25 9 20 5	Ŋ	*0.93 *0.97 0.73 1.18 1.22 0.73 1.67	1.00 0.35 SLOPE 0.935 0.998 0.896 0.906 1.151 1.093
	357 339 339 358 445 400 - 359	379 36 378 23	Ŧ	*1.04 0.90 0.95 1.17 *1.06 *0.95	1.00 0.10 7.77 1.11 1.11 1.00
m	21 12 14 14 20 20 24 32 7	91 8 91 8	M	1.13 0.65 0.75 0.75 *1.08 1.29 1.72 0.38	1.00 0.45 0.45 3.507 4.755 2.969 2.681 7.044 7.044 7.044 7.044 7.044 7.550
ત્ય	129 106 94 103 107 135 78	107 20 105 21	ď	*0.99 0.88 *0.96 *1.00 1.26 0.73	36 0.18 ERCEPT 9.382 -9.850 -5.088 1.385 11.79 11.79 12.240 12.751
_	+ + + + + + + + + + + + + + + + + + +	19 7 15	-	1.26 0.74 1.37 0.84 1.26 0.74 1.37	1.00 1.00 0.36 0.11 INTERCEPT 9.382 -9.850 -5.088 1.385 13.702 -14.179 12.240
PER 10D	MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY SFU	1) IATION IATION	PER 100	MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY SFU	1) MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY SFU
_	DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO CAHILL	MEANCWITHOUT I) STANDARD DEVIATION MEANCO,M,L,G) STANDARD DEVIATION	3 2	DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO CAHILL CAHILL	MEAN(MITHOUT I) STANDARD DEVIATION GRESSION VS Z EPA DZUBAY MDS-A EPA DZUBAY TF-M EPA DZUBAY TF-M EPA DZUBAY TF-P EPA DZUBAY DF-D EPA DZUBAY MDS-S LBL LOO DICOT LBL LOO DICOT UCD CAHILL SMDAY UCD CAHILL SFU
.15		ANCHI TANDA INCD.			ANDA ANDA ANDA ANDA ANDA BO BO C C C C C C C C C C C C C C C C C
RESULTS	S C C C C C C C C C C C C C C C C C C C	Z MEA ST X MEA	RAT10 TO	EPA EPA EPA EPA EPA EPA EPA EPA EPA EPA	MEAN(WITHOU) STANDARD DE REGRESSION VS D EPA DZUBAN N EPA DZUBAN N EPA DZUBAN C LBL LOO L LBL LOO L LBL LOO G UCD CAHILL I UCD CAHILL I UCD CAHILL

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	AVG		7.1	AVG	1.98 (1.10 (1.00	
	16	20 5 7 7 7 7 8 8 8 9 9 9 9 9 9 9 9 9 9 9 9 9	20 10 21 16	16	1.94 0 0.70 M 0.55 N 0.55 N 0.99 C 0.45 L 1.24 S 1.24 S	1.00	
1977.	15	35 13 13 15	20 13 23 23	15	1.92 1.72 0.64 0.54 0.34	1.00	
11-18	*	15 23 23 18 12 23	<u> </u>	<u>+</u>	0.81 1.08 1.24 0.97 0.65 1.24	1.00	
MAY	13	000 000 000 000 000 000 000 000 000 00	24 29 26	13	2.47 0.85 1.19 0.55 0.55	1.00	
5 1-16	12	30 14 13 23 10	18 7 18 11	12	1.70 0 0.79 0 0.79 0 0.74 0 1.30 0 0.57	1.00	
NANOGRAMS/CUBIC METER; PERIODS	1.1	100000000000000000000000000000000000000	01 8 8	Ξ	1.50	1.00	
ETER; 1	10	13 5 10 13 13 13 13 13 13 13 13 13 13 13 13 13	90 CM	10	1.06 0.12 1.18 1.53 0.59 0.71	1.00	COR. COEFF. 0.135 0.760 0.850 0.695 0.435 0.724 0.381 0.381
JBIC ME	თ	56 12 10 10 3	7. 19. 19. 19. 19. 19. 19. 19. 19. 19. 19	on	3.88 0.83 0.69 0.62 0.21 0.75	1.00	COR.
RAMS/CL	œ		<u> </u>	œ	0.88. 1.88. 1.99.	1.00	RMS. DEV. 14.205 7.850 6.385 4.186 4.508 2.535 4.346 0.
NANOG	7	31 77 12 11 15 15 15	15 8 17 13	7	2.03 *1.05 *1.11 0.79 0.33 *0.98 0.39	1.00	ERROR RI 0.927 0.362 0.290 0.188 0.242 0.115 0.298
 D	Φ	17 15 20 20 20 19	14 6 12 7	9	1.80 1.42 1.41 1.41 1.41	1.00	W 0 0 0 0 0 0 0 0
	ស	29 38 16 17 7 19	20 12 25 16	ß	1.47 1.93 0.81 0.36 0.81	1.00	SLOPE 0.358 1.466 1.689 0.581 0.370 0.436 0.360
STUDY OF LARGE	3	20 33 33 28 18 18 16	30 11 31 17	£	0.81 1.70 1.70 *0.95 0.81 0.61	1.00	
SON STUE	m	. 88 88 1 8 E L 1	3 7 1	M	0.95 0.71 1.07 0.71 1.55 0.83	1.00	ERROR 18.291 6.315 5.013 3.282 4.468 2.034 4.796 0.
_	ď	143 18 17 17 15 15	20 12 23 18	u	*0.91 *0.91 *0.91 0.86 0.40 0.76	0.60	ERCEPT 29.544 -5.642 13.962 3.804 9.476 0.573 11.205
INTERCOMPAR	1	15 18 0 7 7 7 8	13 8 8		1.36 1.64 0. 0.64 1.82	1.00	INTERCEPT 29.544 -5.642 -13.962 3.804 9.476 0.573 11.205 0.
-	PER 10D	MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY SFU	G, 1) LATION LATION	PER 10D	MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY SFU	G, I) IATION	MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY
	_	DZUBAY DZUBAY DZUBAY UZUBAY LOO LOO CAHILL	MEAN(WITHOUT G,1) STANDARD DEVIATION MEAN(D,M,L) STANDARD DEVIATION		DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO CAHILL CAHILL	MEAN(WITHOUT G,1) STANDARD DEVIATION	REGRESSION VS Z D EPA DZUBAY M EPA DZUBAY N EPA DZUBAY C LBL LOO L LBL LOO L LBL LOO S LBL LOO S LBL LOO G UCD CAHILL
	RESUL TS	EPA DE CEPA	MEAN(WITHOU STANDARD D MEAN(D,M,L) STANDARD D	RATIO TO Z	EPA DE EPA DE EPA DE LBL LEBL LUCO OCO OCO OCO OCO OCO OCO OCO OCO OCO	1EAN (WI STANDA	SRESSION EPA DE EPA DE EPA DE EPA DE LEBL LEBL LEBL LEBL LEBL LEBL LEBL L
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. 7761	5	80 - 104 - 25 - 26 - 17 - 17 - 88	et 13 57	15 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 -
1-18	ī	116 85 85 130 137 137 102 98 98	116 17 123 10	14 - 100 - 1
NANOGRAMS/CUBIC METER: PERIODS 1-16, MAY 11-18	13	108 113 74 74 108 111 111 92 112 112	103 15 109 11	1.05 1.05 1.05 1.05 1.05 1.05 1.05 1.05
1-16,	12	89 110 89 118 118 107 103 95	104	12 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
ER 1005	Ξ	65 71 71 99 100 74 74 60 93 106	85 71 89 41	0.88 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
TER: F	0.	81 70 63 67 71 73 60 60 60 64	65 65 12	
JB1C TE	o	651 661 572 574 574 574 678 688	55 14 14 14 14	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
RAMS/CI	8	-238 86 86 102 102 113	115 55 106 6	8
NANOG	7	86 63 65 81 81 81 82 77 77 81 82 81 81 81 81 81 81 81 81 81 81 81 81 81	82 18 87 52	- 1.04 - 1.08 - 1.08
 %	ø	11.7 11.3 11.3 11.3 12.2 12.2 12.2 12.2 13.3 11.7	107 17 106 71	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
TOTAL	ß	108 140 129 129 124 134 99 91 126 140	116 20 117 117	0.93 1.21 0.82 1.11 1.11 1.11 1.00 0.78 0.78 0.78 0.78 0.78 0.78 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.0
INTERCOMPARISON STUDY OF TOTAL	3	214 239 239 193 282 269 231 222 200 304	24.2 36 25.4 35	9 8 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9
ON STU	M	126 108 104 135 187 199 110 95	121 30 114	5.05 1.05 1.05 1.05 1.05 1.05 1.05 1.05
MPARIS	N	298 294 297 247 339 344 236 241 241 241	283 40 40	11.5 1.05 95 •1 0+ 10 •1 03 96 •1 0+ 11.20 17. 1.20 17. 1.20 17. 1.20 17. 1.20 18. 1.22 19.
INTERCO	-	100 95 76 76 101 101 107 103	87 16 87 18	-0-0 00 -0 Z
-	PER 10D	MDS-A 1F-P MDS-S 01C0T 01C0T 01C0T 1TLF SFU LS 2 1S 4	SAMPLERS) DEVIATION L.G.I.K) DEVIATION	HDS-A TF-M HDS-A TF-M HDS-S DICOT DICOT DICOT DICOT DICOT DICOT DICOT SFU LERS) LATION HDS-A TF-M HDS-S DICOT DICOT DICOT DICOT DICOT DICOT DICOT DICOT SFU
		DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO CAHILL CAHILL CAHILL HUDSON HUDSON		FPA DZUBAY TF-HE FZU DZUBAY TF-HE FZU DZUBAY TF-HE FPA DZUBAY DZUBAY TF-HE TF-HE DZUBAY DZUBAY DZUBAY TF-HE TF-HE DZUBAY DZUB
	ESULTS	EPA	MEAN(ALL STANDAR(MEAN(D,M STANDAR(EPA DZUBA EPA DZUBA EPA DZUBA EPA DZUBA LBL LOO LBL LOO LBL LOO UCD CAHILL VCD CAHILL FSU HUDSOO FSU HUDSOO FSU HUDSOO EPA DZUBA EPA DZU
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	SO		13	SD C	0.13 0.30 0.30 0.00 0.00 0.00 0.00 0.00		
	AVG		76	AVG	0.99 0	1.00	
	16	54 D D D D D D D D D D D D D D D D D D D	50 4 51 3	16	1.09 D *1.07 M 0.86 R 0.86 R *0.99 L *0.92 S	1.00	
1977.	15	34 338 334 357	38 36 8	15	0.89 1.23 1.36 1.36 0.99 0.89 0.92	1.00	
MAY 11-18	7	70 77 57 88 90 85	77 12 78 11	<u>+</u>	*1.00 0.74 0.74 1.17 *1.10 *0.95	1.00	
. MAY	13	68 61 51 72 74 71	53 8 55 10	13	1.16 1.15 *0.96 0.84 *1.07 *1.05	1.00	
NANOGRAMS/CUBIC METER; PERIODS 1-16,	12	64 71 66 76 70 75 -	71 6	12	0.90 *1.00 *0.94 0.93 *1.07 *0.98 *1.05	1.00	
PER 100		339 37 36 36 47 37 50	, m , m		0.89 0.85 0.85 0.83 0.83 0.85 1.22	1.00	
ETER;	01	30 33 33 33 34 34 36 58	34 36 36	0	0.89 1.36 0.71 0.71 0.98 0.89 0.95 1.39 0.83	1.00	.COEFF. 0.995 0.995 0.990 0.999 0.998 0.991 0.991
UBIC	o	41 33 31 31 27 28 28	32 34 04	σ	1.26 1.20 1.20 1.20 1.20 1.20 1.20 1.20 1.20	1.00	COR
RAMS/C	ω	74 -177 -177 	91 49 74 6	00	0.81 1.94 0.63 - - - - - - 0.74	1.00	RMS. DEV. 6.277 24.532 7.602 2.495 4.737 9.657 13.541
NANO	7	3 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4	39 7 5	7	1.14 1.25 0.69 0.86 0.86 *0.99 *0.99 *1.14	1.00	ERROR F 0.035 0.028 0.109 0.034 0.017 0.021 0.051
 ZN	9	56 50 50 50 50	58 5 5 60	9	1.13 *0.94 *1.05 *0.99 *0.99 *0.94 *1.10	0.00	
SMALL	ū	61 74 58 53 65 63 75 75	65 6 7	Ŋ	0.94 1.14 1.02 0.89 0.89 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.0	0.00	SLOPE 0.926 0.996 1.015 0.882 1.128 1.233 0.948 0.948
STUDY OF	±	170 210 178 165 210 203 220 175	191 22 196 195 22	Ŧ	0.89 1.10 0.93 0.98 0.86 *1.10 *1.06 *1.15	1.00	008 114 114 114 119 119 119 119 119 119 119
	M	77 84 84 95 70 70 80 84 84	80 15 78	ĸ	*1.053 *1.05 0.88 0.88 *1.00 1.43 *1.05 0.86	1.00	ERROR 3.391 2.652 10.314 3.196 1.287 2.001 4.550 6.663 3.188
INTERCOMPARISON	O	239 244 248 248 222 - 222 - 278 278 203	243 27 238 258 26	CJ	. 00.98 . 1.00 . 0.91 . 0.91 . 1.17 . 0.91	1.00	TERCEPT 2.681 7.056 2.585 -0.847 -4.888 -9.819 8.313 1.417
INTERC	-	1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	55	-	11.04 11.17 11.35 10.90 10.93 10.84 10.85	1.00	Z I
	PER 10D	MDS-A TF-P TF-P MDS-S DICOT DICOT SMDAY SFU	SAMPLERS) DEVIATION L.G.I) DEVIATION	PER I OD	MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY SFU	LERS) /IATION	MDS-A TF-P TF-P MDS-S DICOT DICOT DICOT SMDAY
		DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO CAHILL CAHILL	MEANCALL SAMPLERS) STANDARD DEVIATION MEANCO,M,L,G,1) STANDARO DEVIATION	Z (DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO CAHILL	MEAN(ALL SAMPLERS) STANDARD DEVIATION	ION VS Z DZUBAY DZUBAY DZUBAY LOO LOO CAHILL CAHILL
	RESULTS	EPA EPA EPA EPA CCD CCD	Σ Σ	RAT10 TO	EPA EPA EPA LBL LBL UCD UCD	MEANCA	REGRESSION VS DEPA DZUBAY N EPA DZUBAY N EPA DZUBAY C LBL LOO L LBL LOO C LCD CAHILL
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INTERCOMPARISON

	SD		13	SD	0.22 0.24 0.26 0.18 0.23 0.23 0.23		
	AVG		D +	AVG	1.07 1.00 1.12 0.78 1.16 1.26 1.26 0.44	1.00	
	16	346 346 347 317 317 317 317 317 317 317 317 317 31	38 6 36 6	16	*0.96 O *0.91 M O .75 P O .75	1.00	
. / / n	15	4 4 4 4 4 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6	41 9 39	15	1.11 1.26 0.87 0.87 *0.99 *1.09	1.00 0.21	
B	<u>*</u>	10 10 10 10 10 10 10 10 10 10 10 10 10 1	7 B B N	<u>*</u>	*1.05 *0.96 0.64 *0.96 *1.07	1.00 0.18	
- (13	46 -29 51 51 - 5	£8 51 51	13	*0.95 *1.08 0.60 0.60 1.14	1.00	
01-1-0	15	23 44 46 63 73 1 1 5 7 1 5 7 1 1 5 7 1 1 5 7 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	35 12 32 11	12	0.72 0.95 1.23 0.66 1.41 1.38	1.00	
ER1003	Ξ	19 28 35 57 63 63 43	38 17 37 21	Ξ	0.50 0.74 0.92 1.50 1.66	1.00	
NANUGRAMS/CUBIC METER: PERTUUS	10	35 46 33 33 40 41	32 11 27 12	10	*1.08 *1.08 *1.02 *1.02 1.24 1.27 0.40	1.00	COEFF. 0.526 0.841 0.612 0.035 0.840 0.767 0.791 0.636
197	σ	40 30 34 37 37 30 34 34 37 37 37 37 37 37 37 37 37 37 37 37 37	28 9 27 11	Ø	*0.94 *1.09 1.23 0.76 0.80 *1.09	1.00	COR
(AIIS/CI	6 0	60 1 1 88 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	36 17 28 8	ω	1.68	1.00	RMS. DEV. 7.821 8.376 9.799 4.164 8.288 7.692 8.763 8.258 8.855
NANCO	7	41 40 36 31 43 45 57 57	39 11 36 12	7	*1.06 *0.93 0.80 1.11 1.19 1.47	1.00	ERROR RI 0.346 0.315 0.155 0.155 0.333 0.387 0.136 0.389
 N	9	51 58 31 67 67 67 50	50 14 19 19 19	9	*1.02 1.16 0.62 1.34 1.28 1.34 0.40	1.00	# 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
	ß	47 66 37 37 64 61 72 23	50 19 19	ស	1.32 · 1.32 · 1.32 · 1.32 · 1.33 · 1.33 · 1.33 · 1.33 · 1.34 · 1.44 · 1.	1.00	SLOPE 0.605 1.693 1.092 0.020 1.632 1.500 0.318 0.925
5	÷	44 66 71 71 66 67 18	50 19 48	Ŧ	0.88 - 1.28 - 1.28 - 1.28 - 1.32 - 1.32 - 1.32 - 1.36 - 0.36 - 0.94	1.00	
אל אל היי	м	4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4	36 13 35 18	м	1.18 1.21 1.21 96 1.55 0.96 0.42	1.00	ERROR 14.317 12.918 15.710 6.303 13.876 11.862 15.555 5.597
TAKIS	ũ	59 44 75 75 61 16 45	45 17 18 18	S	1.32 *1.11 *0.98 0.56 1.36 1.37 *1.00	1.00	ERCEPT 18.062 10.928 10.928 10.928 10.743
INTERCOTTENENTS ON STOUT OF LARGE	1	43 18 21 27 - 50 51 18	34 17 32 17	-	1.27 0.53 0.62 0.79 1.47 1.79	1.00	10.062 -27.251 0.928 29.441 -18.534 0.743 -8.510 4.686 -2.295
-	PER 100	MDS-A TF-H TF-P MDS-S DIC DI : OT SMDAY SFU	LERS) [IATION] [1]	PER I OD	MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY SFU	LERS) IATION	MDS-A TF-M TF-P MDS-S D1COT D1COT SMDAY SFU
		DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO CAHILL CAHILL	Z MEAN(ALL SAMPLERS) STANDARD DEVIATION X MEAN(D,M,L,G,1) STANDARL DEVIATION	Z 1	DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO LOO CAHILL CAHILL	MEAN(ALL SAMPLERS) STANDARD DEVIATION	ON VS Z DZUBAY DZUBAY DZUBAY LOO LOO CAHILL
	RESUL TS	EPA EPA EPA EPA LBL LBL LBL	MEAN(A STANC MEAN(D STAND	RAT10 T0	EPA EPA EPA EPA LBL LBL LBL UCD	MEAN (A STAND	REGRESSION VS D EPA DZUBAY N EPA DZUBAY N EPA DZUBAY C LBL LOO L LBL LOO S LBL LOO S LBL LOO G UCD CAHILL
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_	PER 10D	MDS-A	M-91	TF-P	MDS-S	DICOT	DICOT	D1C0T	SMDAY	TTLF	SFU	1.0	ATION		AT ION	PER 10D	MDS-A	16-M	1F-P		DICOT	DICOT	DICOT	SMDAY	11.5	SFU	1.5	AT ION		MDS-A		TF-P	MDS-S	DICOT	DICOT	D1C0T	SMDAY	11.6	SFU
	_	DZUBAY	DZUBAY	DZUBAY	DZUBAY	P0	P00	8	CAHILL	CAHILL	CAHILL	MEAN (WITHOUT G. I)	STANDARD DEVIATION	J. E.	STANDARD DEVIATION	2	DZUBAY	DZUBAY	DZUBAY	DZUBAY	00	L00	ر ا	CAHILL	CAHILL	CAHILL	MEAN (WITHOUT G, I)	STANDARD DEVIATION	ON VS Z	DZUBAY	DZUBAY	DZUBAY	DZUBAY	r00	200	S LBL L00	CAHILL	CAHILL	CAHILL
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_	RESULTS			z							_	7		×	UI	RATI								၁ ပ			£	S	REGR	0 E	Σ	22	Œ	C	<u>ر</u> د	S	ر	_ 	<i>-</i>

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1-16,	12	21 81 6 7 1 7 1 7 1	13 15 3	1.14 *0.91 0.46 0.91 *1.07 *1.14	0.29
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NANOGRAMS/CUBIC METER; PERIODS	10	80 80 7 7 9 9 1	7 8 1		.00 1.00 .67 0.30 COR.COEFF. 0.931 0.973 0.971 0.994 0.995 0.995
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INTERCOMPARISON	-	ιτουνουασ	r - r -		1 00 1.0 0.18 0.2 1NTERCEPT 0.368 -1.282 -1.282 -0.884 -0.499 -1.048
£	PER100	MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY SFU	6.1)	00 -A -P -P 01 01 07 AY	MDS-A TF-M TF-P MDS-S DICOT DICOT SMDAY SFU
		DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO CAHILL CAHILL	MEAN(WITHOUT G.1) STANDARD DEVIATION MEAN(D.M.L) STANDARD DEVIATION	D Z Z DZUBAY DZUBAY DZUBAY DZUBAY C COO C CAHILL C CAHILL C CAHILL	MEAN(WITHOUT G,1) STANDARD DEVIATION REGRESSION VS Z D EPA DZUBAY TF-M N EPA DZUBAY TF-M N EPA DZUBAY TF-M N EPA DZUBAY TF-M C LBL LOO DICOT L LBL LOO DICOT S LBL LOO DICOT C
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	AVG		-	AVG	1.34 0 1.17 1 1.02 0 1.22 0 0.59 0 0.86 0 0.75 0	1.00	
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1977.	15	ווטמוט	~ ~ ~	15	1.20 1.80 1.80 1.20 0.60 0.60	1.00	
11-18	<u>*</u>	- - - -	a- ao	<u>+</u>	2.1.20 0.5.0.50 0.0.50	1.00	
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MPAR19	ď	~ M − 1 − − 1 1	טט בא	U	0.63 3.47 3.47 40.95 0.32 0.32 0.32	1.00 1.24	ERCEPT 0.980 -2.245 -0.071 0.862 0.536 0.536 0.592 0.592
INTERCOMPARISON	-	0000111			2.00 0. 2.00 8.1.00	1.00	INTERCEPT 0.980 -2.245 -0.071 0.336 0.538 0.592 0.592
-	PER 1 OD	MDS-A TF-P TF-P MDS-S DICOT DICOT DICOT SMDAY SFU	6.1) (1ATION	PER 1 0D	MDS-A TF-P MDS-S DICOT DICOT SMDAY	6, I)	MDS-A TF-P MDS-S DICOT DICOT SMDAY SFU
		DZUBAY DZUBAY DZUBAY UZUBAY LOO LOO CAHILL	MEAN(WITHOUT G,1) STANDARD DEVIATION MEAN(D,M,L) STANDARD DEVIATION	2	DZUBAY DZUBAY DZUBAY DZUBAY LOO LOO CAHILL	MEAN(WITHOUT G,I) STANDARD DEVIATION	ON VS Z DZUBAY DZUBAY DZUBAY LOO LOO CAHILL CAHILL
	RESULTS	EPA EPA EPA EPA EPA EPA EPA CCO UCO	ΣΣ	RATIO TO	EPA EPA EPA EPA EPA CCD UCD	MEAN(W STAND	EGRESSI EPA EPA EPA EPA LBL LBL UCD
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	AVG		236	AVG	M 1.25 N 1.25 N 1.05 N 1.05 C 1.17 C 1.17 C 1.17 C 1.31 G 0.73 H 0.88 U 0.89 X 0.93	1.00 0.25	
	91	207 D 275 M 222 N 222 N 222 R 222 R 235 C 351 L 350 S L 194 U 194 U 196 K	248 71 244 68	16	0.83 D 0.89 N 0.89 R 0.89 R 1.42 C 1.41 C 1.41 C 0.68 H 0.78 L	1.00	
. 776	5	242 242 128 185 191 193 173 183	17. F. ST. ST.	15	0.78 0.73 0.73 0.73 0.73 0.73 0.79 0.98 0.98	1.00	
MAY 11-18 1977	<u>*</u>	263 235 235 218 344 358 413 413 163 174 174	248 94 234 97	<u>*</u>	1.06 0.95 0.88 1.39 1.44 1.44 1.66 0.66 0.65	1.00	
	13	203 203 203 134 134 135 135 135 135 135 135 135 135 135 135	170 33 167 75	13	0 73 1.23 0.79 0.79 1.11 - - - - - - - - - - - - - - - - -	1.90 0 20	
NANOGRAMS/CUBIC METER; PERIODS 1-16.	51	246 274 240 243 343 345 345 191 191 191	245 60 86	12	1.12 0.98 0.95 1.40 1.40 1.41 0.78	1.00	
ER1005	=	314 250 250 310 331 331 331 331 270 270 281 249	266 47 272 53	Ξ	1.18 0.94 1.102 1.17 1.24 0.74 0.70	1.00	
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MBIC M€	б •	8 1 2 3 3 4 5 5 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6	65 19 72 20	6	0.70 0.56 0.56 0.87 0.98 0.98 0.90 0.90 0.90	1.00	
NAMS/CL	00	300 292 292 208 243 140 221	230 55 224 18	80	1.30	1.00 0.24	RMS. DEV. 18.230 38.819 30.322 27.782 33.028 38.330 27.687 24.423 37.828 37.828
NANOGE	7	226 226 164 164 175 175 175 175 117 117 117 117 117 117	<u> </u>	7	0.79 1.57 1.11 1.14 0.97 1.22 1.22 1.22 0.87 0.97	1.00	₹
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	ď	278 278 187 253 252 289 145 150 150 139	202 55 201 52	ľ	0.90 0.93 1.25 1.25 1.43 0.05 0.69	1.00	SLOPE 1 060 1.366 1.092 1.121 1.182 1.182 1.271 0.483 0.953 0.556
), OF 1	#	279 387 310 231 346 352 	279 77 281 86	£		1.00 0.28	
INTERCOMPARISON STUDY OF TOTAL	м	218 191 200 200 284 284 176 176	190 55 771 55	M	1.05 1.05 1.05 1.20 1.49 0.51 0.74	1.00	ERROR 13.028 27.093 20.711 18.668 29.734 20.962 27.043 21.562 16 411 25.419 46.281
PAR I SC	N	184 690 527 479 597 597 260 365 450	489 126 486 156	C	.0.99 .1.18 .0.98 .0.98 .1.12 .1.22 .0.53 .0.92	1 00 0.26	
TERCOM	-	159 176 177 177 192 210 210 131 93	160 37 155 43	-	1.00 1.08 1.20 1.20 1.32 1.32 1.32	1 00 0.23	-33.103 -33.103 -28.036 -7.24.382 -34.482 -34.582 -8.847 14.322 19.322 19.322 19.322 19.322 19.322 19.322 19.322 19.322
≟	PER 10D	MDS-A TF-P TF-P MDS-S DICOT DICOT SMDAY SFU LS .2	CRS) ATTON ATTON	PER 100	MDS-A • TF-H TF-P MDS-S D1COT D1COT SMDAY TTLF SFU LS 2	z	MDS-A TF-M TF-P TF-P MDS-S DICOT DICOT SMDAY TTLF SFU SFU
	ď	SON CELE	MEAN(ALL SAMPLERS) STANDARD DEVIATION MEAN(D,M,L,G,I,K) STANDARD DEVIATION	8	SON SON	MEAN(ALL SAMPLERS) STANDARD DEVIATION	N
	'n		ICALL INDARC ICD,M,	T0 Z		(ALL NDARD	10
	RESULTS	EPA EPA EPA EPA EPA EPA EPA EPA EPA EPA	MEAN STA MEAN STA	RATIO TO	EPA EPA EPA EPA EPA EPA EPA EPA EPA EPA	MEAN	
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				S	17 17 17 18 18 18 18 18 18 18 18 18 18 18 18 18		
	20		47	SD	0.15 0.28 0.19 0.18 0.16 0.17 0.25		
	AVG		161	AVG	0.85 1.34 1.10 0.88 1.00 1.03 1.14 0.81	1.00	
	16	165 D 234 M 176 N 174 R 256 C 258 L 258 L 254 S	208 47 201 53	16	0.79 D 1.12 M 0.85 N 0.84 R 1.23 C 1.24 L 1.22 S 1.22 S	1.00	
.//61	15	85 140 188 75 111 112 117	120 35 118 25	15	0.71 1.16 1.56 0.62 •0.92 •0.93 •0.93	1.00	
MAY 11-18	<u></u>	219 191 172 263 269 318	219 72 197 85	<u>+</u>	1.00 0.87 0.78 1.20 1.23 1.45	1.00	
	13	78 1167 1116 80 101 101 104	105 30 110 39	13	0.74 1.58 1.10 0.76 0.76 *0.96 *0.99	1.00	
PERIODS 1-16.	12	199 236 188 198 262 261 261	212 45 209 53	12	0.94 1.12 0.89 0.94 1.24 1.23	1.00	
PERIOD	=	228 285 218 203 197 197 216 -	212 36 215 46	11	1.08 1.35 1.35 *1.03 *0.95 *1.02 *1.02 *0.85	1.00	
	10	228 264 254 266 249 256 287 189	238 44 217 49	10	• 0.96 1.11 1.07 1.07 1.12 • 1.08 • 1.21 0.80	1.00	.00EFF. 0.988 0.952 0.981 0.952 0.975 0.975 0.910
UBIC 7	σ	26 85 85 33 35 35 55	45 20 23 23	σ	0.58 1.91 1.91 0.49 0.74 0.79 0.88 1.41	1.00	
NANOGRAMS/CUBIC METER;	80	195 238 231 231 - - 208 164	207 30 189 23	00	0.94 1.15 1.12 1.12 - - - - - - - - - - - - - - - - - - -	1.00	RMS. DEV. 16.011 31.364 28.059 20.958 26.794 24.201 25.551 27.261 32.559
NANOG	7	60 128 128 17 74 79 88 105	95 41 99 53	7	0.63 1.98 1.35 0.75 0.78 0.83 *0.93 *1.11	1.00	70R 048 089 079 059 076 092
 	9	386 329 317 268 267 267 232	300 49 290 67	9	1.29 1.10 1.06 0.89 0.89 0.89 0.77	1.00	m o o o o o o o
SMALL	ß	122 227 192 128 166 164 188 101	158 40 149 49	Ω.	0.77 1.44 1.22 0.81 *1.05 *1.04 1.19 0.64	1.00	SLOPE 1.061 1.131 0.999 1.119 1.094 1.084 1.234 0.540
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MEAN(ALL SAMPLERS)	197	179	206	226	259	363	201	<u>8</u>	29	202	263	207	230	248	218	503	217	98
STANDARD DEVIATION	125	69	<u> </u>	82	Ξ	167	78	57	00	8	137	63	17	85	75	8		
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	6		000		1,00	<u>-</u>		4		cua								

COR. COEFF.	0.841	0.802	0.747	0.899	0.952	0.951	0.931	0.452	0.746
	21.699	+1.515	37.995	21.826	35.238	32.464	44.783	35.977	46.995
ERROR	0.129	0.180	0.164	₩60.0	0.157	0.141	0.199	0.158	0.203
SLOPE	0.630	0.871	0.689	0.724	1.544	1.562	1.528	0.226	0.849
ERROR	26.890	40.698	36.759	21.116	36.527	31.826	44.570	35.883	45.466
INTERCEPT	24.628	-8.439	30.375	2.585	-32.492	-12.247	18.713	53.937	9.199
	MDS-A	TF-M	TF-P	MDS-S	DICOT	DICOT	D1C0T	SMDAY	SFU
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TECHNICAL REPORT DATA (Please read Instructions on the reverse before comp	oleting
1 REPORT NO EPA-600/7-78-118	3 RECIPIENT'S ACCESSION NO.
4 TITLE AND SUBTITLE INTERCOMPARISON OF SAMPLERS USED IN THE DETERMINATION OF	5 REPORT DATE July 1978
AEROSOL COMPOSITION	6 PERFORMING ORGANIZATION CODE
D.C. Camp, A.L. Van Lehn, and B.L. Loo	B PERFORMING ORGANIZATION REPORT N
9 PERFORMING ORGANIZATION NAME AND ADDRESS	10 PROGRAM ELEMENT NO
Lawrence Livermore Laboratory	1NE625D EB-11 (FY-78)
Livermore, CA 94550	11 CONTRACT GRANT NO.
Lawrence Berkeley Laboratory	IAG-D6-0800
Berkeley, CA 94720	IAG-D7-F1108
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERE
Environmental Sciences Research Laboratory-RTP, NC	Final
Office of Research and Development	14. SPONSORING AGENCY CODE
U.S. Environmental Protection Agency	EPA/600/09
Research Triangle Park, N.C. 27711	

15. SUPPLEMENTARY NOTES

16 ABSTRACT

An intercomparison study was carried out to evaluate the performance of 11 different designs of aerosol samplers. The samplers were operated by participating scientific groups having recognized expertise in sampler development and operation. The devices tested include hi-vol, TWO MASS, cyclone, CHAMP, streaker, stacked filter and manual and automated dichotomous samplers. The samplers were operated in Charlesto WV for eight consecutive days duirng May of 1977. The collection surfaces of each sampler were changed at least every 12 hours which enabled the intercomparison to be made for 16 sampling periods. The collected samples were returned to the laboratory of each participant and analyzed for mass, nitrate, sulfur or sulfate, lead, and 9 other elements. Most of the samplers separated the aerosol into two fractions with 50% separation diameters ranging from 2.4 μm to 4.3 μm . The upper 50% cutoff diamete for the various samplers ranged from 14 μm to about 30 μm . Best agreement among samplers was found for elmeents such as sulfur and lead that occurred primarily in the fine fraction. The amount of total mass collected was strongly influenced by the upper 50% cutoff diameter of each sampler. For stacked filter samplers and the tandem filter samplers, the fine fraction appeared to be enriched with crustal elements such as Si, Ca, and Fe, which suggests that there are particle bounce errors. Of all the samplers tested, the automatic dichotomous sampler showed the greatest precision.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a DESCRIPTORS	b identifiers/open ended terms	c. COSATI Field/Group
*Air pollution *Aerosols *Samplers *Comparison *Mass *Sulfur		13B 07D 14B 07B
18. DISTRIBUTION STATEMENT	19 SECURITY CLASS (This Report)	21. NO, OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED 20 SECURITY CLASS (This page) UNCLASSIFIED	151 22. PRICE

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