A COMPARISON OF ACTIVE AND PASSIVE SAMPLING FOR OZONE DETECTION

The Spectrex PAS-500 was used in this experiment and is ideal for active environmental sampling due to its miniature size, weight (4oz.) and duration

(40 hours on one 9 volt alkaline battery).

Phase II Report

Appendix A: Exposure Assessment Methodology

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7.4 RESULTS OF FIELD EVALUATION OF PERSONAL OZONE SAMPLES

The primary objective of the outdoor field experiment was to evaluate the active denuder system under California ambient exposure conditions. A secondary objective was to compare the relative performance of the active system with continuous monitors and passive badges; a one-microenvironment (i.e., ambient) experiment at high-ozone concentrations was selected. An additional objective was to demonstrate that the active systems can be worn by children with minimal intrusion (i.e. that they wear them, and not remove them, and that they can perform their normal activities).

The working hypothesis for this experiment was that active denuders will compare well with continuous monitors, on average, and that precision for active systems will be significantly better than with passive badges. If the hypothesis is true, then active samplers could be used for the remaining personal ozone experiments. The success of the experiment was evaluated against performance criteria similar to those used for the TED/badge sampler: relative precision of that ± 20 percent, relative bias of about ± 10 percent.

In planning and running the experiment, consideration was given to the ozone concentrations required for a successful evaluation of the two samplers, as well as to the potential effect of high-ozone concentrations on the children participating in the experiment.

The children's exposure needed to achieve at least 300 ppb-hr ozone during each experiment, in order to be at least three times above the expected detection limit for the passive badge (about

100 ppb-hr). The detection limit for the active sampler was expected to be much lower (about 10 to 20 ppb-hr). This required an average ozone concentration of over 100 ppb for 3 hours, or a concentration of 150 ppb for over 2 hours.

The South Coast Air Quality Management District (SCAQMD) calls a “health advisory” when ozone concentrations exceed the California standard, but are less than 200 ppb. During a “health advisory”, the SCAQMD recommends that people with respiratory problems stay indoors. If the ozone concentration is expected to be over 200 ppb, the SCAQMD calls a “Stage I Alert”; during an “Alert”, they recommend that people not exercise outdoors during times of the ozone peak. An “Alert” would mean that the children would need to stay indoors during the afternoons.

Thus ozone concentrations between about 100 and 200 ppb were needed. Average ozone concentrations of 105 and 141 ppb were obtained for about 2 ½ hour exposures on the 2 days. In addition, detection limits were lower than expected: about 75 ppb-hr for the passive badge and about 10 ppb-hr for the active sampler. Thus conditions on both days met the required criteria.

The experiment was conducted on July 19 and 21, 1994, at Bobby Bonds Park in Riverside using 6- to 12-year old children who attended a lunch/recreation program from about 1130 until 1600 PDT. On each day about 40 children wore small backpacks for about 2½ hours during normal outdoor activities. The activities included races; playing kickball, soccer, or baseball; reading; doing art projects; going on a nature hike; etc. The children took occasional water and rest breaks, plus a few took bathroom breaks. Adult observers recorded general activities and locations for the children, including when and for how long they might have gone inside or to the bathroom. In general, most of the children spent all of their time outdoors within the area bound by the continuous monitors and the microenvironmental samplers; this means that the active and passive samples should both agree with the continuous monitoring data, since all were exposed to the same air mass. The backpacks did not restrict the children’s activities, and no one took the backpacks off. However, in a few cases, a child complained about the backpack and one of the adult observers helped the child adjust the backpack for a better fit.

Each backpack contained an active sampler with a passive badge attached on the outside. The inlet to the active sampler and the passive sampler were between neck and chest height. In addition, 10 percent carried a collocated passive badge. About 20 percent trip blanks were also collected for both the passive and active samples. The glass denuder tube was encased in a PVC tube, and foam pads surrounded the PVC tube and the pump in the backpack to protect the children from a broken glass tube or other objects. No items broke, and none of the children were hurt by the apparatus (including several who fell on their backpacks playing soccer).

Two continuous ozone monitors were set up about 100 yards apart in the area where the children played, one near the first base line of the baseball field, another near the right field fence. The monitors were calibrated before and after each experiment; the data acquisition system was set up to collect data over 5-min averaging periods, with strip-chart backup.

In addition, four backpacks were designated as outdoor microenvironmental samplers. Each contained two active samplers and had two passive badges attached.

Microenvironmental sampling backpacks were configured exactly like those worn by the children. In particular, the passive sampler used for these microenvironmental samples were not protected by rain caps, as frequently used by the Harvard group. Rain caps were not used in order to keep the microenvironmental samples as similar to the personal sample as possible. The microenvironmental samplers were placed under a tree where the children spend some quiet time, under a tent similar to where they took water breaks, and near the two continuous monitors. On July 19, the tree microenvironmental backpack was accidentally moved to the right field fence next to another backpack.

The same procedures were used each day, including the following tasks:

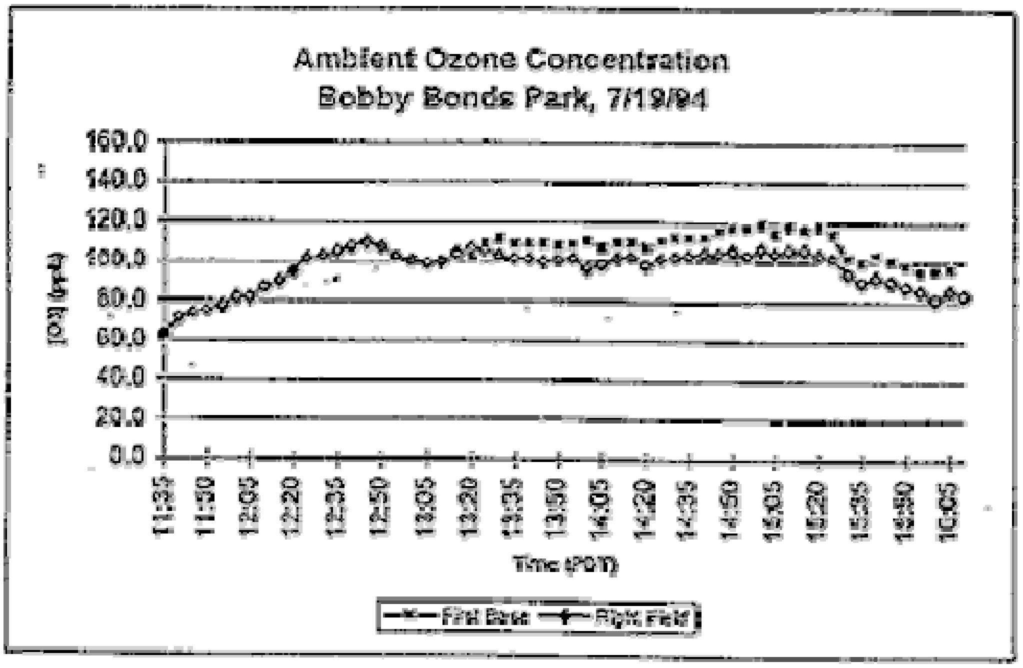
- The continuous ozone monitors were set up and calibrated.
- The active, sampling pumps were warmed up and flow calibrated.
- The active and passive samplers were prepared.
- The packs were first installed on the children, and then the active samplers and passive badges were placed in or attached to the packs.
- Procedures were followed for recording the start and stop times of the active samplers and the passive badges.
- About 10 adult observers watched the children and recorded their activities and general location during the sampling period.
- After sampling, the flow rates of the active sampling pumps were again measured.

The laboratory preparations and analyses were performed by Alison Geyh of Harvard. Samplers were shipped to the field and returned to Harvard using an overnight service. Active samples were kept cool at all times except during sampling; passive samples were kept at ambient temperature. Laboratory analyses were performed in four batches, two for each day's experiment. Laboratory results were returned to STI for data processing. Ozone monitor operations in the field are discussed in subsection 8.4; data processing procedures are discussed in subsections 9.4 and 9.5.

The results of the field evaluation are summarized below, and presented in Figures 7-5 through 7-7 and Tables 7-4 through 7-8. The blank levels and levels of detection (LOD) for the active and passive samplers are shown in Table 7-4. Although there was some variation between analysis batches, the data are consistent: the active LOD was very low, at about 10 ppb-hr; the passive LOD was higher, about 75 ppb-hr, and similar to the LOD results during the chamber evaluation tests. Individual-batch blank levels were used during data processing.

Ozone concentrations at 5-min averages for the two continuous monitors are shown for the time period of the experiments in Figure 7-5. Note that the personal samplers were operated from about 1234 to about 1604 PDT on July 19 and from about 1309 to about 1549 PDT on July 21. The two monitors agreed very well on both days, implying that the gradient in ozone concentrations in the area was small.

Pairs of outdoor microenvironmental samples were placed under a tree, under a tent, and near the two continuous monitors, one near the first base line of the baseball field, another on the right field fence. The results for these samples are listed in Tables 7-5 and 7-6 and illustrated in Figure 7-6. For the active microenvironmental samplers, the pairs agreed quite well with each other. In addition, there was also good agreement between the separate sets of active microenvironmental samplers; this again implies that the gradient in ozone concentrations in the area was small. The pairs of passive microenvironmental samplers (without a rain cap) agreed less well within pairs and with passive samplers at other locations. In addition, the active microenvironmental samplers averaged about 6 percent below the continuous monitors, while the passive microenvironmental samplers averaged about 41 percent higher.



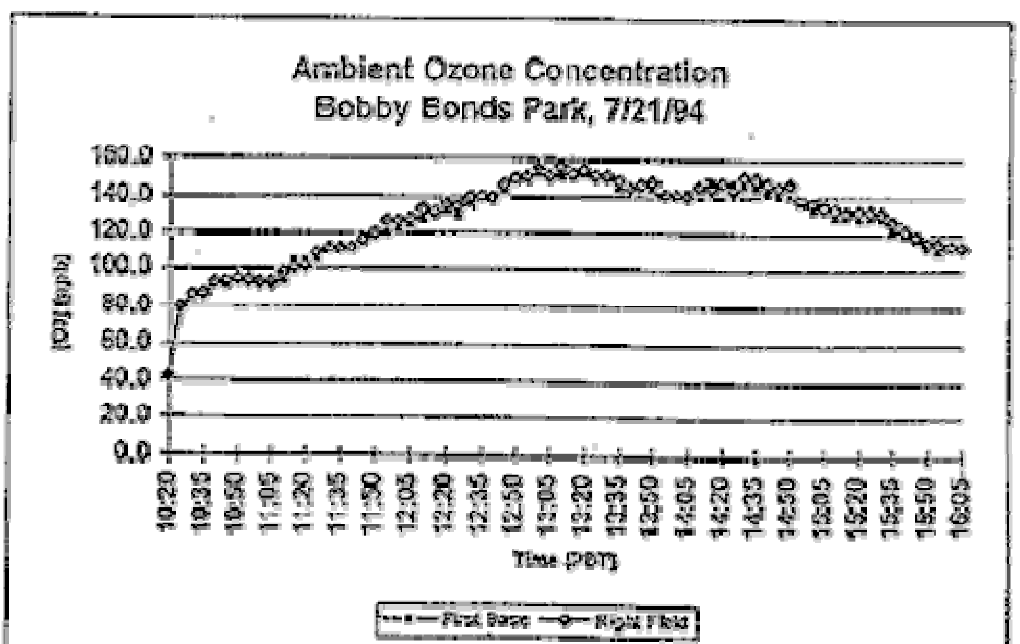
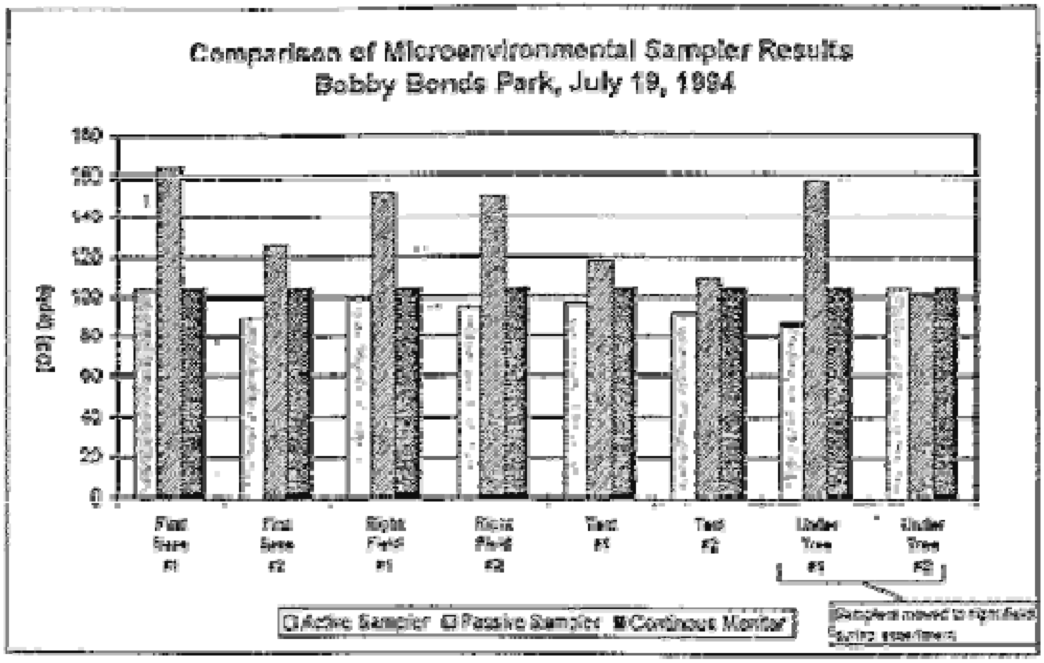


Figure 7-5. Ambient ozone concentrations at Bobby Bonds Park on July 19 and 21, 1994.



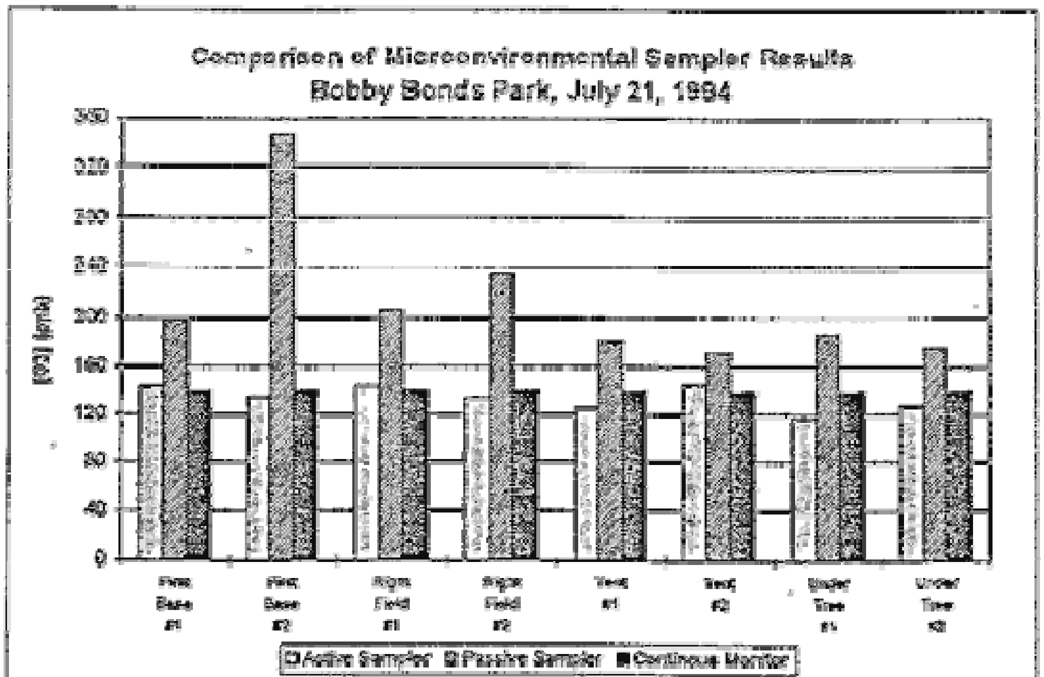


Figure 7-6. Comparison of active and passive microenvironmental ozone concentrations with ambient ozone concentrations at Bobby Bonds Park on July 19 and 21, 1994.

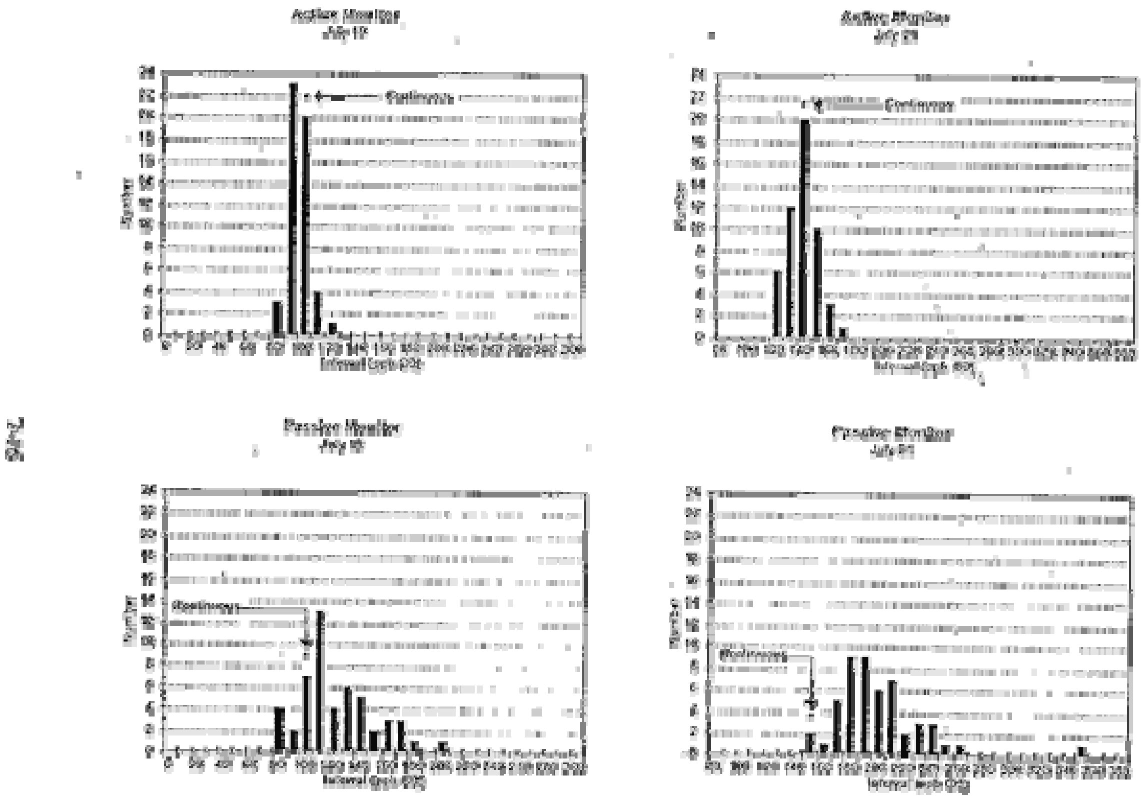


Figure 7-7. Frequency distributions of active and passive personal ozone concentrations at Bobby Bonds Park on July 19 and 21, 1994.

Table -7-4. Blank Levels and Limits of Detection (LOD) for active and passive samplers.

Experiment Date	Analysis Batch	Avg. Active Blank Level NO_3 (mg/mL)	σ_B Active NO3 (mg/mL)	LOD_{Active} O_3 (ppb-h5)	Avg.Passive Blank Level NO_3 (mg/mL)	σ_B Passive NO3 (mg/mL)	$LOD_{Passive}$ O_3 (ppb-hr)
7/19	1	0.0241	0.0072	11	0.1304	0.0142	55
7/19	2	0.0243	0.0098	15	0.1689	0.0213	82
7/21	3	0.0136	0.0016	2	0.1380	0.0223	87
7/21	4	0.0204	0.0081	12	0.1644	0.0201	78
			Mean	10			75

Table 7-5. Comparison of Microenvironmental Sampler Data for 7/19/94.

Location/Sampler	Active [O_3] (ppb)	Active/Cont. Ratio	Passive [O_3] (ppb)	Passive/Cont. Ratio	Continuous [O_3] (ppb)
First Base #1	103	0.99	163	1.57	104
First Base #2	89	0.86	125	1.20	104
Right Field #1	99	0.95	152	1.46	104
Right Field #2	95	0.91	150	1.44	104

Under Tent #1	97	0.93	118	1.13	104
Under Tent #2	92	0.88	109	1.05	104
Under Tree #1	86	0.83	158	1.52	104
Under Tree #2	104	1.00	101	0.97	104
Mean	96	0.93	135	1.39	104

· Sampler moved to right field location during experiment.

7-6 Comparison of microenvironmental sampler data for 7/21/94.

Location/Sampler	Active [O_3] (ppb)	Active/Cont. Ratio	Passive [O_3] (ppb)	Passive/Cont. Ratio	Continuous [O_3] (ppb)
First Base #1	142	1.03	197	1.43	138
First Base #2	134	0.96	346	2.49	139
Right Field #1	143	1.03	206	1.48	139
Right Field #2	133	0.96	236	1.70	139
Under Tent #1	125	0.91	180	1.30	138
Under Tent #2	144	1.04	171	1.24	138
Under Tree #1	117	0.85	185	1.34	138
Under Tree #2	127	0.92	175	1.27	138
Mean	133	0.96	212	1.53	138

Table 7-7. Comparison of active sampler, passive sampler, and continuous ozone monitor data.

Experiment Data	$[O_3]_{average}$ Active Sampler (ppb)	$\sigma_{[O3]}$ Active (ppb)	$[O_3]_{average}$ Passive Sampler (ppb)	$\sigma_{[O3]}$ Passive (ppb)	$[O_3]_{average}$ Cont. Monitor (ppb)	$\sigma_{[O3]}$ Continuous (ppb)
7/19	91	7	113	27	105	1
7/21	136	12	190	25	141	1

Table 7-8. Comparison of averages for active continuous and passive/continuous ozone ratios

Experiment Date	$[O_3]_{active}/[O_3]_{cont.}$ Ratio A	$\sigma_{Ratio\ A}$	$[O_3]_{active}/[O_3]_{cont.}$ Ratio P	$\sigma_{Ratio\ P}$
7/19	0.87	0.069	1.08	0.26
7/21	0.97	0.082	1.29	0.33
Mean	0.92	0.076	1.18	0.30

Ozone concentrations for the active samplers and passive badges worn by the children, and for the continuous monitors are listed in Tables 7-7 and 7-8, and illustrated in Figure 7-7. A total of 78 students wore the samplers, 39 on each day. On July 19, when the continuous monitors averaged 105 ppb, the average for the active samplers was 91 ppb ± 7 ppb; the active results for July 21 are similar: continuous ozone of 141 ppb while the active samplers averaged 136 ppb ± 12 ppb. This is an average negative bias of 8 ± 8 percent, well below (better than) the criteria for acceptance of the active sampler as a personal monitoring device for this study.

The results for the passive badge worn by the children were not as good: the passive badges show a positive bias of about 21 ± 19 percent, based on concentration (Table 7-7), or about 18 ±

30 percent, based on ratio to the continuous (Table 7-8). This bias is lower than the bias for passive microenvironmental samples. In addition, there was at least one outlier well beyond all the rest of the data in both the personal and microenvironmental data sets. The passive badge did not meet the criteria for acceptance as a personal sampling device for this study.

Figure 7-7 shows that the distributions of the active samplers and passive badges are significantly different, both in shape and in bias, relative to the continuous monitors.

Conclusions form this field evaluation experiment are summarized below:

- The active sampler had a lower (better) limit of detection (LOD) than the passive badge: 10 ppb-hr versus 75 pp-hr.
- The ambient ozone concentration, as measured by two continuous monitors, was quite consistent on each day, averaging 105 ppb on July 19 and 141 ppb on July 21.
- The pairs of active outdoor microenvironmental samplers agreed quite well with each other and between pairs. The passive microenvironmental samplers (without a rain cap) agreed less well.
- The personal ozone concentrations as measured by the active samplers averaged about 8 percent below the continuous monitor (bias), with a precision of about 8 percent. These results demonstrate that the active sampler easily meets the acceptance criteria set before the experiment.
- The personal ozone concentrations as measured by the passive badges averaged about 21 percent above the continuous monitor (bias), with a precision of about 19 percent. These results do not meet the acceptance criteria set before the experiment. In addition, there were outliers in the data set.
- There were significant differences in bias and precision between the 2 days of the testing; it is not known if the different ozone concentrations on these 2 days influenced the results, or if other variables did.
- The personal ozone concentrations as measured by the active samplers had a smaller bias and a lower precision than the concentrations measured by the passive samplers.
- The field evaluation suggests that the active denuder personal sampler can provide sufficiently accurate and precise personal ozone data to use in exposure model evaluation studies. The passive badge does not have sufficient precision to meet the needs of this study.
- The small backpack with one or two active samplers inside was worn by students for about 2 ½ hr without significant problems; this setup will likely work for additional experiments.