

# I International

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## **INSTRUMENTATION NEEDS FOR NASA'S GLOBAL TROPOSPHERIC EXPERIMENT**

**A Report on a Workshop Held in Boulder, Colorado,  
October 2001**

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## EXECUTIVE SUMMARY

A workshop was held in Boulder, Colorado, in October 2001, to discuss instrument development needs and priorities for NASA's Global Tropospheric Experiment (GTE). The next scheduled field expeditions in this program are INTEX-NA (Intercontinental Chemical Transport Experiment-North America) to be held in the summer of 2004 and the spring of 2006. This mission will take place in continental air masses and over oceans near continents. Particular needs of INTEX were weighted heavily during the workshop deliberations.

A group of scientists involved or very familiar with GTE campaigns discussed, on the basis of individual compounds or atmospheric properties, needs for future GTE investment in instrumentation. A similar workshop held in 1996 had identified instrument downsizing as the primary need, and this has been successful in several cases. At this time, GTE can look to new approaches or greatly improved instruments in terms of limits of detection and/or time resolution.

A short time was spent at the workshop on the philosophy of blind intercomparisons, and the compounds for which instruments need to be compared. A group of five compounds were highlighted. A future workshop in spring of 2002 will be devoted to the choice of compounds and protocols for an airborne intercomparison in 2003.

At the end of the workshop, a list of priorities was drawn up. Those compounds which were considered of high priority to GTE, and which could be available on at least an exploratory basis by 2004 are, with no ordering:

1. CH<sub>2</sub>O (more instrument development to improve sensitivity)
2. NH<sub>3</sub> (instrument development)
3. H<sub>2</sub>O<sub>2</sub> and ROOH (a new instrument)
4. NO<sub>2</sub> (downsize present instruments, and/or try a different approach)
5. a fast H<sub>2</sub>O capability for the P-3B GTE aircraft.

Fifteen other compounds/properties were selected for medium priority attention. All of those would provide added useful capabilities to GTE, although they are less important than the high priority instruments.

The report discusses the workshop, lists the compounds/properties in terms of priority for needed instrument development and investment, and contains short descriptions of needs and possible solutions for each item on the list.

## PREFACE

This workshop, sponsored by GTE, was held at the Ramada Inn, in Boulder, Colorado, on 8 to 10 October 2001. The format of the workshop was as follows. The first day began with plenary presentations (with considerable interruption and discussion) of five topics: (1) instrumentation lessons learned from the recently completed TRACE-P campaign; (2) plans for the INTEX missions with a special eye toward instrumentation needs; (3) a tutorial on satellite measurements of chemical species, appropriate because INTEX will make underflights for comparison with satellite data; (4) the results of informal intercomparisons during TRACE-P; and (5) a discussion of the results and conclusions from a 1996 GTE workshop. This was followed by discussion of individual items, beginning with a list generated at the 1996 workshop.

The second day began with an approximately two hour discussion of intercomparison issues and needs. The results from this will be used as a starting point for a future workshop on instrument intercomparison alone, with an eye toward test flights in 2003. Following this, and a brief review of the preceding day's deliberations, the group broke into three smaller groups. Each of these set lists of priorities and reasons for those decisions. The day concluded in a plenary session to sort out those priorities with consensus from the entire group.

On the third day, the three smaller groups reconvened. Each was given a third (randomly chosen) of the compounds/properties to discuss in more detail, with short notes written on each topic. These are the major basis for the descriptions presented in the text of the report.

The workshop attendees were:

John Barrick  
Bill Brune  
Tony Clarke  
Vickie Connors  
Jim Crawford  
David Crosley  
Bruce Doddridge  
Jim Drummond  
Fred Eisele  
Greg Huey  
Daniel Jacob  
Dan Murphy  
Paul Novelli  
Brian Ridley  
Glen Sachse  
Stan Sander  
Hanwant Singh  
David Tan  
Paul Wennberg

## BACKGROUND

The Global Tropospheric Experiment (GTE), which had its origins in the late 1970s, is a program of the National Aeronautics and Space Administration (NASA). It is focused on three major scientific topics: (1) biosphere-atmospheric interchange and biological sources; (2) long range transport of chemical species, and their distributions in the atmosphere; and (3) chemical reactions in the troposphere that produce conversion, redistribution, and removal of the trace compounds present. The major part of GTE comprises scientific field missions and modelling efforts to understand these topics. The field missions center on airborne instruments, which are supplemented by ground-based platforms, sondes, and satellite observations. The payloads are designed to emphasize photochemistry, and not such topics as clouds, radiation, aerosols per se, etc.

An important feature of GTE is the attention paid to development and testing of instruments aboard aircraft. (Many earlier missions employed only one aircraft, but the latest three, PEM Tropics A and B, and TRACE-P, as well as and the upcoming INTEX in 2004 utilize both the NASA DC-8 and the P-3B.) This has included design, construction, and testing of new instrumentation. Formal airborne intercomparisons have been made. The formal ones are campaigns in the Chemical Instrumentation Test and Evaluation (CITE) series, and are rigorous, blind intercomparisons among two or more instruments measuring the same species. CITE-1, in 1983 and 1984, focused on OH, CO, and NO; CITE-2 in 1986 concerned the odd nitrogen compounds NO<sub>2</sub>, HNO<sub>3</sub>, and PAN; and CITE-3 in 1989 intercompared the sulfur species SO<sub>2</sub>, DMS, H<sub>2</sub>S, CS<sub>2</sub>, and COS.

Additionally, informal comparisons have also been made. These were done primarily in TRACE-P in 2001, using opportunities when both aircraft were flying in the same air mass. These are described briefly below to indicate where work is needed. More information on GTE can be found on the GTE web page <http://www-gte.larc.nasa.gov/>.

In 1996, a workshop was held at SRI to set priorities for development of new or improved airborne instrumentation for use in GTE science missions. As noted below, the conclusion of that workshop was that the available funds should be focussed on downsizing current instruments, rather than developing new ones. That has been partially successful. A second workshop was convened in Boulder in October of 2001 to discuss opportunities, needs, and priorities for new and improved GTE instrumentation addressing particular compounds and other properties of the troposphere. This report describes the findings of that workshop.

### THE 1996 GTE INSTRUMENTATION WORKSHOP

The 1996 workshop is described in detail in D. R. Crosley, *Instrumentation Development for the Global Tropospheric Experiment*, SRI International Report MP-96-112R, August 1996. Its outcome was quite different from that anticipated at the beginning. The then current state of measurement capabilities for compounds and other properties of the atmosphere were summarized by the workshop participants, as starting points for discussion. One of the topics

included was "aircraft issues", prepared by Jim Hoell. In the presentation and ensuing discussion, it emerged that available space, power, and weight requirements posed a limit on the addition of new instrumentation. The PEM-Tropics A mission was about to begin, and the limitations of both aircraft in all three categories for the existing instruments was very apparent.

After further discussion, both plenary and as three separate groups, it was concluded that many of the GTE instruments are well tested and proven. However, they were in large part extrapolated airborne versions of original prototypes developed and tested under laboratory conditions. Thus, they are often large and heavy, consume large amounts of power (especially 60 Hz), and require operator(s) for constant tuning and intervention. There was felt to be an urgent need to reduce the size, weight, power consumption, and number of operators in future GTE missions. This was the major recommendation from the workshop for future investment of GTE instrument development funds.

Subsequently, proposals were requested for "downsizing" the equipment used aboard both aircraft for future GTE missions. There were mixed results from the proposals funded. Some equipment was significantly improved in several of the categories needed. Others could only be downsized a fraction of the expected improvement. In one case, the failure of a manufacturer to deliver the key hardware prevented any downsizing of one particular system.

Those instruments which were successfully downsized by the time of TRACE-P are:

Georgia Institute of Technology: NO/NO<sub>2</sub>

Drexel: SO<sub>2</sub>

NCAR: spectroradiometer

NCAR: chemical ionization mass spectrometer (OH, H<sub>2</sub>SO<sub>4</sub>, et al.)

NASA Langley: DACOM (H<sub>2</sub>O, CO, CH<sub>4</sub>, N<sub>2</sub>O)

Nonetheless, during the recently completed TRACE-P campaign, and for the upcoming proposed INTEX mission in 2004, there is space available for new instrumentation. (Naturally, instruments that are light, small, consume little power, and could be automated, are most desirable.) During the 1996 workshop, conclusions and priorities were reached concerning those compounds and atmospheric properties that were most in need of measurement capability, whether improved or totally new. Those conclusions formed the starting point for the 2001 workshop.

The list of compounds and atmospheric properties that resulted from the 1996 workshop are given (in altered form) in Table 1. Initial comments from the present workshop about progress since that time, or concerning other topics, are included in the table. For the most part, little advancement has been made in new instruments. Perhaps most notable was the concern in 1996 for accurate radiometry. This issue appears to have been fully solved the spectroradiometer developed by NCAR and flown on both PEM-Tropics missions and on TRACE-P. HNO<sub>3</sub> was at the top of the list for needed measurements in 1996 but now there exist several CIMS instruments that have flown. Their results warrant an intercomparison (see below) but new instrument development is unnecessary. In a few other cases, instrumentation recommended in 1996 has emerged but it has not been fully tested and evaluated.

Some participants in the 2001 workshop felt that GTE should give high priority to combining existing measurement capabilities, thus encouraging a multiplicity of measurements per instrument rack. This would both downsize and create room for new instruments needed for further progress. The philosophy of one instrument per molecule should not be considered feasible in the long term. This is reflected in the inclusion of multiple species measurements but received little further discussion during the workshop.

**TABLE 1**

| Compound                         | Comments                                                                           |
|----------------------------------|------------------------------------------------------------------------------------|
| HNO <sub>3</sub>                 | open path absorption now available > 7 km; CIMS                                    |
| PAN                              | promising instrumentation (Innsbruck)                                              |
| other organic nitrates           | important in continental air masses                                                |
| NMHCs                            | fast but a small suite                                                             |
| NO <sub>x</sub>                  | large values expected in INTEX; NO <sub>2</sub> laser-induced fluorescence         |
| NO <sub>3</sub>                  | cavity ringdown                                                                    |
| N <sub>2</sub> O <sub>5</sub>    |                                                                                    |
| PNA (HNO <sub>4</sub> )          | chemical ionization mass spectrometry                                              |
| NH <sub>3</sub>                  | important regarding aerosols; tunable diode laser                                  |
| J-values                         | spectroradiometry solved; aerosol extinction; actinometric comparison              |
| OH                               | new instruments not needed; OH loss rate measurement                               |
| H <sub>2</sub> O <sub>2</sub>    | new instrument is needed                                                           |
| CH <sub>3</sub> OOH              | new instrument is needed                                                           |
| CH <sub>2</sub> O                | new instrument is needed; diode laser doesn't meet needs for remote air            |
| H <sub>2</sub> O                 | need on P-3B; solicit ideas; dew point is what is really needed                    |
| aerosols                         | need to know when flying in a cloud; inlet improvement                             |
| sulfur species                   | SO <sub>2</sub> intercomparisons yield uncertainty; H <sub>2</sub> SO <sub>4</sub> |
| HO <sub>2</sub> /RO <sub>2</sub> |                                                                                    |
| halogens                         | grab samples good enough for organic halogens                                      |
| oxygenates                       | acetone is important                                                               |
| organic acids                    | sufficiently well done                                                             |
| HCN/RCN                          |                                                                                    |
| -----                            |                                                                                    |
| CO lidar                         |                                                                                    |
| CO <sub>2</sub>                  |                                                                                    |
| Hg                               | in same category as pesticides                                                     |
| wing pods                        |                                                                                    |
| multiple species                 | measure several with one instrument                                                |

(Those topics below the line were added at the present workshop.)

## INTEX-NA

The Intercontinental Chemical Transport Experiment – North America (INTEX-NA) will probably be the next GTE mission, to be held in 2004. It will be performed over North America using both the DC-8 and P3-B aircraft. The purpose is the understanding of the exchange of chemicals between continents and the global troposphere. Of primary interest are O<sub>3</sub> and its precursors (HO<sub>x</sub>, NO<sub>x</sub>, and hydrocarbons), aerosols, and the major greenhouse gases CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O. Inflow and outflow of these chemicals over the North American continent will be examined first in the summer of 2004, when the photochemistry is at its most intense period, and later in the spring of 2006 when influence of East Asian transport to North America is its greatest. The mission will coordinate with and support satellite measurements made at the same time. A draft version of a white paper on INTEX-NA was available for the workshop participants.

Because of the current focus on INTEX-NA, which will probably constitute GTE's scientific missions through the next five years, discussion at the workshop was greater for its needs than for other possible GTE studies. For example, more attention was paid to odd nitrogen compounds than to sulfur species of biogenic origin, the latter being important in a remote marine environment.

## WORKSHOP PRESENTATIONS

The workshop began with five presentations to the entire group. The first of these was by Daniel Jacob, who described lessons learned concerning instrumentation usage and potential problems in TRACE-P. One problem, also recognized in previous missions, was the large amount of heating in the DC-8 as low altitude, boundary layer flights were made. At high temperatures, some instruments malfunctioned. Although this was not discussed subsequently at the workshop, it is clear that new instruments should be designed to use as little power as possible. Flights at low altitudes are included as part of INTEX in studies of chemical outflow and air mass aging. Jacob also discussed qualitatively the behaviour of individual instruments and the several informal intercomparisons (the latter topic was also dealt with later). Because the data and results from TRACE-P are not yet public, those issues will not be discussed here.

The second presentation was by Hanwant Singh on INTEX-NA. He presented the scientific rationale and priorities for the mission, as described above. Portions of flights would be devoted during INTEX to satellite underflights, in order to compare results. It is possible that other groups (NOAA, NSF, etc.) would also take part in the campaign, but it is too early to know now.

A list of priorities for each aircraft was given in the usual GTE format. These are given by each compound or atmospheric property, with priorities running from 1 (mission critical), 2 (very important), 3 (important), 4 (useful), and 5 (exploratory). When an NRA is announced for the mission, this list is used. In many previous missions, all instruments in priorities 1 and 2 were loaded onto the aircraft, with some from category 3, and none in category 4. Nearly always, one or two instruments in category 5 have been added to the payload before being

proven fully tested, provided of course they addresses data of high interest to the mission. Again, as is customary in such GTE priority lists, limits of detection and limits of time resolution are added for each measurement. It was noted in the draft that superior time resolution over that quoted was "highly desirable." Nonetheless, later in the workshop discussion, several comments were made that many existing instruments could provide the detection limits given in the list. However superior (sometimes exceptionally better) performance in that category was also most desirable from the standpoint of instrument development. It is exactly that kind of improvement that the workshop looked for, and such superior performance beyond that in the draft should be a feature in the list of priorities for instrument development.

During the Singh talk there was a lot of discussion concerning fluxes. Because the P-3B flies more slowly than the DC-8, and is designed for long duration, low altitude flights in the boundary layer, it is better suited for flux measurements, although meteorological instrumentation on board the DC-8 does operate at 100 Hz. In the marine boundary layer DMS is a good choice for fluxes, and it was suggested that isoprene would be excellent over continental areas. However it was then pointed out that isoprene cannot be measured rapidly enough to be suitable to determine fluxes. There was considerable discussion at this time on fluxes, including merits of eddy correlation vs. rapid sampling, and other aspects. However when later individual compounds/properties and instruments were discussed, fluxes were not returned to as a topic worth special consideration.

Jim Drummond then discussed satellite measurements, giving an excellent tutorial to this largely aircraft based audience. This is an important topic because of the connection of satellite and aircraft experiments in INTEX and TRACE-P. All the methods used are spectroscopic, utilizing nadir viewing of absorption of earth-reflected solar radiation, or emission/absorption by the earth's surface and atmosphere. Most of the discussion was based on infrared absorption, which includes many compounds of interest to GTE. Satellite limb measurements can have good vertical resolution (1-2 km) but horizontal resolution of a few hundred km. This corresponds to an aircraft averaging time (on an underflight) of tens of minutes to an hour. Measurements in the troposphere are more difficult than those in the stratosphere, largely due to the presence of clouds in the troposphere. If they are present but at low altitude, measurements above them can be done but the altitude of the cloud deck must be known. For validation of satellite measurements via aircraft, one wants of course no species variation and no clouds, whereas the most scientifically interesting information aboard the aircraft arises when there is species variation.

Fred Eisele followed with a discussion of intercomparisons during TRACE-P. He had used actual data sets to compare different instruments, with correlation plots and statistics where appropriate. Sometimes, two instruments flew together on the same plane, but more likely the comparison was aboard two aircraft, one aboard each plane. There were three particular flight tracks, the shortest at 20 minutes duration and the longest one hour in the same air mass, which were used for evaluation. The agreement or lack thereof provided important background information in assessing new and improved instrumentation needs. However, because the data are now available only to the science team, details will not be discussed here. (In fact, at a TRACE-P science team meeting held in Norfolk in November, Eisele used more recently analyzed data to reach slightly different conclusions in a couple of cases.)

The results and the conclusions of the 1996 Instrumentation Workshop were then discussed by David Crosley. He listed the main recommendations from that group, including a table of instrumentation needs for species and atmospheric properties which had been drawn up. This is the basis of Table 1, and the recommendations discussed by Crosley are given above. During this discussion the other compounds and comments in Table 1 were added by the present participants.

## INTERCOMPARISONS

During the second day of the workshop, about two hours were devoted to the topic of intercomparisons, beginning with the recommendations about them reached at the 1996 workshop. A workshop to discuss only intercomparison issues and protocols will be held in the spring of 2002, with an eye toward test flights to take place in 2003. The discussion at the present workshop was to obtain a sense of this group regarding intercomparisons. Major conclusions are given next, but details will not be included.

The discussion had as its background the informal intercomparisons made on TRACE-P and in other field tests known to the participants. It was felt that intercomparisons were needed for several compounds, and that the scheduling of test flights for intercomparison purposes only (that is, no complete suite of compounds to understand atmospheric chemistry goals) is an important aspect. Most felt that only meteorological data, and a compound such as CO and/or O<sub>3</sub> to generally define the nature of an air mass, are all that should be flown in addition to the intercompared instruments. An addition of NO to this suite, to sort out the OH/HO<sub>2</sub> measurements, was suggested but met mixed opinions. The intercomparisons should be blind and the data analyzed by referees. All the results would be published.

From this discussion resulted a list of compounds for which instruments should be intercompared. These are, with no ordering: OH; HO<sub>2</sub> vs. RO<sub>2</sub>; HNO<sub>3</sub>; SO<sub>2</sub>; NO<sub>2</sub>; oxygenated hydrocarbons; and CH<sub>2</sub>O. It was noted that for INTEX, SO<sub>2</sub> was listed as a #3 priority while the others were given a #2 ranking. During later discussion which prioritized instrument development needs, more comments were made concerning intercomparisons. These are included in comments about individual compounds.

## PRIORITIES

Each of the three smaller groups was asked to list priorities for instrument development, with special attention paid to needs of INTEX. These were ranked as high, medium, or low priority for development at this time. After further plenary discussion, the participants reached a general consensus on priorities. These are given in Table 2. There is no ordering within each category, reflecting the fact that total consensus was not achieved within all priority categories. Some brief comments are added; these are given in more detail in the descriptions of each compound/property. Note that some felt high priority should be given to testing and intercomparison of instruments, but those sentiments are not included in this table which deals only with instrument development.

## TABLE 2

### High Priority

CH<sub>2</sub>O (more instrument development to improve sensitivity)  
NH<sub>3</sub> (instrument development)  
H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>OOH (a new instrument needed for crosschecks with the present approaches)  
NO<sub>2</sub> (downsize present instruments from those flown on TRACE-P; try a different approach)  
fast H<sub>2</sub>O instrument for the P-3B

### Medium Priority

Carbonyls  
Aerosol reduction of J-values  
P-3B aerosol lidar  
Organic aerosols  
Cloud indicator  
Fast aerosol composition  
CO lidar  
HO<sub>2</sub>/RO<sub>2</sub> measurements  
Instrument automation and further downsizing  
Use of wing pods on P-3B  
CO<sub>2</sub> flux  
OH loss rate measurement  
Fast PAN  
Fast NMHCs  
PNA  
Forward facing aerosol lidar for the P-3B

### Low Priority

Organic nitrates other than PAN  
NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>  
Halogens  
Organic acids  
HCN/RCN  
Hg  
SO<sub>2</sub>

## INDIVIDUAL COMPOUNDS AND OTHER ATMOSPHERIC PROPERTIES

To conclude the workshop, each group was given assignments to summarize their understanding of the overall thinking of the plenary group. One third of the topics were assigned to each group. Those write-ups are given here, supplemented by other points made during the plenary discussions, as reflected in notes taken by Vickie Connors. Those notes are not comprehensive, but where included provide further detail beyond that in the write-ups.

Following the conclusion of the workshop, I received comments from two participants and one invitee who was unable to attend. These concerned aerosol measurements, CO lidar, and H<sub>2</sub>SO<sub>4</sub>. Excerpts from these are given in the individual write-ups but do not change priorities given in Table 2.

### HIGH PRIORITY

#### CH<sub>2</sub>O

Formaldehyde (CH<sub>2</sub>O) is a high-yield product of the atmospheric oxidation of hydrocarbons. Its photolysis is a major source of HO<sub>x</sub> radicals throughout the troposphere. As a result, CH<sub>2</sub>O is important for tropospheric chemistry both as a tracer and as a driver of photochemical activity. Concentrations of CH<sub>2</sub>O range from over 1 ppbv in the continental boundary layer to less than 50 pptv in the upper troposphere. GTE has identified the need for CH<sub>2</sub>O aircraft measurements with a sensitivity of 10 pptv and 1-minute temporal resolution to serve the needs of future missions.

Existing techniques for CH<sub>2</sub>O measurement from aircraft include wet chemical derivatization and fluorescence, TDL spectroscopy, and gas chromatography. The state-of-the-science limit of detection (LOD) for these techniques is 30-50 pptv. Comparisons of aircraft observations with photochemical models show large discrepancies, both in the upper troposphere where concentrations are of the order of the LOD and at lower altitudes where concentrations are well above LOD. These discrepancies raise substantial concern as to our fundamental understanding of radical photochemistry in the troposphere. However, our ability to move forward on this issue has been hindered by doubt on the reliability of observations. Intercomparisons on the ground and from aircraft indicate large disagreements between techniques, even with concentrations of several hundred pptv. There is a clear need for further instrument development.

Improved diode laser-based sensors appear to be viable future techniques for CH<sub>2</sub>O measurements. These sensors are highly specific, and during post-processing the time response may be varied depending on the CH<sub>2</sub>O concentrations. For example, during encounters with pollution plumes one may use integration times of the order of seconds. Present sensitivities are 25-50 pptv and appear to be limited by the beam quality of the laser source. New laser sources

including difference frequency generation and quantum cascade lasers may provide the greater beam fidelity needed for further improvement of sensitivity.

While closed-path diode laser sensors have participated in several airborne missions, open-path sensors may be feasible, particularly in view of recent advances in powerful quantum cascade lasers. An analysis of open-path measurement sensitivity, specificity, and altitude range is encouraged.

Measurements based on laser-induced fluorescence (LIF) are also technically feasible and should be analyzed. LIF sensors have similar properties to diode laser sensors in terms of specificity and variable time integration, and may be capable of achieving the 10 pptv target sensitivity.

Cost: moderate to high  
Development level: 2-4 years

### **NH<sub>3</sub>**

Ammonia measurements are needed to address several aerosol issues such as acid/base ratios, which in turn can control the uptake of other gas phase compounds such as SO<sub>2</sub>, O<sub>3</sub>, and semi-volatile acids. Ammonium ions play a fairly unique role in aerosols, because there are many acidic compounds found in aerosols, both inorganic and organic, but ammonia is typically the only basic species found at sufficiently high concentration to determine the level of particle neutralization. Ammonia is also believed to play an important role in enhancing aerosol nucleation rates above those that are possible from classical sulfuric acid/water bimolecular nucleation alone. While nucleation increases particle number density, it typically reduces their size and growth rates, thus changing their atmospheric lifetime, light scattering abilities, and influence on clouds. Ammonia is also important as part of the reactive nitrogen budget and its measurement would strongly support efforts to close this budget.

An aircraft ammonia instrument appears to be feasible since NH<sub>3</sub> is presently being measured in ground-based and laboratory studies at ambient concentrations. The major measurement difficulties are: sampling, calibration, and evaporation from aerosols. Due to ammonia's sticky nature, inlet walls can be both short-term sources and sinks of the molecule, particularly during altitude changes that can result in dramatic temperature, water concentration, and pressure changes. Since much ammonium is contained in aerosols, care must also be used to separate gas and particle phases.

There are currently two means of ammonia measurement. These are an photothermal interferometric approach under development at NASA Langley, and CIMS instruments in several laboratories. Measurement down to 10 pptv should be feasible in the 1-10 s time frame, and the costs for developing new instrumentation should be in the moderate range. It is anticipated that aircraft measurements of NH<sub>3</sub> should be possible within the next 2 years.

The question of the possibility of an open path system, such as that built by NASA Ames for the measurement of HNO<sub>3</sub> and NO<sub>2</sub>, to measure NH<sub>3</sub> was raised. Calculations using known spectroscopic parameters should provide the answer fairly quickly.

## **H<sub>2</sub>O<sub>2</sub> and ROOH**

Here particular attention was paid to CH<sub>3</sub>OOH as the single most important member of the family of ROOH. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is produced in the atmosphere by self-reaction of HO<sub>2</sub> radicals, and organic hydroperoxides (ROOH) are similarly produced by reactions of organic peroxy radicals (RO<sub>2</sub>) with HO<sub>2</sub>. They are the principal termination products for HO<sub>x</sub> radical chains in the troposphere, and can also serve as reservoirs for HO<sub>x</sub> radicals which they regenerate by photolysis. Concentrations of H<sub>2</sub>O<sub>2</sub> range from over 1 ppbv in the boundary layer under photochemically active conditions to under 100 pptv in the upper troposphere. Methylhydroperoxide (CH<sub>3</sub>OOH) is thought to be the dominant organic peroxide in the remote troposphere and is present at concentrations comparable to or lower than H<sub>2</sub>O<sub>2</sub>. Higher organic peroxides are predicted by models to be abundant in continental boundary layers due to high emissions of precursor nonmethane hydrocarbons, and represent there a major sink for HO<sub>x</sub>. They have yet to be observed, however. One cannot exclude the possibility that surprisingly high concentrations of these organic peroxides could be present in the global troposphere, paralleling the recent discoveries of high concentrations of carbonyl compounds. GTE has identified the need for development of speciated hydroperoxide measurement capabilities with sensitivities of 10 pptv and 1-minute temporal resolution, although no known method aside from a very old and slow sample collection/EPR approach can differentiate among species of ROOH.

Existing techniques for H<sub>2</sub>O<sub>2</sub> measurement from aircraft include liquid scrubbing followed by HPLC, and TDL absorption spectroscopy. The first technique has been flown for years and has also been applied to speciated CH<sub>3</sub>OOH and total ROOH measurements. TDL methods for H<sub>2</sub>O<sub>2</sub> are at an advanced stage of development. No intercomparisons between techniques have been conducted from aircraft, and the reliability of the measurements is, as a result, uncertain. This uncertainty is a serious limitation for using the observations to test our understanding of HO<sub>x</sub> radical photochemistry. Aside from this reliability issue, the detection limits of current instrumentation for H<sub>2</sub>O<sub>2</sub> and CH<sub>3</sub>OOH are inadequate for testing our understanding of photochemistry in the upper troposphere.

Cost: moderate to high

Development level: 2-4 years for HPLC and TDL; > 5 years for other techniques

## **NO<sub>2</sub>**

The instrumentation for NO and NO<sub>2</sub> measurements recently flown on the DC-8 and P-3B missions during TRACE-P are large and require several on-board operators. It is quite feasible with recent advances in laser technology and photolysis lamps that significant reduction in the size and weight can be made. Combined with increased automation and fewer operators,

there is an excellent opportunity to free up space for other instrumentation, especially on the P-3B. This downsizing can be achieved without sacrificing the current low LOD (e.g., < 5 pptv for NO<sub>2</sub>) and response time necessary for remote atmosphere photochemical studies. This downsizing is possible for both the LIF NO/NO<sub>2</sub> or the chemiluminescence/photolysis NO/NO<sub>2</sub> techniques that have been used in GTE programs. The downsizing is expected to be mostly an engineering initiative and could be completed in the 2-4 year time frame.

Furthermore, a new direct LIF technique for NO<sub>2</sub> measurements has been recently developed in various laboratories, and has been applied to urban and rural atmospheres. Further improvements in this technique are expected to make it an attractive technique, particularly in the upper troposphere where the NO<sub>x</sub> partitioning favors NO. In addition, cavity ringdown is considered a viable technique for NO<sub>2</sub> at low concentration. This will likely be investigated in the near future.

5 ppt is an acceptable LOD for NO<sub>2</sub> for the upcoming INTEX-NA mission, which will take place over the east and west coasts, with flights through Wisconsin to match ground station measurements. All of the instruments currently available are capable of this LOD.

The Georgia Tech NO/NO<sub>2</sub> LIF system has a long track record of providing excellent sensitivity and time response, as well as freedom from interferences, in both the NO and NO<sub>2</sub> measurements. While the system was downsized considerably between PEM-Tropics B and TRACE-P, it remains a large and demanding instrument. Future plans for the system are twofold. One is to reduce the system size and weight by roughly a factor of two while maintaining the sensitivity and response time obtained in the PEM Tropics missions. The second approach is to utilize laser power more efficiently, enabling the addition of other measurement channels (CH<sub>2</sub>O, HONO) but while reducing size and weight. For example, these changes will enable the removal of one of the large YAG lasers, reducing not only size and weight but also power consumption and heat generation. A further emphasis on automation should reduce the in-flight personnel requirements. The time scale for the laboratory downsizing is < 2 yrs, that for aircraft integration is 2-4 yrs.

It is also possible, considering the substantial overlap in calibration and other subsystems, to consider combining present mature instruments, now oriented toward one species, into more efficient combined measurement systems. An example that is considered quite feasible for the P-3B is to unite a NO, NO<sub>2</sub>, NO<sub>y</sub>, and O<sub>3</sub> chemiluminescence instrument with the P-3B PAN GC-ECD instrument. A single rack instrument with external pumps and gas supplies could then provide all the above listed measurement capability (O<sub>3</sub> at 1 s, NO, NO<sub>2</sub>, NO<sub>y</sub>, PAN, PAN homologues) that currently occupies three racks. The current requirement of 3 or more operators for these measurements could be replaced by a single in-flight operator.

### **Fast H<sub>2</sub>O for the P-3B**

Water vapor is an extremely important trace species in the atmosphere. This importance ranges in scope from its strong influence of the earth's radiation balance and budget, through intimate participation in photochemical cycling, and utility as a relatively conserved tracer of

atmospheric motion and transport. Water vapor is dispersed in a highly heterogeneous manner throughout the lower troposphere. Current hygrometer techniques available to NASA GTE aircraft for applications under the INTEX project plan are possibly incapable of characterizing water vapor with adequate resolution and response time, owing to existing problems associated with memory effects and slow response experienced during rapid changes in ambient water vapor sampled during flight tracks and overall accuracy over the wide dynamic range of water vapor sampled over relatively short time scales in flight.

Fast water vapor measurement – at <10% accuracy and 10 Hz acquisition down to concentrations of 20 ppm – for the NASA P-3B operating mostly in the planetary boundary layer and lower free troposphere, is recognized as a key developmental priority for INTEX-NA and future GTE missions. This improved capability is particularly applicable to improving the robustness and integrity of photochemical calculations, some of which rely implicitly on a highly accurate understanding of water vapor abundance and behavior.

Possibilities for new or improved instruments include improved Lyman- $\alpha$  hygrometers, closed- or (preferably) open-path TDL spectroscopy, and open-path IR or millimeter wave remote sensing techniques. High temporal resolution in water vapor is a critical need for eddy correlation flux studies which might be conducted from the NASA P-3B platform in INTEX and future projects. The results of these completed and continuing developmental efforts should be reviewed to select a suitable candidate.

While fast water vapor on the NASA P-3B might be viewed as a “facility” instrument permanent to the aircraft platform, the critical nature and importance of accurate and highly time-resolved measurements to GTE science necessitates a research-like approach to selection, integration, operation and maintenance of a research-grade fast water vapor sensor for the NASA P-3B, possibly with a project investigator responsible for the instrument during field deployment. The need for an instrument at this performance level is viewed as being likely satisfied within a 0–2 year window allowing for use during INTEX-NA Phase A planned for summer 2004. Over the 2–4 year window improvements should be targeted at improving time resolution while maintaining the high accuracy required to satisfy photochemical calculations. As noted below, one possibility for locating the instrument is in a wing pod of the P-3B.

## **Medium Priority**

### **Oxygenates: Carbonyls and Alcohols**

This considers carbon containing oxygenates with two or more carbons, in the form of carbonyls and alcohols; organic acids are low priority and will be treated separately.

This is a new but highly important category of globally present chemicals. The current methods use GC techniques with a variety of detectors (RGD, PID, MS) and can measure a large suite of chemicals. Sensitivities for the detection of important species are adequate. The scientific effort is relatively new and current difficulties need to be resolved.

0-2 year time frame: Keep present methods but resolve potential difficulties and disagreements. There are problems of unknown backgrounds that may or may not be generated by the measuring systems themselves. It is recommended that continued testing and interactivity among groups should take place to sort out problems. The current instrumentation is not yet ready for a blind intercomparison. Currently the relatively slow speed (5-10 min) of these measurements is not an important issue.

2-4 year time frame: Once basic problems have been sorted out, the present methods can be made somewhat faster but not a great deal so. PTR-MS or CIMS techniques offer good possibilities for fast (~1 min) detection of some chemicals in this group. A long term effort is needed to assess this capability. The ability to measure a suite of chemicals is clearly desirable and should be retained.

## **Aerosol Absorption and Extinction**

Absorption of light by aerosols affects the J-values important in tropospheric photochemistry. It was recommended that both an onboard absorption instrument and a column extinction measurement be considered. Additionally, column extinction forms an excellent bridge between aircraft and satellite measurements.

Although coarse particle absorption is possible from larger dust aerosol in the atmosphere it is more common for light absorbing aerosol (at visible wavelengths) to be dominated by submicrometer combustion-derived black carbon (BC) aerosol. This provides a valuable indicator for both anthropogenic and biomass combustion emissions. These measurements are commonly made by a light absorption photometer by continuously monitoring changes in transmission of light through a filter. These measurements are valuable for both real-time indications of air mass characteristics and for post flight analysis of air mass and aerosol properties. In conjunction with light scattering the light absorption coefficient also defines the single scatter albedo, an intensive property of an air mass that is also a key parameter needed for climate models.

Such measurements have been made on GTE missions using a particle soot absorption photometer (PSAP). This single wavelength instrument is commonly used for airborne applications although there are issues regarding artifacts associated with pressure fluctuations and humidity effects. While these can be reduced through careful analysis and correction, there remain uncertainties on the order of 20% that increase as concentrations of absorbing species decrease. Substantial additional uncertainty is introduced when estimating BC from the light absorption measurement because the mass absorption coefficient must be known or assumed. This uncertainty is reduced when coincident size distribution data for BC are available. Even with perfect measurements of light absorbed by aerosols on a filter, there would be uncertainty in converting into absorption in the atmosphere because light absorption changes significantly depending on the mixing state of the particles.

There is room for an improved aircraft light absorption instrument with reduced pressure sensitivity, reduced RH response, increased number of wavelengths (to help differentiate species such as BC or dusts) and increased sensitivity. There are also alternative devices for these measurements (eg. photoacoustic) but these have typically been less sensitive, more complex and unproven for airborne operations. However, due to the interest in this measurement by the radiation and climate community as well as EPA etc., it is likely that improvements to existing technologies can be expected perhaps in a 2-4 year time frame.

Consequently, if these developments result in new or improved airworthy instrumentation that offers performance features better than the PSAP then these should be considered for acquisition by the GTE program. However, because the existing PSAP instrument meets the minimum requirements of GTE missions and because other programs are supporting the development of improved instrumentation, it is not a high priority that GTE funds should be used for the development of improved capabilities.

Aerosol column extinction measurements can describe the decrease in direct solar intensity measured as aircraft move through the atmosphere and/or descend through the column. When molecular extinction is subtracted at visible wavelengths this measurement describes the optical depth of the aerosol for the column of aerosol above the aircraft. Descent through the column provides variation in optical depth directly linked to the aerosol field being descended through. The column integrated extinction also provides the column optical depth that is directly related to measured satellite aerosol column radiances.

The change in measured extinction on descent is also a result of the aerosol size distributions, light scattering, light absorption and aerosol composition measurements made on the GTE aircraft. Hence, a measurement of aerosol extinction provides a quantitative link between the in-situ aerosol aircraft measurements and their column radiative properties seen by satellites. This quantitative link enables the interpretation of satellite aerosol fields in terms of the aerosol properties measured on the aircraft. In this fashion, the aerosol physical and chemical aircraft measurements available over limited spatial and temporal ranges can also be extended by satellite products. Moreover, the strong correlations between aerosol and gas phase species common in the sampled air masses may also allow inferences of gas phase fields from the remotely sensed aerosol data.

The addition of measured aerosol extinction and optical depth to the GTE aircraft would clearly be a valuable contribution to interpreting column aerosol properties and establishing stronger links between mission data and satellite products. It is also felt that this capability might be readily made by inexpensive modifications to existing GTE measurements (e.g., Shettlers' spectroradiometric J-values) with little or no impact on payload. As a result such modifications should be a high priority for immediate addition to future missions. This is of particular value for P-3B measurements focused more on lower altitudes with higher aerosol loading, but should also be considered for the DC-8.

## **P-3B Aerosol Lidar**

Two types of aerosol lidar for the P-3B were discussed. One is a forward-looking lidar that alerts the scientists to upcoming clouds or aerosols. A large device to do this was used on the DC-8 in the SUCCESS mission of the SASS program in 1996, but a smaller version was envisioned here. The second lidar would be nadir pointing, mapping out aerosol fields below the airplane in the way the Ed Browell's O<sub>3</sub>/Aerosol lidar does on the DC-8, but again smaller owing to the less stringent requirements.

The P-3B lidar(s) would have several roles. The first role is real-time information to the mission scientist on the location of layers, plumes, and other atmospheric structure. A second role is to provide links between remote sensing and in-situ aerosol data. A third role is to provide a 2D field for data interpretation of questions such as layer thickness, boundary layer depth, and haze at high humidities just below cloud base.

For these roles, the following capabilities are required: (1) eye safe operation of the lidar; (2) small ( $\leq 50$  kg typical), robust, automated operation; (3) real time display; (4) range of about 3 km is adequate; (5) sensitivity should be high enough to see boundary layer aerosols and plumes with fast time response, but does not need rapid measurement in the clean free troposphere; (6) downward looking geometry would be adequate for the mission support and 2D field roles. A pointing capability would strongly enhance the roles of comparison to in-situ aerosol data and would be essential to studying haze formation. This pointing capability could be scanning or a simpler switch between forward and downward pointing.

Commercial units which are probably adequate for simple downward looking operation are available for \$20-\$60K plus integration costs. Adding pointing capability is certainly feasible but would require some development for both the actual pointing and real-time display software.

Additional information on this topic has been provided since the workshop by an invitee (Browell) who was unable to attend. At NASA Langley, Browell has been assembling a small downward pointing lidar. It has two wavelengths and could go in the baggage compartment of the P-3B or other aircraft for nadir aerosol measurements. It would require about half of a double rack and one person to operate it and act as the laser safety person. It would gather scientifically useful data on aerosol distributions and scattering ratios at two wavelengths. At NASA Goddard a small lidar has been developed; it offers eyesafe nadir data. The cost is about \$100K. Although it has not flown, it is assumed that it will work well on an airborne platform. At Hawaii, Tony Clarke is attempting to modify a small device for use on their 6 passenger Seneca; the goals are <100 lbs, eyesafe so no operator is required, and cost <\$60K.

## **Organic Content of Aerosols**

The organic carbon (OC) content of aerosols is not only a large fraction of aerosol mass in many regions but also influences the aerosol surface properties, heterogeneous chemistry,

humidity response, nucleation capabilities, optical properties and role as cloud condensation nuclei. As a result it is an important measurement that is not presently part of GTE capability. Measurements of organic aerosol have been historically less common than ionic composition due to more demanding analysis requirements as well as concerns over positive and negative artifact associated with the gain or loss of aerosol mass caused by semivolatile aerosol moving in and out of the gas phase. Sampling problems and a poor response time (often >30 min in the free troposphere) have hampered progress. However, improvements in techniques have resulted in ground based technology recently being adapted to aircraft measurements (INDOEX, SAFARI, ACE-Asia). These have employed diffusion denuders to strip gas phase organic species prior to aerosol sampling on filters. These can also be made with a size cut to resolve total and submicrometer organic carbon. Sampling times depend upon flows and aerosol concentrations but 15-30 min lag averages would still be common. Filter samples are then analyzed for OC by thermal desorption and evolved CO<sub>2</sub>. This approach has been shown to work on aircraft but generally requires high flow rates and pumping capacities that may be a burden on P-3B resources. Uncertainties are poorly known but expected to be on the order of 30%. It is unclear whether improved sensitivity will reduce these demands in the near future.

Other OC techniques are also emerging including liquid phase ion chromatography and detection by mass spectrometry (as at Aerodyne and SRI, using electron impact ionization). This and other emerging technologies are actively being pursued and reported. It is likely that improved techniques will become available in the 0-2 or 2-4 year time frame. Hence, while this is a medium priority measurement for the GTE program it is probably not necessary that GTE needs to support its development. However, GTE should be prepared to acquire such a capability and support integration into an aircraft payload as it becomes available.

### **Cloud Indicator**

A short-term, medium priority activity is to provide a sensor for clouds on the DC8. This is not an attempt to add cloud research capabilities. Rather, a facility level instrument needs to be present to determine when the DC8 is in cloud even when the plane is not flying other aerosol or cloud probes. This is required to interpret measurements of soluble gas phase species and radicals. A simple and robust commercial instrument needs to be identified, procured, and provisions made to keep it operating reliably over the long term.

### **Fast Aerosol Composition**

Expansion and extension of capabilities for bulk aerosol composition are a fairly high priority for the medium term. The existing instruments based on IC will continue to be needed but better size resolution, response time, and sensitivity (especially for nitrate) are all desirable. Several approaches can be considered. A recently commercialized aerosol mass spectrometer (AMS) has measured sulfate, nitrate, and, with less confidence, organics at several sites with excellent size resolution. Dedicated instruments based on separating aerosols from the gas phase (with impactors or denuders) followed by a species-specific detector (e.g. N, S, or organics) have

been developed for ground use. Finally, incremental improvements of the ion chromatography (IC) systems could yield benefits in time resolution and/or sensitivity.

Organic aerosols have been discussed earlier as a separate topic, as reflects the fact that organics are a substantial but poorly characterized component of aerosols throughout much of the troposphere. A fast and accurate measurement of aerosol organics is listed as a medium term priority because the techniques still require development. We note that both the AMS and IC techniques bring along important capabilities for organics that should be encouraged.

On a longer time frame, extension of bulk aerosol analysis to more elements (such as Al, Fe, V, As, ...) should be strongly considered in order to characterize aerosol sources and long-range transport of mineral dust. Single particle analysis is not a high priority for INTEX but could be useful for other missions either with more focus on aerosols or if the single particle analysis can provide information on air parcel history.

## **CO Lidar**

Due to the fundamental importance of CO in tropospheric chemistry, and its usefulness as a tracer of anthropogenic emissions, the need for a CO lidar was discussed. Such an instrument, with vertical resolution similar to DIAL, would provide detailed spatial resolution useful for chemical-transport modeling. It could also be useful for satellite validation studies. With no instrument currently available, development is to be encouraged. Feasibility studies are recommended in the 0-2 year time span. Coupling of CO and O<sub>3</sub> lidar would provide a powerful tool in evaluating anthropogenic perturbations on local and regional scales. Full research and development time could require more than is available for INTEX (>4 years).

Again, Browell (invited but unable to attend) provided comments after the workshop. He has been advocating a CO lidar to form a 2D map of anthropogenically influenced flows for several years. At Langley, they have simulated the measurements and determined the necessary requirements. An instrument is by no means ready, but with proper funding it could be put into development.

## **HO<sub>2</sub>/RO<sub>2</sub> Measurements**

The measurement of total peroxy radicals ( $RO_x = HO_2 + RO_2$ ) is highly desired for future GTE missions. Speciation among different RO<sub>2</sub>s would be nice but is of low priority to GTE. RO<sub>x</sub> is a key part of the odd hydrogen budget and is important to ozone production. RO<sub>x</sub> is therefore implicated in nearly all aspects of tropospheric oxidation. RO<sub>2</sub> (organic peroxy radical) is also the immediate product of hydrocarbon oxidation. Accurate measurements of RO<sub>2</sub> will provide a stringent test for present photochemical models. Measurement capability of 0.1 pptv in 60 s, and some confidence that nearly all the RO<sub>2</sub> expected to be of significance is detected, are desirable for GTE purposes.

Traditional RO<sub>x</sub> measurements have not been considered appropriate for GTE missions, either for reasons of uncertainty and interference (chemical amplifier methods) or time response (matrix isolation EPR). One promising method converts RO<sub>2</sub>s to OH by chemical conversion using NO, and the OH is subsequently measured (two techniques used by GTE can measure OH). By adjusting experimental conditions to favor HO<sub>2</sub> conversion over RO<sub>2</sub> conversion, discrimination can be achieved. Such an experiment was flown on an exploratory basis on TRACE-P and showed considerable promise. However much work remains to be done on zeroing, calibration, and testing; an intercomparison of instruments with others (for example, that measure HO<sub>2</sub> only) would be greatly desirable. The time frame for development of this to be GTE-ready is expected to be less than two years, at moderate cost. While this approach of chemical conversion to OH is promising, that fact should not preclude consideration of other approaches especially if they meet the measurement requirements but offer advantages in size, weight, speciation, etc.

### **Instrument Automation and Further Downsizing**

Automation and downsizing of some individual instruments are discussed under individual compounds and instruments. The subject was discussed from a more general approach. It was noted that not all the downsizing funded as a result of the 1996 workshop was successful. Instrument automation and the downsizing of existing instruments provide two benefits: (1) implementation of the latest technologies and instrument control, thus improving instrument performance; (2) reduction of size, weight, and often power that is required by the combination of instrument and investigators, thus increasing the capability of the aircraft to accommodate the measurement of more atmospheric chemical species, aerosol properties, and meteorological variables. Automation and downsizing also permit instruments to be used in aircraft wingpods, thus further increasing aircraft carrying capacity.

As aircraft payloads become more complex in order to better constrain the scientific problems, automation and downsizing will become increasingly more critical. In TRACE-P, P-3B payload weight limitations reduced aircraft scientific measurement capability below what was otherwise possible. Automation and downsizing are feasible to some extent for essentially all instruments currently in the GTE program. The barriers to downsizing are cost of smaller, lighter components, of more careful structural designs, and time. The barriers to automation can be cost, but are primarily technical expertise and time to implement automation procedures that mimic what the scientist does to run the instrument and correct instrument failures. The recommended action item is that automation and downsizing should be an ongoing activity with current instrumentation and should be strongly encouraged for new instrumentation.

The cost is moderate to high, depending on the instrument, and all time ranges (0-2, 2-4, and >5 years) are appropriate, again depending on the instrument.

## Wing Pod Usage

It was noted that the NOAA P-3B and the ER-2 both fly a considerable number of instruments in their wing pods, and these could be added to the NASA P-3B. Obviously the candidate instruments for mounting in wing pods must be automated. The additional weight could be compensated for by less fuel, although that would pose a lower limit on flight time.

The most obvious benefit from the use of wing pods for airborne instrumentation is the potential for expansion and increased diversity in the payload for the NASA P-3B research aircraft. The P-3B payload deployed during the TRACE-P campaign pushed the limits for cabin weight that can be safely flown. Additional weight (e.g., 1000 lbs. per wing) can be added to the wings without compromising the structural integrity of the P-3B airframe.

While putting instrumentation in wing pods frees cabin space for additional instrumentation, candidates for wing pod measurements must be evaluated in terms of both their reliability and their criticality to flight operations. One candidate might be a fast water vapor sensor. These water vapor sensors can be specifically designed to be attached to an aircraft wing. A fast water vapor sensor is of particular interest in supplementing the chilled-mirror hygrometer measurements on the P-3B which can have slow response under rapidly changing conditions (discussed above as a high priority issue). On the other hand, it is not clear that such a reliable enough sensor can be available in the next two year time frame. Another candidate would be a forward/downward looking aerosol lidar (also discussed earlier, of medium priority). This system would be a useful tool in providing data suitable for making real-time information to direct the aircraft during flight. It would not, however, be so critical as to cause a flight to be aborted if it failed during the flight. While ozone is certainly critical to mission success, the reliability with which it can be measured makes it a potential candidate for deployment in a wing pod. There is some development of more complicated measurement systems for which an automated version suitable for a wing pod have been or are being developed (e.g., CIMS and LIF). To the extent that they are not critical to mission success, deployment of these systems from wing pods should be encouraged.

For options involving water vapor or aerosol lidar measurements, the cost appears low since they may only involve purchase and integration with no need for development. Cost for other wing measurements is more difficult to assess, although, some instruments of ER-2 heritage may become suitable for relatively low investment.

Some use of wing pods is reasonable to expect in the near-time frame (0-2 years) with the use of water vapor and aerosol lidar sensors perhaps representing the easier and more promising additions in time for the INTEx mission (note however the caveat expressed above concerning a water vapor sensor. Other wing pod measurements require a commitment over a longer time frame, but the possibility that some might be ready in time for INTEx should not be ruled out.

## **CO<sub>2</sub> Flux**

Presently a flush radome pressure system (Turbulent Air Motion Measurement System, or TAMMS) is available on the Wallops P-3B aircraft to make 3-component wind field measurements. The system is capable of providing vertical winds within an accuracy of 10 cm/sec. Flux measurements were obtained during TRACE-P via the eddy-correlation technique by coupling fast vertical winds with fast CO<sub>2</sub> and SO<sub>2</sub> measurements. All air motion and trace species parameters were recorded at 50 Hz on the TAMMS data acquisition system.

CO<sub>2</sub> measurements can be provided by a modified microprocessor-controlled non-dispersive infrared gas analyzer (NDIR). The instrument measures the difference in light absorption between the sample and a reference gas flowing through identical optical absorption cells. Sensor and flow system are kept relatively insensitive to aircraft altitude by operating at a constant mass flow and pressure. The NDIR is temperature stabilized to minimize environmental temperature sensitivity and a dryer is utilized upstream to eliminate the need for water vapor corrections and apparent fluxes arising from density fluctuations.

A forward-facing Rosemount droplet-excluding probe, located within 1 meter of the NDIR instrument to minimize sampling time, is utilized for sampling. The sampling frequency for CO<sub>2</sub> fluxes during TRACE-P was 10 Hz and measurement precision was ~ 60 ppbv. All indications and results acquired during the TRACE-P mission utilizing the presently available suite of instruments suggest terrestrial CO<sub>2</sub> flux measurements are feasible. For the measurement of oceanic fluxes, where a precision on the order of 10 ppbv is required, a modest investment to upgrade current instrumentation would be necessary.

## **OH Loss Rate Measurement**

Current attempts to reconcile fast photochemical theory with measurements involve comparisons of measured HO<sub>x</sub> (OH + HO<sub>2</sub>) with values predicted using detailed photochemical box models. The availability of these HO<sub>x</sub> measurements as test species represents a significant advance over the use of species like NO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and CH<sub>3</sub>OOH which are more indirect indicators of fast photochemistry. While agreement between measurement and theory for HO<sub>x</sub> species is encouraging, it does not shed light on the rate of cycling for HO<sub>x</sub> through the photochemical system. Any given HO<sub>x</sub> value can result from a wide range of possible production and loss rates. A total OH loss rate measurement provides a critical test of photochemical theory independent of the actual HO<sub>x</sub> concentration. Agreement/disagreement in OH loss would be a valuable tool in determining whether differences in predicted concentrations are most likely due to missing HO<sub>x</sub> sources or sinks.

The total OH loss rate measurement has been developed and deployed in four ground-based field campaigns in 1999-2001. The measurement requires moderately sensitive OH detection, which can be provided as part of instrumentation to measure atmospheric OH and HO<sub>2</sub>. The technique uses the discharge flow technique, in which OH, produced in a moveable probe, is added at different distances from the detection to the flow of ambient air. The decay of

the added OH is measured as the movable probe is pulled back. Adaptation to aircraft requires an increase of the measurement frequency and consideration of pressure effects on the assumptions of the discharge flow techniques.

OH loss rate capability should be encouraged and developed as part of ongoing efforts, with additional cost to GTE. The cost should be low, and the time to adapt it to aircraft will be in time for the INTEX mission.

### **Fast PAN**

The current methods for PAN generally use GC-ECD methods. They have the advantage of high sensitivity (~ 1pptv), high specificity, and the ability to simultaneously measure a suite of other important trace chemicals (e.g., C<sub>2</sub>Cl<sub>4</sub>, PPN, alkyl nitrates). The main disadvantage is that these methods are somewhat slow (2-5 min). To achieve fast PAN two approaches are possible:

1. (0-2 years): Make the current GC-ECD methods as fast as possible. Measurement frequency can probably be cut in half. However, this may require sacrificing the other chemicals (C<sub>2</sub>Cl<sub>4</sub>, alkyl nitrates) measured by these systems. Detection limits may be reduced some (~5 pptv). Clear definitions of needs are appropriate at the present time, and tests of modified GC-ECD instruments could be carried out.
2. (2-4 years): There are no known reliable methods for continuous and sensitive detection of PAN. PT-MS does offer some possibilities and an instrument operated by the University of Innsbruck has flown on an aircraft in TexAQS 2000. An extended research effort is needed to test and evaluate the sensitivity and specificity of such an instrument.

### **Fast NMHCs**

A medium priority is for a fast-response technique for certain NMHCs. The existing grab sample system run by UC Irvine provides an excellent suite of molecules. The number of cans provides adequate temporal coverage (an average of a few minutes with capability to adjust for special events) but much faster time response (a few seconds) as well as real-time information would be very desirable for a subset of species. The scientific goal is to measure a subset that would characterize sources. Specific compounds would vary for identification of urban areas and biomass burning; isoprene is the obvious choice for continental biogenic emissions although no viable methods of rapid measurement is known. However, the exact list of measured species should be determined by the interplay between instrumental capabilities and the tracer value. One example of a promising technique is PT-MS, but at this time a broad array of techniques should be considered.

### **PNA (HNO<sub>4</sub>)**

Pernitric acid plays a critical role in the photochemistry of the upper troposphere but there are no in situ measurements available at the present time. A PNA measurement would be valuable on the DC-8 platform during a photochemical study. In particular, a PNA measurement technique that can be combined with HNO<sub>3</sub>, NO<sub>2</sub>, or NO<sub>y</sub> measurements would provide the greatest value. Several techniques

(CIMS, programmed thermal decomposition followed by NO<sub>2</sub> detection) are in development and a flight ready system should be possible on a two year time scale. The required detection limit is less than 5 pptv in a one minute integration period.

### **Low Priority**

Except for SO<sub>2</sub>, these low priority items received little attention and write-ups were not assigned. The comments are from the workshop as a whole. Though it will not be so important during INTEX, SO<sub>2</sub> has been important in past GTE expeditions in remote marine areas and is therefore included. Comments from Eisele on H<sub>2</sub>SO<sub>4</sub> received after the workshop are also noted.

### **Other Organic Nitrates**

Some of these are currently analyzed at NCAR using some of the UC Irvine sampling can contents. This seems to be sufficient for GTE purposes.

### **NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>**

These compounds were considered as low priority for GTE, although one participant commented that N<sub>2</sub>O<sub>5</sub> may be of interest concerning nitrate aerosol formation.

### **Halogens**

Organic halogen measurements are very good and sufficient for GTE. Measurement of inorganic halogens is still exploratory and it is not clear that GTE should pursue this.

### **Organic Acids**

These are now adequately measured on GTE missions. Their relatively low importance to GTE does not warrant any further instrumentation.

### **HCN/RCN**

The importance of these compounds to GTE is not clear, and instrumentation work is not needed. Specific instrumentation needs were not discussed.

### **Hg**

No comments were made after this was added to the list.

## **SO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>**

Sulfur dioxide (SO<sub>2</sub>), primarily an anthropogenic combustion product, is a valuable tracer of anthropogenic pollution plumes. SO<sub>2</sub> oxidation downwind of sources provides information on combustion sources to pollution plumes and on the oxidation processes that are occurring as the plume moves downwind. SO<sub>2</sub> oxidation results in sulfuric acid, which is a major component of aerosol and acid rain. Thus, SO<sub>2</sub> measurements provide a link between gas-phase and aqueous-phase chemistry and aerosols.

Several techniques exist, but many do not have the sensitivity appropriate to measure SO<sub>2</sub> distant from source regions. Required detection limits are 5 pptv in 300 seconds. A few techniques are available, including the fast mass spectrometric technique at Drexel and the slower technique from the University of New Hampshire (mist chamber with alkaline solution – difference from total sulfate). A preliminary intercomparison suggests large differences between the two techniques. These differences between TRACE-P techniques need to be resolved. In addition, other fast techniques may be desirable.

SO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> have been a key component of previous GTE programs, especially concerning the formation of sulfate aerosols. They are in the priority 3 category for INTEX. H<sub>2</sub>SO<sub>4</sub> is measured adequately using CIMS on the P-3B. Georgia Tech could modify a CIMS instrument to do this on the DC-8 if desired, although there seems to be no near term (4 years) need.

Such development would require moderate costs for existing instruments but high costs for new developments. The time period would be 0-2 years for existing techniques, and 2-4 years for new techniques.