

Annex 2:

Advances in Measurement Methods for Atmospheric Chemistry

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1 **Section 1: Laboratory Methods**

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5 **Recent advances**

6 Our knowledge of the details of tropospheric chemistry has increased
7 tremendously over the last ten years. This increase is in part related to the
8 sheer volume of work done, but is also a consequence of the incorporation of
9 new measurement techniques. The largest source of data has been the
10 environmental or “smog” chambers, which provide integrated pictures of the
11 overall chemistry. However, the methodology often suffers from an inability
12 to isolate the particular reaction of interest. Furthermore, wall reactions are
13 often irreproducible, and differ from chamber to chamber. On the other hand,
14 direct, time-resolved spectroscopic methods can be designed to study a single
15 species undergoing a single reaction. However, the conditions under which
16 that species can be studied are often far removed from those encountered in
17 the atmosphere, and care must be exercised when extrapolating the results to
18 the real world. Clearly, the most progress has been made where direct and
19 indirect methods have been integrated to test our understanding at both the
20 microscopic and macroscopic levels. Some of the major advances in
21 laboratory techniques are highlighted below, along with future trends.

22 **Ozone/HO_x Photochemistry**

23 The photolysis of ozone to produce O(¹D), followed by the reaction of
24 O(¹D) with H₂O, provides the largest source of OH in the lower atmosphere.
25 The study of the quantum yields for ozone photolysis (in particular in the
26 “energy-deficient” region beyond 310 nm) has long fascinated physical
27 chemists and has even been the subject of some controversy over the years
28 [Ravishankara *et al.*, 1998]. However, in the last several years, major
29 advancements have been made in our understanding of the processes involved
30 in ozone photolysis. The techniques used have included traditional methods
31 such as resonance fluorescence or laser induced fluorescence, but have also

1 included more advanced techniques “borrowed” from the chemical physics
2 community. For example, the excited $O(^1D)$ and $O_2(^1\Delta_g)$ photofragments have
3 been detected using a Resonance Enhanced Multi-Photon Ionization (REMPI)
4 technique [Ball *et al.*, 1993] or by vacuum ultraviolet laser induced
5 fluorescence [Takahashi *et al.*, 1996]. Studies conducted in molecular beams
6 have allowed the ozone to be prepared with a minimal amount of internal
7 energy, so that the wavelength of the threshold can be determined with high
8 accuracy. The direct detection of all possible photofragments, $O(^3P)$, $O(^1D)$,
9 $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$, in all possible combinations has now been accomplished
10 and the presence of a clear “tail” in the $O(^1D)$ quantum yields beyond 310 nm
11 (the result of both the photolysis of internally excited ozone and the
12 occurrence of spin-forbidden photolysis pathways) has firmly been
13 established. Corroborative evidence for the existence of this long wavelength
14 tail has been obtained from *in situ* measurements of the $O(^1D)$ production rate
15 using chemical actinometry [Shetter *et al.*, 1996]. Calculated photolysis rates
16 only show a good agreement with such actinometer measurements
17 (particularly at high solar zenith angle) when the long-wavelength tail is
18 incorporated into the calculation.

19 A great deal of improvement has been made in the database for the
20 kinetics of the reactions of OH with organic species (including hydrocarbons,
21 halocarbons, and organosulfur compounds [Atkinson, 1997a]. Improvements
22 in measurement techniques have allowed OH to be measured in pressures up
23 to 600 Torr O_2/N_2 in both flash photolysis [Hynes *et al.*, 1995; Brown *et al.*,
24 1999] and flow tube systems [Abbatt *et al.*, 1990], in spite of the rapid
25 quenching of the fluorescence that occurs under these conditions. The
26 versatility of flow tube experiments has been extended by the use of high
27 pressure turbulent flow systems [Abbatt *et al.*, 1990, Seeley *et al.*, 1996]. The
28 database has particularly been improved at low temperature, in large part due
29 to the care taken in sample purification [Vaghjiani and Ravishankara, 1991].

1 **Isoprene / Terpene Oxidation Mechanisms**

2 Much of the progress in isoprene chemistry has occurred using
3 traditional smog chamber techniques, or variations thereupon. While the major
4 pathways to methylvinyl ketone and methacrolein have been quantified by
5 Atkinson and coworkers using Fourier Transform Infrared Spectrometry/GC
6 [Tuazon and Atkinson, 1990] and by Paulson *et al.* [1992] using GC, there
7 still exist many uncertainties in the yields of minor products, particularly
8 under conditions of low NO_x. The atmospheric pressure ionization (API) mass
9 spectrometric technique has been used by Atkinson's group to identify the
10 presence of hydroxycarbonyls not detected by traditional techniques (Kwok *et*
11 *al.*, 1995). Jeffries and co-workers [Yu *et al.*, 1995] have implemented the
12 technique of derivatization using O-(2,3,4,5,6-pentafluorobenzyl)
13 hydroxylamine hydrochloride (PFBHA) which enables the identification of
14 many reactive carbonyls and acids which otherwise would not be amenable to
15 detection by standard chromatographic methods [Yu *et al.*, 1998; 1999]. Both
16 these new techniques need some development before they can be considered
17 quantitative, but offer the possibility of quantifying multifunctional products.
18 The oxidation of terpenes has been less well studied, with each of the terpenes
19 subject to only 2 or 3 investigations. The range of reaction products is wide,
20 and the mass balances obtained are poor. The chemistry of the oxygenated
21 reaction products remains poorly quantified.

22 Much work in the last few years has been dedicated to understanding the
23 chemistry of alkoxy radicals [Atkinson, 1997b]. Alkoxy radicals provide a
24 branching point in the oxidation of most hydrocarbons, and the competition
25 between the various reaction pathways determines the rate at which the carbon
26 chain gets shortened, and influences the degree of oxidation, and ultimately
27 the solubility, of the stable reaction products formed. The majority of studies
28 have been performed in smog chambers by studying the relative rates of
29 formation of the various products. However, recent chamber studies at lower
30 temperatures have indicated that the oxidation chemistry of even simple
31 organics such as ethene may be more complicated than inferred from room
32 temperature studies [Orlando *et al.*, 1998]. A few studies using direct

1 spectroscopic detection have been performed, but these are limited to small
2 alkoxy radicals derived from alkanes [*Devolder et al.*, 1999; *Blitz et al.*, 1999].

3 **Aerosol Formation / Heterogeneous Chemistry**

4 Several improvements in instrumentation have led to a better
5 understanding of aerosol formation and growth at the microscopic level.
6 Kulmala and coworkers have performed both experimental and theoretical
7 studies on nucleation of sulfuric acid – water mixtures. Ball et al. made use of
8 an ultrafine condensation nuclei counter to detect particles in the early stages
9 of growth (diameter \approx 3 nm), and thereby infer the nucleation rate. The use of
10 Chemical Ion Mass Spectroscopy (CIMS) made detection of very low
11 concentrations of sulfuric acid possible. Both these groups concluded that the
12 functional dependence of the nucleation rate on water and sulfuric acid was
13 much stronger than given by older theory, but in reasonable accord with field
14 experiments. Nucleation was also strongly enhanced in the presence of NH_3 .
15 The electrostatic balance (particle levitation) has been used to follow the
16 deliquescence behavior of NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ particles [*Imre et al.*,
17 1997; *Xu et al.*, 1998]. In this technique, a charged particle is trapped by an
18 electric field, its mass is measured by the magnitude of the restoring force, and
19 its physical state inferred from measurement of scattered laser light.

20 A variety of different aerosol detection techniques have been applied to
21 quantify the formation of aerosol from terpene oxidation. While the potential
22 for the formation of aerosol particles from biogenic hydrocarbons has long
23 been recognized, descriptions of particle growth are still largely empirical,
24 describing the yield of particulate matter as a function of the extent of
25 oxidation [*Odum et al.*, 1996; *Hoffmann et al.*, 1997]. However, it is not clear
26 whether this parameterization can be simply transferred to atmospheric
27 conditions. It is thought that particle nucleation, or initial growth on seed
28 nuclei, involves the deposition of low-volatility products, often formed in
29 small amounts, followed by ad- or absorption of more volatile products into
30 the organic layer formed.

1 Tropospheric heterogeneous chemistry is a relatively new and untapped
2 research area. Atmospheric pressure flow reactors have been used to measure
3 the coefficients for reaction of gaseous N_2O_5 directly on monodispersed,
4 submicron sulfuric acid aerosols [*Mozurkewich and Calvert 1988; Fried et al.*,
5 1994; *Lovejoy and Hanson, 1995*]. The use of the measured reaction
6 coefficients in tropospheric modeling studies [*Dentener and Crutzen, 1993*]
7 indicates strongly that heterogeneous reactions in the troposphere can be very
8 important; for example, it is estimated that for January in the troposphere
9 north of 45°N , more than 90% of all NO_x is removed by the heterogeneous
10 reaction, $\text{N}_2\text{O}_5 + \text{H}_2\text{O}(\text{aerosol}) \rightarrow 2\text{HNO}_3$. Much progress has been made in
11 understanding the uptake of organics onto aqueous or acidic aerosol using the
12 falling droplet technique pioneered by Aerodyne/Boston College [*Jayne et al.*,
13 1992]. These experiments often yield values for both the uptake parameters
14 and the solubility constants, and the suite of molecules investigated includes
15 carbonyls, acids, alcohols and sulfur gases. Less is known about the chemical
16 transformations that occur in aqueous tropospheric aerosols. While the aerosol
17 offers abundant surface area for uptake the small volume may limit the extent
18 to which gas-phase chemistry may be influenced. However, the very
19 concentrated solutions encountered could lead to rapid reaction rates under the
20 right circumstances. The interaction of common atmospheric oxidants with
21 organics, and particularly the effects of ambient light need to be investigated
22 in detail before a full understanding of the impact of aerosol on biogenic
23 carbon (and vice versa) can be determined.

24 **Instrument Intercomparisons**

25 Instrument intercomparisons are vital and indeed as much a part of doing
26 atmospheric research as is gathering data to test a geophysical hypothesis. A
27 reliable estimate of the uncertainty in a measurement is as important as the
28 measurement itself. A great variety of intercomparisons have been carried out
29 during the past ten years. Techniques and methods to measure many of the
30 atmospheric gases have been evaluated quantitatively; for example: NO_2
31 [*Fehsenfeld et al., 1990*]; CH_2O [*Gilpin et al., 1997*]; and hydrocarbons [*Apel*

1 *and Calvert, 1994; Apel et al., 1999*]. Atmospheric scientists should continue
2 to show an honest skepticism about the accuracy of measurements derived
3 from any new atmospheric component measurement technique until such time
4 that it has been proven through adequate testing and evaluation in blind
5 intercomparisons and through other careful laboratory and field testing.

6 **Future trends**

7 **Optical Spectroscopy**

8 The use of cavity ring-down spectroscopy has been demonstrated as
9 being a very sensitive way to detect free radicals. Since it is an absorption
10 technique it is not subject to the effects of quenching as encountered with
11 fluorescence techniques, while the sensitivity may approach that of LIF for
12 larger molecules. Other advances in laser technology (diodes, near UV, near
13 IR) could lead to improvements in techniques for detecting peroxy and/or
14 alkoxy radicals. Part of the reason for the improvements in precision in the last
15 ten years is related to the wider availability of better lasers and signal
16 acquisition hardware. It should also be noted that a better detection sensitivity
17 allows lower radical concentrations to be used, which in turn minimizes the
18 effects of secondary reactions. As further developments in instrumentation
19 occur they will undoubtedly be incorporated into laboratory systems, too.

20 **Hydrocarbon Oxidation**

21 Much work still needs to be done on the chemistry of oxygenated
22 reaction products, particularly multifunctional carbonyls. Derivatization
23 techniques for carbonyls are constantly being improved and incorporated into
24 both laboratory and field studies. Mass spectrometric methods (API, CIMS)
25 have rapid time response and high sensitivity, and could be used in time-
26 resolved laboratory studies if appropriate conditions can be found. The
27 sensitivity and selectivity of CIMS has been demonstrated both for stable
28 molecules [*Lovejoy and Hanson, 1995*] and for free radicals [*Villalta and*
29 *Howard, 1996*].

1 The chemistry of alkoxy radicals remains central to our understanding of
2 hydrocarbon chemistry. Most of the work to date has been done using
3 competitive product studies. Some direct spectroscopic techniques have been
4 used, but at present they tend to be labor intensive. The development of more
5 general techniques, applicable to several different radicals, would be useful.

6 **DMS Oxidation**

7 There still exist many problems in identifying and quantifying the
8 intermediate radicals in DMS oxidation. The intermediates studied directly
9 include CH_3S by LIF [Tyndall and Ravishankara, 1989; Turnipseed *et al.*,
10 1992] and CH_3SO by mass spectrometry [Mellouki *et al.*, 1988; Dominé *et al.*,
11 1990]. Both mass spectrometric and optical techniques should be developed to
12 further investigate the reaction mechanisms. The key branching steps to the
13 formation of SO_3 and MSA and their dependence on temperature and NO_x
14 [Sørensen *et al.*, 1996; Patroescu *et al.*, 1999] need to be identified through
15 direct laboratory studies in conjunction with chamber studies.

16 **Heterogeneous Chemistry**

17 Continuing laboratory studies should elucidate the details of nucleation
18 of particles, particularly those comprised largely of organic materials. Most
19 studies to date have been on “model” mixtures on binary mixtures, e.g.,
20 sulfuric acid – water. A better understanding of the conditions required for
21 nucleation will enable the extent of new particle formation in the atmosphere
22 to be assessed. It is particularly important to isolate the effects of the
23 individual oxidants, e.g., OH, NO_3 or O_3 since these oxidants tend to be
24 important in different regions of NO_x or solar intensity, and each leads to
25 products of differing volatility.

26 Formation of “intermediate” clusters. Study by mass spec; see
27 particle forming. Single particle studies.

28 The question of chemistry inside, and particularly on the surface of,
29 particles needs to be addressed more systematically. Currently, the identity
30 and concentrations of oxidants within aqueous aerosol particles have not been
31 thoroughly studied. The oxidation of partially oxygenated compounds

1 removed from the gas phase could continue inside droplets and influence not
2 only the measured concentrations but also the physical properties of the
3 particles. Finally, the occurrence of reactions on the surface of (organic)
4 aerosol needs to be first demonstrated and then thoroughly investigated. This
5 is a new field which has been the subject of speculation for many years, but
6 which has not been quantified satisfactorily to date.

7 **Intercomparisons**

8 Several different techniques of measurement of the OH radical
9 concentration in the troposphere have been developed, for example the ion-
10 assisted OH measurement [*Tanner et al.*, 1997], laser induced fluorescence
11 [*Hofzumahaus et al.*, 1996; *Mather et al.*, 1987] and long path absorption
12 spectroscopy [*Dorn et al.*, 1996a]. These techniques have been improved
13 greatly during the past ten years, and their use is now extensive throughout the
14 world. It is suggested that the atmospheric scientists plan an IGAC sponsored
15 intercomparison involving measurement of the most important atmospheric
16 transient species, OH radical, using blind tests in air mixtures prepared in a
17 common manifold in the laboratory and in field studies at a common site
18 under a variety of atmospheric conditions.

19 **Summary**

20 Tropospheric homogeneous and multiphase chemistry have both seen
21 impressive expansions in the last ten years. Tropospheric chemistry,
22 particularly relating to biosphere-atmosphere interactions, tends to be complex
23 and, to date, not enough studies have been carried out to fully test the
24 reproducibility of many of the different systems studied in the laboratory. In
25 this sense, the discipline is still immature, and much work remains to be done
26 to validate the current database and further extend it. Our understanding of
27 heterogeneous and multiphase systems is largely based on data from bulk
28 systems at the moment. Further developments in measurement techniques will
29 undoubtedly lead to a continued appreciation of the complexities and
30 subtleties of the chemical reactivity in the atmosphere.

1 **Section 2: *In situ* Aerosol Measurements**

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5 **Introduction**

6 In this section we examine the role of in-situ aerosol measurements¹ in
7 addressing global-scale scientific questions. To do this in a coherent way, we
8 focus on a single, well-defined problem - direct climate forcing by
9 anthropogenic aerosols^{2,3}. As a result of this focus, only a small subset of
10 aerosol measurement techniques will be mentioned. Readers interested in a
11 general review of aerosol measurements are referred to the excellent treatment
12 by McMurry (1998).

13 A major development in climate research over the last decade has been
14 the recognition that anthropogenic aerosol particles - and not just greenhouse
15 gases - are significant players in altering the Earth's energy budget (IPCC,
16 1996). For example, Hansen et al. (1998) have referred to a "paradigm
17 change" wherein "uncertainties in climate forcings have supplanted global
18 climate sensitivity as the predominant issue." Figure 2 from that paper
19 indicates that the *sign* of the net global forcing over the industrial era is
20 unknown, within current uncertainties, and that the largest uncertainties
21 involve anthropogenic aerosols. Thus, it is appropriate that improved
22 quantification of aerosol climate forcings is a major focus of current research.
23 Even for the direct aerosol effect (the best-posed problem), this is a
24 challenging observational undertaking, given the spatial non-uniformity of

¹ Measurements where the instrument or sampling device is collocated with the aerosol; distinct from "remote measurements."

² A "climate forcing" is a *change* in global or regional net irradiance (W m^{-2}) at the top of the atmosphere (or some other height), imposed by some agent (such as human activity) that is external to the climate system.

³ "Direct" forcing by aerosols refers to the scattering or absorption of solar radiation by the particles themselves and is distinguished from "indirect" forcing, which involves particle-induced changes in cloud brightness or extent.

1 aerosol particles and their complex and highly variable optical properties.
2 How well has the measurement community responded to this challenge over
3 the last decade? What are the prospects and challenges for the future? We
4 will address these questions not only in relation to instrumental techniques but
5 also in terms of the development of a practical observational strategy.

6 **Recent advances**

7 **Parameters requiring measurement**

8 A cogent argument for the importance of climate forcing by
9 anthropogenic sulfate aerosols was put forward in 1990 (Charlson et al.,
10 1990). Subsequent papers confirmed and refined this argument (e.g. Kiehl
11 and Briegleb, 1993) and extended it to other anthropogenic aerosol
12 components, primarily biomass smoke (Penner et al., 1992), mineral dust from
13 disturbed regions (Sokolik and Toon, 1996), and light-absorbing soot
14 (Haywood and Shine, 1995). As a result of these and many other studies,
15 direct climate forcing by anthropogenic aerosols was shown to be important as
16 well as highly uncertain. Improved quantification was framed in terms of a set
17 of critical, measurable properties of the aerosol (Penner et al., 1994; Ogren,
18 1995). Table 1, adapted from Ogren (1995), lists the most important of these
19 parameters, separating them into *extensive* and *intensive* categories⁴.
20

⁴ An extensive parameter depends on the amount of aerosol material present while an intensive parameter (frequently the ratio of two extensives) does not.

Table 1: Measurable parameters for quantifying direct aerosol forcing

a. Extensive parameters

$\sigma_{sp}(\lambda)$, $\sigma_{bsp}(\lambda)$, $\sigma_{ap}(\lambda)$	Scattering, hemispheric backscattering, and absorption components of the aerosol light extinction coefficient, $\sigma_{ep}(\lambda)$ (also called the volume extinction cross-section), at wavelength λ , all with units of m^{-1} .
M_i	Mass concentration of aerosol component i (or of the total aerosol), with units of $\mu g\ m^{-3}$.
$\tau(\lambda)$	Aerosol optical depth, defined as the vertical integral of $\sigma_{ep}(\lambda)$, dimensionless.
$\tau_{180}(\lambda)$	180° backscattering coefficient, with units of $m^{-1}\ sr^{-1}$.

1

b. Intensive parameters

$b(\lambda)$	The hemispheric backscatter fraction, defined as $b_{\text{bsp}}(\lambda) / s_{\text{sp}}(\lambda)$.
$s_{\text{sp}}(\lambda)$	Aerosol single scattering albedo, defined as $s_{\text{sp}}(\lambda) / e_{\text{p}}(\lambda)$.
α	Ångström exponent describing the wavelength dependence of extinction, defined as the exponent in the functional relationship, $e_{\text{p}}(\lambda) = e_{\text{p}}(\lambda_0) (\lambda / \lambda_0)^{-\alpha}$, where e_{p} can refer to $s_{\text{sp}}(\lambda)$, $b_{\text{bsp}}(\lambda)$, or $a_{\text{p}}(\lambda)$.
$CF_i(\lambda)$	The fraction of e_{p} due to coarse mode particles, where the coarse mode is operationally defined as all particles with low-RH aerodynamic diameters larger than $1 \mu\text{m}$ and e_{p} can refer to $s_{\text{sp}}(\lambda)$, $b_{\text{bsp}}(\lambda)$, or $a_{\text{p}}(\lambda)$.
$f_j(\text{RH})$	Hygroscopic growth factor for parameter j , a multiplier that describes dependence of the parameter on relative humidity (RH). Parameter j can be $s_{\text{sp}}(\lambda)$, $b_{\text{bsp}}(\lambda)$, $a_{\text{p}}(\lambda)$, α , M_i , or $m_i^*(r)$.
$f_{i,j}(\lambda)$	Mass extinction efficiency for component i and parameter j , defined as $f_{i,j} = \frac{f_j}{fM_i}$, where f_j can be $s_{\text{sp}}(\lambda)$, $b_{\text{bsp}}(\lambda)$, or $a_{\text{p}}(\lambda)$, with units of $\text{m}^2 \text{g}^{-1}$.
$m_i^*(r)$	Normalized distribution of the mass of component i (or of the total aerosol) with respect to particle radius, r , defined as, $m_i^*(r) = \frac{1}{M_i} \frac{fM_i}{f \log(r)}$
$S_a(\lambda)$	Aerosol extinction-to-backscatter ratio, defined as $e_{\text{p}}(\lambda) / b_{\text{bsp}}(\lambda)$.

1

2

3 **Observational strategies**

4 Table 1 begins to show the complexity of the observational challenge.

5 The dimensions over which aerosol properties display important variations

6 include space (from turbulent to continental scales), time (from turbulent to

7 interannual scales), height, relative humidity, chemical composition, size

8 parameter (particle size relative to wavelength), and scattering angle. Thus,

1 the observational task amounts to filling in a seven-dimensional matrix of
2 required information, where five of the dimensions have of order 10 elements,
3 the geographical/spatial dimension has 4 million elements (for 10 km global
4 resolution), and the time dimension has 9000 elements (for hourly time
5 resolution over one year.) Clearly, a brute force approach is not an option.
6 Rather, a feasible measurement program must be highly strategic in nature and
7 must involve tight coupling with both satellite observations and numerical
8 models. The measurement strategy has two basic elements: the *development*
9 of suitable measurement methods and their *deployment* in the field.

10 **Method development**

11 In-situ instruments and sampling techniques must be developed to
12 enable demonstrably accurate measurements of a small but highly leveraged
13 subset of optical properties. These measurements are needed for initializing
14 and testing aerosol optical models, chemical transport models, and satellite
15 retrieval algorithms. Two difficult and frequently neglected aspects of method
16 development are critical to the direct forcing problem. *Standardization* of
17 instruments, sampling methods, and data reduction procedures is required
18 since measurements from different times and places must be comparable. In
19 addition, robust procedures for *determination of uncertainties* are required
20 both to allow measurement error to be distinguished from ambient variability
21 and so that the degree of constraint imposed by the measurements on models
22 and satellite retrievals is known. Much of the progress during the 1990's has
23 been in these two areas.

24 Light scattering

25 A large fraction of the parameters listed in Table 1 flow from the
26 measurement of light scattering by nephelometry. Nephelometer technology
27 has steadily evolved over the past 50 years (Heintzenberg and Charlson,
28 1996), with demonstrated accuracy improving from roughly a factor of two in
29 the 1960's to around 10% in the 1990's. Recognizing the need for a
30 standardized instrument, a group of scientists collaborated with TSI, Inc. in
31 the early 1990's to develop a high-sensitivity, commercial version. This

1 instrument (TSI model 3563) has been subjected to rigorous noise and
2 calibration tests (Anderson et al., 1996) and protocols for sampling, field
3 calibration, and data reduction have been published (Anderson and Ogren,
4 1998). Since becoming available, it has been broadly embraced by the
5 measurement community and is now routinely deployed in field experiments
6 by a large number of research groups.

7 The model 3563 nephelometer measures σ_{sp} and σ_{bsp} at three
8 wavelengths spanning the visible range (450, 550, and 700 nm). It therefore
9 allows a direct calculation of backscatter fraction, b , which is a proxy for the
10 asymmetry parameter, g , used in many radiative transfer models (Marshall et
11 al., 1995). In addition, it allows ω_0 to be calculated over two discrete
12 wavelength ranges.

13 When combined with size segregation at 1 μm diameter as
14 recommended by Anderson and Ogren (1998), the nephelometer allows a
15 calculation of the coarse-mode fraction of scattering, CF_{sp} . This parameter is
16 a useful predictor of many other optical properties, since the optical
17 characteristics of sub- and super-micron particles are quite distinct. In
18 addition, it is strongly related to aerosol composition and source, since super-
19 micron aerosol mass is generally dominated by mechanically-produced
20 particles (e.g. dust, seasalt, flyash, or vegetative debris) while sub-micron
21 mass is generally dominated by secondary or combustion-derived particles
22 (e.g. sulfates, organics, or soot).

23 Because of its enclosed chamber, the nephelometer is suitable for
24 controlled-RH measurements (Covert et al., 1972), which allows a direct
25 determination of $f_{sp}(\text{RH})$. Nephelometer measurements also contribute to
26 determining component scattering efficiencies, $\omega_{i,sp}$, and single scattering
27 albedo, ω_0 , discussed below.

28 Recently, nephelometer technology has been extended to the
29 measurement of the 180° backscatter coefficient (Doherty et al., 1999),
30 permitting a tight coupling of in-situ and lidar techniques. In particular, it
31 permits a calibrated, in-situ measurement of the extinction-to-backscatter

1 ratio, S_a , which is the primary aerosol property required for quantitative lidar
2 retrievals.

3 Mass scattering (and absorption) efficiencies

4 The scattering efficiency of an aerosol component is the essential
5 parameter linking its mass concentration (which can be predicted from source
6 emissions and chemical transport models) to the scattering of visible light for
7 calculations of its direct radiative forcing. In a review of this topic, focused
8 on the example of sulfate scattering efficiency, Charlson et al. (1999) describe
9 a number of important and often subtle complications. In part, these arise
10 from inherent difficulties in any attempt to apportion a population effect
11 among members of that population⁵. However, Charlson et al. show that
12 consistent and useful results can emerge from a strategy based on practical
13 realities of both aerosol chemistry and aerosol instruments. Approaches to
14 measuring scattering efficiencies divide into two, complementary categories:
15 (1) multiple linear regression of the scattering coefficient against aerosol
16 component masses and (2) Mie calculations based on the size distribution of
17 chemical components combined with other information on refractive index
18 and state of mixture. For sulfate, Charlson et al. show that consistent results
19 emerge from these approaches and support about a factor-of-two range in
20 values for anthropogenically-perturbed aerosols. This consistency requires,
21 however, that the sulfate component includes the masses of chemically bound
22 cations and water but not but masses of other aerosol compounds that are
23 merely correlated with sulfate due to collocated sources or common sinks. In
24 this sense, the sulfate ion - which can be measured readily and with high
25 accuracy - is used as an indicator species for the sulfate component but must
26 not inadvertently be taken as an indicator for pollution aerosol in general.
27 Other issues discussed by Charlson et al. include relative humidity effects, the
28 need to treat ammonia species differently from sulfates, and the need to assess

⁵ Consider, for example, the shadow cast by a grove of trees. The question, "What fraction of the shadow is due to this individual tree?" is ultimately ambiguous. Other examples, specific to extinction apportionment are discussed by White (1986).

1 covariances between scattering efficiencies and other parameters that control
2 direct radiative forcing.

3 For the case of light absorption, an alternative to the mass-based
4 approach has been proposed by Bond et al. (1998). These authors show that
5 current estimates of mass emission rates for black carbon (the dominant
6 aerosol absorber) are fraught with difficulties and are likely to be seriously in
7 error. As a complementary (and possibly preferable) approach, they propose
8 that the emission rate of light absorption be measured directly for various
9 types of combustion and that transport models use light absorption, not black
10 carbon mass, as the prognostic variable. Demonstration of this technique at a
11 coal-burning power plant revealed emission rates of light absorption that were
12 an order of magnitude lower than what would be inferred from published
13 mass-based emission factors.

14 Single scattering albedo

15 The radiative effects of atmospheric aerosols are critically sensitive to
16 the relative amounts of scattering and absorption, expressed in the parameter
17 (Haywood and Shine, 1995). While the measurement of τ_{sp} is relatively
18 mature and accurate (see 1.1), the measurement of τ_{ap} is not. The latter,
19 therefore, is what limits the accuracy of current measurements of τ_{sp} .

20 The measurement of the aerosol light absorption coefficient, τ_{ap} , by
21 differential transmission photometry has a long history (dating back at least to
22 Lin et al., 1973), but a standardized, calibrated, real-time measurement has
23 only recently become available. This instrument (the Radiance Research, Inc.
24 PSAP) has been subjected to noise, calibration and intercomparison tests
25 (Bond et al., 1999; Reid et al., 1998) and a detailed set of field use and data
26 reduction protocols have been published (Anderson et al., 1999). Many
27 research groups have adopted this instrument, bringing a measure of
28 standardization to the field.

29 Significant problems remain, however, regarding the accurate
30 determination of τ_{ap} (and, thus, τ_{sp}). First, the optical properties of particles on
31 a filter cannot fully mimic those of suspended particles. If the response

1 depends on particle morphology or chemistry, the calibration with laboratory-
2 generated particles may be inaccurate. Recognizing this possibility, Bond et
3 al. (1999) estimate that the 95% confidence uncertainty of the PSAP is at least
4 +/-20%. Similarly, intercomparison tests by Reid et al. (1998) for biomass
5 smoke aerosols were inconclusive but suggested a PSAP uncertainty of
6 +/-40%. Calibration experiments with a variety of absorbing aerosol types are
7 needed. The PSAP is also limited in that it measures at only one wavelength
8 (the calibration applies to 550 nm), although the technique could readily be
9 applied to other wavelengths. Finally, by collecting particles on a filter prior
10 to measurement, the PSAP does not permit studies of the humidity
11 dependence of light absorption, $f_{ap}(RH)$. Indeed, there is no available method
12 for measuring this important parameter.

13 Recent improvements in the photoacoustic method (Moosemüller et al.,
14 1997; Arnott et al., 1999), which senses light absorption by suspended
15 particles in an enclosed volume, may offer a route to both improved accuracy
16 and the measurement of $f_{ap}(RH)$.

17 Aerosol composition and size distribution

18 The distributions of particle number, mass and composition as functions
19 of size are needed to build aerosol optical models for closure tests and for
20 extrapolating measurements across wavelength and scattering angle.

21 Regional- to global-scale versions of these models are presently based on a
22 very limited number of measurements with large uncertainties (see, e.g., Pan
23 et al., 1997). Considerable improvements in measurement accuracy have
24 occurred in the 1990's. Sources of uncertainty have been compiled by Quinn
25 et al. (1996). Measurements with these newer methods have been made in
26 many regions, revealing large-scale patterns (Covert et al., 1996; Porter and
27 Clarke, 1997) that could form the basis for improved, global-scale models.
28 Some caution, however, is warranted. Already there is a common tendency to
29 fit size distributions with analytical functions without evaluating the resulting
30 errors. These errors can be large, particularly when converting between
31 moments of the distribution (e.g. from number to mass). A much needed, but

1 difficult, first step is to compile the existing measurements (from many
2 different campaigns and investigators) into a common data base for general
3 use.

4 Sampling inlets

5 Coarse mode aerosols (largely mineral dust and seasalt) dominate the
6 variation in optical properties over many regions and are known to play
7 significant roles in the cycling of secondary aerosol species (e.g. biogenic or
8 anthropogenic sulfate.) Thus, a major problem for in-situ measurements is the
9 loss of coarse mode aerosols during sampling from high-speed aircraft
10 (Huebert et al., 1990; Huebert et al., 1998). The losses are significant for
11 diameters above 1 or 2 μm and may be 90% or more for diameters larger than
12 5 μm . No solution has yet been found (other than sampling at low speed) -
13 indeed, a definitive means of calibrating inlet efficiency as a function of size
14 has yet to be developed. A solution to the calibration problem might lie in the
15 use of identical, non-aspirated, particle sizing probes both outside the aircraft
16 and inside the sample plumbing (see, e.g., Noone et al., 1992). A promising
17 approach to solving the inlet loss problem is currently being pursued. This
18 approach involves removing the turbulent surface layer in the deceleration
19 zone by sucking a large fraction of the flow through porous walls. The
20 resulting inlet would produce size-dependent, over-sampling of large particles,
21 which would require accurate calibration. However, this would be a much
22 more manageable problem than under-sampling and would have the advantage
23 of improving large particle counting statistics.

24 **Field deployment**

25 The measurement strategy must select a judicious combination of long-
26 term and intensive deployments from ground-based, ship-based, and airborne
27 platforms. Goals are to characterize the major aerosol types and dominant
28 scales of variability. In addition, the measurement plans should be optimized
29 to provide rigorous tests of internal consistency (e.g. among methods and
30 platforms) and to detect errors in transport models and satellite retrievals.

1 Intensive field campaigns have been the focus of effort in the 1990's and will,
2 accordingly, be discussed in greatest detail.

3 Long-term monitoring

4 Measurements at *ground-based stations* can be used to develop
5 instrumental methods, to study temporal variations in aerosol properties over
6 all time scales, and to serve as baseline stations for intensive campaigns.
7 There are presently about a dozen such stations (e.g. Cape Grim baseline
8 station) that conduct routine measurements of aerosol optical properties
9 intended for studying direct climate forcing. Ideally, the number and location
10 of these stations would span the full range of regional aerosol types and the
11 sampling and measurement protocols would be identical at all stations such
12 that their results could be strictly compared. It is important, but difficult, to
13 assess the vertical and regional representativeness of in-situ measurements
14 from fixed surface stations. One promising approach to this problem involves
15 coupling to collocated lidar measurements.

16 Transects and vertical profiles

17 *Ship-based* measurements have been used extensively to study spatial
18 variations in aerosol optical properties. As a result, the marine boundary layer
19 aerosol is one of the best understood components of the tropospheric aerosol
20 system. Oceanic measurements have the advantage that they can be coupled
21 to reasonably well understood satellite aerosol retrievals. On the other hand,
22 being confined to the ocean surface - where aerosol mass and optical
23 properties are generally dominated by seasalt - is a serious limitation for
24 studying the effects of anthropogenic aerosols.

25 *Airborne* aerosol measurements have also been used extensively to study
26 spatial variations. The overwhelming majority of in-situ data on vertical
27 variations comes from airplanes. Their main limitations are expense, payload
28 capacity, difficulty of operating and calibrating instruments in flight, and
29 losses of coarse-mode particles in sample inlets (see 1.4, above.)

1 Intensive campaigns

2 During *intensive field campaigns*, an integrated suite of observational
3 and modeling methods are focused on one region over a several-week time
4 period. These campaigns serve both an exploratory function - characterizing
5 the aerosol and the factors controlling it - and as opportunities for testing the
6 internal consistency among various measurement methods and platforms.

7 Ideally, the outcomes of an intensive campaign would be

- 8 (1) rigorous field-assessments of aerosol measurement methods,
9 showing where improvements are most needed,
- 10 (2) rigorous tests of key hypotheses regarding the processes that control
11 aerosol properties,
- 12 (3) a thorough characterization of a regional aerosol at one specific
13 time, and
- 14 (4) an optimal, long-term measurement strategy for achieving
15 representative sampling and monitoring changes to that region.

16 Results from two of the many intensive campaigns conducted during the
17 1990's will now be used to illustrate the type of progress that has been
18 achieved.

19 ACE-1⁽⁶⁾ was the first large-scale, international field campaign
20 explicitly devoted to quantifying aerosol properties with regard to their
21 climate forcing effects (Bates et al., 1998). It was conducted during one
22 month in the late Spring of 1995 in the Pacific Ocean, south of Australia. A
23 wealth of data on aerosol optical and chemical properties relevant to the direct
24 effect was acquired from three platforms - a coastal ground station, a ship, and
25 an airplane. Notable accomplishments include the following.

- 26 • Definitive tests of airplane inlet efficiency were conducted, showing
27 that sub-micron, non-sea-salt sulfate was efficiently sampled and
28 that coarse-mode sea-salt was not (Huebert et al., 1998).
- 29 • Using airborne and ground measurements, seven hypotheses
30 concerning the latitudinal, vertical, and diurnal variations of aerosol
31 chemistry were tested and, in two cases, rejected (Huebert et al.,
32 1998).
- 33 • The humidity dependence and the coarse/fine partitioning of light
34 scattering were documented at the ground station (Carrico et al.,
35 1998).

⁶ The International Global Atmospheric Chemistry (IGAC) Project's first
Aerosol Characterization Experiment (ACE-1).

- 1 • The closure approach to measurement error analysis (Quinn et al.,
2 1996) was effectively applied to chemical mass and light scattering
3 data from the ship (Quinn and Coffman, 1998).
- 4 • Distinctive features of this minimally polluted marine environment
5 were observed in terms of extremely high values of τ and extremely
6 low values of sub- μm sulfate scattering efficiency (Quinn et al.,
7 1998).

8
9 The TARFOX campaign⁷ investigated the direct radiative effects of
10 North American industrial pollution aerosols as they advected off the East
11 coast of the United States (Russell et al., 1999). Vertical profiles of aerosol
12 chemical and optical properties were measured from an aircraft during 18
13 flights in July of 1996, yielding several important results.

- 14 • A robust, local closure method was developed whereby extinction
15 from airborne in-situ instruments is compared to extinction derived
16 from differential, airborne optical depth measurements. Results
17 showed significant discrepancies (beyond estimated experimental
18 error) in 5 of 11 cases and a systematic bias that was tentatively
19 ascribed to inlet losses of volatile organic species (Hartley et al.,
20 2000).
- 21 • Organic carbon, rather than sulfate, was found to dominate the
22 aerosol mass on most occasions (Novokov et al., 1997).
- 23 • Measured humidification factors for light scattering were found to
24 be considerably higher than values used in previous climate forcing
25 calculations (Kotchenruther et al., 1999).
- 26 • An apparent discrepancy was found between the τ -values yielding
27 best agreement with radiative flux measurements (0.89-0.93; Russell
28 et al., 1999) and the ambient τ -values derived from the in-situ
29 measurements (0.95 \pm 0.03; Hartley et al., 2000).

30 **Summary and future trends**

31 The problem of direct forcing by anthropogenic aerosols is an excellent
32 example (by no means unique) in which (i) a theory has been developed
33 primarily in relation to numerical models, (ii) the models are largely empirical
34 in nature, and (iii) the models are only weakly constrained by observational
35 data. These features characterize research in an exploratory mode. Having
36 identified an important problem and the key parameters needed for improved
37 quantification, a major effort is now underway to move from this exploratory
38 mode to a definitive one.

1 This transition requires a careful measurement strategy, given the
2 extremely complex and variable nature of the atmospheric aerosol
3 phenomenon. Direct measurements must be effectively coupled to aerosol
4 optical models, chemical transport models, and satellite observations. This
5 coupling must take into account the respective virtues and limitations of each
6 approach. In-situ measurements can never sample a significant fraction of the
7 atmosphere, but they do offer detailed and, above all, calibrated measurements
8 of aerosol properties. Their key advantage is that uncertainties can be
9 quantified with minimal assumptions; if this is done rigorously, they can
10 provide a firm anchor to the reality of aerosol optics, physics, and chemistry.

11 Over the last decade, the aerosol research community has made
12 substantial efforts to develop and standardize measurement techniques, to
13 better quantify uncertainties (e.g. through closure experiments), and to
14 measure aerosol properties from many different regions. In-situ data relevant
15 to direct forcing have been acquired from long-term monitoring activities,
16 geographical transects, and intensive field campaigns, with a strong emphasis
17 on the last. The resulting large data sets are rapidly reaching the point where
18 they can be used, in conjunction with models, to characterize important
19 features of the aerosol on a global scale.

20 Weaknesses do exist, however, that undermine the ability of in-situ
21 measurements to constrain optical properties for models and satellite
22 retrievals. Uncertainties in the measurement of aerosol light absorption are
23 high, even for the case of low relative humidity, and there is no available
24 method for measuring the humidity dependence of light absorption. In
25 addition, there is no effective method at present for sampling coarse mode
26 aerosols from high-speed, research airplanes. At the level of experimental
27 design, there is need for more rigorous uncertainty analysis and for more
28 active testing of hypotheses.

29 Looking ahead to the next decade, a major challenge will be to devise
30 optimal ways to couple in-situ measurements to satellite observations. We are

⁷ Tropospheric Aerosol Radiative Forcing Observational Experiment.

1 only beginning to learn how to do this. A shift is clearly underway (see
2 Section 3) whereby satellites will map out aerosol spatial and temporal
3 variations while targeted in-situ measurements will establish the limits and
4 uncertainties associated with satellite data interpretation. An important step in
5 this direction will be to assess the scales of variability for various extensive
6 and intensive aerosol properties. For example, there is an implicit assumption
7 in all quantitative aerosol retrievals from satellites that certain intensive
8 aerosol properties are conserved over broad regions, even though extensive
9 properties undergo wide variations. Existing in-situ data sets are already ripe
10 for testing this and many related assumptions. Future in-situ measurements
11 should make these tests ever more definitive.

1 **Section 3. Satellite Instruments for Tropospheric** 2 **Chemistry**

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5 **Introduction**

6 It is possible to adequately monitor long-lived tropospheric species with
7 a limited number of measurement stations distributed around the globe.
8 Satellite-based measurements are necessary, however, to obtain global
9 observations of short-lived species and species with sources that are variable
10 in space and time. Satellite-based measurements must, of necessity, use
11 remote sensing techniques. Current techniques are based on the passive
12 sensing of scattered or transmitted sunlight, or emitted thermal or microwave
13 radiation. These passive techniques have employed viewing along limb
14 (horizontal) paths, nadir viewing, or a combination of the two to perform the
15 required measurements. Observations from instruments such as TOMS,
16 SBUV, and SAGE, since the late 1970's, and the UARS satellite during the
17 1990's have provided the scientific community with a comprehensive picture
18 of the chemical composition of the stratosphere and mesosphere. These
19 measurements will be continued during the next decade by the NASA EOS-
20 CHEM and ESA ENVISAT satellites. Table 1 summarizes a selection of past,
21 present, and future satellite instruments designed for sensing atmospheric
22 composition.

23 Initially, the remote sensing of atmospheric composition by satellite
24 sensors was limited to the stratosphere. The primary difficulty in satellite
25 remote sensing of trace gases and aerosols in the troposphere is the limited
26 number of techniques available. A persistent problem has been limited
27 vertical resolution and difficulty in separating tropospheric concentration from
28 the total column. Tropospheric chemistry will be advanced in the coming
29 decade by satellite sensors with new capabilities for observing the
30 troposphere: from passive sensors with improved spectral coverage; from
31 passive sensors in geostationary and L1 orbits providing regional and

1 continental-scale observations with high spatial and temporal resolution; and
 2 from lidars, active sensors based on lasers, which offer the potential for
 3 observations of aerosols and some trace gases with greatly improved vertical
 4 resolution, at the cost of restricted geographic coverage. Development of
 5 these new sensors has been enabled by technologies which have matured
 6 during the 1990's. These new technologies and the advances expected from
 7 them are discussed in this section. Several satellite instruments flown during
 8 the 1990's which are forerunners of the next generation of satellite sensors are
 9 used to illustrate the discussion.

10 **Recent advances**

11 **Ozone and other trace gases**

12 Satellite measurements of aerosols and chemical species in the
 13 troposphere are much more difficult than in the upper atmosphere and
 14 measurement capabilities from space have been much more limited. The limb
 15 viewing geometry is characterized by horizontal resolutions on the order of
 16 400 km, which is inconsistent with the spatial variability of many tropospheric
 17 trace species. Additionally, tropospheric clouds interfere with limb viewing
 18 measurements, so observations of tropospheric composition must rely
 19 primarily on nadir- or near-nadir-viewing instruments. Passive nadir-viewing
 20 instruments have limited vertical resolution, however, and separation of the
 21 tropospheric amount from the total column concentration can be very difficult.

22

23 **Table 1.** Summary of instruments discussed in this section. The list is not
 24 comprehensive but gives an example of past, present, and future capabilities.
 25 Only measurements of primary significance to atmospheric chemistry are
 26 listed.

Instrument	Satellite	Agency	Relevant Measurements	References
AVHRR	TIROS-N, NOAA-6 through NOAA-14, 1978 – present	NOAA	aerosols	Husar et al., 1997
TOMS	Nimbus 7, 1979 – 1992;	NASA	ozone, aerosols	Herman et al., 1997

	Meteor, 1992 – 1994; ADEOS, 1996 – 1997; Earth Probe, 1996 – present			
SAGE I/II	Atmospheric Explorer, 1979 – 1981; Earth Radiation Budget Satellite, 1984 – present	NASA	O ₃ , NO ₂ , and aerosols in stratosphere and upper troposphere	
MAPS	Space Shuttle, 1981, 1984, 1994	NASA	CO	Neil and Fishman, 2000
LITE	Space Shuttle, Sept. 1994	NASA	aerosols	Winker et al 1996
GOME	ERS-2, 1995 - present	ESA	O ₃ , NO ₂ , H ₂ O, BrO, OClO, SO ₂ , HCHO, aerosols	Burrows et al. 1999
IMG	ADEOS, 1996 – 1997	NASD A	O ₃ , N ₂ O, H ₂ O, CH ₄ , CO	Ogawa et al 1994
MISR	Terra, 12/99 – present	NASA	aerosols	Diner et al. 1991 Martonchik, 1997
MODIS	Terra, 12/99 – present; Aqua, 12/2000	NASA	aerosols	Kaufman et al 1997 Tanre et al 1997
MOPITT	Terra, 12/99 – present	CSA	CO, CH ₄	??
SCIAMACHY	ENVISAT, 2000	ESA	O ₃ , NO, NO ₂ , N ₂ O, H ₂ O, BrO, OClO, CO, CH ₄ , SO ₂ , HCHO aerosols	Bovensmann et al. 1999
EPIC	Triana/2001	NASA	ozone, aerosols	??
OMI	EOS Chem, 2002	ESA	O ₃ , SO ₂ , NO ₂ , aerosols	??
TES	EOS Chem, 2002	NASA	O ₃ , NO, N ₂ O, CO, CH ₄ , HNO ₃ , etc.	??
GIFTS	commercial satellite, 2003	NASA	O ₃ , CO, H ₂ O, etc.	??
lidar	PICASSO-CENA, 2003	NASA , CNES	aerosols	Winker and Wielicki, 1999
GeoTRACE	TDRS	NASA	O ₃ , CO, aerosols	??

1

2 UV/Visible Techniques

3 Total column ozone has been derived since 1979 from ultraviolet
4 measurements of scattered sunlight by the TOMS instrument. In the late

1 1980's, a technique was developed to derive tropospheric column of ozone as
2 the residual of the total column measured by TOMS and the stratospheric
3 column from co-located SAGE II measurements (Fishman *et al.*, 1990). The
4 drawback of applying this technique to SAGE II data is that only
5 climatological studies can be done, as SAGE II longitudinal coverage is sparse
6 and full latitudinal coverage is obtained only over about 40 days.

7 The Global Ozone Monitoring Experiment (GOME) has operated since
8 its launch in April 1995 as part of the ERS-2 satellite payload, and flies in a
9 780 km sun-synchronous orbit. GOME is a nadir-viewing spectrometer
10 designed for trace gas measurements by observing reflected sunlight in the
11 ultraviolet and visible (Burrows, *et al.*, 1999). In contrast to TOMS and
12 SBUV which operate at a number of discrete wavelengths, GOME observes
13 the entire spectrum between 240 nm and 790 nm with an improved spectral
14 resolution which varies from 0.2 nm in the UV to 0.4 nm in the red. The
15 improved coverage of the ozone spectrum by GOME and the improved signal
16 to noise ratio of the measurements provide GOME with enhanced capabilities
17 relative to TOMS and SBUV. In the troposphere and lower stratosphere,
18 GOME is able to resolve the vertical profile of ozone with an effective
19 resolution of 10 km. For other gases, the tropospheric column is determined
20 by subtracting the stratospheric column from the total column, assuming local
21 longitudinal homogeneity of the stratosphere. Using this residual technique,
22 GOME has been used to observe tropospheric NO₂ (Figure 1), formaldehyde
23 (HCHO), and SO₂ resulting from pollution and biomass burning. GOME is
24 the first satellite instrument suitable for studying halogen oxides in the lower
25 troposphere and has been used to observe the global distribution of BrO.

26 The observations begun by GOME will be continued by three GOME-2
27 instruments scheduled to be flown on the EUMETSAT/ESA METOP series of
28 satellites, as well as by the conceptually similar OMI instrument, scheduled to
29 be flown on EOS-Chem. The capabilities of GOME will be extended by
30 SCIAMACHY, planned for launch on ESA-ENVISAT in early 2000.
31 SCIAMACHY is similar to GOME in design concept but with spectral
32 coverage extended into the near infrared, between 240 nm and 2380 nm, and

1 with three viewing geometries: nadir viewing, limb-scanning, and occultation
2 (Bovensmann, et al., 1999). Extended spectral coverage and matched
3 limb/nadir measurements allow the tropospheric column amounts of a variety
4 of trace gases to be determined: O₃, NO₂, N₂O, BrO, CO, CH₄, H₂O, and,
5 under polluted conditions: HCHO and SO₂. Additionally, SCIAMACHY will
6 measure vertically resolved profiles of O₃, H₂O, N₂O, and CH₄.

7 **Infrared Techniques**

8 Many trace species exhibit spectral signatures in the thermal infrared,
9 and infrared techniques hold the potential to observe many species which
10 cannot be observed using UV/visible techniques. Satellite measurements of
11 tropospheric gases have been performed using the gas filter correlation
12 technique and by inversion of the radiance spectrum observed at high spectral
13 resolution. In the gas filter correlation technique, an onboard gas cell filled
14 with the target gas provides measurements of a specific gas without requiring
15 high spectral resolution and tight spectral requirements. This technique does
16 not require the absorption lines to be resolved and is characterized by high
17 SNR. The first satellite measurements of CO were obtained by the MAPS
18 (Measurement of Air Pollution from Satellites) instrument using this
19 technique in the mid-IR. MAPS flew on the space shuttle in 1981, 1984, and
20 1994 and provided the scientific community with valuable insights into the
21 importance of biomass burning as a source of CO (Neil and Fishman, 2000).
22 The utility of MAPS was limited by the short duration of shuttle missions,
23 however. Global observations of CO on a continuing basis are planned to be
24 provided by MOPITT on the NASA Terra platform in low Earth orbit,
25 launched in December 1999.

26 High spectral resolution infrared spectrometers hold the potential to
27 observe a broader range of species than is feasible using the gas filter
28 correlation technique. Limited vertical resolution of CO, CH₄, and O₃ is
29 possible if spectral resolution is high enough to resolve the absorption line
30 structure. The TES (Tropospheric Emission Spectrometer) instrument, part of
31 the EOS-Chem payload, is a Fourier Transform Spectrometer observing the

1 spectral region between 3.2 microns and 15.4 microns at a resolution of 0.025
2 cm^{-1} . TES is expected to provide tropospheric measurements of O_3 , CO , CH_4 ,
3 HNO_3 , NO , and N_2O with vertical resolutions of 2 km to 6 km. The IMG
4 (Interferometric Monitor for Greenhouse Gases) instrument, which operated
5 between October 1996 and June 1997 on the Japanese ADEOS satellite,
6 illustrates the potential of high spectral resolution observations from
7 instruments such as TES. IMG is a nadir-viewing Fourier Transform
8 Spectrometer (FTS) operating between 3.3 microns and 14.0 microns with 0.1
9 cm^{-1} spectral resolution (Ogawa, et al., 1994). The instrument has an $8 \times 8 \text{ km}^2$
10 footprint and 32 km swath. As shown in Figure 2, IMG data has provided
11 global measurements of tropospheric CO, using a neural net retrieval approach
12 (Clerbaux et al. 1999; Hadji-Lazaro et al. 1999).

13 **Future Trends**

14 **Observations from Geostationary and Lagrange Orbits**

15 Among the issues in tropospheric chemistry which cannot be addressed
16 by instruments in low Earth orbit are those processes which take place on
17 small scales and require measurements with spatial resolutions on the order of
18 10 km and temporal resolutions on the order of fractions of an hour to a few
19 hours. Satellites in low earth orbit require a full day or more to provide full
20 global coverage and any given region is revisited no more than twice a day.
21 Instruments on satellites in geostationary or Lagrange orbits are required in
22 order to document the spatial distribution, temporal trends, and variability of a
23 number of environmentally significant shorter-lived atmospheric species. A
24 satellite in geosynchronous orbit - at an altitude of about 36000 km - orbits the
25 Earth once per day and so has a stable and continuous view of a large portion
26 of the Earth's surface. Four to five satellites in geosynchronous orbit, spaced
27 longitudinally, are required to obtain full coverage of the Earth up to a latitude
28 of 50-60 degrees. A Lagrange orbit is an orbit at a point between the Sun and
29 the Earth where the gravitational pulls from both bodies are balanced such that
30 the satellite maintains a constant distance from both the Sun and the Earth.
31 The L1 and L2 points lie along a line between the Earth and the Sun. The L1

1 point is between the Earth and the Sun, at a distance of about 1.6 million km
2 from the Earth, and the L2 point is beyond the Earth's orbit. The L1 point
3 provides a continuous view of the full solar-illuminated Earth disk, and the L2
4 point provides a view of the night side of the Earth.

5 The use of sensors in geosynchronous and L1 orbits to observe
6 tropospheric composition has been enabled by the development of large
7 format detector arrays, and their associated low-noise readout electronics, high
8 bandwidth satellite communications links, and high volume data handling
9 facilities. These large arrays enable sensors to make quasi-continuous
10 measurements over the full Earth disk with high spatial, spectral, and temporal
11 resolution. These new satellite platforms will allow the investigation of a
12 whole new class of atmospheric phenomena, including processes occurring at
13 small spatial scales and the transport of pollutants from local source regions to
14 the global atmosphere. Instruments in these orbits can also give the synoptic
15 context for measurements from ground networks or field campaigns.

16 GIFTS is a mission recently selected for NASA's New Millennium
17 program for launch in 2003 to demonstrate new technologies and the potential
18 for high spectral resolution infrared observations from geosynchronous orbit.
19 GIFTS is an imaging Fourier Transform Spectrometer which will provide
20 spectra in two bands in the thermal infrared. The spectral resolution is
21 programmable, from 18 cm^{-1} to 0.6 cm^{-1} . The primary focus of GIFTS is to
22 demonstrate an improved capability for temperature and humidity sounding to
23 improve the accuracy of weather forecasts. However, observations at the
24 highest spectral resolution will provide vertically resolved profiles of ozone,
25 CO, and other constituents. Views of mesoscale-sized regions can be obtained
26 every half hour.

27 Triana is a NASA mission scheduled to launch in early 2001 which will
28 fly several instruments at the L1 point to provide continuous observations of
29 the sun-illuminated side of the Earth from this unique vantage point. A 10-
30 band imaging filter radiometer called EPIC will provide hourly measurements
31 of ozone over the full sunlit disk of the Earth at a spatial resolution of 8-14
32 km. This is done using the UV-backscatter technique developed for TOMS.

1 GeoTrace is an instrument which is somewhat similar to the Triana
2 EPIC camera, but with higher spectral resolution. GeoTrace has been
3 proposed to the NASA New Millennium Program to fly in a geosynchronous
4 orbit and would provide measurements similar to GOME but with continuous
5 full-disk coverage. GeoTrace gives atmospheric column amounts, is aimed at
6 monitoring, distribution, diurnal changes, and transport.

7 Instruments such as GIFTS, GeoTrace, and Triana will provide unique
8 insights into the temporal behavior of atmospheric composition and dynamics
9 at small to medium scales. Rapid changes in tropospheric constituents will be
10 observed, providing a means of separating the tropospheric burden from the
11 relatively slowly changing stratospheric burden.

12 **Active Sensing of Aerosols and Trace Gases**

13 The global distribution of tropospheric aerosol is highly variable due to
14 the variety and variability of sources and the short residence time of aerosols
15 in the atmosphere. Due to the current limited knowledge of aerosol source
16 strengths and production and transformation mechanisms, aerosol distribution
17 cannot be adequately determined by modeling. Improved satellite
18 measurements are necessary to obtain a more complete picture of the global
19 aerosol.

20 Aerosols can be detected and characterized from satellite measurements
21 of scattered sunlight in the UV and near-IR, but the retrievable information is
22 limited. The Advanced High Resolution Radiometer (AVHRR), flying on a
23 series of NOAA satellites, has provided aerosol observations since 1979
24 (Husar et al, 1997). Algorithms using two of the AVHRR wavelengths (0.65,
25 0.865 μm) have been used to retrieve aerosol optical depth and Angstrom
26 coefficient (the spectral coefficient of aerosol scattering). Operational aerosol
27 products, however, have been limited to ocean regions due to the difficulty of
28 retrieving aerosol over inhomogeneous and/or bright land surfaces. More
29 recently (Herman, et al., 1997) aerosol retrieval algorithms have been
30 developed and applied to TOMS UV measurements to detect absorbing
31 aerosols, primarily dust and smoke, over land as well as marine surfaces. This

1 recent work has resulted in new insights into the global sources, production
2 mechanisms, and transport of dust and smoke, but retrieval of quantitative
3 parameters is difficult.

4 The payload of the Terra satellite, launched in December 1999, includes
5 the MODIS and MISR instruments which provide new capabilities for aerosol
6 sensing. MODIS is a nadir-viewing imaging filter radiometer with 36 spectral
7 channels and improved calibration relative to AVHRR. Seven of those
8 channels, between 550 nm and 2100 nm, will be used for retrievals of aerosol
9 optical depth over dark vegetation as well over ocean (Kaufman et al. 1997;
10 Chu et al. 1998). Over the ocean, it will also be possible to retrieve the mean
11 aerosol size and the relative contribution to the aerosol optical depth of the
12 accumulation and coarse modes (Tanré et al. 1997; Tanré et al. 1999). The
13 Multi-angle Imaging Spectro-Radiometer (MISR) will provide multi-angle
14 observations in 4 spectral bands between 446 nm and 866 nm. Each band is
15 imaged with 9 view angles spread out along the flight path between 70
16 degrees forward and 70 degrees aft. These multi-angle measurements provide
17 additional information on aerosol angular scattering characteristics and allow
18 the classification of aerosols into one of about a dozen types, distinguished by
19 size, composition, and shape (spherical/non-spherical) as well as
20 measurements of aerosol optical depth (Kahn et al., 1997).

21 The new observing capabilities provided by the Terra instruments will
22 provide major improvements in knowledge of the global aerosol. None of
23 these instruments, however, is sensitive to aerosols at very low concentrations
24 or provides any information on the vertical profile of aerosols. Active lidar
25 sensors, based on short-pulse lasers, are required.

26 The Lidar In-space Technology Experiment (LITE) provided the first
27 demonstration of the promise of satellite lidar for aerosol studies. LITE was a
28 lidar system using a high power pulsed laser operating at 355 nm, 532 nm, and
29 1064 nm (Winker et al. 1996) which flew on the Space Shuttle in September
30 1994. Figure 3 illustrates the capability of satellite lidar to detect and profile
31 aerosols over land as well as over ocean. Observation of the vertical profile of
32 aerosol also facilitates assimilation of the data by models.

1 The relatively recent development of rugged, long-life, and efficient
2 diode-pumped solid-state lasers has enabled the development of lidars which
3 can be operated from long-term satellite platforms in low Earth orbit.
4 PICASSO-CENA is a recently approved NASA mission which will launch in
5 early 2003 and is planned for a three-year mission (Winker and Wielicki,
6 1999). The PICASSO-CENA instrument suite includes two instruments
7 optimized for aerosol studies: a two-wavelength lidar (532 nm, 1064 nm) and
8 a high-resolution spectrometer viewing the A-band of oxygen. The
9 spectrometer will demonstrate a new approach to the passive sensing of
10 aerosols. Combination of channels with large and small column oxygen
11 optical depth allows the separation of atmospheric scattering from surface
12 scattering, providing improved retrievals of aerosol over land surfaces.

13 To provide a comprehensive picture of the global aerosol distribution,
14 data from many diverse sources - both satellite and ground-based in situ and
15 remote sensing instruments - will have to be integrated, using model
16 assimilation techniques. The PICASSO-CENA satellite will fly in formation
17 with the Aqua (formerly EOS PM) satellite, allowing the combination of
18 MODIS and lidar observations. The OMI instrument, on EOS-Chem, will be
19 used to detect aerosols using the TOMS retrieval approach (Herman et al.
20 1997). The unknown vertical distribution of aerosol results in significant
21 uncertainties in quantitative retrievals using this algorithm. Use of near-
22 coincident aerosol profiles from PICASSO-CENA can be used to improve the
23 accuracy of OMI aerosol retrievals.

24 It should also be mentioned that technologies required for space-based
25 sensing of trace gases by differential absorption lidar (DIAL) systems are
26 being developed. DIAL systems have not yet been flown in space, but have
27 proven their utility through many years of use in ground-based and airborne
28 measurement campaigns. Laser technology has now progressed to the point
29 where spaceborne DIAL systems are in the early planning stages and it is
30 likely that DIAL systems to measure tropospheric ozone and water vapor will
31 be in orbit by the latter part of the decade. Because active sensors provide
32 limited horizontal coverage, assimilation techniques will need to be developed

1 to merge high vertical resolution data from lidar with broad spatial coverage
2 data from passive sensors.

3 **Summary**

4 Global remote sensing of atmospheric constituents is essential to
5 understand the natural processes which determine the composition of the
6 global atmosphere and to assess the impact of human activities on the
7 atmosphere. Following successes in the development of capabilities for
8 satellite measurements of the stratosphere, the next challenge is to develop
9 capabilities for measurements in the troposphere. In contrast to the
10 stratosphere, higher spatial and temporal resolution is required for
11 tropospheric studies. New developments in satellite sensor technologies
12 during the last decade have enabled more capable sensors to meet these
13 challenges. Pathfinder instruments such as GOME, IMG, and LITE have
14 indicated the potential for the new generation of instruments to be flown
15 during the next decade. These new satellite sensors will provide major
16 advances in our understanding of the composition of the troposphere on
17 regional and global scales.

18 **Acronyms:**

19 EPIC - Earth Polychromatic Imaging Camera

20 GIFTS - Geostationary Imaging Fourier Transform Spectrometer

21 OMI - Ozone Monitoring Instrument

22 SCIAMACHY - SCanning Imaging Absorption spectroMeter for Atmospheric
23 CartographY

24

25

1 **Section 4. *In situ* Gas Phase Measurements**

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4 **Recent Advances**

5 Major advances in instrumentation over the past decade, particularly in a
6 few specific areas, have greatly enhanced understanding of gas phase
7 chemical processing and are also providing a whole new view of the
8 production, growth, and interaction of particles in the atmosphere. The rate at
9 which the earth's atmosphere cleanses itself is largely dependent on its ability
10 to produce the hydroxyl radical (OH), yet only a decade ago very few if any
11 credible in situ tropospheric measurements of this compound existed [*Crosley,*
12 1993]. By 1991, a sensitive new in situ ground-based OH instrument was
13 successfully intercompared to a long path instrument [*Mount and Eisele,*
14 1992; *Eisele et al., 1994*], and several other successful intercomparisons took
15 place over the next few years [*Crosley, 1997; Hofzumahaus et al., 1998*]. By
16 the mid 1990's OH measurements were being included on tropospheric aircraft
17 campaigns [*Mauldin et al., 1998; Brune et al., 1998*]. While still not common
18 place, OH and HO₂ measurements have contributed significantly to several
19 major aircraft and ground-based campaigns. Large increases in the sensitivity
20 of long-path absorption instruments have led to new folded-path instruments,
21 which can now also make ground or ship-based in situ measurements
22 [*Brandenburger et al., 1998*].

23 Another area of major progress is the measurement of biogenic
24 compounds. Over the past decade or so, the previously held view of
25 vegetation as an emission source of a few fairly passive organic compounds
26 has changed to one in which vegetation plays a central interactive role in
27 ozone production and atmospheric chemistry in general. Its role, however, is
28 extremely complex, and the number of measurements required to fully
29 quantify biogenic emissions and their products is truly huge. Unlike the
30 difficulties encountered in measuring the hydroxyl radical, the compounds of
31 importance are neither in the sub-parts per trillion concentration range, nor so

1 reactive that they are lost on first contact with a surface. Rather, the problem
2 is specificity because of the sheer number of compounds to be measured and
3 the fact that many of the compounds are so similar. In addition, many of the
4 product compounds of interest are quite sticky and can react if deposited on
5 surfaces. Not only are chemical identification and the measurement of
6 concentrations important; flux of the compounds is also of great interest.
7 Much progress has been made using customized GC and GCMS measurement
8 schemes combined with eddy accumulation techniques to inventory both
9 primary biogenic emissions and their products [Guenther *et al.*, 2000]. While
10 such techniques are highly specific they are typically quite slow, requiring
11 10^2 - 10^3 seconds. They are thus not well suited to flux or aircraft studies
12 unless accompanied by some type of eddy accumulator. Advances in diode
13 lasers technology have led to several new measurement techniques for making
14 faster measurements of some biogenic and anthropogenic emissions such as:
15 formaldehyde, ammonia, CO, NO₂, H₂O₂, N₂O and SO₂ [Silver *et al.*, 1991;
16 Roths *et al.*, 1996; Mackay *et al.*, 1996; Fried *et al.*, 1999]. While these
17 measurements are highly specific and typically have sensitivities allowing
18 measurements into the mid ppt range, it is unlikely that they will be able to
19 sort out and individually identify the bulk of major biogenic emissions and
20 their products (particularly complex compounds with more than 5 atoms) over
21 the next decade. Recently, a modified chemical ionization mass spectrometry
22 technique which operates at low pressures and uses electric fields to enhance
23 collision energies in the ion reactive region was introduced into the
24 atmospheric measurements arena. The instrument is called a Proton Transfer
25 Reaction Mass Spectrometer (PTRMS) [Lindinger *et al.*, 1998a,b] It offers
26 several advantages over existing hydrocarbon measurement techniques: fast
27 measurements (in the 1 second time frame), a reasonable amount of specificity
28 using mass analysis to identify compounds, measurements down to the mid to
29 upper ppt concentration range, and the ability to be used on an aircraft
30 [Crutzen *et al.*, 2000]. To measure the large number of organic compounds
31 present in the atmosphere in an unambiguous way may require more analytical

1 power than is provided by the present PTRMS, but this can be greatly
2 improved through the use of tandem mass spectrometers or ion traps.

3 Another area in which large strides have been made is sulfur chemistry
4 and its relation to particles. For many years, particle nucleation was thought
5 to occur even in the remote atmosphere but direct quantitative evidence for
6 such processes was lacking. In the past decade, new developments in both the
7 gas and particle side of nucleation have dramatically enhanced observations
8 and understanding. On the particle side the development of ultrafine particle
9 detectors now allows particles as small as 2.5 nm diameter to be measured and
10 size-resolved, even at concentrations below $0.1 \text{ particles cm}^{-3}$ [*Stolzenburg*
11 *and McMurry*, 1991]. Gas phase precursors such as sulfuric acid [*Eisele and*
12 *Tanner*, 1993] are also now commonly measured in conjunction with ultrafine
13 particles, and this combination for the first time provides a means of directly
14 comparing nucleation theory to field observations [*Weber et al.*, 1995]. Even
15 the transitional growth steps between gas phase molecular clusters and stable
16 particle formation are now observable [*Eisele and Hanson*, 2000].

17 Exciting new breakthroughs have also made possible real time chemical
18 composition measurements of particles. A variety of laser evaporation/laser
19 induced ionization time-of-flight mass spectrometry instruments are now
20 being used to chemically analyze individual particles in laboratories and in
21 field studies. The result has been a surprising diversity between individual
22 particles and a complex chemical mixture of many trace constituents,
23 including many metals. These instruments still have limited capabilities for
24 determining absolute chemical concentrations, but rapid progress is being
25 made in this direction.

26 While lidars are not new, their improved capabilities and extended use
27 are. They are presently included in many aircraft payloads and provide
28 valuable information about the larger environment in which the aircraft in situ
29 measurements are made. In addition, they provide an extended real time
30 survey of local conditions, and as such can be used to direct aircraft flight
31 planning during an ongoing mission.

1 **Future Trends**

2 The better we come to understand atmospheric chemistry, the more
3 complex we realize it is. This complexity takes on several forms, each of
4 which poses a different set of measurement problems. Part of this complexity
5 occurs because observed chemical concentrations are typically a result of
6 dynamics as much as chemistry. In order to understand the influences of each,
7 more chemically speciated lidar and satellite measurements are needed. The
8 development of more rapid measurement techniques which can determine
9 fluxes would also contribute much, as would the measurement of a wider
10 range of compounds, many of which could be used as tracers. The use of
11 multiple measurement platforms could also provide additional insight,
12 especially near localized sources or convective systems. As measurements
13 move down near the surface, particularly in industrialized or urban areas, the
14 complexity increases in part because the sheer number and types of sources
15 increase. If such areas are to be studied in detail, far more compounds need to
16 be measured, and if accomplished on an aircraft, the measurement time needs
17 to be decreased to the order of a few seconds so that individual sources or
18 plumes can be distinguished from each other. This will require new, more
19 sensitive measurement techniques, which will probably be mass spectrometry
20 based. Chemical ionization mass spectrometry offers the required speed and
21 sensitivity and can be applied to large/complex biogenic and anthropogenic
22 molecules. More powerful analytical capabilities, such as tandem mass
23 spectrometers and ion traps will, however, be required. Optical techniques
24 can make fast sensitive measurements for small molecules and continue
25 progress in this area is needed, but these techniques have difficulty, for
26 example, in speciating large organics.

27 Another area that deserves far more attention in the next decade is
28 aircraft inlets. As an ever larger number of field studies are mounted from
29 aircraft platforms, and as measurement capabilities are extended to include
30 more reactive and/or sticky compounds, sampling becomes a major issue. An
31 instrument that works perfectly on the ground or even in an aircraft will add
32 little to an aircraft mission if the compound of interest can not be transported

1 in a well understood way between ambient outside conditions and the
2 measurement instrument. This problem is particularly acute for aerosols, but
3 affects many gas phase measurements as well. Some of the issues that need to
4 be addressed are: Large air speed changes and the associated temperature
5 changes, even if measurements are made outside the aircraft, temperature
6 changes associated with bringing air into the aircraft, re-equilibration of
7 compounds found both on particles and in the gas phase as temperature and
8 relative humidity change, loss to and evaporation from inlet surfaces as
9 altitude, temperature, and relative humidity change, the influence of pressure
10 changes, aircraft boundary layer thickness, inlet orientation and position
11 relative to other inlets, high speed droplets, droplet shattering, and icing.
12 Finally the influence of heterogeneous reactions on tropospheric gas phase
13 chemistry needs to be explored in far more detail particularly in urban air
14 masses. This will require new more sophisticated measurement techniques
15 probably involving both lasers and mass spectrometers to quantify not only
16 acids and ammonia but also the large number of organic compounds found in
17 both the gas and particle phases.

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