Acetone in the atmosphere: Distribution, sources, and sinks

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Acetone (CH_3COCH_3) was found to be the dominant nonmethane organic species present in the atmosphere sampled primarily over eastern Canada (0-6 km, 35°-65°N) during ABLE3B (July to August 1990). A concentration range of 357 to 2310 ppt ($=10^{-12}$ v/v) with a mean value of 1140 ± 413 ppt was measured. Under extremely clean conditions, generally involving Arctic flows, lowest (background) mixing ratios of 550 ± 100 ppt were present in much of the troposphere studied. Correlations between atmospheric mixing ratios of acetone and select species such as C_2H_2, CO, C_3H_8, C_2Cl_4 and isoprene provided important clues to its possible sources and to the causes of its atmospheric variability. Biomass burning as a source of acetone has been identified for the first time. By using atmospheric data and three-dimensional photochemical models, a global acetone source of 40-60 Tg ($=10^{12}$ g)/yr is estimated to be present. Secondary formation from the atmospheric oxidation of precursor hydrocarbons (principally propane, isobutane, and isobutene) provides the single largest source (51%). The remainder is attributable to biomass burning (26%), direct biogenic emissions (21%), and primary anthropogenic emissions (3%). Atmospheric removal of acetone is estimated to be due to photolysis (64%), reaction with OH radicals (24%), and deposition (12%). Model calculations also suggest that acetone photolysis contributed significantly to PAN formation (100-200 ppt) in the middle and upper troposphere of the sampled region and may be important globally. While the source-sink equation appears to be roughly balanced, much more atmospheric and source data, especially from the southern hemisphere, are needed to reliably quantify the atmospheric budget of acetone.

INTRODUCTION

Natural and anthropogenic nonmethane hydrocarbons (NMHCs) are released into the atmosphere at a rate of nearly 10^3 Tg/yr [*Duce et al.*, 1983; *Singh and Zimmerman*, 1992]. Atmospheric reactions of these NMHCs with ozone (O_3) and free radicals result in the formation of a variety of intermediate oxygenated species of which carbonyls (RR'C=O) form an important group [*National Academy of Sciences (NAS*, 1976; *Lloyd*, 1979; *Atkinson*, 1990]. There is further evidence that direct emissions of carbonyl species from both natural and manmade sources are also quite common [*NAS*, 1976; *Isidorov et al.*, 1985; *Sigsby et al.*, 1987]. Carbonyl compounds are of interest to atmospheric chemists because of their potential toxicity, their ability to photolyze and produce free radicals, their ability to form stable atmospheric products, and their interactions in the smog cycles. Because they are frequently intermediate products of atmospheric oxidation, these molecules can serve as excellent tracers for the validation of photochemical models.

While several carbonyl species have been studied in polluted atmospheres [*Vairavamurthy et al.*, 1992], formaldehyde is the only one to receive significant attention in global tropospheric chemistry studies. One of the most abundant reactive oxygenated species in the remote atmosphere is acetone. It was first measured by *Cavanagh et al.* [1969] at a concentration of about 1 ppb in the uncontaminated Arctic air of Point Barrow, Alaska. *Singh and Hanst* [1981] used a photochemical model to suggest that acetone is an ubiquitous atmospheric species resulting from the oxidation of propane. They also showed that acetone can produce free radicals which sequester reactive nitrogen in the form of PAN. Recent photochemical studies have used one-dimensional and two-dimensional models to describe its atmospheric structure based on its source resulting from the oxidation of molecules such as propane and isobutane [*Kasting and Singh*, 1986; *Chatfield et al.*, 1987; *Singh and Kasting*, 1988; *Henderson et al.*, 1989; *Kanakidou et al.*, 1991]. Data to support these model results unfortunately are extremely sparse, in part because of lack of suitable measurement techniques [*Vairavamurthy et al.*, 1992]. Table 1 summarizes available measurements of acetone, most of which were made at rural surface sites using a variety of direct and indirect techniques. The only measurements that are not made on the ground are those of *Arnold et al.* [1986] who used an indirect chemical ionization technique, applicable in the upper troposphere and the lower stratosphere, to estimate acetone abundances. The wet chemical derivative techniques such as the DNPH/HPLC method have also been used for aldehydes and ketones in semipolluted environments, but these require long sampling times and suffer from potential interferences [*Vairavamurthy et al.*, 1992]. Overall, few reliable measurements of acetone

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TABLE 1. Acetone Concentrations in the Rural/Remote Atmospheres

Acetone Mixing Ratio, ppb	N	Altitude	Method	Location	Source
1.0 .(ND-2.9)	25	surface	grab sample GC/FID	Point Barrow, Alaska, 71°N	*Cavanagh et al.* [1969]
1-3	-	surface	grab sample GC/FID	western United States	*Robinson et al.* [1973]
0.47±0.09	5	surface	grab sample GC/MS	Atlantic air, 35°N	*Penkett* [1982]
2.8±0.8	18	surface	condensate GC/FID	rural sites in Arizona	*Snider and Dawson* [1985]
0.1-0.2	19	upper troposphere, 6-10 km	CIMS, indirect method	over Europe, 45°N	*Arnold et al.* [1986]
1.7±0.8	96	surface	DNPH/HPLC, wet chemical	rural sites in southern Canada, 45°N	*Shepson et al.* [1991]
1.14±0.41	123	free troposphere, 0-6 km	cryosample GC-RGD	North America, 35-65°N	this study

ND, not detectable; N, number of data points. CIMS, chemical ionization mass spectrometry; DNPH, Dinitrophenyl hydrazine; HPLC, high performance liquid chromatography; RGD, reduction gas detector.

are available in the global troposphere and very little about its sources and sinks is known.

During the summer (July to August) of 1990, NASA GTE/Arctic Boundary Layer Expedition (ABLE)3B experiment provided an opportunity to utilize a recently developed instrument to perform real-time airborne measurements of acetone between 35°N and 65°N to an altitude of 6 km. In addition, a comprehensive set of trace chemical (O_3, NO_x, NO_y, PAN, HNO_3, C_2-C_6 NMHC, CO, halocarbons) and meteorological parameters were also measured. Here we present the first airborne measurements of acetone based on its direct real-time detection and use these to characterize its distributions and variabilities in the troposphere. Relationships between the atmospheric concentrations of acetone and other key chemical parameters are explored. Based on the interpretation of these field measurements and the exercise of photochemical models, we construct a rough picture of its sources and sinks.

EXPERIMENT

ABLE3B utilized a Lockheed Electra for all aircraft measurements. Instrument integration and flight tests were performed at Wallops Island, Virginia. Aircraft missions were conducted from July 5 to August 15, 1990, primarily from North Bay (46.3°N, 79.5°W) and Goose Bay (53.3°N, 60.4°W), Canada. Field missions were divided into generic types that included boundary layer flux measurements, midtropospheric distributions, and vertical profiles. A latitude of 35°-65°N over 60°-80°W longitude was covered during this experiment. Transit flights provided limited opportunities to study the latitudinal distribution of species. Geographical extent covered during the ABLE3B missions and a summary table of individual flights are provided in the overview paper by *Harriss et al.* [this issue].

The PANAK instrument was designed to measure peroxyacetylnitrate (PAN) and select aldehyde and ketones using a pair of airborne gas chromatographs. Results based on the measurements of PAN and other reactive nitrogen species are discussed in a companion paper [*Singh et al.*, this issue]. The initial focus for carbonyl measurements was on acetone and acetaldehyde. The instrument used depended on cryogenic collection of about 300 ml of air, separation of

key species with glass capillary column, and sensitive detection by a mercuric oxide reduction gas detector (RGD). The RGD is based on the UV detection of mercury vapor released when a species X reacts with heated (285°C) mercuric oxide (X+HgO(solid) → XO+Hg(vapor)). It has been previously shown by *O'Hara and Singh* [1988] that RGD can detect acetone and acetaldehyde (and possibly formaldehyde) with a sensitivity that is 20 to 30 times greater than that of FID. Since the RGD is also sensitive to other species such as alkenes, sulfur compounds, and some higher hydrocarbons, the analytical technique devised used a precolumn (with time-programmed backflush) to reduce potential chromatographic interferences.

Species of interest, such as acetone, were cryogenically (-170°C) enriched from a 300 ml (0°C, 1 atm) air sample in a multistage open tube trap connected to a ten-port gas sample valve. The concentrate was then injected into a precolumn containing two stationary phases. The first section of the packed precolumn was 20 cm x 0.18 cm ID section of 10% carbowax 600 on Supelcoport connected to a second section of 30-cm length containing 0.2% carbowax 1500 on Carbopack. The precolumns and valve assembly were held at 42°C. The compounds flushed through the precolumn were cryofocused in second dual stage trap attached to a six-port valve. When acetone was collected in the second trap (time program), the two phase precolumn was backflushed to substantially eliminate potential interferences such as water and high boiling organics. Trapped material from the second precolumn was injected into the main analytical column by heating it to 70°C. The main analytical column itself was a 30 m x 0.75 mm 1 μm Supelcowax 10 glass capillary column fitted with a 0.2 m x 1 mm 10% carbowax 1000 on Supelcoport guard column. A helium carrier gas flow rate of 10 cm^3/min and an isothermal oven temperature of 47°C were employed. A make up flow of 10 cm^3/min was provided to allow the RGD to receive a total of 20 cm^3/min of helium.

In-flight calibrations were performed with the help of an acetone permeation tube (VICI-Metronics) held at 0°C in an icepoint flight dewar. This tube permeated at a mean rate of 58 ng/min of acetone. A dynamic dilution system using compressed ultrazero air was used to generate acetone standards in the 50 to 3000 ppt range bracketing actual tropospheric measurements. To ensure that the permeation
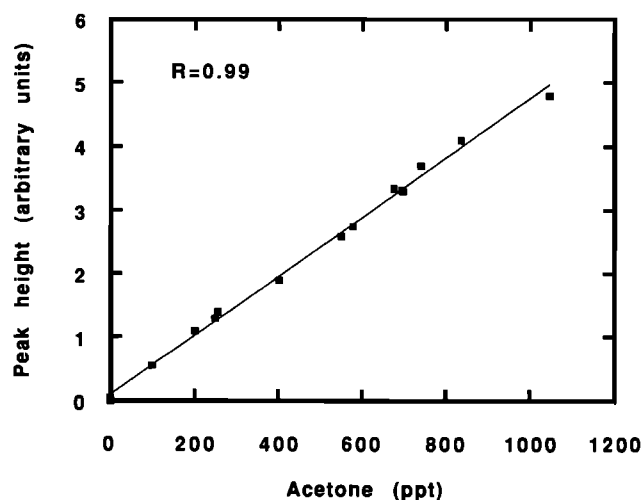
Fig. 1. Linearity of acetone calibration over a typical concentration range using the gas chromatographic-reduction gas detector (GC-RGD) system.
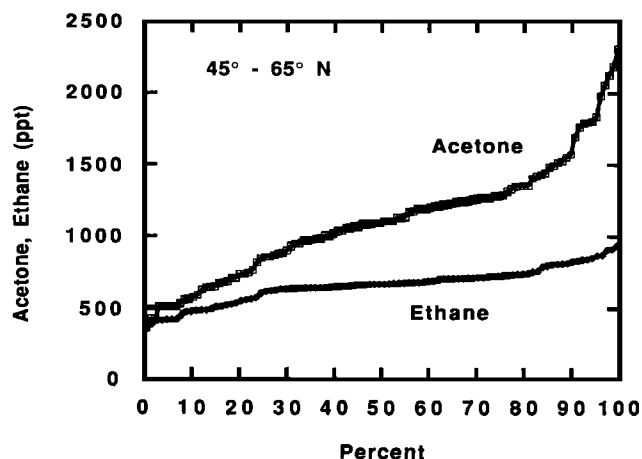

Fig. 2. Frequency distribution of acetone and ethane mixing ratios. Ethane data correspond to those missions for which acetone measurements were also available (missions 13-22). Unless otherwise stated, all data presented in this and subsequent figures represent measurements over 45°-65°N latitude and 60°-80°W longitude.

tube was uncontaminated and behaved properly, laboratory standards were prepared in a variety of liquid medium and compared with the acetone standards generated from the acetone permeation tube. These comparisons agreed to typically within 10% and confirmed the purity of the acetone emission. It is noted that the same studies also showed that the acetaldehyde permeation tube did not work properly and the gravimetric loss rates did not correspond to acetaldehyde emissions over a period of several weeks. One of the causes was found to be the slow oxidation of acetaldehyde to acetic acid. In the field, all calibrations were performed with the acetone permeation system. As is shown in Figure 1, the detector is linear in the concentration range of interest. ABLE3B provided the first opportunity for the deployment of this GC-RGD system aboard an aircraft. During field operation the system had a sensitivity of 10 ppt acetone (300-ml standard sample) and a measurement was made about every 12 min. The sampling frequency was in part dictated by the fact that the RGD system shared its computer control with the PAN instrument. A precision of ±10% and an overall accuracy of about ±15% are estimated.

RESULTS AND DISCUSSION

Acetone measurements were made starting with the Goose Bay operation and continued till the end of ABLE3B (missions 13-22). An integrated data file, containing acetone data and the corresponding mixing ratios of a large variety of trace species measured by ABLE3B investigators, was created for the purpose of data analysis. These complementary data were averaged within the acetone sampling window. In the analysis and interpretation that follows, it is important to remember that all measurements are not exactly overlapping in time and space.

Atmospheric Distribution of Acetone

Acetone was found to be an ubiquitous component of the atmosphere and was measured in a concentration range of 357 to 2310 ppt. Substantial variability in the atmospheric abundance of acetone was observed and its vertical structure varied from day to day. This variability was associated with

meteorological patterns responsible for the transport of acetone and other trace species from a variety of source regions. Since acetone has significant secondary sources and a relatively short lifetime, differences in chemical production and destruction rates can also cause atmospheric gradients and variability. As is discussed later in this paper, atmospheric lifetime of acetone is longer than 10 days and
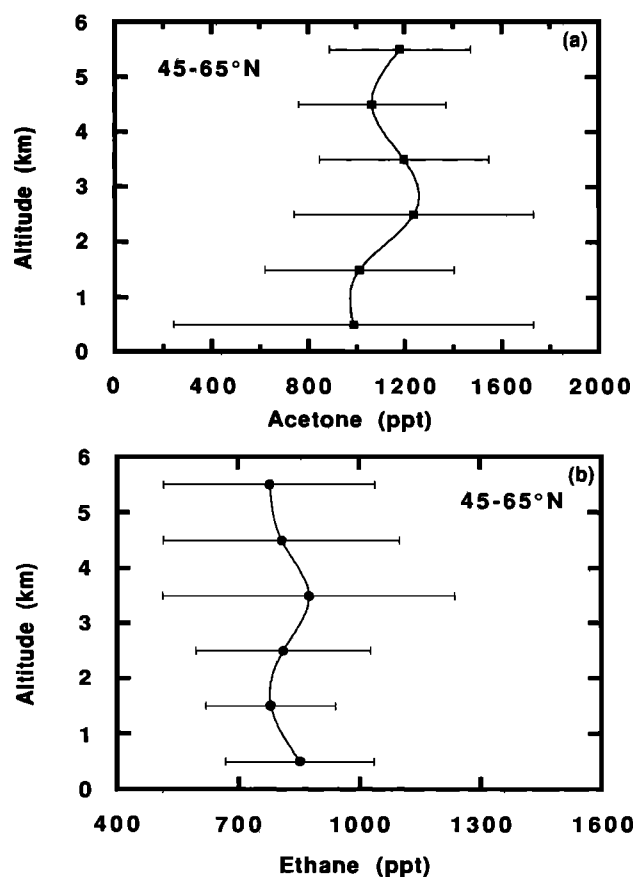

Fig. 3. Mean vertical structure of (a) acetone and (b) ethane. Horizontal bars show one standard deviation.

long-range transport is clearly possible. The mean acetone concentration observed during this entire effort was 1140 ± 413 ppt (n=123). Figure 2 shows the frequency distribution of acetone and ethane based on data collected during ABLE3B. Ethane is thought to be the most abundant non-methane organic species in the global atmosphere [*Singh and Zimmerman*, 1992]. It is clear from Figure 2, that acetone was more abundant than ethane during this entire experiment. The possibility clearly exists that oxygenated species (such as carbonyls, alcohols, ethers) are important components of the global atmosphere but have not yet been fully investigated.

Figure 3 shows the vertical structure of acetone and ethane as measured in the $45°$-$65°N$ latitude belt. The mean acetone vertical profile is nearly constant with substantial variability at all levels. Frequently mixing ratios were higher aloft than near the ground. The lowest mixing ratios were found during clean Arctic air episodes and coincided with low CO, NMHC, C_2Cl_4, and O_3 values. Table 2 shows data involving two such periods encountered in the free troposphere (4-6 km, mission 14) and the boundary layer (0-2 km, mission 18). Trajectory analysis performed by *Shipham et al.* [this issue] indicate that the air masses encountered during mission 14 probably originated in the subtropical Pacific some 15 days earlier and were influenced by the Arctic/subarctic air en route to the sampling area. The lowest mixing ratios observed in the free troposphere were in the 500-to 600-ppt range, while the lowest levels encountered in the surface air were in the 350-to 400-ppt range. The latter were found in clean Arctic air masses and over water bodies (e.g., missions 18 and 19 over Frobisher Bay). As will be discussed later in this paper, it is possible that important amounts of acetone are exchanged (but probably not lost) across water bodies. Table 2 also shows the extremely low levels of other primary and secondary tracers present in these air masses. For example, the PAN concentrations measured in this 4-to 6-km altitude were among the lowest ever encountered. It is evident that background mixing ratios of at least 400 to 600 ppt could be found in much of the troposphere studied during ABLE3B (0-6 km). The surface mean of 1140 ppt and clean background mixing ratios of $\approx$500 ppt are in general agreement with the limited surface data from the Arctic reported by *Cavanagh et al.* [1969] and over the Atlantic reported by *Penkett* [1982]. The results in this study, however, show significantly higher acetone abundances at 6 km than those indirectly estimated by *Arnold et al.* [1988] from a technique based on chemical ionization mass spectrometry (CIMS). The reasons for these differences are not clear.

Missions 18-22 provided an opportunity to study the latitudinal behavior of acetone and other trace chemicals over a latitudinal belt of $35°$-$63°N$ ($60°$-$80°W$ longitude) during early August. These limited data cannot be considered to provide a robust latitudinal profile given the observed variability in the atmospheric abundance of acetone. However, a general behavior similar to that of CO (and C_2H_2) is indicated. Figure 4 uses data from four select missions to show the vertical structure of acetone and CO at four latitudes. A significant change in the boundary layer concentrations is evident. This is direct evidence for substantial surface emissions of acetone and its precursors at lower latitudes. This general feature is also seen in the corresponding vertical profiles of tracers with significant anthropogenic sources

TABLE 2: Acetone and Tracer Concentrations Under Clean Background Conditions

Date	Latitude, °N	Altitude, km	Acetone (ppt) Mean±σ	Acetone (ppt) Range	CO, ppb	O3, ppb	C2Cl4, ppt	C2H2, ppt	NOy, ppt	PAN, ppt	Comment
August 7, 1990 (M14)*	53-55	4-6	554±81	512-713	71	42	12	42	200	99	NW trajectories. Very low CO, O3, NMHC and PAN
August 13, 1990 (M18)	60-64	0-2	538±100	357-646	87	24	13	58	236	52	N to NW trajectories. Lowest aerosol. Low NMHC.

*Mission Number

ships point to the common sources of CO, C_2H_2 and C_3H_8, and acetone. The relationship with C_2Cl_4 is weaker in part because of the difficulty in resolving small changes in its measured concentrations of less than 20 ppt (precision≈2 ppt) above a background of about 10 ppt. This background itself is somewhat variable because of hemispherical scale gradients in the mixing ratio of C_2Cl_4 due to its moderately short lifetime (≈6 months). Other tracers such as CFCs showed worse precision problems and were not used. Indeed, air masses were strongly influenced by biomass burning in this region [Shipham et al., this issue]. Figure 7 shows the same relationships with oxidized species such as NO_y, PAN, and O_3. Although these data are much more scattered, they still suggest that the sources that impact the distribution of acetone also have a substantial impact on NO_y, O_3, and PAN. These relationships in the context of ABLE3B support biomass burning and industrial pollution as two important sources of acetone which are also responsible for much of the observed atmospheric variability.

Case Studies of Biomass Burning and Industrial Pollution

Biomass burning as a source of acetone. Air masses strongly affected by forest fire plumes were sampled during ABLE3B. In virtually all cases an enhancement of acetone was observed. Figures 8 and 9 present examples of cases where the sampled air was impacted by forest fire plumes. During mission 13 a forest fire plume was sampled between 1 and 3 km altitudes (Figure 8). The unaffected C_2Cl_4 (as well as several anthropogenic halocarbons) rule out the possibility of significant urban/industrial influences. The corresponding enhancement in CO and C_2H_2 and slight
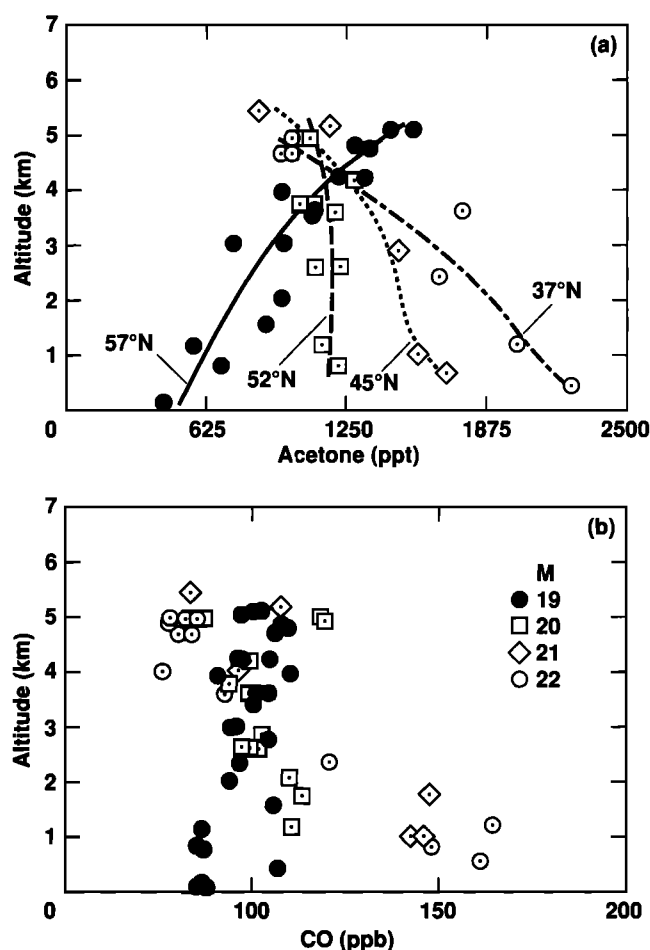

Fig. 4. Variations in the vertical structure of (a) acetone and (b) CO at four latitudes. Data are from missions 19 (solid circle), 20 (open square), 21 (open diamond), and 22 (open circle) representing latitudes of 57°N, 52°N, 45°N, and 37°N, respectively.

(CO, NMHCs, NO_y, and C_2Cl_4). Figure 5 shows the latitudinal behavior of acetone, CO, and C_2H_2 in the free troposphere for altitudes above 4 km. The CO and C_2H_2 mixing ratios are median values from a 5° latitude band. It is evident that free tropospheric concentrations of all these species are larger at the subpolar latitudes. In large part this is due to the slower removal rates and the influence of northerly sources such as fires.

Relationships Between Acetone and Selected Tracer and Oxidized Species

As has been previously stated, the measured concentration of acetone showed significant variability above its geochemical background of 400-600 ppt. The relationship between acetone and other primary and oxidized species is explored to get a better understanding of the nature of its sources. Figure 6 shows these correlations with select molecules such as C_2H_2, CO, C_3H_8, and C_2Cl_4. The first three are tracers of both urban and biomass-burning sources, while the last is purely indicative of urban/industrial pollution. Propane is also an eventual precursor of acetone. The data are segregated to show mixing ratios in the boundary layer (0-2 km) and aloft (>2 km). Figure 6 indicates that a significant association between the variability of acetone and that of key species is present. These relation-

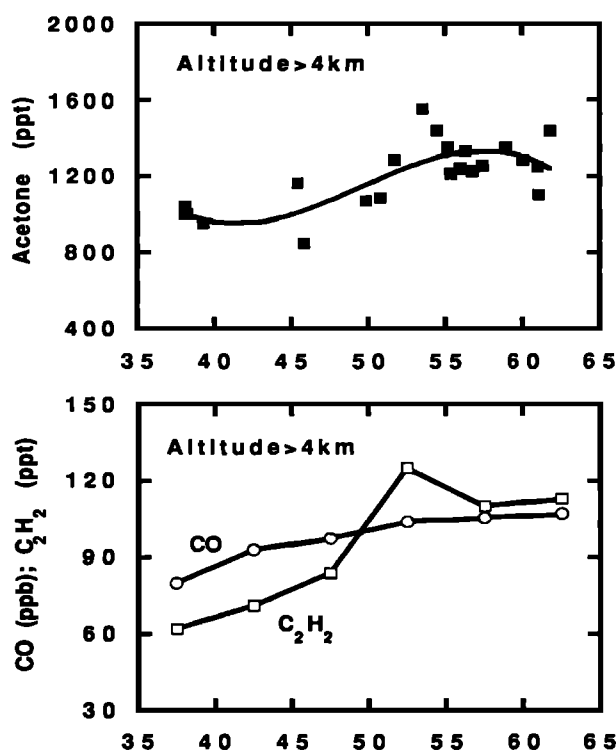Fig. 5. Latitudinal distribution of acetone, CO, and C_2H_2 in the free troposphere. Data are from missions 18-22 for altitudes above 4 km. CO and C_2H_2 data are median mixing ratios within a 5° latitudinal band.
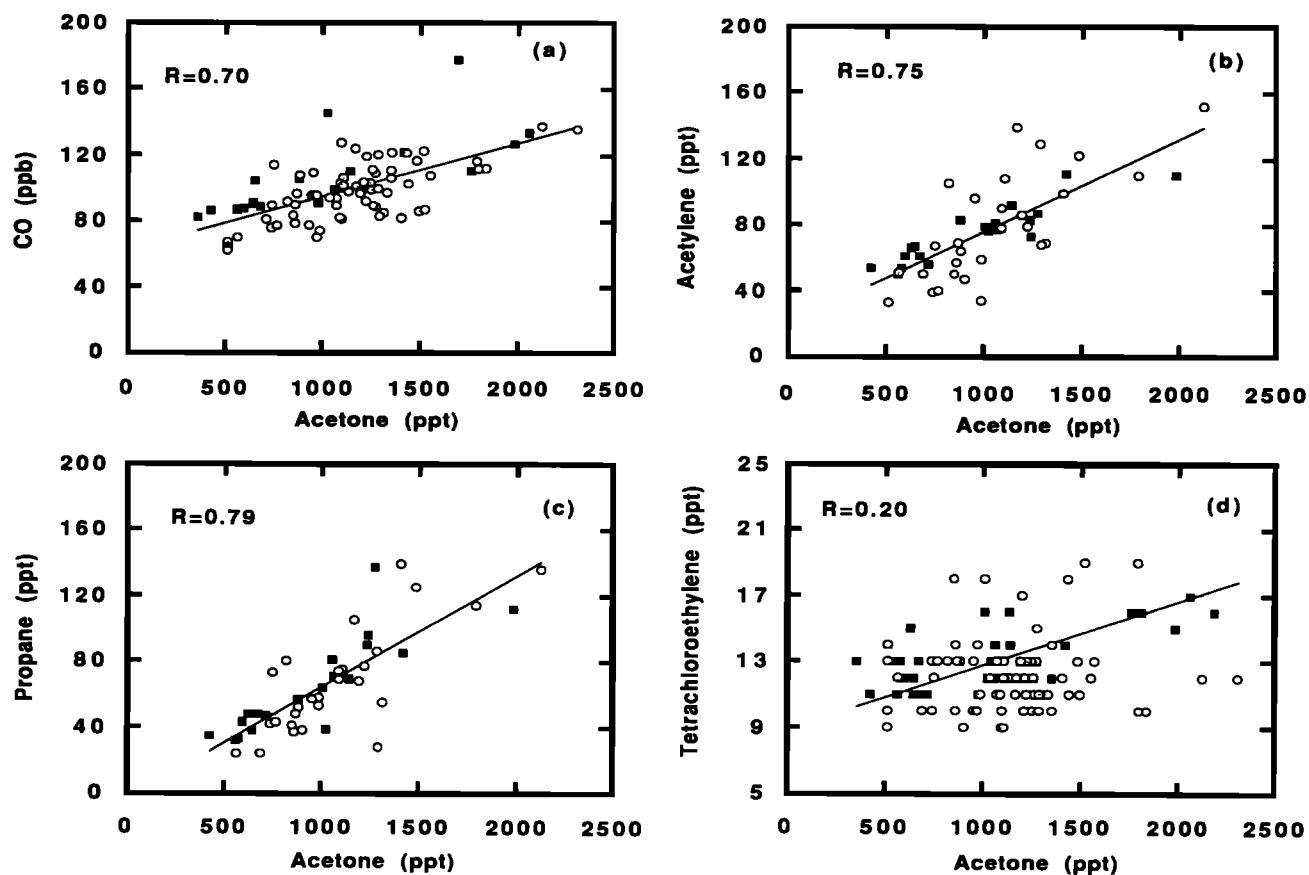
Fig. 6. Relationship of acetone with selected (CO, C_2H_2, C_3H_8, and C_2Cl_4) tracers. Squares and circles represent data collected below and above 2-km altitudes, respectively.

enhancement in O_3 are generally consistent with the combustion source of the air mass. Fires were also visible in the area and, in addition, aerosols were significantly enhanced suggesting a young moist fire plume [Browell et al., 1991]. The general low-level wind flow (associated with the potential temperature of 285 K) varied with convergence of trajectories from the northerly and easterly directions. A second increase in acetone at 4 km coincides with C_2Cl_4 increase and is suggestive of some urban contamination. Indeed, trajectories at the 305 K potential temperature level ($\approx$ 3 km) had a significant southwesterly component suggestive of urban influences.

Figure 9 shows the vertical distribution of acetone, C_2Cl_4, C_2H_2, and CO during transit flights from Goose Bay (53°N) to Frobisher Bay (63°N) and back (missions 18 and 19 on August 13, 1990). Compared to the boundary layer, the free tropospheric levels of acetone and other tracers (e.g., C_2H_2 and CO) are enhanced without commensurate enhancement of C_2Cl_4 or of other anthropogenic halocarbons. Trajectory analyses by Shipham et al. [this issue] also show the general influence of clean Arctic air during the entire flights. Near Goose Bay the upper air masses had high aerosol levels and were probably impacted by biomass-burning plumes that had been somewhat aged [Browell et al., 1991]. Figure 9 acetone distribution implies a very clean boundary layer decoupled from a free troposphere. It is further noted that the very low boundary layer concentrations were also over large water bodies. Acetone is highly soluble and substatial concentrations in the water may exist. Most probably, the low

boundary layer concentrations are due to this exchange with water. As we shall discuss later, while water may act as a reservoir of acetone, the possibility of acetone decomposition in water is unlikely.

Urban/Industrial influences. Two examples of acetone levels in air influenced by urban/industrial sources are shown in Figure 10. During mission 16 (August 9, 1990), which was intended as a marine air mission over the Atlantic, high concentrations of acetone were encountered in the marine boundary layer. These elevated acetone mixing ratios coexisted with high levels of C_2Cl_4 along with tracer species such as CO, NMHC, and NO_y. The corresponding O_3 mixing ratios were not significantly enhanced, suggesting a relatively fresh plume and conditions unfavorable for photochemical activity. In this regard it is noted that the boundary layer air had relatively cold temperatures (15°-20°C) that are generally not conducive to significant O_3 synthesis. Southwesterly trajectories were consistent with the view that these air masses may have originated over the North American continent [Shipham et al., this issue].

Figure 10 shows a second episode of pollution that was encountered in the free troposphere during mission 17. High concentrations of acetone and C_2Cl_4 were seen to coexist between 3 and 6 km altitudes although a great deal of structure was evident. At around 3.5 km a layer containing high aerosol, O_3, and CO (>150 ppb) was seen coincident with high C_2Cl_4 and NO_y concentrations. It is possible that the plume layer between 3 and 4 km had some forest fire smoke mixed in it, while the 4- to 6-km layer was more directly
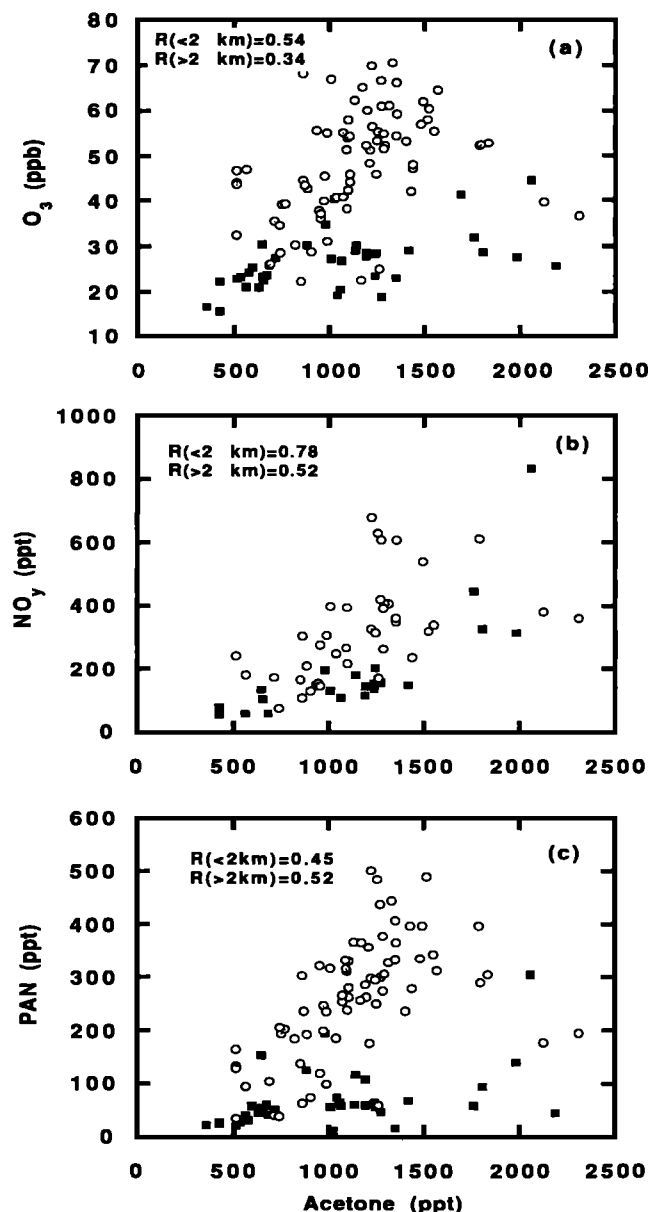
Fig. 7. Relationship of acetone with selected oxidized species (O_3, NO_y, PAN). Symbols are same as in Figure 6.

ment of 2.9 ppb NO_y, 60 ppb CO, 1.2 ppb PAN, 0.07 ppb C_2Cl_4, and 0.3 ppb C_3H_8. Assuming that this is a relatively fresh and a typical urban plume, urban concentrations of acetone can be estimated by scaling up from the urban abundances of known tracers. Typical urban mixing ratios above the background levels can be determined from the available literature to be 20-50 ppb for NO_y, 500-2000 ppb for CO, 0.2-0.5 ppb for C_2Cl_4, and 3-6 ppb for C_3H_8. This suggests that mean concentrations of acetone in polluted regions are only marginally elevated and may be in the 2- to 6-ppb range. It is noted that there was a striking difference in the relative enhancement of industrial pollutants in air masses that had been significantly aged. For example, in two instances (missions 16 and 17 shown in Figure 10) Δacetone/ΔC_2Cl_4 was found to be in the vicinity of 50-60 as opposed to 3 in a fresh plume (mission 21). As we shall see in the next section, the most important source of acetone is secondary in nature, and Δacetone/ΔC_2Cl_4 would increase with the age of the air mass. The secondary sources, however, may take many days to produce acetone and considerable dilution would have occurred. It is noted however, that these estimated 2- to 5-ppb urban acetone mixing ratios are lower than the 12 (±4) ppb reported by Snider and Dawson [1985] in Arizona but comparable to the 0.2- to 3- ppb levels reported by Grosjean et al. [1990] from several Brazilian cities. Isidorov [1990] reports of studies from West Berlin in 1977 where acetone mixing ratios as high as 120 ppb were measured. In all of these cases, substantially different measurement techniques were employed.

Sources, Sinks and Lifetime of Acetone

While the basic steps that determine the atmospheric chemistry of acetone and its precursors are relatively well defined, its sources are not well understood. The job is made further difficult by the fact that very little atmospheric data are available to construct its budget and the removal rates are both a function of season and latitude as acetone is removed by reaction with free radicals, by photolysis and dry and wet deposition. By using both photochemical models and measurements, we make a first attempt to develop a budget for acetone and compare our estimates of sources and sinks to describe areas of uncertainties.

Sources of Acetone

Primary man-made emissions. There is little doubt that direct anthropogenic emissions of acetone are present. Acetone is a commonly used solvent that is manufactured in large quantities. In the United States an attempt has been made to determine its stationary source emissions as part of the NAPAP emissions inventory. Its aggregated emissions from use as a solvent and chemical intermediate in the United States are estimated to be 0.2-0.25 Tg/yr [Middleton et al., 1990]. Acetone has also been identified as a direct emission from automobile tail pipes [Sigsby et al., 1987]. In a study of exhaust from 46 cars it was found that acetone emissions from the tail pipe were highly variable and constituted 10-70% of the total aldehyde fraction which in turn was 2-3% of the total hydrocarbon emission (J. Sigsby, private communication, U.S. EPA, 1991). From these studies one

impacted by urban transport. Trajectories at the 305 K and 315 K potential temperature level show that air masses originated in the Arctic and the Pacific oceans but accumulated pollution during transit over northern United States and southern Canada [Global Tropospheric Experiment (GTE), 1990].

Although this study was not primarily designed to measure polluted atmospheres, opportunities presented themselves to sample polluted air masses which indicated evidence of fresh as well as aged contamination. During the return flight (August 15, mission 22), acetone concentrations in the marine boundary layer, impacted by the east coast urban plume, of 2.3 ppb were measured. A fresh urban plume was also sampled in the boundary layer during mission 21 (August 14, 2207 to 2210 UT). In this plume, levels of all urban tracers registered significant increases. An in-plume enhancement of 0.2 ppb acetone coincided with an enhance-
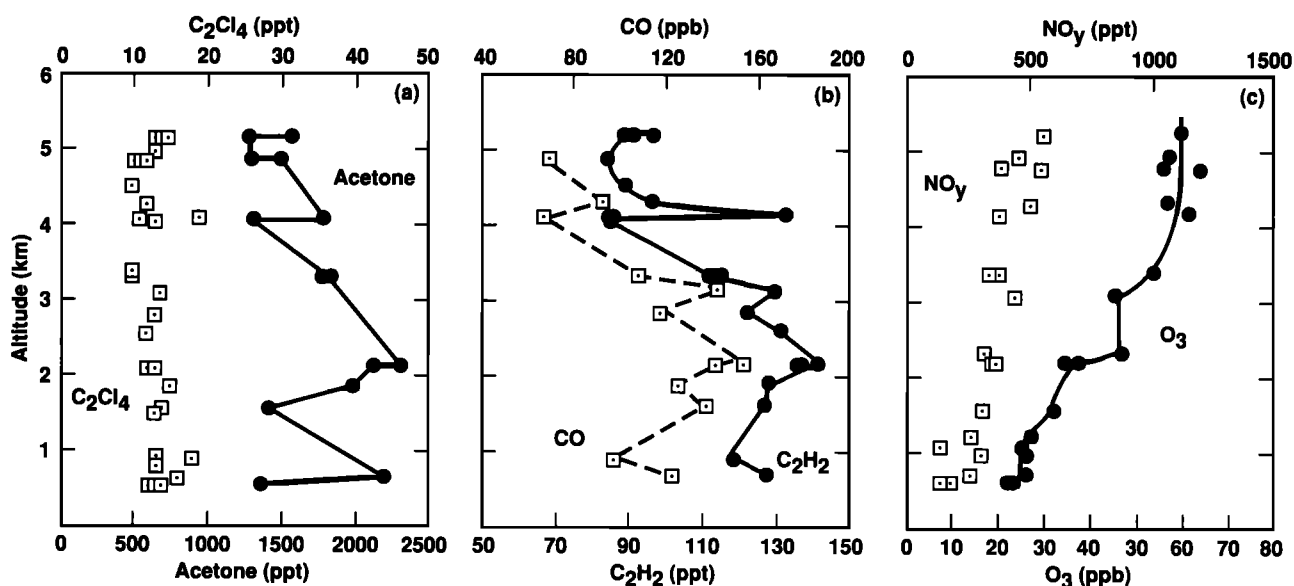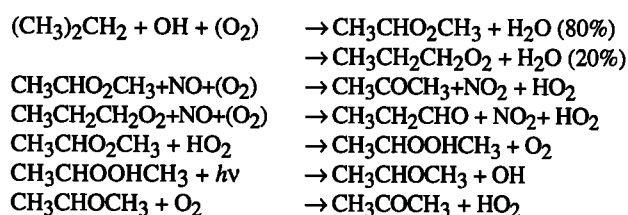
Fig. 8. Evidence of acetone enhancement in a forest fire plume on August 5, 1990 (mission 13). C_2Cl_4 distribution is used to rule out significant industrial pollution.

can estimate that on the average about 1% of the exhaust emission is acetone. In the United States, total hydrocarbon emitted from mobile sources are in the vicinity of 6-7 Tg/yr [*Singh and Zimmerman*, 1992]. Thus an acetone auto exhaust source of 0.05-0.1 Tg/yr can be estimated for the United States. Extrapolation to the world suggests that 0.6-0.8 Tg/yr and 0.2-0.3 Tg/yr of acetone are emitted from stationary and mobile sources, respectively.

Secondary sources of acetone. As has been suggested by *Singh and Hanst* [1981], nearly 80% of propane on a carbon basis is oxidized by OH radicals to produce acetone; the remainder 20% producing propionaldehyde. The following mechanism shows the formation of acetone from propane.

$$(CH_3)_2CH_2 + OH + (O_2) \rightarrow CH_3CHO_2CH_3 + H_2O \ (80\%)$$
$$\rightarrow CH_3CH_2CH_2O_2 + H_2O \ (20\%)$$
$$CH_3CHO_2CH_3 + NO + (O_2) \rightarrow CH_3COCH_3 + NO_2 + HO_2$$
$$CH_3CH_2CH_2O_2 + NO + (O_2) \rightarrow CH_3CH_2CHO + NO_2 + HO_2$$
$$CH_3CHO_2CH_3 + HO_2 \rightarrow CH_3CHOOHCH_3 + O_2$$
$$CH_3CHOOHCH_3 + h\nu \rightarrow CH_3CHOCH_3 + OH$$
$$CH_3CHOCH_3 + O_2 \rightarrow CH_3COCH_3 + HO_2$$

Thus acetone is a product of propane oxidation both in high and in low NO_x environments. The above mechanism actually applies to any alkane with a similar structure (CH_3CHRCH_3) where R is an alkyl group. In the real world the most important candidates in this category are propane,
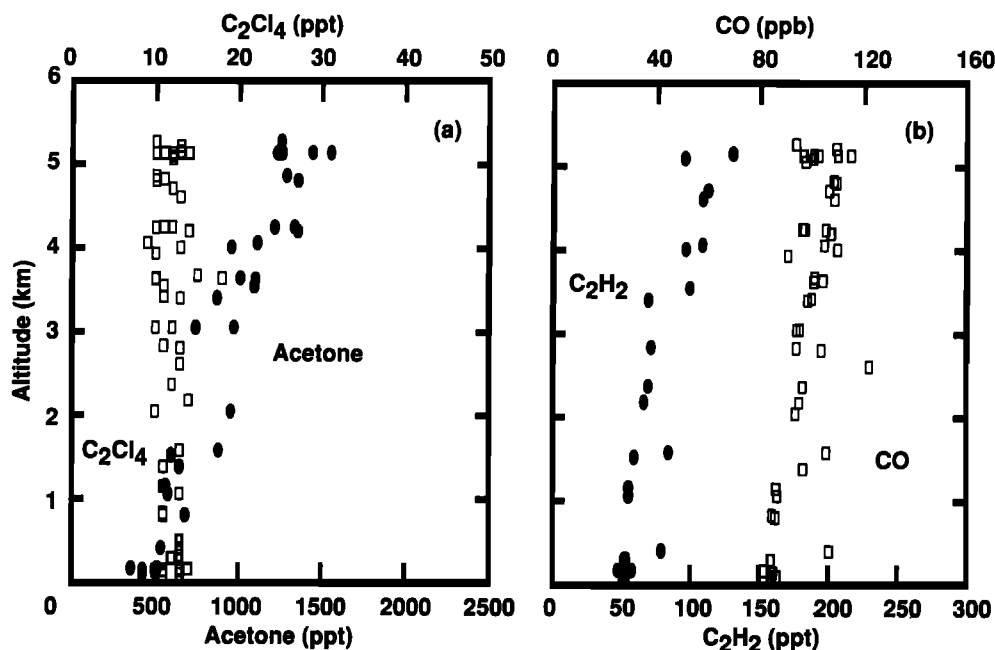

Fig. 9. Acetone and tracer mixing ratios present in the troposphere on August 13, 1990 (missions 18 and 19). Data were collected during to and from transit between Goose Bay (53°N) and Frobisher Bay (63°N).
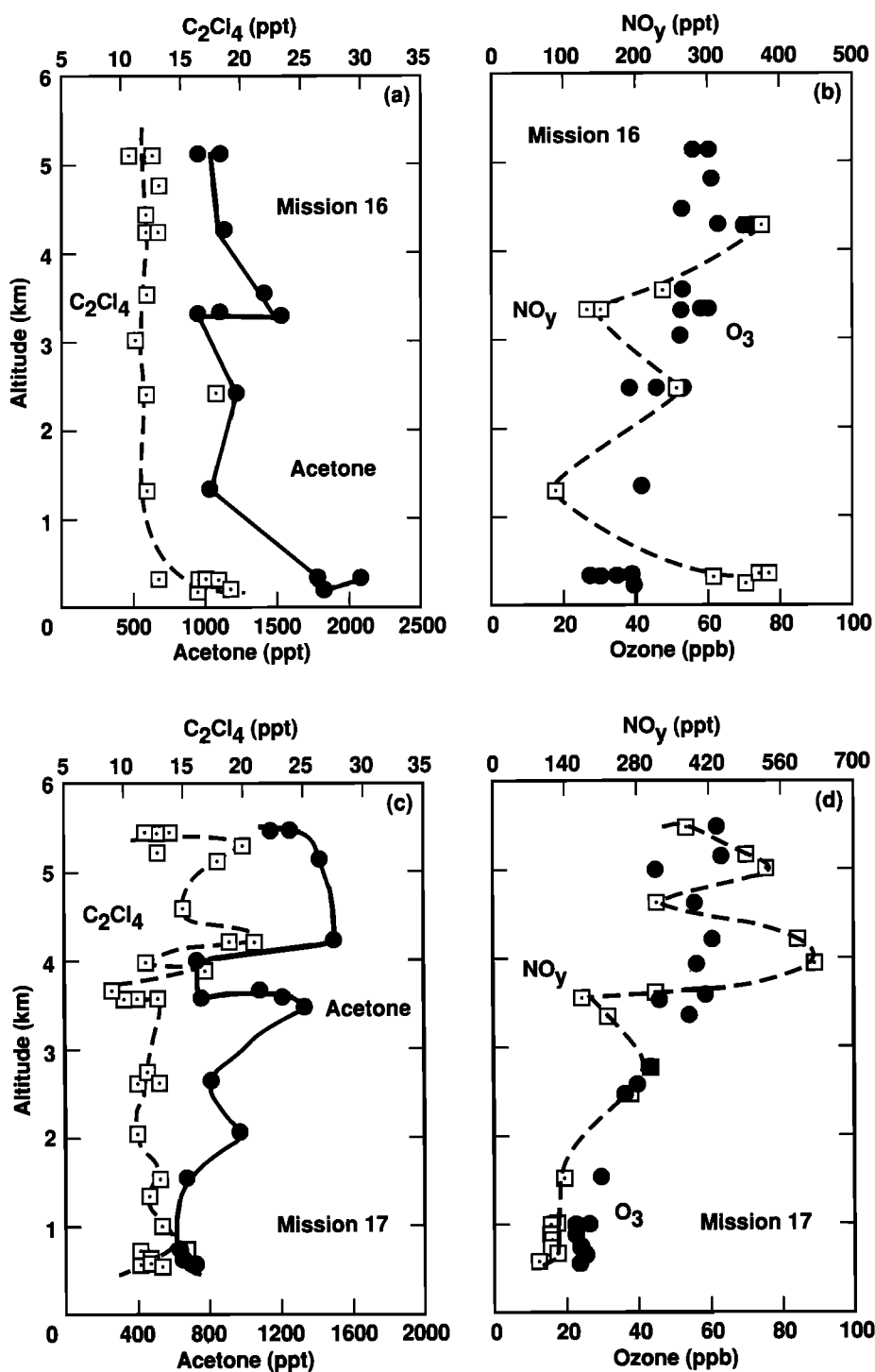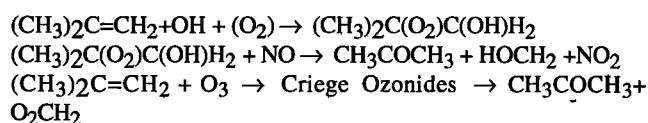
Fig. 10. (a and b) Evidence for acetone enhancement within a polluted air mass in the boundary layer (mission 16, August 9, 1990) and (c and d) the free troposphere (mission 17, August 11, 1990). C_2Cl_4, O_3, and NOy distributions are also shown.

isobutane, and isopentane [Singh and Zimmerman, 1992]. The global source of propane has been estimated to be 15-20 Tg/yr based on direct atmospheric measurements and its calculated removal rate. Known sources add up to only about 5 Tg/yr and large unknown sources (probably natural/biogenic) are presumed to exist. This 15-20 Tg/yr propane source has the potential to produce 16-21 Tg/yr of acetone. Emissions of isobutane and isopentane are less

certain but can be expected to be in the 1-2 Tg/yr range. Thus these aliphatic hydrocarbons alone can produce 17-23 Tg/yr of acetone.

Alkanes are not the only hydrocarbons that can lead to significant acetone formation. Many alkenes, both natural and man-made, also lead to acetone production. The following reactions show the oxidation of isobutene with OH and O_3 leading to the formation of acetone.

$(CH_3)_2C=CH_2+OH + (O_2) \rightarrow (CH_3)_2C(O_2)C(OH)H_2$
$(CH_3)_2C(O_2)C(OH)H_2 + NO \rightarrow CH_3COCH_3 + HOCH_2 +NO_2$
$(CH_3)_2C=CH_2 + O_3 \rightarrow$ Criege Ozonides $\rightarrow CH_3COCH_3+$
O_2CH_2

In many studies involving ozonolysis, acetone has been identified as a product of C_4-C_6 alkene oxidation [*NAS*, 1976]. Indeed, any molecule with a structure similar to $(CH_3)_2=CR_2$ is a potential source of acetone. Of course, as these molecules get more and more complex, competing reactions will cause the yields of acetone to drop. It is estimated that isobutene and other similar alkenes can result in the formation of about 2-3 Tg/yr of acetone.

The above discussion also applies to natural molecules which have structures similar to $(CH_3)_2=CR_2$. The most abundant of these is probably myrcene. Myrcene has been identified as an emission from a variety of plants and vegetation and is often present in measurable atmospheric concentrations [*Isidorov et al.*, 1985; *Singh and Zimmerman*, 1992]. Based on emission studies of deciduous, evergreen, and mixed forests, J. Greenberg and P. Zimmerman (NCAR, Boulder, Colorado, private communication, 1992) find that myrcene emissions range from 0 to 5% of those of α-pinene. The lowest myrcene emissions appear to be from evergreen forests. Plant species such as Scots pine have been found to produce significantly higher emissions of myrcene. Assuming a 200 Tg/yr global source of α-pinene, myrcene emissions can be estimated to be about 5 Tg/yr. Chamber studies of *Arnts and Gay* [1979] suggest that 4% of myrcene carbon may be converted to acetone. This yield may be on the low side because many intermediates that may produce acetone can be lost to chamber walls. Assuming a 4% yield from myrcene, an acetone source of about 0.2-0.3 Tg/yr can be calculated.

A much larger but much more uncertain source of acetone, from the OH oxidation of α-pinene, has been proposed in an unpublished work by Gu et al. (1984). In their laboratory studies they find that 15 (±10)% of α-pinene by mole is converted to acetone. Assuming that about half the α-pinene is removed by reaction with OH, a large source of acetone (6±4 Tg/yr) can be calculated. Unfortunately, no independent corroboration of this result can be found in the published literature. Recent attempts to identify acetone as a product of α-pinene oxidation have been unsuccessful (R. Atkinson, private communication, 1992). Clearly more definitive work is needed to ascertain or rule out this potentially important pathway.

Direct biogenic emissions. Acetone has been identified as a direct biogenic emission from a large number of plants. In one study, 22 plant species characteristic of northern hemisphere forests were studied for organic emissions and acetone was found to be emitted in all cases [*Isidorov et al.*, 1985]. Recent studies in the United States (P. Goldan and R. Falls, NOAA, Boulder, Colorado, private communication, 1992) have also seen these emissions in a variety of rural locations in southeastern United States. It appears that evergreens are the most productive source of acetone and the least productive sources of myrcene. These investigators have also performed limited laboratory studies to evaluate emission fluxes. In laboratory studies with Colorado blue spruce, Alberta spruce, loblolly pine, and aspen, acetone emissions were determined to be 2.10^{-4} to 3.10^{-5} g acetone(C)/g CO_2 (C) uptake. A CO_2 plant uptake of 9 $(\pm 2).10^{16}$ g(C)/yr (gross
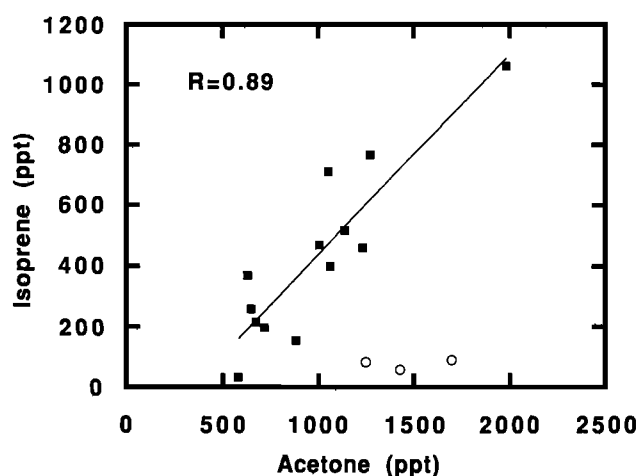

Fig. 11. Relationship between mixing ratios of acetone and isoprene in the boundary layer (0-2 km, 45°-65°N). Data are for overlapping measurements made during missions 13-22. The circles represent data points where the air was heavily influenced by urban pollution (mission 21) and smoke plumes (mission 13).
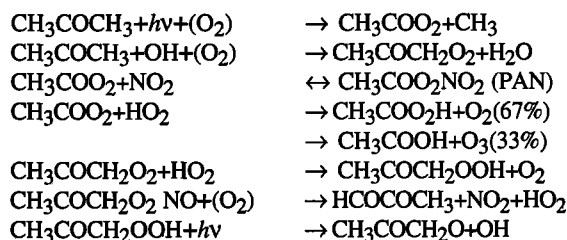
primary productivity) is considered to be a reasonable estimate for the globe. Assuming that the lowest emission rate is representative of plants associated with 80% of CO_2 uptake and the highest rate, typical of evergreens, associated with 20% of CO_2 uptake, an acetone global source of 9 Tg/yr can be calculated. Assuming the lowest emission rate to be representative of all vegetation, a 4 Tg/yr source is possible.

To further explore the existence of biogenic sources of acetone we compared its atmospheric behavior during ABLE3B with that of a well-known biogenic hydrocarbon, namely, isoprene. Figure 11 shows the relationship between measured isoprene and acetone mixing ratios for the overlapping periods during ABLE3B. Since isoprene was rarely measured in the free troposphere, these data are from the boundary layer only (0-2 km). The three outlier data points are shown as circles as they represent conditions where the air sample was strongly influenced by an urban plume (mission 21) or a smoke plume (mission 13). While the available data are limited, Figure 11 is strongly suggestive of the biogenic sources of acetone in the sampled region. It is certainly plausible that direct biogenic emissions of acetone are significant. A great deal more research is needed to understand its biochemistry and to have meaningful quantitative data on its biogenic emissions.

Biomass burning source. The sampled area was impacted by local and distant fires burning over the Hudson Bay lowlands and over Alaska [*Shipham et al.*, this issue]. Acetone has not yet been identified as a direct emission from fires. However, these field data (e.g., Figure 8) leave little doubt that this indeed is the case. Acetone in instances where fire plumes were sampled was clearly elevated along with other species such as CO and C_2H_2. By carefully analyzing measurements within fire plumes, a Δacetone/ΔCO(v/v) = 0.025 (0.02-0.03) could be calculated. This acetone enhancement was probably an upper limit as some formation of acetone from hydrocarbon oxidation may already have occurred within the sampled plumes. The same plumes had a $\Delta C_2H_2/\Delta CO$ ratio in the vicinity of 0.001-0.002 in near agreement with results from studies over Alaska [*Wofsy et al.*, 1992]. It is further noted that the overall mean correlation of acetone and CO is also linear with a slope of 0.03 (Figure

6a) suggesting that much of the acetone-CO correlation is probably dictated by the influence of fires in the region. Assuming a CO source from biomass burning of 200 Tg/yr [Lobert et al., 1991], and a Δacetone/ΔCO of 0.025, an acetone source of 10 (8-12) Tg/yr can be calculated. Clearly more work needs to be done to better quantify this source, but preliminary results from this study suggest that acetone is a significant product of biomass combustion.

Sinks and atmospheric lifetime of acetone. Acetone photolysis and its reactions with OH are probably its major loss pathways. Acetone is capable of producing free radicals and intermediate oxygenates. Among the many products of acetone oxidation are PAN, acetic acid, peroxyacetic acid, methyl glyoxal, and complex peroxides. More detailed chemistry is provided elsewhere [Singh and Hanst, 1981; Henderson et al., 1989; Kanakidou et al., 1991], but the following are some of the salient chemical steps in the atmospheric decomposition of acetone:

$CH_3COCH_3 + hv + (O_2)$ → $CH_3COO_2 + CH_3$
$CH_3COCH_3 + OH + (O_2)$ → $CH_3COCH_2O_2 + H_2O$
$CH_3COO_2 + NO_2$ ↔ $CH_3COO_2NO_2$ (PAN)
$CH_3COO_2 + HO_2$ → $CH_3COO_2H + O_2(67\%)$
                          → $CH_3COOH + O_3(33\%)$
$CH_3COCH_2O_2 + HO_2$ → $CH_3COCH_2OOH + O_2$
$CH_3COCH_2O_2\ NO + (O_2)$ → $HCOCOCH_3 + NO_2 + HO_2$
$CH_3COCH_2OOH + hv$ → $CH_3COCH_2O + OH$

A lesser amount of removal may also occur through wet and dry deposition. Although acetone is highly water soluble, its partition coefficient strongly favors the gas phase (H = 32 M atm^{-1} at 25°C) and there appears to be no known mechanism for hydration and significant photolytic loss in aqueous medium [Chatfield et al., 1987; Betterton, 1991]. The possibility of acetone loss by microbial processes after dissolution in seawater cannot be ruled out. Based on present information, it appears that gas phase losses are favored and removal by any process involving dissolution should be small. Seawater algae may also provide a small marine source of acetone [Whelan et al., 1982]. No direct measurements of acetone in seawater are available, but essential equilibrium with the atmospheric abundance can be expected.

We have used a two-dimensional photochemical model to calculate acetone lifetimes based on photolysis and OH removal alone. Absorption cross sections used are those of Emrich and Warneck [1988] and the OH field is consistent with a methyl chloroform atmospheric lifetime of 6.2 years. Details of the nature of these two-dimensional calculations have already been described by Kanakidou et al. [1991]. Figure 12a shows these calculated atmospheric lifetimes at 55°N. In summer (July 1), acetone lifetime is calculated to be 10-30 days with OH removal dominating in the boundary layer and photolysis dominating in the free troposphere. This lifetime is significantly longer in other seasons approaching 1-3 months in April and 6-36 months in January. Figure 12b shows the dependence of acetone lifetime (July 1) with latitude and height. As can be expected from the OH and UV distribution in the atmosphere, the lifetime of acetone is substantially shorter in the tropics, approaching 10-20 days.

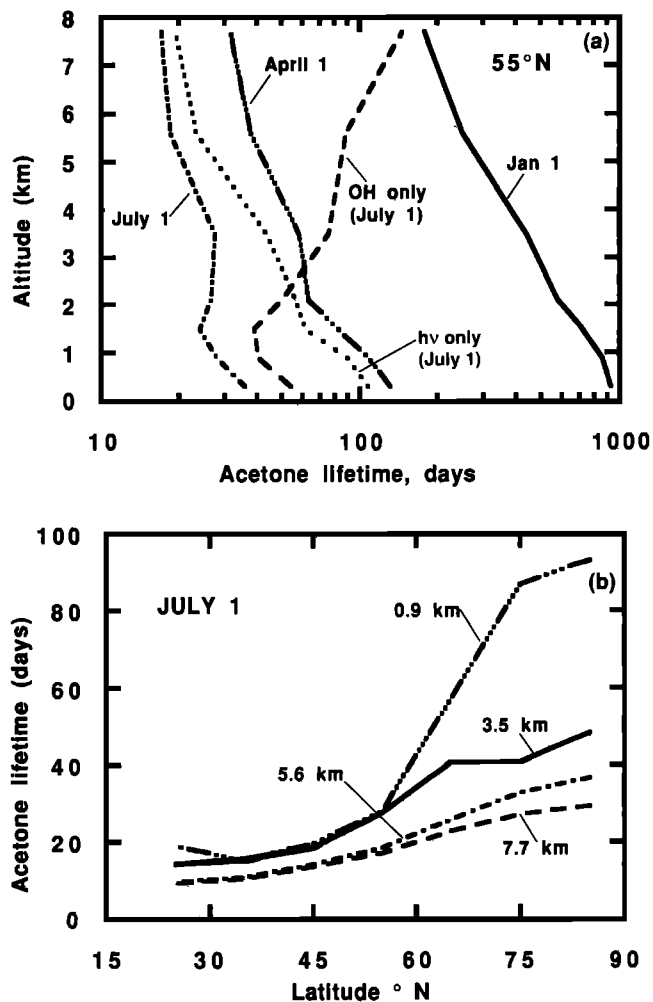To ascertain the sink strength of acetone both two-

Fig. 12. (a) Calculated atmospheric lifetime of acetone as a function of season and height at 55°N and (b) as a function of latitude and height for July 1. Lifetimes are based on two-dimensional model calculations with removal by photolysis and reaction with OH only. In (a) the lifetime (for July 1) due to photolysis (hv only) and OH (OH only) is also shown separately .

dimensional and three-dimensional models of the atmosphere were used [Kanakidou et al., 1991, 1992]. In both of these models the only source of acetone was that resulting from propane oxidation. The chemical scheme used in both two-dimensional and three-dimensional models described the O_3-OH-NO_x-CO-CH_4-C_2H_6 and C_3H_8 chemistry [Kanakidou et al., 1991]. The model calculations incorporated seasonal and vertical resolution for the OH and the UV field as well as a measure of dry deposition. The deposition velocity (V_d) of acetone is probably extremely small and may be negligible [Wesely, 1989]. In the three-dimensional model run, a uniform deposition velocity of 0.05 cm/s, typical of similar species, was applied for acetone. In these model runs, nearly 64% of acetone was removed by photolysis, 24% by reaction with OH, and the remaining 12% by dry deposition. A global mean lifetime of acetone of about 16 days was derived from the three-dimensional model. The three-dimensional model required a global propane source of 17 Tg/yr to fit the propane budget: 12 Tg of this source is distributed according to NO_x industrial emissions, 1 Tg is assumed to be emitted by tropical biomass burning, 2 Tg from plants, and 2 Tg
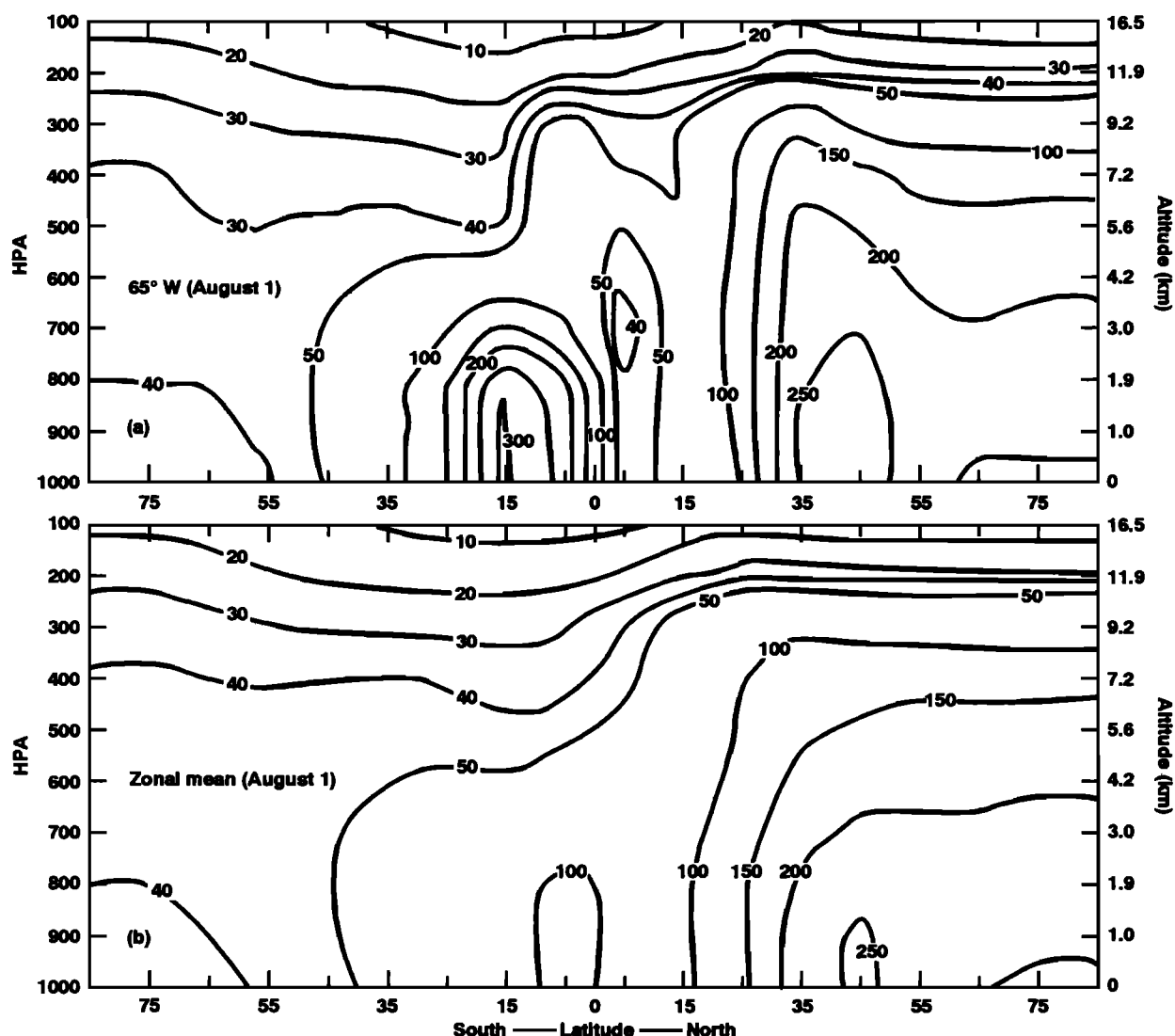
Fig. 13. Calculated atmospheric distribution of acetone for August 1 based on a three-dimensional model of the troposphere. (a) The isopleths show acetone mixing ratios (ppt) as a function of latitude for 65°W longitude and (b) for zonal mean conditions. The acetone source is exclusively due to propane oxidation and a uniform acetone deposition velocity of 0.05 cm/s is used. A 17 Tg/yr propane source, as described by *Kanakidou et al.* [1992] is employed.

from oceans [*Kanakidou et al.*, 1992]. An 18 Tg/yr global acetone source is generated from this propane oxidation in the model. On an annual basis, 90% of this source is in the northern hemisphere (NH). In the NH, maximum values of acetone are computed for February and minimum values for the end of July when photochemical destruction of acetone is near its peak.

Figures 13a and 13b show the model-derived diurnal mean acetone abundance for 65°W longitude and zonally mean conditions for August 1 as a function of latitude and height. The relatively short lifetime of acetone and its precursors, of the order of a few weeks, results in sharp latitudinal and longitudinal gradients. The meridional distribution of the zonal mean acetone concentration is relatively regular decreasing with latitude and height. In the southern hemisphere (SH) an acetone zonal mean concentration of 20-40 ppt is calculated for August. A model-distributed global photochemical acetone source of 18 Tg/yr results in about 200 ppt background acetone concentration in the lower troposphere at 55°N in August. Based on actual measurements

between 35° and 65°N, a true background concentration of acetone in this region was 500-600 ppt. Earlier, more limited data of Penkett from 35°N suggests a similar background level. Scaling up the model results at least for the NH would suggest that a global acetone source of 40-60 Tg/yr would be consistent with these NH measurements. This estimate assumes that all acetone sources have a distribution similar to the source resulting from propane oxidation.

Acetone Global Budget

Table 3 summarizes all the sources that have been quantified above in a rough fashion. Although substantial uncertainties exist, an acetone global source of about 40 Tg/yr probably exists. Nearly half of this source is as a result of oxidation of NMHC with propane being the dominant precursor. Substantial biogenic (20%) and biomass burning (25%) sources are estimated. At present it appears that the atmospheric acetone abundance and its removal rates would be compatible with a global acetone source/sink of

TABLE 3. Global Sources and Sinks of Acetone

Source Type	Global Annual Emissions, Tg/yr	Comment
Primary anthropogenic		≈95%NH
Stationary sources	0.5 (0.4-0.7)	extrapolated
Mobile sources	0.3 (0.2-0.3)	from U. S. data
Primary biogenic	9 (4-18)	≈60%NH, poorly quantifiable
Secondary anthropogenic		≈80%NH
And biogenic		
propane oxidation	17 (15-20)	
isobutane/isopentane oxidation	2 (1-3)	
isobutene/isopentene oxidation	1 (1-2)	
myrcene oxidation	0.2 (0.2-0.3)	
α-Pinene oxidation*	---	highly uncertain chemistry
Biomass burning	10 (8-12)	from this study, ≈80%SH
Total Source strength	40 (30-46)	≈60%NH;40%SH
Total sink strength[+]	40-60	2D/3D model calculation

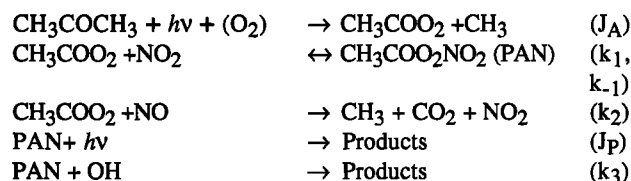NH, northern hemisphere; SH, southern hemisphere.

*A large acetone source (≈6 Tg/yr) may be postulated from the oxidation of α-pinene based on the kinetic study of Gu et al. (1984). No independent verification of this result has been possible.

[+]Sink estimate is based on scaling up of model output to fit measurements at 55°N. In the model used, acetone loss is due to photolysis (≈64%), OH reactions (≈24%), and dry deposition (≈12%).

40-60 Tg/yr. However, this calculation is constrained by rather limited atmospheric data largely collected from the northern hemisphere in one season. Based on estimates shown in Table 3, the source-sink relationship for acetone is roughly in balance but the uncertainties are quite large and in many cases unquantifiable. Clearly a body of atmospheric data that defines the seasonal, vertical, and latitudinal distribution of acetone is needed. Much more accurate information on the direct emissions of acetone from vegetation and biomass combustion are required to further improve the budget of acetone. It is possible that atmospheric abundances of acetone can also be derived from the Jungfraujoch spectra [Ehhalt et al., 1991] and this possibility should be further explored.

Acetone As a Source of Peroxyacetylnitrate (PAN)

Singh and Hanst [1981] have proposed that photolysis of acetone produces peroxyacetyl radicals which can lead to PAN formation. A zero dimensional model as used by Singh and Hanst [1981] and new rate constants as presented by Demore et al. [1992] and Kanakidou et al. [1991] have been used to further evaluate this possibility in light of these new acetone measurements. The basic chemical mechanism is described as follows with a steady state solution for PAN.

$$CH_3COCH_3 + h\nu + (O_2) \rightarrow CH_3COO_2 + CH_3 \quad (J_A)$$
$$CH_3COO_2 + NO_2 \leftrightarrow CH_3COO_2NO_2 \ (PAN) \quad (k_1, k_{-1})$$
$$CH_3COO_2 + NO \rightarrow CH_3 + CO_2 + NO_2 \quad (k_2)$$
$$PAN + h\nu \rightarrow Products \quad (J_P)$$
$$PAN + OH \rightarrow Products \quad (k_3)$$

$$[PAN]_{ss} = J_A[CH_3COCH_3]/\{(1 + k_2[NO]/k_1[NO_2])(k_3[OH] + J_P) + k_{-1}k_2[NO]/k_1[NO_2]\}$$

Using available kinetic data, the above equation can be used to calculate steady state PAN mixing ratios for typical atmospheric conditions and acetone abundances. These, as a percentage of acetone mixing ratio, are calculated to be about

2% at 280°K (≈2 km), 10% at 270°K (≈4 km), and 100% at 250°K (≈7 km). The higher yield of PAN with altitude is due to the greater thermal stability of PAN at lower temperatures and to the fact that photolytic decomposition rate of acetone increases with altitude [Kanakidou et al., 1991]. These zero-dimensional calculations suggest that in the middle and upper troposphere, 100-500 ppt of PAN may result from acetone photolysis alone. Needless to say, vertical mixing and advection would tend to reduce the actual yield of PAN.

Three-dimensional model runs were made to more accurately address the role of acetone in PAN formation. Model results showed that in the high northern latitudes (55°N) for August, the contribution of the calculated acetone (≈200 ppt) to the zonal average PAN concentration is 40-50 ppt in the middle and upper troposphere and lower (≈10 ppt) near the surface. Scaling up to the measured concentrations of acetone (500-1000 ppt) one can estimate that some 100 to 200 ppt of the middle/upper tropospheric PAN may have resulted from acetone oxidation alone. It is reasonable to postulate that acetone was probably a major PAN precursor over northeastern Canada during ABLE3B [Singh et al., this issue] and would play an important role everywhere if substantial concentrations are found to be globally present.

CONCLUSIONS

Acetone, an oxygenated organic hydrocarbon, has been found to be the dominant nonmethane organic species present in the subarctic atmosphere sampled during ABLE3B. A substantial global source in the vicinity of 40-60 Tg/yr is estimated to be present. It is suggested that nonmethane hydrocarbon oxidation, biomass burning, and direct biogenic emissions are important sources of acetone. Insufficient data are available to reliably quantify these source strengths. By using atmospheric data and photochemical models, a rough atmospheric budget of acetone has been presented. While the source-sink equation appears to be roughly balanced, much more atmospheric and source data are needed to reliably estimate these relationships. Atmospheric abundance of acetone is expected to have strong latitudinal and seasonal

variations, but no direct observations are available. The possibility of deriving acetone abundances from atmospheric spectra (such as the Jungfraujoch spectra) should be explored. It is postulated that acetone photochemistry may be responsible for a significant fraction of the observed free tropospheric PAN. Oxygenated molecules are important components of the atmosphere even though very little about their sources and fate is known.

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