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BIBLE A whole-air sampling as a window on Asian biogeochemistry

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[1] Asian trace gas and aerosol emissions into carbon, nitrogen, and other elemental cycles will figure prominently in near term Earth system evolution. Atmospheric hydrocarbon measurements resolve numerous chemical species and can be used to investigate sourcing for key geocarriers. A recent aircraft study of biomass burning and lightning (BIBLE A) explored the East Asian atmosphere and was unique in centering on the Indonesian archipelago. Samples of volatile organics taken over/between the islands of Japan, Saipan, Java, and Borneo are here examined as a guide to whole-air-based studies of future Asian biogeochemistry. The midlatitude onshore/offshore pulse and tropical convection strongly influence concentration distributions. As species of increasing molecular weight are considered, rural, combustion, and industrial source regimes emerge. Methane-rich inputs such as waste treatment and rice cultivation are evidenced in the geostrophic outflow. The Indonesian atmosphere is rich in biomass burning markers and also those of vehicular activity. Complexity of air chemistry in the archipelago is a direct reflection of diverse topography, land use, and local economies in a rapidly developing nation. Conspicuous in its absence is the fingerprint for liquefied petroleum gas leakage, but it can be expected to appear as demand for clean fossil fuels rises along with per capita incomes. Combustion tracers indicate high nitrogen mobilization rates, linking regional terrestrial geocycles with open marine ecosystems. Sea to air fluxes are superimposed on continental and marine backgrounds for the methyl halides. However, ocean hot spots are not coordinated and suggest an intricate subsurface kinetics. Levels of long-lived anthropogenic halocarbons attest to the success of international environmental treaties while reactive chlorine containing species track industrial air masses. The dozens of hydrocarbons resolvable by gas chromatographic methods will enable monitoring of upcoming Asian modernization. Crucial uncertainties are underscored. Signatures for Asian combustion processes and megacities have been obtained only indirectly or at a distance. Detailed fingerprinting must be combined with regular aircraft and ground station measurements to maximize utility of the database. *INDEX TERMS:* 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0394 Atmospheric Composition and Structure: Instruments and techniques; *KEYWORDS:* hydrocarbons, troposphere, Indonesia, sources, biogeochemistry

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1. Introduction

[2] Demographics dictate that during the era of global change, the human condition will evolve most rapidly in Asia. The continent contains over half the global population but has only begun to industrialize [*World Resources Institute* (*WRI*), 1992; *United Nations* (*UN*), 1994]. Economic growth has been sporadic but even at average rates will create a focus for energy consumption and the emission of climate altering substances [*Office of Science and Technology Policy* (*OSTP*), 1997; *Elliott et al.*, 1997a, 1997b]. Several types of source transition can be expected to occur as Asia modernizes. With accumulation of wealth, demand for the locally clean petroleum gases will rise [*Ausubel et al.*, 1988; *Lu*, 1993; *McCreary et al.*, 1996]. A coastal migration is likely to shift and concentrate the population base eastward [*WRI*, 1992; *Streets et al.*, 1999]. Sharp and extensive boundaries will be created between remaining natural ecosystems, their managed counterparts and the new megacities [*UN*, 1992; *Chameides et al.*, 1994; *Vitousek et al.*, 1997]. The attendant changes will be among the largest ever

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experienced by the Earth system, and will come under close scientific scrutiny [*Elliott et al.*, 1999a, 1999b]. A crucial perspective on Asian growth will be the biogeochemical [*Schlesinger*, 1997; *Elliott et al.*, 1999a, 1999b]. Carrier species of interest can be classified and monitored according to the major elemental cycles [*Cicerone and Oremland*, 1988; *Duce et al.*, 1991; *Vitousek and Matson*, 1993; *Intergovernmental Panel on Climate Change* (*IPCC*), 1995].

[3] Techniques of analytical chemistry which discriminate large numbers of elements or molecules constitute powerful tools for examining the sources and fate of substances moving through the Earth system [*Hopke*, 1985]. The couple of whole-air sampling and gas chromatography now resolves dozens of the gas phase hydrocarbons, simultaneously and in air from across the global troposphere [*Blake et al.*, 1992, 1994, 1996a, 1996b, 1996c]. A variety of secondary groups are identifiable including oxygenates, nitrates and halogens. The volatile organics are carriers of direct and indirect greenhouse potential [*IPCC*, 1995; *Elliott et al.*, 1996]. Their concentration distributions will also elucidate sourcing for compounds in other phases and in other elemental cycles. We are currently engaged in a general effort to adapt whole-air methods to the study of Asian growth [*Blake et al.*, 1997; *Elliott et al.*, 1997a, 1997b, 1999a, 1999b]. Preliminary work has been conducted under the NASA Pacific Exploratory Mission series of aircraft campaigns (PEM) [e.g., *Hoell et al.*, 1996, 1997, 1999; *Blake et al.*, 1997, *Fuelberg et al.*, 1999]. PEM attempted to characterize regions of the Pacific Rim environment in sequence. We have participated recently in a Japanese sponsored aircraft study which complements the NASA projects in many respects. Much of the East Asian atmosphere was within range during the month long experiment. Penetration of lightning plumes was a major objective so that transit to Indonesia was required and a majority of flights radiated from the island of Java. The focus upon Indonesia/Malaysia is unusual among aircraft chemistry studies and provides the opportunity to push our interpretations southwestward.

[4] In the present work we examine whole-air data gathered during the Japanese mission, from Asian growth and Earth system perspectives. Signatures for various combustion types are prominent even as the suite of pure hydrocarbons is studied alone. Methyl halides serve in part as tracers of sea to air flux and so link the terrestrial and marine regimes. The anthropogenic halocarbons clearly indicate the wax and wane of industrial activities. We are able to identify and locate many sources, and demonstrate that the detectable hydrocarbons trace major geocycles either directly or indirectly. Some results regard design of future experiments. We argue that a coordinated application of whole-air-based hydrocarbon measurements is needed, conducted at regular intervals in position/time. The capability is at hand to monitor human alternations to Asian biogeochemistry in an abstract but highly informative hydrocarbon space.

[5] Our text begins with a description of the Japan/Indonesia flights, and of hydrocarbon measurements conducted en route. We down-select segments which offer cross cutting coverage of the biogeochemosphere. Throughout the results section the organization is chemical. We step through families of organics d by their major functional groups: alkanes, olefins, alkynes, aromatics, natural halides/nitrates and anthropogenic halogenates. Following inspection of the measurements we survey the types of statistical analyses which may be relevant. Hydrocarbon detection methods have advanced over the last decade such that data sets are rich but unwieldy [e.g., *Blake et al.*, 1997]. A systematic approach to pattern extraction is advisable if the techniques are to be fully exploited. In a concluding discussion section we make geochemical connections to data on the organic gases. Here the hierarchy is elemental, then geographical. We treat linkages to the carbon and nitrogen cycles, and move from the continent to the coast to open waters.

[6] The Earth system level conclusions we draw are manifold and diverse. The single carbon species can be regressed against one another to show that anaerobic methane production is operative from within China [*Khalil and Rasmussen*,1983; *Cicerone and Oremland*, 1988; *Schlesinger*, 1997]. The different combustion signatures alternate in the alkane distribution, with C5 marking gasoline consumption [*Mayrsohn and Crabtree*, 1976; *Logan et al.*, 1981; *Cullis and Hirschler*, 1989, 1990; *Blake and Rowland*, 1995; *Guenther et al.*, 1995]. Flights from Java to Borneo illustrate the complexity of the atmosphere in the Indonesian microcosm. The larger, sparsely populated island exhibits a strong biomass burn signature [*Andreae*, 1991; *Blake et al.*, 1996c]. Over Java vehicular activity can be discerned. The oil-based but eclectic (developing) economy of Indonesia [*WRI*, 1992; *Brown*, 1995a, 1995b] makes its presence felt in the database. Automotive emissions are also detected in and around Japan, which boasts one of the world's wealthiest populations. Triple bonded and aromatic compounds are useful tracers in this regard. A special effort is made to observe the input of the methyl halides and methyl nitrate from the ocean to continental and marine air masses [*Singh et al.*, 1983; *Liss*, 1986; *Lobert et al.*, 1995]. Flux balances can be constructed for the atmospheric boundary layer, but hot spots for the sea sourced species do not regularly correspond with each other. Man made halocarbons serve their usual role as tracers of industrial activity [*Rowland and Molina*, 1975; *IPCC*, 1995; *Blake et al.*, 1997]. Short lived perchloroethylene maximizes in certain plumes over the open ocean but the peaks may be distinct from those of the methyl halides. Distributions for all the molecular groups are shaped by the meteorological pulse of the Asian landmass. Winter/spring flow is westerly, summer/fall monsoonal. Over Indonesia convective vertical mixing dominates [*Kao*, 1948; *Thompson*, 1951; *Schmidt*, 1952].

[7] We provide highlights of our analyses as two dimensional species versus species plots. Ethane is often used as the baseline compound because it is simple in structure and ubiquitous in source fingerprints [*Mayrsohn and Crabtree*, 1976; *Blake et al.*, 1992, 1994]. For many of the graphs we note that movement through the space is likely to occur as Asia modernizes. For example, the economy of the People's Republic of China is coal intensive but demand for the fossil fuels perceived to be locally clean will almost certainly grow [*Smil*, 1988; *Lu*, 1993; *Finkelman et al.*, 1999]. The fingerprint for liquefied petroleum gas leakage [*Blake and Rowland*, 1995] is today missing from our Asian samples. Propane and butane relationships to baseline species may evolve in time. We argue that it is migration

of data through the total (n dimensional) species space which should be examined. In this spirit we conduct principal components analysis of the Japan/Indonesia hydrocarbons [*Henry and Hidy*, 1979, 1981a, 1981b; *Hopke* 1981; *Hopke et al.*, 1983] and extract signatures which are recognizable from the literature.

[8] The biogeochemical linkages discussed in the present work permeate the Earth system. The human population of mainland Asia is dense, immense and anxious to contribute to the global economy [*Lu*, 1993; *Brown*, 1995a, 1995b]. There will be a tendency to pass quickly through the standard energy market series, from biofuels and coal to oil products and natural/liquefied petroleum gas [*Ausubel et al.*, 1988; *Ausubel*, 1995; *Elliott et al.*, 1999a, 1999b; *Streets et al.*, 1999]. Combustion signatures for the alkanes will shift toward the pentanes or butanes. Combustion mobilizes nitrogen which will transfer to both managed and natural terrestrial ecosystems, enhancing soil nutrient pools [*Luizao et al.*, 1989; *Keller and Matson*, 1994; *Galloway*, 1996; *Vitousek et al.*, 1997]. The hydrocarbons oxidize in the presence of NO_x to give ozone which can damage crops and impact harvests [*Chameides et al.*, 1994]. The ozone in turn may cross the entire Pacific Basin and increase background levels in western North America [*Elliott et al.*, 1997a, 1997b]. The open North Pacific is downwind of Asia in the geostrophic sense and is nitrogen limited by and large [*Berger and Wefer*, 1991; *Longhurst et al.*, 1995; *IPCC*, 1995]. Ocean fertilization is a possibility [*Fanning*, 1989; *Owens*, 1992; *Michaels*, 1993]. Whole-air hydrocarbon analysis can help to apportion sourcing of fixed nitrogen. A feedback loop exists through the production of the dissolved trace gases in seawater [*Elliott et al.*, 1997b; *McNair et al.*, 1998]. Marine distributions and fluxes would be shifted by aeolian fertilization. The phenomenon is yet another which can be tracked through the whole-air methods.

[9] Our analysis of the Japan/Indonesian campaign underscores the power of whole-air hydrocarbon sampling to elucidate effects of Asian growth. However, it also points toward key uncertainties which must be dealt with. For example, olefins other than ethylene consistently fell below detection limits on the flights investigated. Most air masses encountered were remote from surface contact so that shorter lived molecules had reacted away (alkene lifetimes <days [*Singh and Zimmerman*, 1992; *Blake et al.*, 1997]). There is a strong need to conduct aircraft missions closer to Asian input zones. Longer flight legs must be arranged within the marine boundary layer since gas distributions may be influenced by subsurface features at the oceanic mesoscale [*Semtner*, 1986; *Semtner and Chervin*, 1992; *Chu et al.*, 1999]. Major uncertainties can also be associated with the source profile library. Hydrocarbon signatures for the combustion types are similar with respect to alkane/alkene ratios. Emissions are thus difficult to segregate. An organized fingerprinting exercise would be desirable, cutting across the spectrum of Asian land use and fuel types. Several mission design refinements are envisioned which might lead to biogeochemically weighted programs.

2. Methods

[10] The Japanese aircraft campaign under consideration took as its themes bio rn and lightning chemistry. It is identified by the acronym BIBLE (Biomass Burning and Lightning Experiment), and by the postscript A (first in a series). The project was sponsored by an equivalent of the U.S. NASA, the Japanese National Space Development Agency (NASDA). Detailed background information and descriptions of instruments can be found at the Web site www.Eorc.nasda.go.jp/Sciences. A map of the study area and flight tracks is offered in Figure 1. The major flights numbered 1 through 15 were carried out in the late summer and early fall of 1998. One training flight is also shown, conducted in April of 1998. The basic experimental strategy was transit to Indonesia, a convectively active area [*Kao*, 1948; *Thompson*, 1951] which was the site of a massive biomass burning episode in 1997 [*Brauer and Hishamhashim*, 1998; *Levine*, 1999]. A strong suit of the Japanese atmospheric chemistry community has traditionally been NO_y measurement [*Kondo et al.*, 1987, 1996], and both lightning and the burns would be expected to yield strong plumes of oxidized nitrogen.

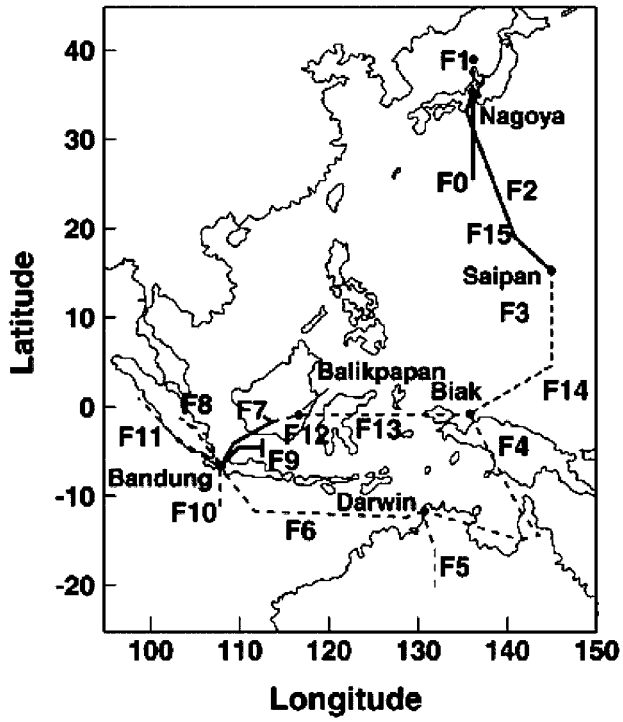

Figure 1. Tracks for the 1998 BIBLE A (first Biomass Burning and Lightning Experiment) aircraft atmospheric chemistry campaign. Flight 0 was a test conducted in April 1998. Flights 1 through 15 constituted the expedition proper. Only highlighted legs are analyzed in the current work.

[11] We will restrict our hydrocarbon analysis to the flights highlighted on the map. The April test excursion ran almost due south from the Nagoya command center to 26 degrees north latitude. We have arbitrarily labeled it 0 here, to distinguish it from the others. Flight 2 of the campaign proper consisted of transit south over the Volcano and Northern Marianas islands to Saipan. Flight 7 began on the Indonesian island of Java after several more transits and intensives, and included a descent over Borneo (Kalimantan portion). Flight 9 followed a similar trajectory but the single

Table 1. A Subset of Hydrocarbons Detected and Analyzed Under BIBLE A for Their Relevance to Asian Growth and Biogeochemical Issues[a]

	Detected Compounds
One carbon species	carbon monoxide and methane
Alkanes	ethane, propane, normal butane, isobutane, normal pentane, isopentane, a variety of hexanes, heptanes, octanes and nonanes
Alkenes	ethylene, propylene, 1-butene, trans-2-butene, cis-2-butene, several pentene isomers
Alkynes	ethyne (acetylene) and propyne
Aromatics	benzene, toluene, p-xylene, m-xylene, o-xylene, ethylbenzene
Halogenated methanes	methyl chloride, methyl bromide, methyl iodide, methylene bromide, bromoform
Organic nitrates	methyl nitrate; two, three, four and five carbon nitrates
Anthropogenic halogenates	carbon tetrachloride, chloroform, fluorocarbons 11 and 12, perchloroethylene
Sulfur species	carbonyl sulfide, dimethyl sulfide

[a]Species are grouped roughly into chemical families and listed in order of increasing structural complexity.

descent was made over the Java Sea. Most of the BIBLE A air time was spent at high altitude. The G2 (Gulfstream) aircraft employed is designed for high, fast flying and it was anticipated that the lightning NO_x signal would be strongest aloft. In this sense the experiments are less than ideal from the biogeochemical perspective, yet we are able to demonstrate the utility of our concepts nonetheless. The flights we have selected for closer investigation are those with the longest legs near the surface, whether over land or sea. Numbers 0 and 2 section the geostrophic outflow aloft during the seasons when continental high and low pressure systems respectively dominate. The latitude 25 degrees is identified as a region of sharp transition between regimes of midlatitude and tropical air chemistry [*Blake et al.*, 1997]. Flight 2 continues southward beyond this threshold (Saipan is located at 15 degrees north latitude). A long leg was included in the marine boundary layer approaching and above the Marianas islands.

[12] The Indonesian and Malay archipelago is a prime frontier of biogeochemistry. For example, it has thus far been bypassed by the PEM series [*Hoell et al.*, 1996, 1997, 1999]. It can be thought of as a microcosm for the global tropics. Densely populated cities exist in close proximity with open ocean and unexplored rain forests. Flight 7 is among those we have selected because it enters the boundary layer over Borneo, which is sparsely inhabited and undergoing deforestation [*WRI*, 1992; *Brown*, 1995a, 1995b, 1998; *Sawa et al.*, 1999]. Descent over the Java Sea offers a useful complement. In Northern hemispheric fall, surface flow is toward the Asian landmass and the ITCZ is indistinct [*Kao*, 1948; *Thompson*, 1951; *Schmidt*, 1952]. Convective activity occurs year-round with a slight seasonality.

[13] The Blake whole-air sampling and gas chromatography team has expanded and improved its capabilities steadily over the last decade. In early aircraft campaigns only a limited number of pure hydrocarbons could be quantified through the whole-air retrieval methods. Today over one hundred species are resolvable, down to pptv levels. Technical details of separation procedures, lower limits of detection, accuracy and precision are discussed in the series of papers *Blake et al.* [1992, 1994, 1996a, 1996b, 1996c, 1997]. Sets of canisters are mounted on board research aircraft prior to take off, then are opened manually en route over cales ranging from 10 seconds to several minutes. The sample spacing depends on ambient atmospheric pressure and the need for local resolution. The cans are returned to a ground-based laboratory, which is usually (though not always) the main facility at the University of California, Irvine. Aliquots are distributed to several gas chromatographic systems, each equipped with column materials and detectors chosen to separate/identify specific suites of compounds. Some of the molecules measured and studied in the present work are itemized in Table 1. They are organized in the listing by functionality in most cases.

[14] The aircraft techniques generate a very large volume of data. 50 to 150 canisters may be filled during a single flight. There are generally 10 to 20 flights involved in a campaign. Up to 100 species are measured from within each sample. Even after zooming in upon the four flights which promised to provide cross cutting biogeochemical information, we felt that a streamlined analysis strategy was called for. We have examined data from flights 0, 2, 7 and 9 by plotting all measured concentrations together within the Table 1 chemical groupings, for each individual flight. Data were displayed first as a function of flight time, then against altitude. Species to species graphs and correlations were constructed as deemed necessary. Most often we have used ethane as the major correlate or X axis compound. Ethane is selected for this role because it is the simplest hydrocarbon displaying significant concentrations in all the source signatures we refer to. Earlier Blake group papers have adopted this convention as well [*Blake et al.*, 1992, 1994].

[15] The fingerprints themselves are given in Table 2. The most important references we have consulted in order to compile this information are the Blake et al. aircraft series [*Blake et al.*, 1992, 1994, 1996a, 1996b, 1996c], supplemented by *Blake and Rowland* [1995] for liquefied petroleum gas composition. There are large uncertainties in almost all values in the table. LPG species ratios are highly variable from economy to economy. For example, mole fractions for propane and the butanes are roughly equal in the typical Mexican product, while in Los Angeles (California) the composition is almost entirely propane. In fact all the signatures we present should be thought of as surrogates for their true Asian counterparts. The natural gas leakage data for nonmethane compounds were obtained near the Alaskan Prudhoe Bay facility. Actual compositions worldwide are highly variable. The CH_4 fraction is in fact

Table 2. Hydrocarbon Source Fingerprints Referenced in the BIBLE A Interpretation[a]

HC	LPG1	LPG2	Burns	Autos	NG	Waste	China	Veg
CH4	0	0	10	10	20	5000		
C2H6	1	1	1	1	1	1	1	+
C3H8	100	100	0.25	0.3	0.1		0.4	+
nBut	60	0.2	0.1	2	0.05		0.1	
iBut	30	1	0.01	0.3			0.1	
nPent	1	<0.01	0.03	3	+		0.05	
iPent	3	0.03	0.01	1	+		0.05	
C2H4	0	0	1	8			0.1	+
C2H2	0	0	0.5	6			0.5	
C6H6	0	0	0.4	4			0.2	
CH3Cl			0.1	low				
CH3Br			0.001					
CH3I			0.0001					

[a]All concentrations are normalized to those of ethane. HC, hydrocarbon species; LPG1, liquefied petroleum gas sampled in Mexico City; LPG2, liquefied petroleum gas sampled in Los Angeles (California); Burns, biomass burning; NG, natural gas; Waste, waste treatment in landfills and sewers; China, a plume tracked to eastern China as point of origin; Veg, terrestrial vegetation. The abbreviations But and Pent signify the butanes and pentanes. References are itemized in the text. Where data are available, sources are arranged in order of increasing methane to ethane ratio. Pluses mean that emission occurs for that particular species under that particular source but that we did not have a value available for the process.

an industry average. Methane to ethane ratios for the anaerobic sources in landfills and sewers are unpublished for the moment and constitute rough estimates from data local to the Irvine campus. They may not translate directly to the developing situation in East Asia. We are currently in the process of obtaining coal combustion samples from the vicinity of Beijing, under sponsorship from the NASA ChinaMAP project [*Chameides et al.*, 1994]. References such as those collected by *Logan et al.* [1981] and *Cullis and Hirschler* [1989, 1990] suggest that while carbon dioxide content of the effluent varies from 95 to 100%, carbon monoxide to methane proportions resemble biomass burning [*Andreae*, 1991]. Residential and commercial coal combustion tend to be the most inefficient types, while industrial and power plant applications release only negligible amounts of the trace gases. China of course remains coal driven. Tremendous residential consumption occurs along the eastern seaboard. The nonmethane hydrocarbon output should be skewed toward short chain byproducts.

[16] Terrestrial vegetation is a significant global source of nonmethane species. Inventories assembled from the biogeochemical perspective have emphasized the distinctions between isoprene and monoterpenes, then reactive and stable organics [*Guenther et al.*, 1995]. Some concept of the role of land ecosystems in individual NMHC budgets can be gleaned from Table 3, a set of heuristic organic source distributions. We have not attempted to generalize a fingerprint for Asian vegetation. The reader will note that methyl halide ratios are included for only a few of the inputs in Table 2, and that the halocarbon composition of industrial effluent has not been specified. Our feeling is that the pure hydrocarbons must form the core of Asian source characterization because of their potential to discriminate human activities such as waste treatment and energy consumption. These are the processes which will be altered and focused on the eastern edge of the continent during the era of global change, and which closely regard the carbon and nitrogen cycles. The industrial halocarbons, however, will function as sensitive tracers for urban air masses so that their source signatures will also be valuable.

3. Results

[17] Many dozens of concentration versus time/altitude plots have been inspected, along with the species to species comparisons necessary for preliminary interpretation. We highlight the graphics and conclusions which are most enlightening from the Asian growth perspective. Since we wish to argue that whole-air sampling should be applied to characterize the continental system of the future, emphasis is placed upon the likelihood that hydrocarbon relationships will transition through geochemical space; the evolution of Asian land and energy use will alter relative source strengths [*Chameides et al.*, 1994; *Brown*, 1995a, 1995b; *Elliott et al.*, 1997a, 1997b; *Brown*, 1998]. Analysis is restricted to two dimensions (two species) in this section.

Table 3. Qualitative Source Apportionment for Some of the Pure Hydrocarbons, Based Largely on Global Budgeting Exercises[a]

	Sources
Methane	managed and natural wetlands, enteric fermentation, landfills, human and animal waste, natural gas, coal combustion
Ethane	fossil fuel combustion, natural gas, liquefied petroleum gas, biomass burning, the ocean, grasses and other vegetation
Propane	natural gas, liquefied petroleum gas, biomass burning, the ocean, grasses and other vegetation
n-butane	fossil fuel combustion, natural gas, liquefied petroleum gas, biomass burning, the ocean
i-butane	fossil fuel combustion, natural gas, liquefied petroleum gas, biomass burning, the ocean
n-pentane	fossil fuel combustion, natural gas, liquefied petroleum gas
i-pentane	fossil fuel combustion, natural gas, liquefied petroleum gas
Ethylene	fossil fuel combustion, biomass burning, the ocean, vegetation
Propylene	fossil fuel combustion, biomass burning, the ocean
Acetylene	fossil fuel combustion, biomass burning
Benzene	fossil fuel combustion, biomass burning, solvents
Toluene and xylenes	fossil fuel combustion, solvents, biomass burning

[a]Adapted from *Cicerone an land* [1988], *Singh and Zimmerman* [1992], *Guenther et al.* [1995], *Schlesinger* [1997], and our compilation in Table 2.

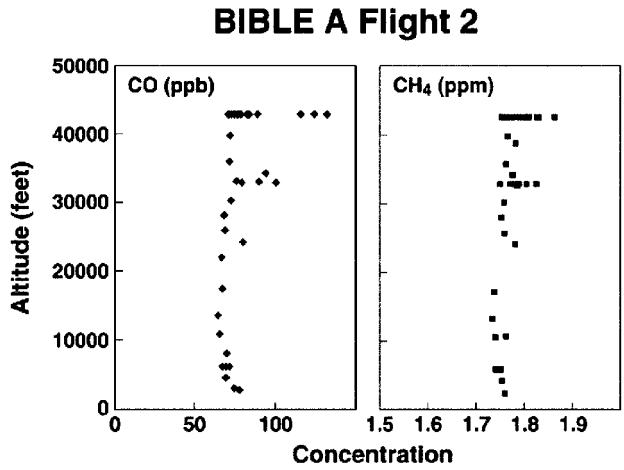

Figure 2. Flight 2 data for carbon monoxide and methane, as altitude profiles.

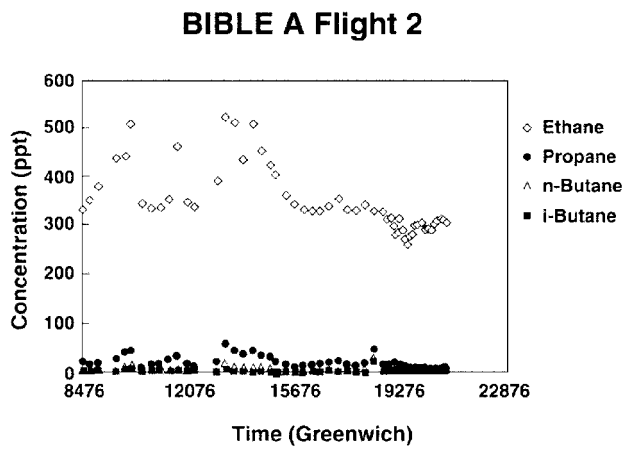

Figure 4. Concentrations of light alkanes over the course of flight 2. The Japan to Saipan transit lies about 9 hours east of the prime meridian.

The major hydrocarbon families are discussed in the structural group order of Table 1.

[18] The single carbon species measured through the whole-air samples and chromatography are carbon monoxide and methane. The molecules are kinetically related along the methane photooxidation sequence [*Crutzen*, 1988]. On several of the flights periodic dips in CH_4 concentration of the order of 10 ppbv correlated with corresponding rises in CO. The Blake measurements may thus provide direct monitoring of photooxidation rates and mechanisms. Seasonality of the Asian general circulation was evidenced. For example, in Figure 2 both of the single carbon species are elevated in air sampled aloft. In Figure 3 methane data are plotted against those for carbon monoxide on the Nagoya to Saipan transit. High carbon monoxide readings aloft suggest combustion sources. Both biomass and coal burning emission ratios for CO/CH_4 are about 10 [*Cullis and Hirschler*, 1989, 1990; *Andreae*, 1991; *Blake et al.*, 1996a, 1996b, 1996c]. Samples taken at higher altitude reflect the influence of these combustion types. Methane-rich sources contribute in the dilute CO samples. China is a center of rice cultivation and so of the managed wetlands fostering anaerobic methane production [*Cicerone and Oremland*, 1988; *WRI*, 1992; *Brown*, 1995a, 1995b]. It is also the most populous nation on Earth. Treatment of human waste is another methane-rich input prominent in the global budget.

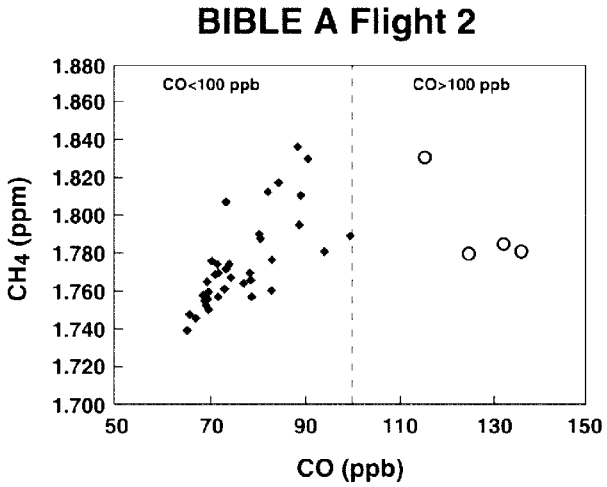

Figure 3. Methane to carbon monoxide relationships in the flight 2 data.

[19] The high pressure/low pressure pulse of the general circulation was again manifested in measurements for higher molecular weight alkanes. Furthermore the effect of extensive convective mixing over Indonesia [*Kao*, 1948; *Schmidt*, 1952] was seen for species in all families, provided that photochemical lifetimes were longer than a few days. Altitude plots will not be presented for the alkanes. Concentrations for some of the more stable saturated organics are plotted in Figure 4 against time for the Nagoya to Saipan leg. Patterns in the ethane series are the most instructive. Variability aloft probably reflects encounters with combustion plumes. A strong transition was experienced near 25 degrees north (15000 seconds Greenwich time). *Blake et al.* [1997] demonstrate that this latitude is a typical threshold for the transition to tropical air. A drop in concentration is observed for many species and by many groups [*Singh and Zimmerman*, 1992]. Note that propane behavior is similar in Figure 4. The dip in ethane concentration at 19000 seconds was detected on descent toward the marine boundary layer near the Northern Marianas Islands. It may signify penetration of a clean maritime layer.

[20] Complexity of the Indonesian atmosphere is demonstrated when heavier alkanes are compared with ethane (Figure 5). Typical tropical background levels form a baseline for alterations by the major combustion types. Descent over Borneo in flight 7 yielded a signature low in the pentanes and suggestive of aged biomass burning. The island is heavily forested but wildfires and conversion for agriculture are taking a toll [*WRI*, 1992; *Brown*, 1995a, 1995b, 1998; *Sawa et al.*, 1999]. By contrast, the return leg of flight 9 (descent to the airfield on Java) produced several samples with delta pentane/delta ethane exceeding 0.1. The best match in the Table 2 fingerprint collection is provided

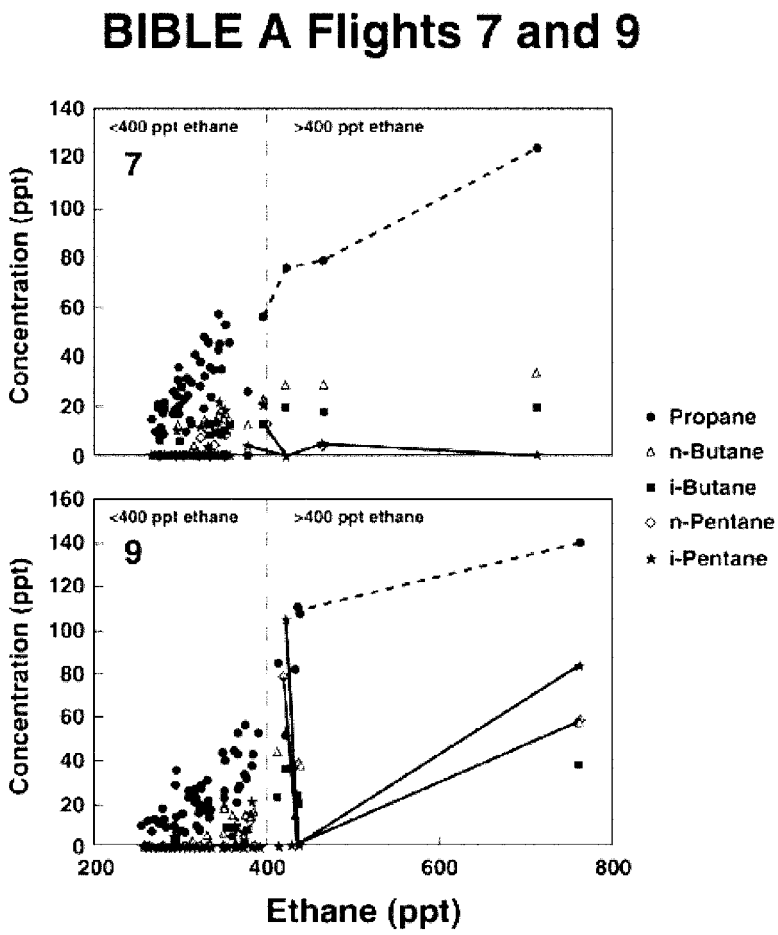

Figure 5. Species to ethane relationships for some major alkane combustion tracers. (top) Flight 7 from Java to Borneo with descent and return. (bottom) Flight 9 from Java to the open Java Sea with descent and return. Propane and pentane data points are connected in the high ethane field for emphasis.

by automotive activity. The developing Indonesian economy is petroleum based. Java is among the most densely populated areas on Earth and supports heavy vehicular traffic. A striking omission from the alkane spectrum cuts across all the BIBLE A data we have inspected, from Indonesia to Japan. The propane and butane peaks associated with liquefied petroleum gas leakage are not obvious [*Blake and Rowland*, 1995] (Table 2). LPG is among the cleanest of fossil fuels and is considered an end-member in the energy market penetration series [*Ausubel et al.*, 1988; *Ausubel*, 1995]. It is likely that the developing economies of East and Southeast Asia will adopt it as a residential fuel type. In China it will serve with natural gas as a substitute for coal in wealthy coastal cities. A key migration through the chemical space will likely be increase in the propane and butane to ethane ratios. LPG emission ratios vary greatly around the globe but are distinct in their C_3/C_4 bias.

[21] BIBLE A was partly intended to elucidate the chemistry of lightning plumes, and the Gulfstream platform is particularly well suited to upper tropospheric operations. Much of the total mission time was thus spent in air remote from continental sources. The olefins (double bonded species) tend to photooxidize within a few days. From this chemical fa nly ethylene was observed in the whole-air samples on a regular basis. Propylene and the isomeric butenes (1- cis and trans-2) went largely undetected. Unsaturated species are crucial components of hydrocarbon signature sets and will become more important as a complete catalog is compiled. The ethylene time series taken alone brims with information. Comparisons have been made with standard baseline compounds for the April test (Figure 6). Surface flow was from the continent. Cleaner air at upper levels shows no consistent pattern in ethene/ethane ratios. A logical interpretation is that the olefin is input from a variety of sources and that individual parcels have disparate photochemical histories. Mixing of continental and maritime air may take place. Although it is the least reactive of the alkenes, C_2H_4 survives only a few days against oxidation in the troposphere. Cloud coverage and day/night proportions can vary during transit.

[22] In the surface air under continental influence (elevated ethane), ethylene concentrations ranged up to 50 pptv. Photochemical trajectories must again figure in the explanation. However, the air has spent several days over the coastal and open western Pacific. Boundary layer alkenes have also been acquired from surface waters, which are typically supersaturated in most of the pure hydrocarbons

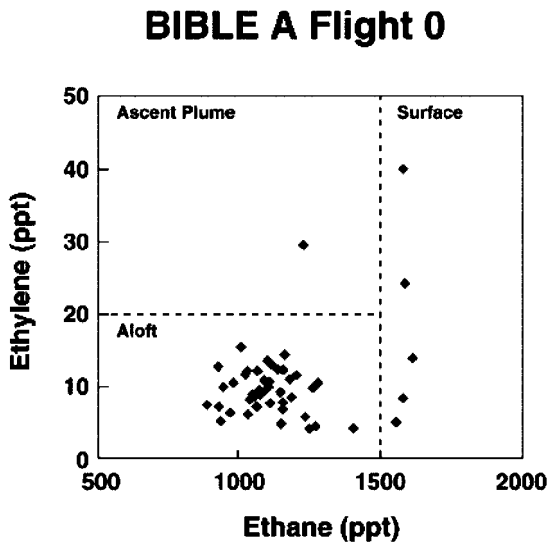

Figure 6. Ethylene to ethane ratios in the April test flight, here labeled 0.

[*Ratte et al.*, 1993]. The variability can thus also be attributed to inconsistency in the degree of ocean supersaturation. We have argued elsewhere [*McNair et al.*, 1998; *Chu et al.*, 1999] that seawater concentration maxima will in general occur in different places for the dissolved trace gases. Marine biological activity is fundamentally advective. Dissolved gases are exuded from distinct links in the transition of carbon atoms from fixed to mineralized forms. Currents and eddies are at their most intense in/near the western edges of the major Northern Hemispheric ocean basins [*Bowden*, 1975]. We anticipate intricate and shifting oceanographic patterns of release.

[23] A single data point from the April flight stands out for its large delta ethylene/delta ethane ratio. This sample was collected on ascent during departure from Nagoya. We infer that a plume was intersected containing Japanese emissions. Note that the wealth of the economy is reflected in the hydrocarbon composition. Ethylene is a standard tracer for vehicular activity [*Blake and Rowland*, 1995]. As the era of global change unfolds, eastern Asia is expected to embrace the automobile [*Smil*, 1988; *Lu*, 1993; *McCreary et al.*, 1996]. Japan lies just downwind, directly in the path of the geostrophics. It will bear the brunt of the implied long range pollutant transport [*Elliott et al.*, 1997a, 1997b]. Because the Asian population base is huge and migration must mainly be coastal, the emission zone is and will remain an extensive south north corridor. There is literally no latitude for dilution as air masses pick up pollutants on the continent and then move over the North Pacific. Transoceanic pollution is likely to be one of the major environmental security issues of the next century. Aircraft whole-air experiments should be repeated many times within the outflow in order to document its onset.

[24] The alkynes and aromatics are grouped together here as a matter of expedience, and because the triple and resonant double bonds are similar in strength/reactivity. Family members without side chains survive for several weeks in the troposphere and thus act as tracers of the seasonal circulation just as do stable, saturated hydrocarbons [*Singh and Zimmerman*, 1992; *Blake et al.*, 1997]. Ethyne distributions, for example, mimic those of ethane in the BIBLE A data. Enrichments in continental outflow are punctuated independent of season by the sharp peaks characteristic of plume encounters. Ethyne and benzene altitude profiles are plotted in Figure 7 for the Japan to Saipan flight. Ethylene is shown as a short-lived comparison species; note that its concentrations fall to zero at upper levels. During a low altitude leg approaching the Northern Marianas in flight 2, a minimum in C_2H_2 concentration was detected over the ocean surface. Air to sea flux and consumption within the water column offer a potential explanation. The compound is one of the few nonmethane organics known to be undersaturated in the open surface ocean on a regular basis [*Plass et al.*, 1992; *Ratte et al.*, 1993]. South of the 25 degree transition the tropospheric alkynes and aromatics adopt tropical composition patterns. Background altitude distributions over Indonesia indicate the dominance of convection.

[25] Simpler members of the triple bond and aromatic families are classic combustion tracers. Ratios of ethyne and benzene to ethane can be used under some circumstances to distinguish biomass or biofuel burning from gasoline consumption. In the Table 2 signatures C_2H_2 and C_6H_6 concentrations are about an order of magnitude larger for automobile exhaust. Ethane relationships from the April test flight resemble organic spectra reported by *Blake et al.* [1997] for Asian cities including Tokyo and Hong Kong. Data for the same species from flight 2 provided some of the tightest linear correlations obtained in the present analysis (Figure 8). The delta ratios are consistent with aged biomass/biofuel combustion. However, it is difficult to exclude a contribution from vehicular sources, and coal burning measurements are not at hand. Despite the strong difference in alkyne/aromatic fingerprints for major combustion sources, they are difficult to distinguish at a distance. The Blake group has described similar problems in the analysis of earlier remote tropospheric measurements [e.g., *Blake et al.*

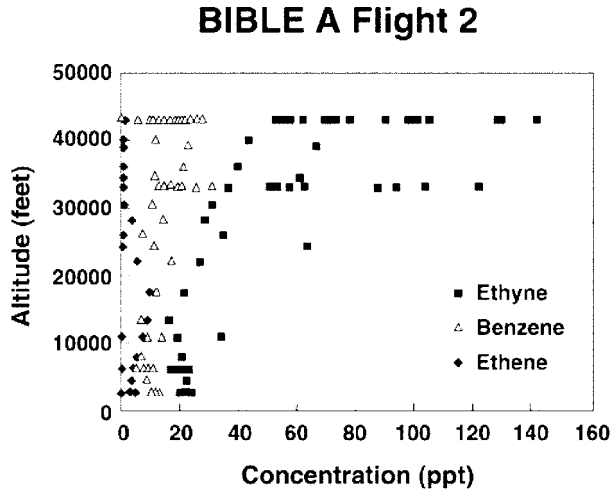

Figure 7. All flight 2 data for ethyne and benzene, presented as altitude profiles. Ethylene points are included to demonstrate that photochemical decay has taken place in air aloft.

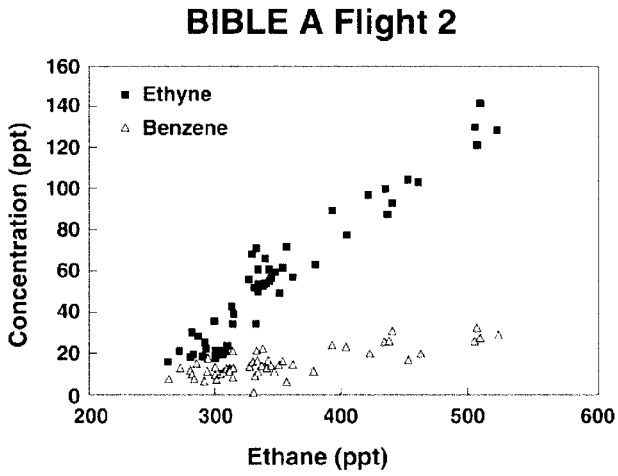

Figure 8. Ethyne and benzene measurements from flight 2 (Nagoya to Saipan) plotted against those for ethane.

1994, 1996a, 1996b, 1996c]. Two issues emerge which are relevant to Asian growth. Again the need for nearer-source sampling is highlighted. It is also the case that meteorological back trajectories could be used to compute the time since surface contact [e.g., *Merrill*, 1996; *Merrill et al.*, 1997]. For Indonesian flights 7 and 9 the plots of ethyne and benzene against ethane were similar in appearance and slope (Figure 9). Samples collected over populous Java and rural/remote Borneo in fact correlated together. This could be a coincidence, but may also serve as an indication that biomass/biofuels still pervade. As the Asian automobile culture expands over the next few human generations, we expect the correlations to remain relatively tight but to rise upward in delta ethane space.

[26] Methyl halides, methyl nitrate and several of the bromomethanes have been analyzed together , as a class of substituted C1 compounds for which the sea figures prominently in global budgets [*Singh and Zimmerman*, 1992; *Lobert et al.*, 1995; *Blake et al.*, 1996a, 1996b, 1996c; *McNair et al.*, 1998; *Chu et al.*, 1999]. Typical behavior over the open ocean is displayed in Figure 10. Descent at 26 degrees north into the marine boundary layer yielded rapid increases in concentration for several of these single carbon species. The methyl iodide peak in particular suggests strong inputs from surface waters. Photolysis removes the molecule from tropospheric air in on the order of one day except under cloudy skies. Note, however, that maxima for the several species occur in different samples. Again we submit that the intricacies of subsurface ecology/photochemistry may be involved. Other aspects of the BIBLE A data set imply strongly that the situation will be difficult to elucidate. Some of the potential pitfalls can be illustrated beginning with data in Figures 11 and 12. Altitude profiles from the second summer/fall flight are readily interpreted for the methyl halides. Flux from the sea surface raises CH_3I concentrations in the boundary layer, in this case in the vicinity of the Marianas. The scale height of perhaps one kilometer is consistent with a one day removal time constant [*Blake et al.*, 1997] and tabulated lower tropospheric eddy diffusion coefficients [*Elliott et al.,* 1996, 1997a, 1997b]. Both the iodide and romide are released during combustion as well as from seawater. CH_3Br concentrations are more obviously elevated at upper levels because the molecule is longer lived (on the order of two years). Further, the bromide concentrations are variable in the boundary layer, in keeping with our arguments on marine hot spots. Methyl nitrate, on the other hand, peaks in the middle troposphere. A possible explanation is that Asian nitrogen oxides have augmented photochemical activity in general and so also the oxidation rate for methane passing from/over the landmass [*Crutzen*, 1988; *Elliott et al.*, 1997a, 1997b]. CH_4 decomposition in NO_x-rich air would be channeled in small part into the nitrate.

[27] Determining relative contributions of the continent and adjacent coastal waters to regional budgets for the halides is likely to require coupled modeling of the ocean/atmosphere system. Aircraft chemistry campaigns have as a rule devoted only limited resources (flight time) to the marine boundary layer. BIBLE A-9 offers a case in point, as illustrated in Figure 12. The central Java Sea is biologically productive [*Berger and Wefer*, 1991] and far enough removed from the islands of Indonesia to yield valuable information on sea/air fluxes. However, only a handful of whole-air samples were collected in the boundary layer. Scaled concentrations in Figure 12 are suggestive of complex marine source signatures but the data are inconclusive. We advocate increased attention to whole-air sampling near the sea surface, and in particular from aircraft platforms.

[28] In air aloft over Indonesia the halides register biomass burning. Emissions ratios for the bromide and iodide normally fall between 10^{-3} and 10^{-4} against ethane as a normalizing agent. Descent over the Kalimantan area of Borneo gave delta ratios for CH_3I to C_2H_6 of roughly one thousandth (Figure 13). Under the Table 2 signatures, fresh combustion sourcing is implicated. Data from the Japan to Saipan transit are superimposed upon Figure 13 as a contrast to the tropical measurements. Distribution in the two dimensional chemical space is hyperbolic. The two

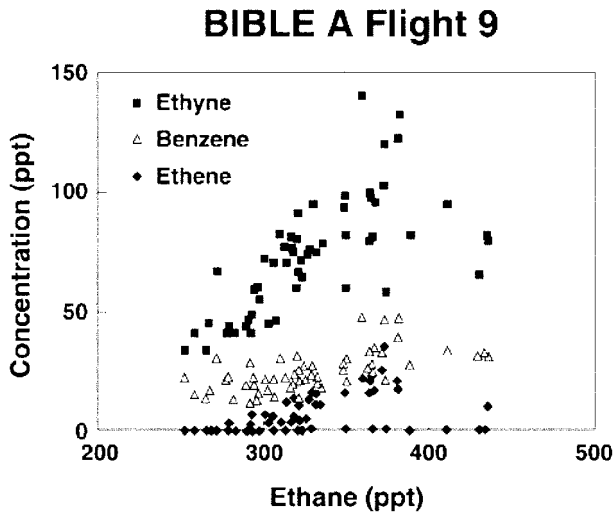

Figure 9. Ethyne and benzene measurements from flight 9 (Java to open Java Sea and return) plotted against those for ethane. Ethylene again manifests photochemical activity.

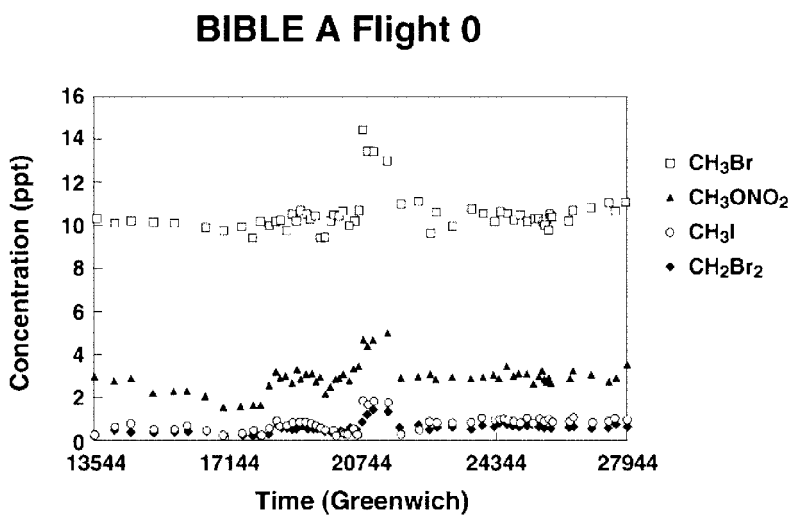

Figure 10. Concentration versus flight time for halogenated methanes and methyl nitrate along the course of the April test flight. The Nagoya meridian lies about nine hours east of Greenwich.

lobes of the data population represent continental air aloft from which the iodide has been photolyzed en route so that concentrations are near zero, and the variable open marine input.

[29] The anthropogenic halocarbons can be divided into two classes based on their lifetimes, which range up to 100 years [*Rowland and Molina*, 1975]. The longer lived species chlorofluorocarbons 11 and 12 and carbon tetrachloride have been regulated under the system of international environmental treaties initiated by the Montreal Protocol. Their stability renders them especially dangerous carriers of halogen material to the stratosphere. Global monitoring networks record the success of Montreal and its followers [*IPCC*, 1995]. The tropospheric CFC burden is peaking. Methyl chloroform is another regulated species but possesses a shorter residence time (several years). Its concentrations are steadily dropping. The BIBLE A data assessed here confirm results from the network studies but in the Southeast Asian context. The stable halocarbons are evenly distributed with background levels approaching ppb. They are best seen as tracers for the largest scales of atmospheric motion [*Prather et al.*, 1987]. Interhemispheric gradients are apparent in the BIBLE measurements, along with mixing of northerly and southerly air masses along the indistinct Indonesian ITCZ.

[30] On the regional scale the more reactive anthropogenic halocarbons become useful indicators. Perchloroethylene is now recognized as a workhorse marker for urban and industrial activity [*Blake et al.*, 1996a, 1996b, 1996c]. It has been catalogued in several Asian urban air masses [*Blake et al.*, 1997]. The perchloroethylene time series from BIBLE A flight 2 is given in Figure 14. A lone concentration greater than 3 ppt was obtained on descent toward the open sea surface. Propane and ethyne levels in the sample were 40 and 20 ppt respectively. The combined halocarbon/hydrocarbon signature matches closely the Blake et al. spectrum for Tokyo and Hong Kong. It is likely that a city plume was intercepted on approaching the Northern Marianas. Irregularities in C_2Cl_4 concentrations along the high altitude segment (9000 to 1500 nds Greenwich) bear a superficial resemblance to data for some of the pure hydrocarbons, and in particular those of ethane and ethyne. In the delta ethane space, however, an interesting story unfolds (Figure 15). At less than 350 ppt C_2H_6 a positive relationship is evident. Perchloroethylene concentrations then begin to fall. In dirtier air masses encountered aloft, the industrial and combustion tracers anticorrelate. This observation may in fact be fundamental for large, developing economies. In the historical fuels substitution series, transition is typically from biomaterials to coal to oil and finally to natural and liquefied petroleum gases [*Ausubel*, 1995]. Several Asian combustion types yield significant quantities of ethane, but C_2Cl_4 can only be generated by industry. It is expected that the economy of the People's Republic of China will grow steadily during the era of global change [*Lu*, 1993; *McCreary et al.*, 1996; *Elliott et al.*, 1997a, 1997b]. Again we can operate in a conceptual chemical space and consider detailed evolution of the whole-air measurements. Chinese growth should involve a high degree of industrialization. By

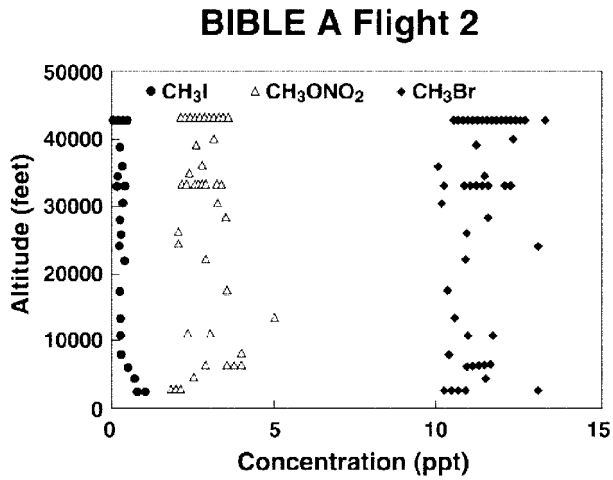

Figure 11. All flight 2 data for methyls iodide, bromide, and nitrate presented as altitude profiles.

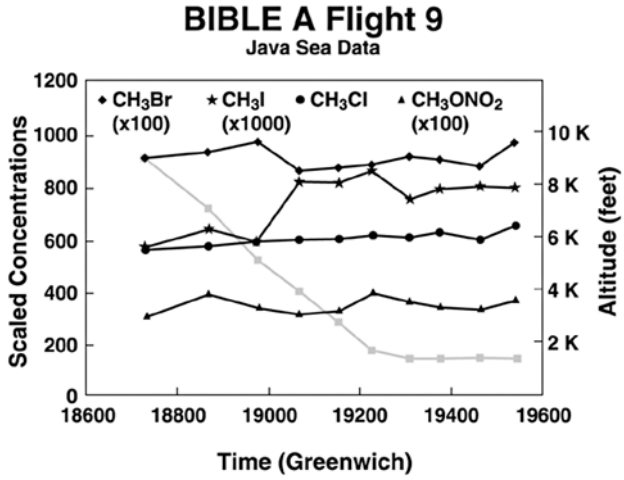

Figure 12. Methyl halide and nitrate data versus flight time during descent to the open Java Sea. Concentrations are scaled by factors of 10 so that they can be plotted with those of methyl chloride. The shaded curve and right-hand axis labels give aircraft altitude.

analogy with the west, short-lived halocarbons may be adopted as solvents and degreasing agents. At the same time, environmental concerns will lead to reductions in the combustion of solids. Petroleum-based products will be imported to compensate. The direction of movement is not entirely clear, but it is expected that the downward tail of the C_2Cl_4 to ethane distribution will be altered in future transects of the Asian outflow.

[31] Since man-made halocarbons are distinct tracers for continental air, combined analysis with natural halocarbons and other ocean sourced species promises to shed light upon sea-air transfer. Perchloroethylene concentrations happen to fall between those of methyls iodide and bromide through most of the BIBLE A data set. In Figure 16 we juxtapose C_2Cl_4 values with concentrations measured for some substituted methanes, as measured over the open ocean during

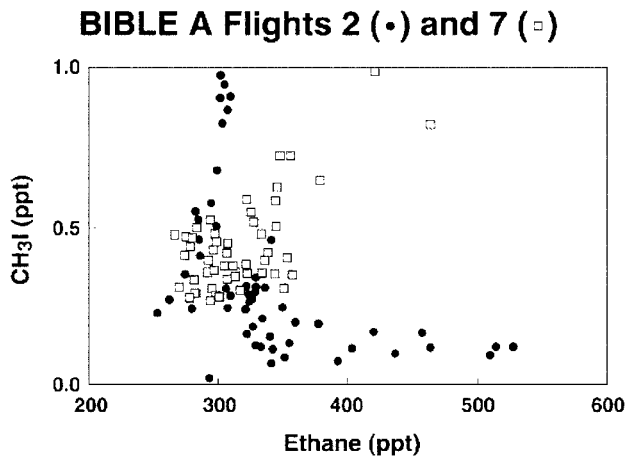

Figure 13. Methyl iodide concentrations in the ethane space for flight 2 which included descent over the northern Marianas Islands and flight 7 with its descent over Kalimantan (central Bo

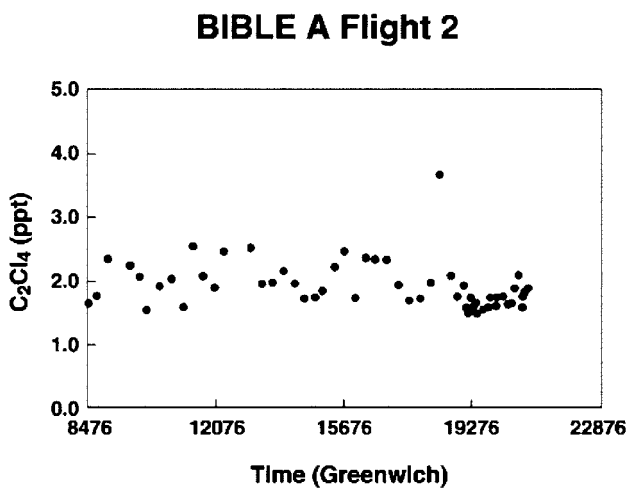

Figure 14. Time series for perchloroethylene during flight 2. The Japan to Saipan transit lies about 9 hours east of the prime meridian.

the April test. The aircraft entered the marine boundary layer due south of Nagoya and near the 25 degree latitude (tropical) transition zone. Maxima for methyls bromide and nitrate bracket a perchloroethylene peak. Methyl iodide is very evenly distributed through the boundary layer. These relationships may well reflect nonurban inputs for CH_3Br, CH_3ONO_2 and CH_3I. If sea to air flux is contributing to their surface concentrations, it occurs coastally or from the Kuroshio and associated warm and cold core eddies. It is thus superimposed on the pollution content of the surface outflow.

4. Statistical Considerations

[32] Aircraft hydrocarbon measurement has become an extraordinarily data-rich technique over the last decade

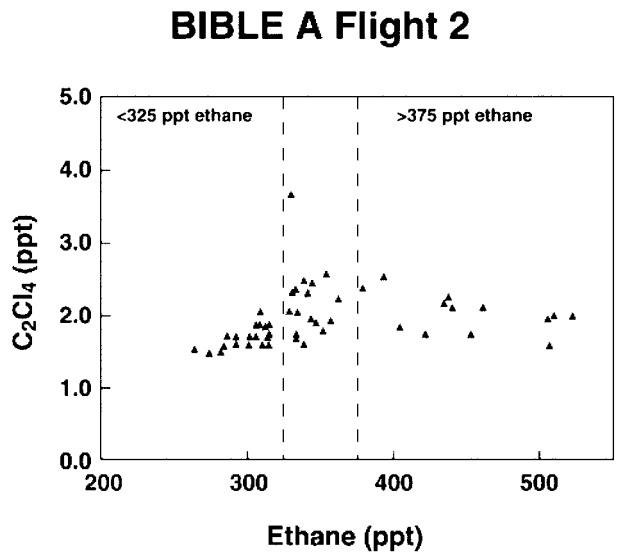

Figure 15. Perchloroethylene concentrations from the Japan to Saipan flight, depicted in the ethane space.

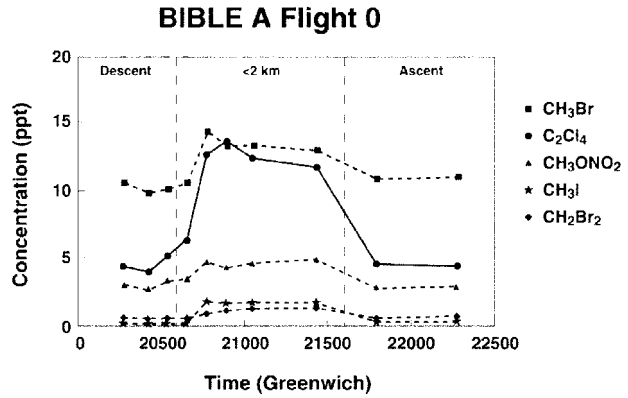

Figure 16. Time series for substituted methanes and for perchloroethylene during descent toward and flight within the open ocean boundary layer (the April test).

[e.g., *Blake et al.*, 1992, 1994, 1996a, 1996b, 1996c, 1997]. Roughly speaking, dozens of canisters may be filled on each of hundreds of flights per year, with a hundred species determined per sample. It is of course crucial to begin interpretation from the geophysically intuitive foundation of concentration versus time/altitude/concentration plots. However, the data structures are sufficiently complex to warrant analyses which are global and multidimensional in the chemical and statistical senses. Traditionally, the Blake group has analyzed in at most two species dimensions at a time from among the large number available; concentrations for one compound may be correlated against those of one other. Investigators of urban air quality have developed statistical approaches which allow rapid assessment of the patterns embedded in measurement data sets [*Hopke*, 1985]. The methods have been applied to volatile organic molecules as well as to the elements [e.g., *Mayrsohn and Crabtree*, 1976; *Watson*, 1983; *Baldasano et al.*, 1999]. In this section we explore application of the multidimensional statistics to regional scale hydrocarbon measurements, and to the special challenge of aircraft campaigns.

[33] The structure of large environmental chemistry data sets may be examined preliminarily using one of the many types of factor decomposition [*Henry and Hidy*, 1979; *Hopke*, 1981; *Hopke et al.*, 1983]. We concentrate our efforts here on Principal Components Analysis (PCA). The correlation matrix is cast into a linear algebraic eigenformat. The resulting eigenvectors and -values are related respectively to source signatures and fractional mass contributions. We have performed PCA upon hydrocarbon measurements from several of the BIBLE A flights. Data were transferred into the 1998 version Statistics Program for the Social Sciences (SPSS package). A standard VARIMAX rotation was conducted to maximize the grouping of final values around readily interpretable extrema. Sample results are offered in Tables 4 and 5 for the key transit from Japan to the Northern Marianas. Communalities of 0.8 or greater indicate that much of the variability in a particular quantity is explained by the procedure.

[34] Table 5 values resemble some of the Asian fingerprint surrogates, and oceanic hot spots are revealed in the PCA procedure as wel example, Factors 1 and 3 as computed for flight 2 are associated with combustion and urban photochemical processing. The propyl and butyl nitrates are enhanced in air moving through cities because precursor alkane emissions are high and oxidation takes place in a NO_x intensive environment. Note that the urban/industrial tracer perchloroethylene loads with the nitrates. Factor 4 appears to represent mainly a flux of OCS from the sea surface. The source loads only with brominated species from among members of the suite of dissolved, oceanic trace gases. Individuality of the PCA response to sea-air transfer may follow from lack of correlation for marine hot spots. Carbonyl sulfide is produced in the water column by photolysis of dissolved organic matter [*Weiss et al.*, 1995; *McNair et al.*, 1998]. The photons required may be absorbed by chlorophyll. Emission may thus occur mainly from waters which have passed their prime biologically. The sulfide is removed rapidly through hydrolysis [*Andreae*, 1986; *Elliott et al.*, 1987, 1989; *Elliott and Rowland*, 1990]. Methyl iodide is much longer lived in the water column and is exuded directly by phytoplankton [*Elliott and Rowland*, 1993, 1995]. However, it is low in PCA communality and does not figure in our analysis here. The anthropogenic halocarbons tend to group together with industrial solvents. The pentanes appear together in Factor 8 and may point to internal combustion.

[35] Principal components analysis underlies some of the techniques available for apportionment of source fractions [*Hopke et al.*, 1983; *Baldasano et al.*, 1999]. The eigenvalue problem identifies inputs; multiple linear regression is then applied. Mass balance can also be computed directly [*Watson*, 1983]. The calculations have been standardized by the U.S. Environmental Protection Agency with regard to source apportionment in urban aerosol studies. They have been several times applied to measurements of volatile organics in city air [e.g., *Mayrsohn and Crabtree*, 1976; *Baldasano et al.*, 1999]. We suspect that chemical conservation could be very fruitfully adapted to larger scales and to aircraft whole-air measurements. The methods are at their simplest when referred to nonreactive entities such as the individual chemical elements. The spectrum of hydrocarbons now resolvable from aircraft samples is so large that stable tracers can be found to represent many source types. Variations of the mass balance methods have also been developed which treat reacting systems. They involve incorporation of diurnal cycling information from full three dimensional photochemical models and the establishment of

Table 4. Some Communalities Above 0.9 and Eigenvalues Above 1.0, for a Principal Components Analysis Applied to BIBLE A Flight 2 (Nagoya to Saipan)

Hydrocarbon	Communality	Factor	Eigenvalue
Ethane	.96510	factor 1	11.74196
Ethyne	.96367	factor 2	4.06982
n-Butane	.96295	factor 3	3.06146
i-Pentane	.95222	factor 4	2.68755
Methane	.92544	factor 5	1.99837
Methyl Chloride	.93410	factor 6	1.66809
Propane	.92328	factor 7	1.32184
Ethyl Nitrate	.91774	factor 8	1.14957
Methyl Nitrate	.91671	factor 9	1.05433
i-Butane	.91617		

Table 5. Hydrocarbons With the Largest Positive Factor Loadings as Deduced in the Flight 2 Principal Components Analysis

	Species 1	Species 2	Species 3	Species 4
Factor 1	Propane (.93940)	n-Butane (.93136)	Methane (.90818)	Ethyne (.88857)
Factor 3	Butyl Nitrate (.81604)	Propyl Nitrate (.74287)	C_2Cl_4 (.54719)	Ethyl Nitrate (.43156)
Factor 4	OCS (.85487)	CH_2Br_2 (.54876)	CH_3Br (.42479)	F22 (.41201)
Factor 6	CCl_4 (.87634)	CH_3CCl_3 (.69784)	$CHCl_3$ (.31139)	CO (.20912)
Factor 8	i-Pentane (.74518)	n-Pentane (.70718)	CH_3Br (.23602)	Methane (.20177)

basis sets which are Fourier series fit to emissions inventories. Essentially, spatial and temporal components are superimposed on classical source receptor relationships [*Hopke*, 1985]. Photochemical simulations are generally performed in conjunction with aircraft studies of regional tropospheric chemistry [e.g., *Liu et al.*, 1996; *Schultz et al.*, 1999]. Ultimately we feel that inverse modeling of the hydrocarbon distributions will prove to be a key analysis tool. In this connection we argue that cataloguing of Asian emissions fingerprints should be made a priority.

5. Discussion

[36] We have analyzed a suite of hydrocarbon measurements made during the Japanese BIBLE A tropospheric chemistry experiment. Our interpretation is conducted from the broad perspective of biogeochemistry. The BIBLE mission sampled two air masses crucial to understanding of the Earth system -Asian outflow and the tropical atmosphere of Indonesia. With this geography in mind, we have attempted to elucidate the role Asia now plays in the Earth system, and we extrapolate into the era of climate change. Rural and biomass/biofuel combustion sources of organics are segregated from urban and industrial. Methane indicates emissions from wetlands and waste management facilities, CO and saturated/unsaturated species point to the various combustion types, and man-made halocarbons trace city air. Directions for future movement through the multidimensional chemical sample space can be anticipated and will reflect Asian economic growth and evolution of the energy use spectrum. Gases crossing the sea/air interface influence species distributions in the marine boundary layer, but do not closely correlate one another.

[37] Beyond such preliminary results, our work suggests areas where the whole-air method can be refined as a biogeochemical tool. Source fingerprints are often unavailable from Asia proper, so that surrogates have been substituted (Table 2). Emissions ratios are thus highly uncertain, and the ability to differentiate varieties of combustion is compromised. Short-lived hydrocarbons such as the olefins went largely undetected because much flight time was devoted to remote locations. Rationale for the remote sampling was contextual; BIBLE A adopted the study of lightning plumes as one of its themes, and the Gulf Stream platform was designed for operation at high altitudes. However, aircraft-based measurements conducted nearer to the major continental sources hold the potential to signature broadly and to quantify reactive species. Aircraft intensives in general provide snapshot mode vertical sections of the atmosphere [*Hoell et al.*, 1996, 1997, 1999]. We support repetition of BIBLE-like studies, perhaps on a seasonal basis. The logistics and politics of regular Asian experiments will of course be challe Nevertheless, time series is an ideal which must be approached. Ground-based measurements could be conducted more frequently and would provide time filling information relative to aerial work. Benefits of an organized Asian hydrocarbon network would be manifold. Over half the world population resides on the continent, and excepting the People's Republic of China growth rates are high [*UN*, 1994; *OSTP*, 1997]. This pool of humanity is only beginning to industrialize, and to modernize from the biofuels and coal toward petroleum [*Ausubel et al.*, 1988; *Smil*, 1988; *WRI*, 1992; *Lu*, 1993]. Shifts in energy and land use patterns will alter regional atmospheric composition [*Elliott et al.*, 1997a, 1997b]. A large number of volatile organics can now be resolved from one another and accurately measured through whole-air techniques [*Blake et al.*, 1997]. Conducted at interval, experiments would closely document the Asian component of global change. The opportunity to do so is unprecedented. Asian growth over the next century will constitute one of the largest pulses of climate altering substance in all of geological history [*OSTP*, 1997; *Elliott et al.*, 1999a, 1999b].

[38] It is worth detailing some geochemical transitions which lie on the horizon, and their likely effects on hydrocarbon and halocarbon spectra. The consensus among economists and policy makers is that Asian development is ultimately inevitable [*Smil*, 1988; *WRI*, 1992; *Lu*, 1993; *UN*, 1994; *McCreary et al.*, 1996; *OSTP*, 1997]. Strong driving forces naturally exist for the incorporation of aspects of western culture. Urbanization and a sharp increase in per capita energy consumption will follow. The rate of growth cannot be predicted. Yet it may determine in part the fate of the Earth system. Rapid but partial industrialization in Latin America has led to a city size distribution skewed heavily toward a few megazones [*UN*, 1992; *Kretzschmar*, 1993, 1994]. They are internally immensely polluted. Studies of change in per capita emissions relative to the rural have yet to be undertaken [*Elliott et al.*, 1997c; *Decker et al.*, 2000]. However, indications are that the outputs of most climate altering trace substances will increase. Slow economic growth in Asia may actually be a worst case scenario as global change unfolds. Topography dictates that Chinese and Indochinese urbanization will consist of coastal migration [*UN*, 1994]. Emissions will thus collapse against the seaboard. Since the prevailing winds are geostrophic, this may mean that effects are felt dominantly on the offshore islands Japan, Taiwan and the Phillipines. For historical reasons short range transport thus represents a volatile environmental security issue. The coastal and open waters of the Pacific are also at risk [*Duce*, 1986; *Elliott et al.*, 1997a, 1997b]. Transport to North America may present additional political difficulties.

[39] Against this backdrop the composition of the atmosphere will evolve, and analytical chemists will provide monitoring. Increases in per capita gross domestic product

will raise demand for clean fuels [*WRI*, 1992; *Lu*, 1993]. The government of China is already under pressure from its vast populous to permit and encourage imports of petroleum. As Asia builds systems for the shipment of gas and LPG, losses would be detectable as methane, propane and butane richness in whole-air samples. Nonmethane hydrocarbons oxidize downwind to generate ozone, so that they are classified as indirect greenhouse gases [*Liu et al.*, 1987; *Crutzen*, 1988; *National Research Council (NRC)*, 1991]. Photochemical oxidants have been tied to the reduction of harvests in China [*Chameides et al.*, 1994], a nation which must struggle in the next century to feed itself [*Brown*, 1995a, 1995b].

[40] The coastal migration will be part of a broad-based shift in land use types on the mainland [*Luizao et al.*, 1989; *WRI*, 1992; *Chameides et al.*, 1994]. As the global human population concentrates into Asian cities and megacities, waste treatment problems will follow. Sewers and landfills are strong methane emitters [*Khalil and Rasmussen*, 1983; *Cicerone and Oremland*, 1988]. It is not yet clear that urbanization reduces emissions from these sources within developing nations. Population growth will be significant even in the People's Republic, and is now averaging 2% outside it [*UN*, 1994]. The managed wetlands of rice cultivation will continue to contribute to methane inventories. With wealth will come an Asian automobile culture, potentially patterned after that in the west [*Elliott et al.*, 1997a, 1997b]. Fuel use and combustion will redistribute. Much of the rural population of the developing world still relies on wood for its energy needs [*Ausubel et al.*, 1988; *Ausubel*, 1995]. Animal husbandry and shift agriculture are major motivations for biomass burns [*Andreae*, 1991]. Primitive energy economies thus emit light alkanes preferentially. We fully anticipate that adoption of the automobile will enhance pentane, ethylene and ethyne populations in the whole-air database.

[41] We have so far restricted discussion to the function of trace hydrocarbons within the Earth system, in their capacities as direct and indirect greenhouse forcers. As volatile organics move through the atmosphere they can be viewed as geocarriers for elemental carbon. The global nitrogen cycle is second only to that of carbon in terms of climate relevance [*Vitousek and Matson*, 1993; *Vitousek et al.*, 1997]. For many of the combustion types which have been fingerprinted and monitored through whole-air techniques, nitrogen oxide emission ratios can be established [*Andreae*, 1991; *Elliott et al.*, 1997a, 1997b]. The NO_x comes almost entirely from high temperature equilibration of the major atmospheric constituents N_2 and O_2 into oxidized products. It is thus new N from the biogeochemical perspective [*Schlesinger*, 1997]. Combustion is also a major source of the primary gas phase pollutants which undergo particle conversion and generate haze (both in the nitrogen and sulfur cycles [*Streets et al.*, 1999]). Vertically integrated optical depths are now so great over Asia that penetration of photosynthetically available radiation is reduced significantly (W. Chameides, personal communication, 1999). Both managed and natural ecosystems may suffer losses of productivity.

[42] We have intended here to consider not just terrestrial biogeochemistry but also long range transport to the open ocean, and processes t place in the sea itself. Mobile nitrogen forms a link between combustion on land and the ecology of the ocean [*Duce*, 1986; *Duce et al.*, 1991; *Galloway*, 1996]. Marine biological production is most often limited by nitrate as a nutrient. The pending Asian vehicle fleet, other energy use types and the general circulation will conspire to inject bioavailable N into the prevailing geostrophics. The sea surface will be the major receptor [*Elliott et al.*, 1997a, 1997b]. The eastern U.S. is currently fertilizing the open North Atlantic on the atmospheric mesoscale [*Fanning*, 1989; *Owens*, 1992; *Michaels*, 1993; *Elliott et al.*, 1997b]. The automobile fleet involved is less than a hundred million strong. The potential for Asian motorization to alter biogeochemistry of the Pacific basin seems very real. Long term inputs of bioavailable nitrogen would be expected to percolate into and become stored within the main thermocline. Water masses of the middle ocean hold an excess of only 10% phosphate relative to nitrate. The potential may exist to switch large volumes of the North Pacific from N to P limitation.

[43] Marine biological material cascades through a series of fixed, degrading and detrital forms after nitrogen triggers phytoplankton blooms [*Doney et al.*, 1996]. Trace gases which flux from the sea surface to influence tropospheric chemistry are exuded at various points along the cycle [*McNair et al.*, 1998; *Chu et al.*, 1999]. Methyl halides appear to be released directly from phytoplankton [*Lobert et al.*, 1995] and their geocycling includes both bacterial consumption [*King and Saltzman*, 1997] and chemical removal [*Elliott and Rowland*, 1993, 1995]. Nonmethane hydrocarbons are produced by the photolysis of poorly characterized dissolved organic material [*Ratte et al.*, 1993]. The whole-air hydrocarbons may initially be conceived of as tracers for continental combustion processes responsible for the mobilization of nitrogen. Mobile forms of the nutrient enter the sea to enhance/alter plant productivity. A reflection of these changes will be new distributions for the dissolved trace gases, and so also for their hot spots. Surface maxima are detected in the aircraft hydrocarbon data sets, to the extent that the boundary layer has been sampled. The whole-air method can thus be used to investigate a long but critical circuit through the Asian component of the Earth system, from combustion through mobile nitrogen to marine ecology to sea/air transfer.

6. Summary

[44] The human population of Asia already constitutes over half of humanity, and it is rapidly modernizing and continuing to grow [*UN*, 1994; *OSTP*, 1997]. Impacts to biogeochemical cycling of the major elements are expected at the regional, Pacific Rim and global scales [*Duce*, 1991; *Vitousek and Matson*, 1993; *Chameides et al.*, 1994; *Galloway*, 1996; *Elliott et al.*, 1997a, 1997b; *Vitousek et al.*, 1997]. Whole-air sampling coupled to gas chromatography is capable of quantifying dozens of hydrocarbons which act as tracers for anthropogenic sourcing to the atmosphere and Earth system. Detection limits of parts per trillion by volume can often be achieved [*Blake et al.*, 1992, 1994, 1996a, 1996b, 1996c, 1997]. A Japanese sponsored, international aircraft campaign recently covered large portions of the East Asian atmos-

phere and included the whole-air method in on-board experiments. The campaign took as its themes the study of biomass burning and lightning emissions. Flight legs were concentrated around the Indonesian archipelago. Here we examine the Japanese whole-air sampling results for insights into evolving Asian biogeochemistry and techniques for monitoring it. Our strategy for analysis is (1) to select flights with large horizontal distance fractions spent in the boundary layer, (2) to plot and consider all data as functions of flight time and altitude, and (3) to organize our treatment by chemical family. Comparisons are made with Asian source signatures where available and otherwise with surrogates.

[45] The meteorological rhythm of winter/spring offshore and summer/fall onshore flow [*Bachmeier et al.*, 1996; *Merrill et al.*, 1997] is evident at middle latitudes for many of the longer lived species. The Indonesian tropics are among the most convectively active areas on Earth [*Schmidt*, 1952; *Fuelberg et al.*, 1999] and strong vertical mixing effects are apparent there. Molecules emitted from the open sea surface can be tracked entering both continental and marine air masses. It is argued that Indonesia is a microcosm of the global tropics in that island regimes exist with dense and sparse human populations near one another, separated by productive ocean waters [*Berger and Wefer*, 1991; *WRI*, 1992]. Ethane is chosen as a major correlate for the other hydrocarbons because of its simple structure and high concentration in many emissions fingerprints [*Singh and Zimmerman*, 1992; *Blake et al.*, 1992, 1994]. Plots of concentrations for key species against those of C_2H_6 manifest combustion signatures in some cases and sea-air transfer in others. As the Asian human population industrializes and expands, source distributions and therefore integrated signatures are likely to change. This implies motion through the chemical species space, and it can be tracked if regular hydrocarbon sampling can be conducted. Major uncertainties regard fingerprints for the different combustion processes. Ratios of single carbon, alkane, unsaturated, aromatic and halocarbon species may be similar for the disparate sources biomass burning, incineration and automotive activity [*Blake et al.*, 1996b, 1997].

[46] The whole-air method has become particularly rich in chemical detail in recent years and invites the application of several advanced statistical techniques [*Mayrsohn and Crabtree*, 1976; *Watson*, 1983; *Hopke*, 1985; *Baldasano et al.*, 1999]. We apply a classical principal components analysis to discriminate major source factors, and outline chemical mass balance computations which may permit the resolution sources along a flight path. Although our BIBLE A data and approach are restricted to organic species several elemental cycles are elucidated, because secondary groups contain other atoms and release mechanisms are shared. Alkyl nitrates trace oxidation of alkanes in the presence of nitrogen oxides. They are thus indicators for urban modification of air masses, and perhaps also for lightning activity. Methyl nitrate is an exception, because methane excesses in city air tend to be small [*Blake et al.*, 1984; *Blake and Rowland*, 1995]. Methyl halides are indicators for both biomass burning and sea-air transfer, but at distinct species ratios. The long-lived anthropogenic halocarbons have stabilized in co ation or are being removed [*IPCC*, 1995], testimony that the Montreal protocol and its followers are reversing the global atmospheric halogen buildup. The short-lived industrial halocarbons distinguish urban emissions [*Blake et al.*, 1997] and we investigate their utility in identifying continental air masses over the open sea.

[47] The BIBLE A whole-air samples analyzed here provide in and of themselves a detailed glimpse of the role Asia will play in evolution of the Earth system over the next few human generations. Through the database, we characterize current mainland emissions as rich in methane at times, rich in combustion signatures as a rule. Terrestrial climate is most dependent on the elemental geocycles of carbon and nitrogen [*Vitousek and Matson*, 1993; *IPCC*, 1995]. The combustion products detected under BIBLE A indicate N mobilization on the continental scale, with potential consequences for soil nutrient storage and terrestrial ecosystem integrity [*Schlesinger*, 1997; *Matson et al.*, 1997]. Long range transport will move the nitrogen to the open North Pacific as well. The hydrocarbons serve as either direct or indirect greenhouse gases. Methane emissions from rich source types such as rice cultivation, landfills and sewers may be detectable in the BIBLE data. We emphasize, however, the absence of certain signatures and also changes that are likely to occur as Asia industrializes. The propane and isomeric butane combination characteristic of liquefied petroleum gas leakage [*Blake and Rowland*, 1995; *Elliott et al.*, 1997c] has not been identified from among the BIBLE A samples. As Asia urbanizes it is expected that incomes will rise and infrastructures for the distribution of the cleaner fossil fuels will be developed. A key question will be their extent of leakage [*Muller*, 1992]. At the regional scale oxidation of the hydrocarbons produces ozone [*NRC*, 1991]. A case has been made for detrimental effects on crop yields, in a nation which will struggle to feed itself in the long term [*Chameides et al.*, 1994; *Brown*, 1995a, 1995b].

[48] Data from the BIBLE A campaign can thus be interpreted to demonstrate the promise of whole-air hydrocarbon sampling to monitor and elucidate biogeochemical change in the western Pacific. However, the measurements also point to refinements which will be necessary in order for the developing method to reach its full potential. The BIBLE A flights were necessarily prejudiced toward the upper troposphere, because lightning studies were a chief motivation. Future aircraft missions can reveal more about the Earth system role of Asia if they favor surface processes and if they are conducted closer to or over the continent. Coordination with regular ground-based measurements would be reasonable as a means to achieve temporal space filling. Overflights and surface measurements may of course be difficult to arrange from a political standpoint. Our analysis highlights their potential scientific value. Crucial uncertainties in our work here are traceable to a lack of Asia-specific source fingerprint information. We recommend that a compilation be undertaken in close conjunction with any intensification of general air sampling activity.

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