Internal Mixture of Sea Salt, Silicates, and Excess Sulfate in Marine Aerosols

MEINRAT O. ANDREAE,* ROBERT J. CHARLSON, FRANK BRUYNSEELS, HEDWIG STORMS, RENE VAN GRIEKEN, WILLY MAENHAUT

Individual aerosol particles from the remote marine atmosphere were investigated by scanning electron microscopy and electron microprobe analysis. A large fraction of the silicate mineral component of the aerosol was found to be internally mixed with sea-salt aerosol particles. This observation explains the unexpected similarity in the size distributions of silicates and sea salt that has been observed in remote marine aerosols. Reentrainment of dust particles previously deposited onto the sea surface and collision between aerosol particles can be excluded as possible source mechanisms for these internally mixed aerosols. The internal mixing could be produced by processes within clouds, including droplet coalescence. Cloud processes may also be responsible for the observed enrichment of excess (nonsea-salt) sulfate on sea-salt particles.

SILICATE DUST PARTICLES OF CONTINENTAL origin are transported in the atmosphere over long distances to remote oceanic regions (*1*) and contribute most of the nonbiogenic component of pelagic marine sediments. These particles have been characterized by bulk chemical and mineralogical analysis (*1, 2*). The particle size distribution of silicate aerosols over the remote oceans has shown two paradoxical characteristics. First, the mass median diameter of the particles does not always decrease with transport distance as much as would be expected from differential settling of the larger particles (*3, 4*). Second, over the open oceans far from continents, the apparent size distribution of the silicate component (mass median diameter, 1.5 to 4 μm) often approximates that of the sea-salt particles (mass median diameter, 4 to 8 μm) (*3–5*), a phenomenon that is unexpected in view of the different origin and atmospheric residence time of the two types of particles.

We report here the results of a microchemical investigation of individual silicate particles collected over the remote oceans. These observations are interpreted in terms of the possible modes of transport of these particles, the processes of cloud and aerosol physics that control their atmospheric behavior, and their bulk chemical composition as a function of particle size. Our results demonstrate that it is feasible to use aerosol composition as a test of the validity of hypotheses regarding chemical and physical processes in clouds (*6*).

Aerosol samples were collected from a ship in the equatorial Pacific Ocean between Ecuador and Hawaii. The cruise track and the bulk characteristics of the aerosols have been described (*5, 7*). The coarse fraction of the aerosol was collected on Nuclepore filters [50% cut-off diameter, 1.2 μm (*8*)]. Electron microscopic inspection of the filters showed that they collected only a few particles smaller than 1 μm in diameter (the median particle diameters were 2 to 3 μm). The particles present on the filters were well separated from one another, typically by about ten particle diameters; thus the likelihood that composite particles originate from the deposition of a particle onto a previously deposited one is very low.

The samples were analyzed first in an automated mode (magnification, ×300) in which several thousand particles were located, sized, and analyzed by energy-dispersive x-ray spectrometry. Particles containing silicon were then imaged by scanning electron microscopy (SEM). We analyzed individual components of composite particles by focusing the electron beam onto these components at high magnification (×10,000). We calibrated the x-ray spectra against mineral standards by using a series of fitting and correction programs.

The three particle types and their statistical distributions are shown in Fig. 1 and Table 1. This classification is based on cluster analysis of the automated scans (*9*). The first class of particles, "sea salt," includes particles that are composed predominantly of sodium, chlorine, and variable amounts of potassium, magnesium, calcium, and sulfur, and are the result of the crystallization of seawater droplets (*10*). In sample C6, collected relatively close to the coast of South America, a number of mixed-cation sulfates were commonly associated with sea-salt particles: some have the composition of evaporite deposit minerals, for example, glauberite, $Na_2Ca(SO_4)_2$, and bloedite, $Na_2Mg(SO_4)_2$. Others have compositions that cannot be explained stoichiometrically on the basis of the x-ray analyses, for example, $NaCa(SO_4)_2$, $NaMg(SO_4)_2$, $NaSO_4$, $KMg(SO_4)_3Cl$, $Na_3Mg(SO_4)_{1.5}$, and Na_3K. It is likely that the missing components in these formulas are ammonium and nitrate ions, which were observed in the ion chromatographic analysis of this sample. Although some of these crystal phases are probably an artifact of the drying process and may not represent the phase relations under atmospheric conditions, their presence gives evidence of the reaction of sea-salt particles (present in the atmosphere as a mixture of brine with evaporite minerals) with atmospheric nitrogen and sulfur species, such as NH_3, HNO_3, H_2SO_4, and SO_2. The resulting replacement of chloride by nitrate and sulfate is confirmed by the ion chromatographic analysis of this sample, which showed a loss of chloride relative to sea-salt composition.

The second class of particles consists of $CaSO_4$ particles containing little or no other sea-salt ions. These particles are especially abundant in sample C11 from the equatorial upwelling region. They could be produced by the breakup of a sea-salt particle containing a gypsum crystallite upon impact on the filter surface. A more interesting possibility, which could also explain the calcium excess often observed in remote marine aerosols (*4, 5*), is that they result from the reaction of atmospheric SO_2 with marine biogenic $CaCO_3$ particles (coccoliths), which, because of their alkalinity, would provide a suitable chemical environment for this reaction. Alternatively, $CaCO_3$ could react with H_2SO_4 as a result of aerosol interactions within clouds.

The third particle class ("silicates") contains all particles with detectable amounts of silicon. It can be further broken down into pure silicate mineral particles and particles also containing sea salt. In all three samples, the fraction of silicate particles associated with sea-salt particles (internally mixed sea-salt and silicate aerosol) is between 80 and 90%, an unexpected finding in view of predicted rates of collision between aerosol particles of this size and their atmospheric abundance. The observed internal mixing of

---

M. O. Andreae, Department of Oceanography, Florida State University, Tallahassee, FL 32306.
R. J. Charlson, Department of Civil Engineering, University of Washington, Seattle, WA 98195.
F. Bruynseels, H. Storms, R. Van Grieken, Department of Chemistry, University of Antwerp (Universitaire Instelling Antwerpen), B-2610 Antwerp-Wilrijk, Belgium.
W. Maenhaut, Instituut voor Nucleaire Wetenschappen, Rijksuniversiteit Gent, B-9000 Gent, Belgium.

*To whom correspondence should be addressed.

Table 1. Concentrations and characteristics of coarse aerosol particles (>1.2 μm in diameter) from the atmospheric boundary layer over the equatorial Pacific Ocean as determined by electron probe microanalysis. Air-mass back-trajectories show that the air masses sampled had in all cases come from the east and remained over the ocean in the trade wind region for at least 5 days.

Sample	Sampling period (1982)	Latitude, longitude	No. of particles analyzed	Particles per cubic meter	Particle types (%)			
					Sea salt	$CaSO_4$	Silicate–sea salt	Pure silicate
C6	7–8 July	2° to 0°S, 82° to 88°W	1492	129,000	85.6	6.0	6.8	1.6
C11	16–19 July	1°N, 118° to 125°W	2629	106,000	88.4	9.4	1.9	0.3
C15	29 July–2 August	6° to 17°N, 140°W	912	90,000	64.7	3.1	28.0	4.2

sea-salt and silicate aerosols could be responsible for the similarity in the size distribution of the silicate and sea-salt aerosols and the lack of a decrease in silicate particle size with distance from land (*3–5*).

To verify whether the observed silicate particles were representative and did not incorporate a storage or analytical artifact, we derived a bulk aerosol composition from the individual particle analyses by using the spot analyses of the silicate particles and the particle geometry as obtained from the SEM images. The results were compared with the composition of the bulk aerosol obtained by proton-induced x-ray emission (PIXE) on the same filters as used for this study, and by instrumental neutron activation analysis (INAA) of simultaneously collected high-volume samples [Table 2, PIXE and INAA data from (*5*)]. All analyses were in agreement to within a factor of 2 or better.

Two mechanisms could explain an internally mixed sea-salt/silicate aerosol: (i) the reinjection during sea-spray formation of mineral particles that have previously settled onto the sea surface, or (ii) the collision of sea-salt and silicate particles in the atmosphere. If 90% of the silicate aerosol particles are associated with sea salt, the first mechanism would imply that more than 90% of the particles deposited onto the sea surface are reinjected into the atmosphere. The feasibility of this mechanism can be tested by comparing the enrichment of aluminum (relative to sodium) in the aerosol with the aluminum enrichment in sea-spray droplets (Table 3). The observed values are higher by more than two orders of magnitude than the enrichment of aluminum observed in sea-spray material [4200 in the Atlantic, 200 in the Irish Sea (*11*)]. Furthermore, on the basis of the aluminosilicate particle density in open ocean seawater [10^5 particles per liter (*12*)] and the upper end of the estimates of sea-spray enrichment (5×10^3), we predict aluminosilicate aerosol particle densities of 50 to 100 m^{-3}, in contrast to the observed values of 2×10^3 to 3×10^4 (Table 3). Clearly, the reinjection mechanism cannot explain the observed abundance of internally mixed sea-salt/silicate aerosol particles.

Several mechanisms may bring salt and mineral particles together in the atmosphere: (i) collision due to different settling velocities, (ii) Brownian coagulation of aerosol particles, (iii) electrostatic attraction, (iv) collision of a mineral particle with a cloud droplet containing sea salt, and (v) coalescence of a cloud droplet containing a mineral particle with a droplet containing a salt particle. The first two processes are not likely to be important because of the small settling velocities of the particles involved and their small number densities. Model calculations based on the use of aerosol characteristics representative of our sample set suggest that the lifetime due to capture via differential sedimentation is greater than 10 days (*13*) and that the lifetime for a silicate particle prior to contacting a salt particle by Brownian diffusion is on the order of 100 years, both longer than the overall lifetime of a coarse aerosol particle. We shall examine possible cloud-related processes instead.

Inside clouds, there are two steps in the processing of coarse particles: activation and coalescence. If the surface of a mineral dust particle has a coating of even a small amount of water-soluble material (the residue from the last rainwater that fell on it or the product of chemical weathering), it will probably be a cloud condensation nucleus (CCN) activated at low supersaturation because of its large size. If, on the other hand, the mineral particle is hydrophobic, because of a lack of soluble material on its surface or because of a nonpolar organic coating, then it might not be a CCN. When a rising air parcel first enters a region of supersaturation, droplets grow on the existing CCN's. Subsequently, if the dust is not a CCN, the still dry dust particles can collide with and be enveloped in droplets. This initial scavenging of the mineral particles into cloud droplets is itself the result of several simultaneous processes: Brownian motion of the mineral

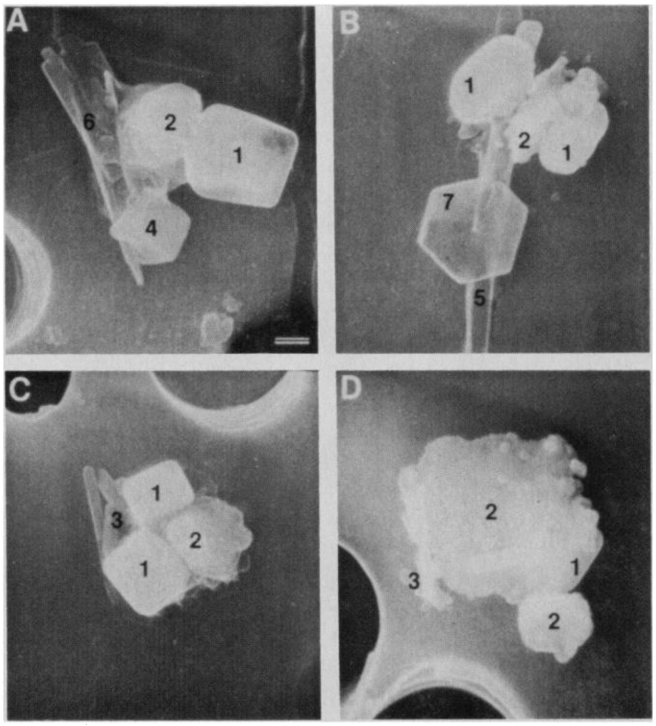

Fig. 1. Internally mixed sea-salt/silicate aerosol particles: (A and B) particles from the equatorial Pacific off Ecuador (sample C6); (C and D) particles from the intertropical convergence south of Hawaii (sample C15). Chemical composition of the component particles: 1, NaCl; 2, silicate; 3, $CaSO_4$; 4, "$NaMg(SO_4)_2$"; 5, "$Na_3Mg(SO_4)_{1.5}$"; 6, "$NaMg_2Ca(SO_4)_3$"; and 7, "Na_3K." (The formulas in quotation marks are not charge-balanced, since they include only the ions detectable by x-ray fluorescence.) Magnification, ×10,000; scale bar, 1 μm.

Table 2. Chemical composition of the coarse fraction (>1.2 μm in diameter) of aerosols from the marine boundary layer (sample origin as in Table 1) as determined by electron probe microanalysis (EPMA), ion chromatography (IC), proton-induced x-ray emission (PIXE), and instrumental neutron activation analysis (INAA).

Sample	Concentration (ng m^{-3})							Sulfur enrichment factor#	Mass % XSO$_4$
	Al	Si	Ti	Fe	Na	SO$_4$-S	XSO$_4$-S*		
C6	50† <40§ 57‖	93† 41§	0.9† 1.1§	25† 19§ 25‖	1760† 1080‡	280‡	189‡	3.08	14.1
C11	6.6† <40§ 9.0‖	17† <17§	0.4† <0.8§	2.3† 2.3§ <12‖	1450† 1840‡	207‡	53‡	1.34	2.6
C15	77† 36§ 80‖	176† 131§	3.5† 2.6§	48† 27§ 34‖	1090† 850‡	153‡	81‡	2.14	8.2
Equatorial Pacific¶								1.46 ± 0.15	3.5 ± 1.1

*Excess (nonsea-salt) sulfate. †Determined by EPMA. ‡Determined by IC. §Determined by PIXE (*5*). ‖Determined by INAA (*5*). ¶Average of eight aerosol samples collected during the same cruise. #$(\text{S/Na})_{\text{aerosol}}/(\text{S/Na})_{\text{seawater}}$.

grains, turbulent diffusion in microscale eddies, convection, electrical effects, diffusiophoresis (which pushes particles in the direction of water vapor diffusion), thermophoresis (which pushes particles down temperature gradients), and differential sedimentation of droplets relative to dust grains (*14*). The time required for the wetting of an initially hydrophobic dust particle is not precisely calculable. Simple consideration of the time required for differential sedimentation to be effective in a marine cloud with 100 droplets per cubic centimeter of 40-μm radius suggests times on the order of 10^3 to 10^4 seconds. Williams (*14*) reported a similar range of lifetimes for 1-μm particles. Because droplets in marine cumuli also have lifetimes on the order of 10^3 to 10^4 seconds, the passage of dust particles through clouds even a few times would ensure that the silicate particles are wetted with cloud water.

Since most cloud droplets do not fall as rain but evaporate, the solute from the original CCN is left behind as a residue on the surface of the mineral particle. The next time such a particle enters a cloud, it will act as a CCN because of the soluble material on its surface and its large size. A similar history of events occurs for salt particles that enter a cloud, except that they are always active CCN's and therefore are solution droplets throughout their residence in the region of supersaturation. All cloud droplets undergo coalescence processes with other droplets and accumulate whatever solute was in those droplets.

Most cloud droplets in marine settings form on CCN's that are composed of sulfates; a small fraction of the droplets have sea-salt particles as their CCN's. The fraction of CCN's containing sea-salt is variable and can be estimated from the population of cloud droplets in marine clouds and from determinations of the typical number concentration of sea-salt particles. Radke (*15*) reported simultaneous measurements of both sodium-containing particles and CCN's in mid-latitude marine air. Sodium-containing particles larger than 0.2 μm that could be CCN's ranged in concentration from 0.1 to 1 cm^{-3}, which is consistent with our data (Table 1). These particles accounted for only 1% or less of the total CCN concentration (typically in the range of 50 to 100 cm^{-3}). That excess (nonsea-salt) sulfate particles dominate the remaining 99% or so of the CCN population is not directly provable in these experiments, but data on aerosol and rainwater composition in remote settings are consistent with this inference (*16*).

Any cloud coalescence process that brings sea salt together with mineral particles must also lead to interactions between sulfate-containing and sea-salt–containing droplets and therefore enrich sea-salt particles with excess sulfate. The observation of such an enrichment in coarse sea-salt particles would therefore be an independent test of our collision hypothesis. The amount of enrichment depends on the number of coalescence events that a sea-salt particle experiences during its atmospheric residence and on the concentration of excess sulfate in cloud droplets. Taking $10^{-5}M$ as a typical concentration of excess sulfate in remote marine clouds (based on rainwater composition), the expected value of 100 coalescence events needed to bring a mineral grain into contact with one of the 1% of the cloud droplets that contain sea salt, a mean droplet size of 10^{-3} cm, and a radius of 10^{-4} cm for the dry mineral and salt particles, we predict that the sea-salt particles should accumulate 10% of their mass in excess sulfate. An excess sulfate percentage of this magnitude was indeed observed in our samples (average excess sulfate content: 3.5 ± 1.1% by weight; $n = 8$) (Table 2). Such an enrichment is also consistent with our observations on sea-salt aerosol samples: we find an enrichment of sulfate on coarse (>1.5 μm in diameter) particles on the order of 2 to 5% in samples from the Southern Ocean (*17*), the tropical and temperate Atlantic (*3*, *18*), and the tropical Pacific (*4*). The reaction between acid sulfates and silicate minerals brought together by in-cloud processes can also account for the presence of CaSO$_4$ particles on silicate aerosol particles (Fig. 1) and the low calcium concentrations in the silicate component of these particles (*18*), since the calcium extracted from the minerals by H$_2$SO$_4$ would crystallize as CaSO$_4$ upon evaporation of the cloud droplet.

Table 3. Comparison of the observed concentration of silicate aerosol particles with that expected from the sea-spray reentrainment of dust particles settled onto the sea surface.

Sample	Concentration (ng m^{-3})		Al/Na ratio (× 10^6)	Enrichment factor‡	Silicate particles (m^{-3})	
	Na*	Al† (*11*)			Predicted	Observed
C6	1,080	50	46,000	1,000,000	54	10,800
C11	1,840	6.6	3,600	78,000	92	2,300
C15	850	77	90,000	2,000,000	43	29,000
Seawater	10.8 g kg^{-1}	0.5 × 10^{-6} g kg^{-1}	0.046	1		

*Determined by IC. †Determined by EPMA. ‡$(\text{Al/Na})_{\text{aerosol}}/(\text{Al/Na})_{\text{seawater}}$.

REFERENCES AND NOTES

1. R. A. Duce, C. K. Unni, B. J. Ray, J. M. Prospero, J. T. Merrill, *Science* **209**, 1522 (1980); J. R. Parrington, W. H. Zoller, N. K. Aras, *ibid.* **220**, 195 (1983); M. Uematsu *et al.*, *J. Geophys. Res.* **88**, 5343 (1983).
2. M. Blank, M. Leinen, J. M. Prospero, *Nature (London)* **314**, 84 (1985).
3. W. Maenhaut, A. Selen, P. Van Espen, R. Van Grieken, J. W. Winchester, *Nucl. Instrum. Methods* **181**, 399 (1981).
4. W. Maenhaut, H. Raemdonck, A. Selen, R. Van Grieken, J. W. Winchester, *J. Geophys. Res.* **88**, 5353 (1983).
5. H. Raemdonck, W. Maenhaut, M. O. Andreae, *ibid.*, in press.
6. *Global Tropospheric Chemistry: A Plan for Action* (National Academy Press, Washington, DC, 1984).
7. H. Raemdonck, W. Maenhaut, R. Ferek, M. O. Andreae, *Nucl. Instrum. Methods Phys. Res.* **B3**, 446 (1984).
8. W. John, S. Hering, G. Reischl, G. Sasaki, S. Goren, *Atmos. Environ.* **17**, 373 (1983).
9. P. Van Espen, *Anal. Chim. Acta* **165**, 31 (1984).
10. C. E. Harvie, J. H. Weare, L. A. Hardie, H. P. Eugster, *Science* **208**, 498 (1980).
11. C. P. Weisel, R. A. Duce, J. L. Fasching, R. W. Heaton, *J. Geophys. Res.* **89**, 11,607 (1984); M. I. Walker, P. S. Liss, N. J. Pattenden, W. A. McKay, *Searex Newsl.* **8**, 18 (1985).
12. C. E. Lambert, C. Jehanno, N. Silverberg, J. C. Brun-Cottan, R. Chesselet, *J. Mar. Res.* **39**, 77 (1981).
13. S. K. Friedlander, *Smoke, Dust, and Haze* (Wiley, New York, 1977), p. 193.
14. A. L. Williams, in *Precipitation Scavenging*, R. G. Semonin and R. W. Beadle, Eds. (Energy Research and Development Administration, Washington, DC, 1977), p. 258.
15. L. F. Radke, thesis, University of Washington, Seattle (1968).
16. E. K. Bigg, *J. Appl. Meteorol.* **19**, 521 (1980); J. N. Galloway *et al.*, *J. Geophys. Res.* **87**, 8771 (1982).
17. M. O. Andreae, *J. Geophys. Res.* **87**, 8875 (1982).
18. ———, unpublished data.
19. The electron probe microanalysis measurements reported here were made during a sabbatical stay of M.O.A. at the Department of Chemistry, University of Antwerp (Universitaire Instelling Antwerpen); thanks are due to F. Adams for making this visit possible. We acknowledge the help of R. Nullens with the operation of the SEM and of P. Van Espen with the analysis of the data. This research was supported by the National Science Foundation (grant ATM-8407137), the Belgian Nationaal Fonds voor Wetenschappelijk Onderzoek, and the Belgian Ministry of Science Policy (grant 84-89/69).

9 December 1985; accepted 8 April 1986

Atmospheric Trace Gases: Trends and Distributions Over the Last Decade

R. A. RASMUSSEN AND M. A. K. KHALIL

Concentrations of the halocarbons CCl_3F (F-11), CCl_2F_2 (F-12), CCl_4, and CH_3CCl_3, methane (CH_4), and nitrous oxide (N_2O) over the decade between 1975 and 1985 are reported, based on measurements taken every January at the South Pole and in the Pacific Northwest. The concentrations of F-11, F-12, and CH_3CCl_3 in both hemispheres are now more than twice their concentrations 10 years ago. However, the annual rates of increase of F-11, F-12, and CH_3CCl_3 are now considerably slower than earlier in the decade, reflecting in part the effects of a ban on their nonessential uses. Continued increases in these trace gas concentrations may warm the earth and deplete the stratospheric ozone layer, which may cause widespread climatic changes and affect global habitability.

IN RECENT YEARS CONCERN HAS BEEN growing that the buildup of man-made trace gases in the atmosphere may warm the earth by contributing to the natural greenhouse effect and cause widespread climatic changes (*1*). Some man-made trace gases may deplete the O_3 layer in the stratosphere and therefore increase the amount of biologically active ultraviolet radiation that reaches the earth's surface (*1, 2*). Although it is recognized that the buildup of CO_2 is likely to increase the earth's temperature during the next century, it is also possible that continued increases of CH_4, CCl_3F (F-11), CCl_2F_2 (F-12), and N_2O may together be as effective as CO_2 in warming the earth (*3*). F-11, F-12, and N_2O may also be most effective in depleting stratospheric O_3 (*2*). Other trace gases such as CH_3CCl_3 and CCl_4 may contribute to both these phenomena but in lesser amounts (*1–3*). While singly their effects may be small, continued increases in the concentrations of these six trace gases have the potential for changing the global environment.

Table 1. Concentrations of atmospheric trace gases over the period from 1975 to 1985 based on measurements taken each January at the South Pole (SP) and in the Pacific Northwest (PNW). The global rates of increase are given at the bottom with 90% confidence limits. The concentrations are in parts per trillion by volume for the four chlorocarbons and in parts per billion by volume for N_2O and CH_4.

Year	CCl_4		CH_3CCl_3		CCl_3F (F-11)		CCl_2F_2 (F-12)		N_2O		CH_4	
	PNW	SP	PNW	SP	PNW	SP	PNW	SP	PNW	SP	PNW	SP
1975	104	96	70	36	120	86	200	165	297	297	1525	1400
1976	106	97	78	46	133	109	217	185	299	298	1555	1425
1977	115	102	86	56	148	122	239	205	300.3	300.3	1573	1442
1978	123	98	94	68	159	139	266	232	302.1	301.2	1596	1463
1979	116	110	112	74	167	148	283	255	302.0	301.8	1619	1483
1980	121	110	126	80	179	159	307	270	303.4	303.8	1639	1500
1981	122	113	127	90	185	170	315	288	304.3	305.0	1656	1516
1982	121	114	133	97	193	179	330	304	306.8	305.4	1671	1539
1983	126	117	144	100	205	188	350	319	306.7	306.5	1663	1549
1984	130	118	150	105	213	195	366	336	306.2	306.5	1689	1567
1985	130	116	158	109	223	205	384	354	307.3	307.5	1711	1570
Annual increase, $C \pm \delta C$	2.4 ± 0.3		8.2 ± 0.6		10.6 ± 0.8		18.5 ± 0.9		1.04 ± 0.14		17.5 ± 1.3	

These trace gases are expected to play a prominent role in changing the earth's environment because they have reached relatively high concentrations in the atmosphere and persist for long times. Moreover, the increases in CO_2, CH_4, and N_2O are closely related to the production of food and energy, whereas the other gases mentioned above are used in modern industrial processes (*1, 4, 5*). Therefore, it is likely that, for a long time to come, the concentrations of these trace gases will continue to increase with increasing population. Here we report data that are useful for evaluating the future environmental consequences of the increased concentrations of six trace gases believed to have the greatest potential for contributing to global environmental changes. These data, which span the last decade, represent, as far as we know, the longest internally consistent record of atmospheric trace gas concentrations (*6*).

Table 1 shows the global concentrations (C) of F-11, CCl_4, CH_3CCl_3, F-12, CH_4, and N_2O for the last 10 years. These measurements were taken every January at the South Pole (SP) and in the Pacific North-

---

Institute of Atmospheric Sciences, Department of Chemical, Biological, and Environmental Sciences, Oregon Graduate Center, Beaverton, OR 97006.