

fate phases at low pH . The data of Driscoll *et al.* (2) are from Adirondack lakes, which should have greater mineral contact time than Leviathan stream waters. This greater residence time could be reflected in the bias of their data toward lower free aluminum a values, representing the solubility of a more stable phase of gibbsite (Fig. 3). In addition, the aluminum concentrations in Adirondack lake waters were achieved from undersaturation by dissolution of aluminosilicates by acidified meteoric input, whereas those in the Leviathan drainage waters were achieved from supersaturation by dilution. Hence, a range of gibbsite stoichiometries might be achieved in natural waters that reflect the residence time of the water. For $pH < 4.6$ the Leviathan data should reflect the maximum aluminum activities derived by simple

mixing, whereas lower activities, down to the limits of alunite or jurbanite solubilities, should reflect increased residence times.

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Interannual Variability of Atmospheric Methane: Possible Effects of the El Niño–Southern Oscillation

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Nearly continuous measurements at Cape Meares, Oregon, revealed that methane was increasing in the earth's atmosphere and that its concentration varied cyclically with the seasons. After 6 years of measurements, results show that the rate of increase in methane undergoes interannual variations; the most prominent of these coincided with the last major El Niño–Southern Oscillation, when methane concentrations fell far below expected levels. One of the consequences of the interannual variability is that the long-term rate of increase at Cape Meares is now about 16 parts per billion by volume per year, or about 1 percent annually, which is significantly less than that indicated by the earliest calculations.

UNTIL A FEW YEARS AGO, IT WAS believed that the concentration of methane (CH_4) in the atmosphere is unchanging. Recent experiments have shown, however, that it not only varies with latitude and the seasons, but is steadily

increasing in the earth's atmosphere (1, 2). Here we report that the rate of increase is not constant and that El Niño–Southern Oscillation (ENSO) (3) events may trigger substantial short-term variations in atmospheric CH_4 .

The increase in CH_4 is probably attributable to industrial and agricultural activities. Over the past century, human activities may also have depleted the concentration of hydroxyl (OH) radicals in the troposphere, thus reducing the capacity of the atmosphere for removing CH_4 and many other trace gases (4). The concentrations of CH_4 found in bubbles of air extracted from polar ice cores suggest that these processes of increasing emission and of decreasing removal have caused atmospheric CH_4 to more than double over the past 200 years (4, 5). A continued increase in CH_4 could cause global climatic changes, including warming of the earth by adding to the greenhouse effect and changes in the physics and chemistry of the earth's atmosphere (6).

For more than 6 years we have made continuous measurements of CH_4 at Cape Meares on the Oregon coast (45°N, 124°W) using an automated gas chromatographic system with a flame ionization detector (1, 7). Early results suggested that atmospheric CH_4 is increasing and provided an estimate of the rate of increase (1). Measurements at other locations from the arctic to the South Pole have confirmed that the trends observed at Cape Meares are representative of a global change. Now the record is sufficiently complete to allow the interannual variability of the trends to be evaluated.

The rate of increase does indeed vary from year to year. The largest of the short-term variations coincided with the last (and somewhat anomalous) ENSO event of 1982 to

Table 1. Effects of interannual variability of CH_4 and the long-term rate of increase at Cape Meares. The annual rates of increase in parts per billion by volume and percent are based on the models $C = a + bt$ and $C = a \exp(bt)$, respectively, where C is the monthly average concentration. The initial value reflects the calculated concentration in the first month of each period. N is the number of data and months in each period. The $\pm$ values are the 90 percent confidence limits for the rate of increase over the times spanned by each segment of the data (t -statistic) (12). $S_{yx} = [\sum d_i^2 / (N - 2)]^{1/2}$, where $d_i = (C_i - \hat{C}_i)$ are the deviations of the measured concentrations (C_i) from those predicted by the model equations ($\hat{C}_i$).

Item	Jan. 1979 to Aug. 1980	Aug. 1981 to May 1982	May 1982 to Feb. 1983	Feb. 1983 to Jan. 1985	Average (total)
Annual rate of increase ($b + \delta b$)					
ppbv	29 $\pm$ 6	14 $\pm$ 3	−3	13 $\pm$ 3	16
Percent	1.8 $\pm$ 0.3	0.8 $\pm$ 0.2	−0.2	0.8 $\pm$ 0.2	1.0
a (ppbv)	1603	1652	1676	1673	1661 $\pm$ 5*
N	20	21	9	22	72
S_{yx} (ppbv)	7	7	9	5	5

*Mean of all the data.

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1983. The effect on CH₄ at Cape Meares is portrayed in Figs. 1 and 2. Figure 1a shows the monthly averaged concentrations after seasonal cycles of 1 year or less are removed (8) and Fig. 1b shows the Southern Oscillation index (SOI), which represents the difference in barometric pressure between Tahiti and Darwin, Australia. The SOI is an indicator of ENSO events. During the time that the SOI registered the last major ENSO event, the concentration of CH₄ reached levels substantially less than expected on the basis of the trend in previous years.

ENSO events affect the concentration of atmospheric CO₂ (9), causing the rate of increase to decline. While records of the relation between CO₂ and ENSO span nearly three decades and many events, this is the first record of a possible influence of ENSO on CH₄. The known systematic measurements of CH₄ do not extend back to earlier ENSO events. The close relations among CH₄, CO₂, and ENSO are shown in Fig. 2, which depicts the rates of change in the gases and the SOI over 12-month overlapping periods (9, 10). For comparison, we also included the behavior of CO₂ during the last ENSO event. The CO₂ trends represent a global average of measurements taken by the National Oceanic and Atmospheric Administration's program of global monitoring for climatic change (10). Figure 2 suggests that ENSO events may be the common cause for the dip in the rates of increase in both CH₄ and CO₂, although the mechanisms for these actions are bound to be different.

The results in Figs. 1 and 2 imply that ENSO events may underlie the observed decrease in CH₄, although the mechanisms for this are not understood—as is also the case for the connection between ENSO and CO₂. The decrease in CH₄ during the ENSO event may have been caused by a greater than normal removal during that year, a lower than normal production, an anomaly in the transport of air to Cape Meares, or combinations of these processes. After the ENSO event, CH₄ at Cape Meares was 5 to 10 parts per billion by volume (ppbv) lower than expected from the trend before the onset of the event. Measurements at other latitudes support the conclusion that the concentration of CH₄ was 5 to 10 ppbv below expected levels on a global scale during the last ENSO. This disappearance of some 20 to 30 million tons of CH₄ is probably due to a greater than normal removal during ENSO. It can be ascribed to a higher concentration of water vapor over warmer sea-surface waters producing higher than normal levels of OH that would remove an unusually large amount of CH₄ from the atmosphere. At Cape Meares the

remaining influence of ENSO may have been caused by anomalous transport of air (11).

The long-term rate of increase in CH₄ is probably considerably lower than the rates observed over periods less than the interannual cycles. Estimates of future concentra-

tions of CH₄ must include interannual variations. When our experiment began (January 1979), CH₄ was increasing rapidly. The rate of increase slowed for about 2 years before the last ENSO event, when concentrations fell abruptly. After the event, CH₄ continued to increase at about the same rate as before the event. The trends of CH₄ over the past 6 years are summarized in Table 1 (12), which shows that the average annual rate of increase is 16 ppbv, or about 1 percent.

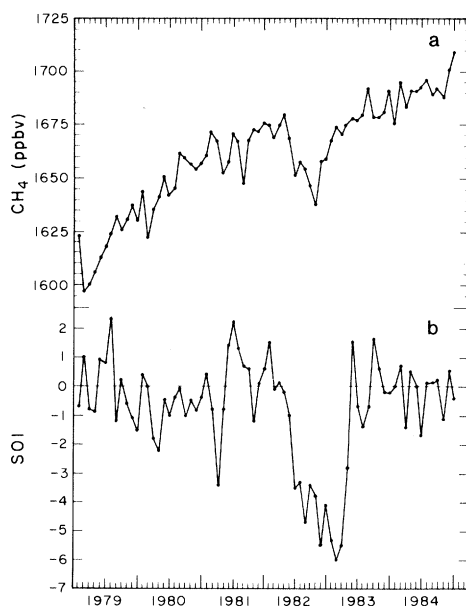


Fig. 1. Decline in CH₄ concentrations during the last ENSO event. (a) Monthly average concentrations of CH₄ at Cape Meares. Cycles that last 1 year or less have been removed. (b) Monthly SOI.

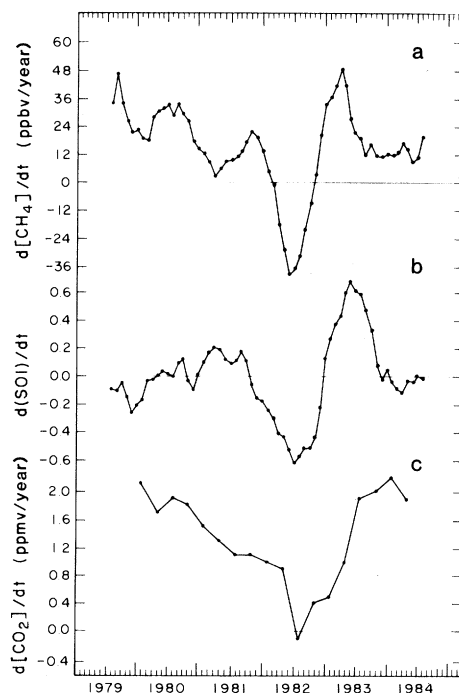


Fig. 2. (a) Rate of change of CH₄ calculated over successive 12-month overlapping periods (8). (b) Rate of change in the SOI over 12-month overlapping periods. (c) Global rate of change in CO₂ (10).

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7. The instrument consists of a modified Carle 211-MS gas chromatograph. The air is dried before being injected into the gas chromatograph. A Spectra Physics Minigrator is used to integrate the chromatographic peaks and data are stored on a magnetic tape with a Techtran 816 Data Logger. The tapes are read by a computer for analysis. Over the 6 years, about 87,000 individual measurements of CH₄ have been taken at Cape Meares. Less than 0.5 percent of the measurements have been discarded because of errors in the integration of the chromatographic peaks or recordings on magnetic tape. The instruments have functioned about 70 percent of the time on average (with no data being obtained in the remainder of the time). The precision of measurements is ≤ 0.5 percent and accuracy is estimated to be ± 5 percent.
8. The seasonal cycles are removed by subtracting a seasonal index, which is the average monthly ratio of the centered smoothed concentrations calculated by 12-month moving averages to the actual monthly data. In Fig. 2, a and b, we have calculated "moving slopes." The first point is the rate of change calculated by linear regression over months 1 to 12, the second point is for months 2 to 13, and so on.
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11. Concentrations of CH₄ fell rapidly, but some of the deficit was made up by a sharp increase toward the latter part of the cycle. Such an effect may be caused by transport anomalies. The remaining deficit that persisted after the ENSO event was caused by either a greater removal or a lesser production of CH₄ during ENSO. Greater removal is a likely explanation; however, ENSO events also affect temperature and rainfall patterns in the Northern Hemisphere that may change microbial processes in soils and other ecosystems where CH₄ is produced naturally. These effects may have contributed to the observed deficit. Data from Alaska, Hawaii, Samoa, and Tasmania are more than 100 times less frequent than those from Cape Meares. A preliminary analysis shows that the change in concentration was largest at Cape Meares and Alaska, but the effect occurred at all sites.
12. The data are represented by a piecewise linear model. The record is divided into four periods or segments over which the trend of CH₄ is represented by the linear function $C_i = A_i + B_i t$, where C_i is the concentration of CH₄ in the i th period and t is time. The first segment (I) consists of 20 months and is followed by second period (II) of another 21

months of slower growth. The third period (III) spans the ENSO event of 1982–83 and is made up of two segments: a phase of rapidly decreasing CH₄ (IIIa) followed by a rapid increase (IIIb). The last period (IV) spans the 22 months after the event. A_i and B_i for the first and last periods are estimated by least-squares techniques. For the second period the starting concentration is fixed by the endpoint of the linear function describing the first period. Therefore, only one degree of freedom is used to estimate the slope. Segment IIIa is treated similarly. For segment IIIb the last point of the equation for segment IIIa and the first point of the equation for segment IV are joined. The rates of change in atmospheric CH₄ during the four periods are summarized in Table 1. The average increase in CH₄ is estimated by $b = \sum w_i b_i$ and $w_i = \delta T_i / \sum \delta T_i$, where b_i is the slope in each of the segments I, II, IIIa, IIIb, and IV and T_i is the time over which these rates of change are estimated. The uncertainty of the overall changes in CH₄ that have occurred over the past 6 years may be estimated by propagating the errors so that $S_b = [\sum (w_i)^2 S_{b_i}^2]^{1/2}$. By this method the 90 percent confidence limits of the average increase (16 ppbv per year) are ± 3 ppbv per year for the entire 6-year period, so that the total increase was 96 ± 18 ppbv. The rates of increase varied considerably from

year to year (Table 1). When the trends are estimated by linear least-squares methods over each 12-month period except for the year of the ENSO event the average of the five yearly rates of increase is 20 ± 10 ppbv. Since observations have been obtained over only one event, an uncertainty of the rate of change during ENSO years cannot be estimated. While the tendency of CH₄ to increase can be explained by growing anthropogenic contributions to the global sources and weakening of the removal processes, these processes are probably changing systematically so that the mean trends and statistical uncertainties in the present record may not be sufficient to allow accurate predictions about CH₄ in the distant future, when perceptible environmental effects are expected.

13. We thank P. Turner and D. Joseph for data management and computer calculations; S. Crawford and D. Stearns for field and laboratory work; E. M. Rasmusson and C. F. Ropelewski for supplying data on the SOI; and R. Gammon for data on CO₂, Fig. 2c, and many discussions. Supported in part by NSF grant ATM-8414020 and by the resources of the Biospherics Research Corporation and the Andarz Company.

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Role of Platelet-Activating Factor–Acether in Mediating Guinea Pig Anaphylaxis

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The pathophysiology of anaphylaxis is very complex, and the sequelae of events are not fully explained in terms of the effects of histamine and peptide leukotrienes alone. Platelet-activating factor (1-*O*-alkyl-2-acetyl-sn-glyceryl-3-phosphorylcholine, PAF-acether) has been detected in animals undergoing anaphylaxis. Injection of synthetic PAF-acether induces similar effects, including bronchoconstriction, respiratory arrest, systemic hypotension, neutropenia, and thrombocytopenia. The results reported here demonstrate that the histamine- and leukotriene-independent component of guinea pig anaphylaxis *in vivo* and in isolated lung parenchymal strips *in vitro* is mediated by PAF-acether. However, PAF-acether is not responsible for the anaphylaxis-induced thrombocytopenia.

A VARIETY OF HUMORAL MEDIATORS, including histamine and the leukotrienes, are involved in the pathogenesis of anaphylaxis in the guinea pig (1, 2). The precise role of these mediators and their interaction with one another have not been well defined. Moreover, the role of platelet-activating factor–acether in mediating some of the components of the anaphylaxis has not been clarified (3–6). We therefore set out to investigate the temporal sequence and role of histamine, PAF-acether, and leukotrienes in the pulmonary response to immunochallenge in guinea pig anaphylaxis. We found that histamine is responsible for the early component, PAF-acether for the middle component, and leukotrienes for the late component of pulmonary anaphylaxis in pulmonary parenchymal strips. All three mediators must be blocked if the bronchoconstrictor response is to be totally eliminated.

Male Hartley guinea pigs (500 to 700 g) were sensitized by the injection of ovalbu-

min (OA) (100 mg intraperitoneally and intramuscularly) 2 to 3 weeks before immunologic challenge. For *in vitro* studies of the responsiveness of airway smooth muscles, we prepared lung parenchymal strips (20 mm long and 3 mm in diameter) from the outer segments of the upper lobes of the lung. The strips were transferred to a water-jacketed organ bath (20 ml) preloaded with 1 g of resting force containing oxygenated (95 percent O₂ + 5 percent CO₂) Krebs-Henseleit buffer. We measured changes in smooth muscle tone isometrically as developed force (in milligrams), using Grass FT-03 force-displacement transducers and a Grass model 7 oscillographic recorder. For the *in vivo* experiments, sensitized guinea pigs were anesthetized with pentobarbital (35 mg/kg). A catheter was introduced into the left carotid artery for measurement of arterial blood pressure, and a special double-lumen cannula was inserted into the distal jugular vein. This cannula allowed continuous withdrawal of peripheral venous blood

(85 μ l/min) for measurement of the platelet count with a Technicon Autocounter. We prevented blood coagulation by adding sodium citrate (3.8 percent; 1:7 by volume), without allowing citrate to flow into the animal (7). Another catheter was inserted into the jugular vein for injection of drugs or their respective vehicles. Airway pressure was measured with a Statham differential gas-pressure transducer connected to a tracheal cannula while the animals breathed spontaneously. All values presented in this study are means $\pm$ SEM. All statistical comparisons were made by *t* test and confirmed by analysis of variance (ANOVA).

Isolated guinea pig lung parenchymal strips challenged by the addition to the bath fluid of OA (2 μ g/ml) showed an increase in force of 184 ± 16 mg ($n = 38$). This increased force persisted for more than 1 hour. Although the amplitude of the OA-induced increases in force showed considerable individual variation, the responses of the four strips taken from each animal were approximately equal. For this reason, the results are given either in absolute values or as a percentage of the responses of control strips taken from the same animal. Addition to the bath of the antihistamine diphenhydramine (30 μ M) or of BW-755c (30 μ M), the dual inhibitor of arachidonic acid lipooxygenase and cyclooxygenase pathways, prior to the addition of OA did not significantly alter the increase in force (178 ± 19 and 194 ± 28 mg for ten and eight strips, respectively). When both inhibitors were added together,

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