

have, however, been observed by Ayrapet'yants *et al.* (11), who classified them as echolocation pulses.

The waveforms in Figs. 2B and 3B are similar to the velocity resolvent signals derived by SIR maximization.

Velocity-sensitive echolocation waveforms are well suited to a situation characterized by (i) unfamiliarity with the environment and (ii) a second (moving) animal in the tank. With no information about environmental reverberation, a reasonable way to detect a moving target in stationary clutter is to use a waveform that recognizes the target by its motion. In radar theory (12), such a strategy is commonly called moving target indication.

A laboratory simulation of the dolphin waveforms can be accomplished by band-pass filtering a time-gated sinusoid. The bottom signals in Figs. 2C and 3C were obtained by band-pass filtering the waveforms immediately above them. In order to simulate the waveform of Fig. 2B, the sinusoid of Fig. 2C (top signal) must have a frequency of  $f_0 = 1$  kHz and be band-pass filtered with high- and low-frequency cutoffs  $f_H \approx 2$  kHz,  $f_L \approx 0.8$  kHz, respectively. For Fig. 3C,  $f_0 = 0.86$  kHz,  $f_H \approx 3.43$  kHz, and  $f_L \approx 0.62$  kHz.

It is interesting to compare the above frequencies with the frequency range that dolphins actually have at their disposal. According to Johnson (13), *Tursiops* is capable of utilizing frequencies between  $f_L \approx 0.1$  kHz and  $f_H \approx 150$  kHz. Most of the signal energy in Figs. 2B and 3B is therefore restricted to a comparatively narrow band. It is the ratio of bandwidth to carrier (centroid) frequency, however, that is important to deciding whether a signal is narrow band or wide band (6, 14). By such a criterion, the dolphin signals are extremely wide band. Because of the large bandwidth-to-carrier frequency ratio, the doppler effect must be described by a compression factor  $s$  rather than by a frequency shift.

The reason for the dolphins' use of such a narrow frequency range is an open question. A possible explanation is that the signal is meant to detect objects at comparatively large distances. Because attenuation in water increases with frequency, a low-frequency waveform with small bandwidth is most likely to retain its structure and strength over long distances. Since the maximum output of a correlation processor is proportional to echo energy, a signal with comparatively long time duration is also to be recommended for long-

distance propagation (if correlation is used).

It has been shown that optimum wide-band waveforms for velocity resolution are similar to certain dolphin signals. The optimum waveforms were derived by assuming a cross-correlation processor, that is, a filter whose output is the integrated product of input signals with a time function that may not be identical to the waveform that is sought. The resemblance between Figs. 2A and 2B, and 3A and 3B, would seem to suggest that *Tursiops truncatus* uses a generalized form of correlation processing. Similar evidence, for auto-correlation processing, has been found for the little brown bat (*Myotis lucifugus*) (6, 15) and the red bat (*Lasiurus borealis*) (6).

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#### References and Notes

1. E. J. Kelly and R. P. Wishner, *IEEE (Inst. Elec. Electron Eng.) Trans. Mil. Elec.* MIL-9, 56 (1965).
2. D. F. DeLong, Jr., and E. M. Hofstetter, *IEEE Trans. Info. Theory* IT-13, 454 (1967).
3. C. A. Stutt and L. J. Spafford, *IEEE Trans. Info. Theory* IT-14, 280 (1958).
4. W. D. Rummier, *IEEE Trans. Aerospace Elec. Sys.* AES-2, 689 (1966).
5. R. A. Altes, *IEEE Trans. Info. Theory* IT-17, No. 3 (May 1971).
6. ———, "Methods of wideband signal design for radar and sonar systems," thesis, University of Rochester (1971).
7. Pictures of the corresponding cross-ambiguity functions are available from the author.
8. If constraints to an optimization problem are imposed one at a time (adding more constraints only when necessary), the solutions to a comparatively unconstrained problem will sometimes be satisfactory from the viewpoint of the unwritten constraints. Such situations can occur because of implicit constraints imbedded in the formulation, such as the description of all waveforms in terms of a given incomplete set of basis functions.
9. T. Bullock (University of California at San Diego), private conversation.
10. W. E. Evans (Naval Undersea Research and Development Center, San Diego), private conversation.
11. E. Sh. Ayrapet'yants, A. G. Golubkov, I. V. Yershova, A. R. Zhezherin, V. N. Zvorykin, V. I. Korolev, *Dokl. Akad. Nauk SSSR* 188, 1197 (1969). English translation: Joint Res. Pub. Service, No. 49479.
12. IT&T Corp., *Reference Data for Radio Engineers* (American Book-Stratford Press, New York, ed. 4, 1956), p. 873.
13. C. S. Johnson, *J. Acoust. Soc. Amer.* 43, 757 (1968).
14. P. M. Woodward, *Probability and Information Theory with Applications to Radar* (Pergamon, London, ed. 2, 1964), p. 101.
15. R. A. Altes and E. L. Titlebaum, *J. Acoust. Soc. Amer.* 48, 1014 (1970).
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## Fate of Air Pollutants: Removal of Ethylene, Sulfur Dioxide, and Nitrogen Dioxide by Soil

Abstract. *The ultimate sink for many air pollutants is unknown. Data are presented here in support of the idea that reaction with soil, through microbial or chemical means, can remove ethylene, other hydrocarbons, sulfur dioxide, and nitrogen dioxide from the air.*

Large quantities of ethylene, an air pollutant and plant hormone, are produced in the United States each year.

Table 1 presents data on the relative amounts of ethylene produced by natural sources and human activities. In

Table 1. Ethylene emissions from major sources in the United States, 1966.

| Source*                                      | Quantities utilized<br>( $\times 10^9$ tons) | Emission factor† | Ethylene emission<br>( $\times 10^9$ tons) |
|--|--|------------------|--|
| Coal combustion                              | 486  | 0.001            | 0.5  |
| Fuel oil combustion                          | 235  | .001             | .2   |
| Motor fuels                                  |  |                  |  |
| Gasoline                                     | 280  | .05              | 14.0                                       |
| Diesel                                       | 27   | .008             | 0.2  |
| Jet  | 28   | .001             | .03  |
| Refuse burning                               |  |                  |  |
| Good incineration                            | 8  | .000025          | .0   |
| Poor incineration                            | 16   | .015             | .2   |
| Open burning                                 | 56   | .001             | .06  |
| Ethylene production from industrial leakage‡ | 11.2   | .001             | .01  |
| Vegetation§                                  | 2000   | .00001           | .02  |

\* Values for sources except leakage from industry obtained from (8). † Estimated values based on information from (9). ‡ From (9). § Assumes a ton of vegetation per acre and an area of  $3 \times 10^9$  square miles for the United States. || Calculated on the assumption of 0.5 ml of ethylene produced per gram (fresh weight) per hour, 24 hours a day, 365 days a year.

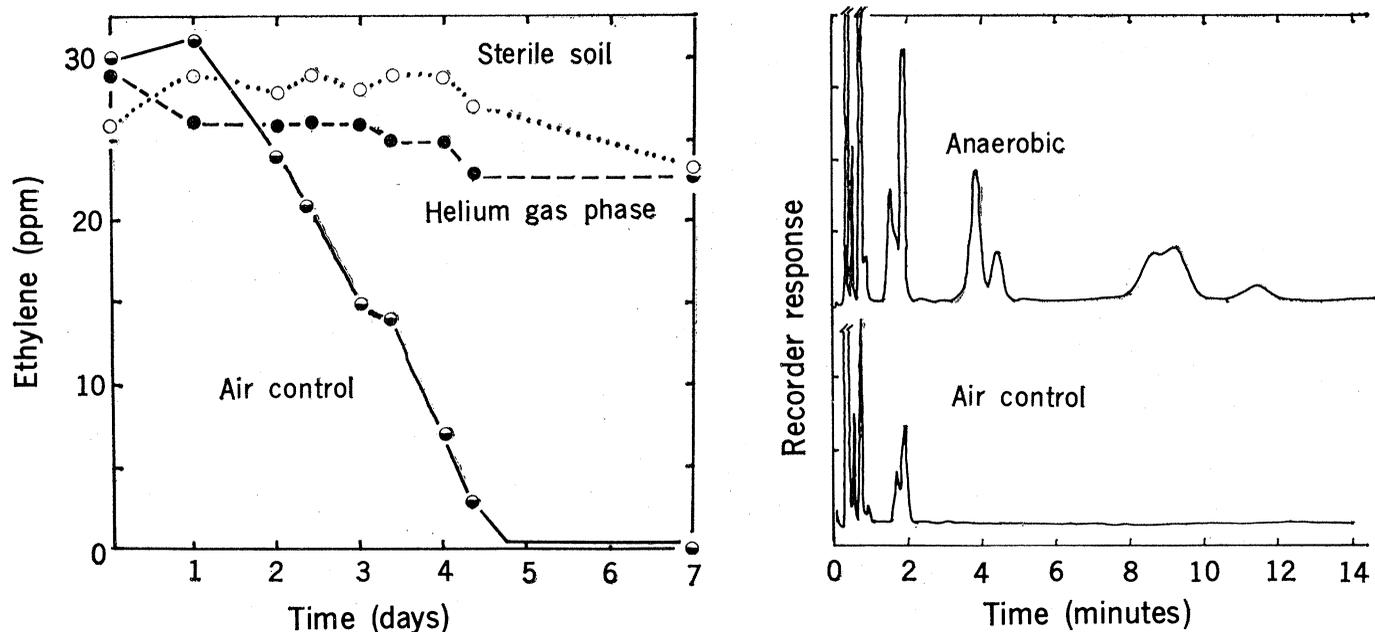


Fig. 1 (left). Effect of soil on concentrations of ethylene in air. Soil samples of 50 g were either autoclaved or used as controls and incubated in 2.5-liter desiccators in the presence of air or helium. Fig. 2 (right). Gas chromatographs showing reduction in the concentrations of hydrocarbons from dilute auto exhaust in the presence of soil after 5 days. The initial distribution of hydrocarbons was similar to that of the anaerobic sample.

1966  $15 \times 10^6$  tons ( $13.5 \times 10^6$  metric tons) of ethylene were released as a pollutant, whereas only  $11.2 \times 10^6$  tons were produced as a raw material for industry, and the amount produced by plants was only 0.13 percent of that produced by man. As a comparison, estimates for the total production of hydrocarbons, sulfur dioxide, nitrogen dioxide, and carbon monoxide are  $32 \times 10^6$ ,  $33 \times 10^6$ ,  $20.6 \times 10^6$ , and  $100 \times 10^6$  tons, respectively (1). However, even though large quantities of ethylene are produced, concentrations in nonurban areas do not increase and remain low— $< 5$  parts per billion (ppb) ( $5.75 \mu\text{g}/\text{m}^3$ ). Two mechanisms for ethylene degradation are known: oxidation by ozone and reaction with an oxide of nitrogen in the light (2). The purpose of this report is to show that, in laboratory experiments, soil acts as an important sink for ethylene through microbial degradation, and for sulfur dioxide and nitrogen dioxide primarily through chemical action.

Soil samples (50 g for ethylene, 250 g for sulfur dioxide and nitrogen dioxide) were placed on petri plates in desiccators (2.5-liter capacity for ethylene, 10-liter capacity for sulfur dioxide and nitrogen dioxide) equipped with sleeves on their lids. Gases were introduced and removed through a rubber vaccine cap fitted on the side arm of the lid collar. Soil samples for ethylene uptake were obtained from Beltsville and Frederick, Maryland, and soil samples

for sulfur dioxide and nitrogen dioxide uptake were taken from Waltham, Massachusetts. The concentrations of ethylene and other hydrocarbons were measured by flame-ionization gas chromatography on an alumina column, sulfur dioxide was measured according to the method of Adams *et al.* (3) with the use of a fixed gas volume, and nitrogen dioxide was measured according to the evacuated bottle method of Saltzman *et al.* (4).

Figure 1 shows the effect of sterilization ( $110^\circ\text{C}$  for 15 minutes) and anaerobiosis (helium gas phase) on the uptake of ethylene by soil. Ethylene uptake by soil does not occur in the absence of oxygen. A ratio of oxygen to nitrogen of 2 percent to 98 percent (by volume) satisfied the oxygen requirement, and 1 percent oxygen resulted in a rate of ethylene uptake equal to half the maximum rate. A ratio of carbon dioxide to nitrogen of up to 10 percent to 90 percent had no effect on the rate of ethylene consumption. Inhibition of ethylene uptake was also observed when the soil was sterilized with ethylene oxide, an indication that the effect of autoclaving was not due to thermal modification of the soil structure. As shown in Fig. 1, a 24-hour lag in uptake occurred after ethylene was added to the gas phase. A similar lag was not observed when subsequent amounts of ethylene were added. The fact that bacteria are known to consume hydrocarbons, including ethylene

(5), and the fact that ethylene uptake by soil is heat-sensitive, requires oxygen, and occurs after a lag period suggests that microorganisms are the major sink for ethylene. The ability of soil to reduce ethylene concentrations is extremely effective. The soil atmosphere in Beltsville was free of measurable amounts of ethylene (5 ppb is the limit of detection), whereas concentrations in the air above vary from 10 to 40 ppb.

Figure 2 shows that soil is able to absorb a number of hydrocarbons in the presence of oxygen. The soil sample completely removed some hydrocarbons and partially removed others from a sample of dilute auto exhaust. A curve similar to the one labeled "anaerobic" was observed when the experiment was initiated. Although we were unable to identify all the peaks, we know that the normal composition of hydrocarbons is reported to be 27 percent acetylene, 20 percent ethylene (third peak from the left), 8 percent propene, 7 percent butane, 5 percent toluene, 5 percent of the various isomers of pentane, and various amounts of 42 other gases (6).

The soil was also able to remove sulfur dioxide and nitrogen dioxide. The rate of removal of these gases was faster than that observed for ethylene. Sulfur dioxide was reduced from 100 to 8 parts per million (ppm) in 15 minutes in the presence of soil. Autoclaving the soil prior to the experiment reduced the rate of uptake to 20 ppm after 15 minutes. The reaction with nitrogen

dioxide was slower. Concentrations of nitrogen dioxide dropped from 100 to 3 ppm after 24 hours, and autoclaving the soil reduced the uptake to 13 ppm after 24 hours. These results indicate that the major portion of sulfur dioxide and nitrogen dioxide is removed by some chemical reaction. However, a microbial contribution cannot be entirely excluded.

Uptake of carbon monoxide by soils was recently demonstrated by Inman *et al.* (7). They found that their soil samples reduced carbon monoxide concentrations from 120 ppm to near zero within 3 hours.

Extrapolating from our laboratory experiments, we calculated that  $7 \times 10^6$  tons of ethylene may be removed from the air in the United States by means of microbial degradation. Since the rate of production ( $15 \times 10^6$  ton/year) exceeds uptake by soil by a factor of 2, other mechanisms of degradation are probably important. The uptake of sulfur dioxide and nitrogen dioxide was more rapid than that of ethylene. Our calculations yield values of  $6 \times 10^8$  tons of nitrogen dioxide and  $4 \times 10^{10}$  tons of sulfur dioxide per year. These values are large enough to accommodate all the sulfur dioxide and nitrogen dioxide produced in the United States (sulfur dioxide =  $32 \times 10^6$  tons, nitrogen dioxide =  $33 \times 10^6$  tons) each year.

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#### References and Notes

1. "Environmental Quality: First Annual Report of the Council on Environmental Quality" (Government Printing Office, Washington, D.C., 1970).
2. P. A. Leighton, *Photochemistry of Air Pollution* (Academic Press, New York, 1961).
3. D. F. Adams, M. Corn, C. L. Harding, J. B. Pate, A. L. Plumley, F. P. Scaringelli, P. F. Urone, *Health Lab. Sci.* 7, 4 (1970).
4. B. E. Saltzman, W. A. Cook, B. Dimitriades, E. L. Kothny, L. Levin, P. W. McDaniel, J. H. Smith, *ibid.* 6, 106 (1969).
5. C. E. ZoBell, *Advan. Enzymol.* 10, 443 (1950).
6. D. M. Anderson *et al.*, "Air Quality Criteria for Hydrocarbons," *Nat. Air Pollut. Contr. Admin. Publ. FS2,3000 AP 64* (1970).
7. R. E. Inman, R. B. Ingersoll, E. A. Levy, *Science* 172, 1229 (1971).
8. L. S. Jaffe, *J. Air Pollut. Contr. Ass.* 18, 534 (1968).
9. Q. R. Stahl, "Preliminary Air Pollution Survey of Ethylene," *Nat. Air Pollut. Contr. Admin. Pub. APTD 69-35* (1969).

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## Eight-Membered Cyclosilicate Rings in Muirite

**Abstract.** *The determination of the crystal structure of muirite,  $Ba_{10}(Ca,Mn,-Ti)_7Si_8O_{24}(Cl,OH,O)_{12} \cdot 4H_2O$ , revealed the presence of discrete cyclic silicate anions,  $(Si_8O_{24})^{16-}$ , formed by the condensation of eight silicate tetrahedra. This first reported occurrence of eight-membered rings is of particular interest, because rings with eight tetrahedra are reported to be energetically less stable than rings with six tetrahedra, which have been found in many minerals.*

Muirite has been found with many other barium-containing silicate minerals in metamorphic rocks in Fresno County, California. Its composition has been given as  $Ba_{10}Ca_2MnTiSi_{10}O_{30}(OH,Cl)_{10}$ . On the basis of the chemical analysis and the x-ray data supplied with the original description, it is not apparent to which group of silicates muirite belongs (1). Because of its tetragonal symmetry the formulation  $Ba_5CaTiO_4(Si_4O_{12}) \cdot 3H_2O$ , with four-membered silicate rings, has been proposed (2).

A crystal of muirite (3) of approximately isometric shape (0.2 by 0.2 by 0.2 mm) was used for data collection on an automatic four-circle diffractometer with graphite crystal-monochromatized  $AgK\alpha$  radiation (wavelength  $\lambda = 0.56083$  Å). From the usual processing and averaging (4) of 10,476 measured intensities 978 unique observed structure factors  $F_{obs}$  were obtained (maximum  $\sin \theta/\lambda = 0.75$  Å<sup>-1</sup>). No absorption correction was applied to the observed data (absorption coefficient  $\mu = 53$  cm<sup>-1</sup>; the maximum corrections would have been  $\pm 8$  percent on  $F_{obs}^2$ ). The unit cell parameters (the figures in parentheses represent the standard deviations in units of the least significant digit) are  $a = 14.030(10)$  Å and  $c = 5.635(4)$  Å. Because no systematic absences of intensities have been observed, the space groups  $P4/mmm$ ,  $P4mm$ ,  $P422$ ,  $P4m2$ , and  $P42m$  are possible (1). The structure was solved by Patterson methods in space group  $P4/mmm$  and refined by full-matrix least-squares analysis to a discrepancy index  $R$  of 0.065 for all observed reflections. In the calculation the X-sites were assumed to be populated only by calcium atoms. The relatively low value of the isotropic temperature factor  $B$  (Table 1) for the X-sites reflects partial occupancy by Ti and Mn, as also evidenced by the chemical analysis (1). The occupancy factors of 0.5 for Ba(3) and O(2) (Table 1) are based on the Fourier maps and on the least-squares refinement. They may possibly be related to either a lower-symmetry space group for muirite ( $P4mm$ ) or to the occurrence of a superstruc-

ture, since reflections on highly overexposed precession photographs indicate a doubling of the  $c$  cell constant. Because of the inconclusive evidence for either of these possibilities, we are reporting here the structure in space group  $P4/mmm$  and are ignoring the superstructure reflections. Thus the statistical occupation of these two atomic sites either may reflect true disorder or may mean that we are describing an averaged structure. The fact that the temperature factors of most of the atoms (Table 1) in the structure are fairly high is another indication that some kind of disorder is present.

The eight-membered rings,  $(Si_8O_{24})^{16-}$ , of silicate tetrahedra, centered around the origin of the unit cell (Fig. 1), are the most striking and unusual feature of this crystal structure. The eight-membered rings are connected to neighboring rings both in the  $a$  and the  $c$  directions by the trigonal prismatic coordination polyhedra around the X-sites (populated by Ca, Mn, and Ti), thus forming a polyhedral three-dimensional framework of tetrahedra and trigonal prisms of composition  $(Ca,Mn,-Ti)_4Si_8O_{24}(OH,O)_4$ . The spaces around this framework are filled with barium and chlorine atoms and  $H_2O$  molecules, so that the correct chemical and structural formula of muirite must be  $Ba_{10}(Ca,Mn,Ti)_4Si_8O_{24}(Cl,OH,O)_{12} \cdot 4H_2O$  with one formula unit per unit cell. The assignment of particular atomic species to the different equipoints (Table 1) is based on the following: (i) the observed interatomic distances, (ii) the scattering factors giving the best agreement between observed and calculated structure factors, (iii) the multiplier refinement, and (iv) partly on the original chemical analysis (1).

The main differences between the original formulation (1) and the one arrived at here are that in this formulation: (i) there are only eight silicon atoms per unit cell, and the structure does not contain any space in which additional silicon atoms would fit; (ii) there is more chlorine per formula unit; and (iii) although most of the O(h4) atoms must be OH groups (in