Reports

Ozone Formation in Air Exposed to Cobalt-60 Gamma Radiation

Abstract. *The amount of ozone formed in air exposed to a 4000-curie cobalt-60 radiation source was determined. In closed glass containers exposed to about 1 Mrad of gamma radiation, ozone concentrations up to 18 parts per million (by volume) were recorded. In air flowing through a glass structure placed near the source, ozone contents up to 0.1 parts per million were observed. It is suggested that ozone formation might be a factor in the reported germicidal effects of ionizing radiations and that damage to plant tissues, ascribed to radiation, might have resulted from exposure to ozone. The possible health hazards from the ozone produced during irradiation should not be overlooked.*

Exposure of air to ionizing radiations is known to lead to ozone formation (*1*). It is also well known that ozone, even in low concentrations, has a strong germicidal effect (*2*) and may cause injury to plant tissues (*3, 4*). It is, therefore, surprising that the possibility of ozone being active in the preservation of food by ionizing radiations has neither been explored, nor mentioned in several reviews of the subject (*1, 5, 6*). Hannan (*5*) mentions that ozone may be formed in the airspaces of irradiated meat but that "the amount would be small."

When the cobalt-60 radiation source (4000 c, panoramic) was installed at this experiment station in 1961, we noted in the source room the characteristic pungent odor of ozone. On one occasion, when the ventilation system was out of order, slight skin irritation was noted by some persons entering the source room when the equipment had just been used.

The presence of ozone was established both by the well-known iodometric method and by the ferric thiocyanate paper test of Deckert (*7*). This latter test is not affected by NO. The air tested was first passed over some $NaHCO_3$ to remove acid impurities. The reaction was strongly positive in all air samples exposed to irradiation.

For quantitative estimation, several modifications of the iodometric method (*8*) were tried, but they failed to provide a sufficiently sensitive and specific procedure for our purposes. We found the fluorescein method of Egorow (*9*) satisfactory. This method is claimed to be specific for ozone and not influenced by NO_2, N_2O, or other nitrogen compounds formed from air. An alkaline fluorescein solution is first treated with zinc dust. After disappearance of the green color, the solution is filtered through an asbestos mat, and then diluted with 0.125*N* NaOH. For ozone measurements, the metered air sample is bubbled through a measured volume of this solution in a fritted glass absorption tower and the color formed is measured using a Beckman Model B spectrophotometer at the sharp absorption peak at 490 mμ. The amount of leuco-fluorescein (fluorescin) oxidized was read from a standard curve obtained with unreduced (green) dye. Egorow's value of one part by weight of fluorescein produced by 0.96 part by weight of ozone was used in the calculations.

We made three types of measurements. In the first test, the ventilation system of the room containing the radiation source was turned off and an oscillating electric fan was placed in the room to mix the air. After activation of the radiation source, air samples were collected from the adjacent shielded control room by means of a small glass tube reaching a point 1 meter from the source. The power of the source at 1 meter was 3183 rad/hour. The initial ozone content of 0.003 part per million (by volume) of the room increased to 0.093 ppm in 2 hours and to 0.116 ppm in 18 hours. Subsequent determinations during the following 6 hours showed no further increase in the ozone content.

In the second set of measurements, air samples were collected through glass tubing, 5 mm in diameter, bent in such a manner that 120 cm of the tubing covered a flat surface of approximately 15 × 17 cm. This structure was placed at various distances from the radiation source and ozone and moisture-free air was drawn through at various rates. As expected, ozone formation increased with decreasing distance from the source and longer duration of exposure (slower movement) of the air (Table 1).

In the third set of experiments, we irradiated closed glass containers and measured the ozone formed within (Table 2). There was considerable variation in the rate of ozone formation as well as in the maximum concentrations reached. It is quite obvious that some factors, in addition to the extent of gamma radiation, were influencing ozone formation and stability (*10*).

As an aid in the cold storage of

Table 1. Ozone formation in air passing through glass tubing near a cobalt-60 radiation source (approximately 4000 c).

Distance from source (cm)	Rate of air movement (lit./hr)	Ozone content of air (ppm)
15.7	8.2	0.079
15.7	51.8	.057
15.7	56.7	.042
15.7	124.0	.038
25.7	1.2	.102
25.7	50.0	.018
25.7	104.8	.010
45.7	50.0	.002
45.7	72.8	.004

Table 2. Ozone formation in irradiated closed glass containers.

Dose rate at center (rad × 10^3/hr)	Total dosage (rad × 10^3)	Ozone (ppm)
Gas-collecting tube (330 ml)		
10	10	1.60
20	40	4.85
346	1728	11.13
1000	19,000	7.75
20-liter flask (with paraffined cork)		
49	850	7.78
49	120	7.00
49	206	8.78
49	1004	18.53
49	1127	13.45*
49	1127	8.56†

*, † 3 hours and 141 hours, respectively, after completion of irradiation.

foods, the use of ozone in concentrations of 1 to 3 ppm has been recommended (*2*). The results obtained with glass containers indicate that the ozone concentrations found might be of significance from the standpoint of inhibiting microbial growth. Although rapidly dissipated in the presence of organic matter, ozone is continuously replenished during irradiation. Thus ozone might have possibly contributed to the microbial inhibition observed with foods irradiated in air or in packages containing some air. One may also wonder if some of the detrimental effects of radiations on foods, particularly on flavor, might have resulted from the ozone formed during irradiation.

Many plants, including tomatoes, Pinto beans, spinach, and potato, are sensitive to ozone at concentrations below 0.1 ppm (*4*). Lettuce leaves, after irradiation, develop epidermal lesions (freckles) consisting of rust-colored spots, mostly on the midvein; when irradiated in nitrogen the spots do not appear (*11*). We were able to produce these spots by exposing lettuce leaves to the irradiated air from which we obtained the results shown in Table 1. But when lettuce leaves were irradiated in the presence of activated charcoal, the spots did not appear. These results indicate that ozone might cause the development of "freckles." Thus, "radiation injury" to plants might sometimes be due to the ozone.

Finally, the public health aspect of these findings should not be overlooked. The ozone concentrations which can be detected by odor and the concentrations which may have harmful effects have not been firmly established. The maximum allowable concentration established by the American Council of Governmental and Industrial Hygienists (*12*) is 0.1 ppm ozone in air, although different concentrations have been reported by others (*2, 13*). Breathing air containing 0.1 ppm ozone may cause respiratory discomfort, headaches, depression, and other undesirable symptoms (*12*). It would seem that for continued exposure, especially when more powerful radiation sources are used, the health hazards from ozone should be taken into consideration. (*14*).

Z. I. KERTESZ*
GRACE F. PARSONS
New York State Agricultural Experiment Station, Cornell University, Geneva

References and Notes

1. U.S. Army Quartermaster Corps, *Radiation Preservation of Food* (U.S. Government Printing Office, Washington, D.C., 1957).
2. V. A. Hann and T. C. Manley, in *Interscience Encyclopedia of Chemical Technology*, (Interscience, New York, 1952), vol. 9, pp. 735–753; W. C. Frazier, *Food Microbiology* (McGraw-Hill, New York, 1958); F. W. Tanner, *The Microbiology of Foods* (Garrard, Champaign, Ill., ed. 2, 1944).
3. C. Homan, *Plant Physiol.* **12**, 927 (1937).
4. M. C. Ledbetter, P. W. Zimmerman, A. E. Hitchcock, *Contrib. Boyce Thompson Inst.* **20**, 275 (1959); S. M. Siegel, *Plant Physiol.* **37**, 261 (1962).
5. R. S. Hannan, *Scientific and Technological Problems Involved in Using Ionizing Radiations for the Preservation of Food* (Her Majesty's Stationery Office, London, 1955).
6. N. W. Desrosier and H. M. Rosenstock, *Radiation Technology in Food, Agriculture and Biology* (Avi, Westport, Conn., 1960); D. K. Salunkhe, *Econ. Botany* **15**, 28 (1961); W. M. Urbain, *J. Agr. Food Chem.* **8**, 340 (1961).
7. W. Deckert, *Z. Anal. Chem.* **153**, 189 (1956).
8. C. E. Thorp, *Ind. Eng. Chem.* **12**, 209 (1940); B. E. Saltzman and N. Gilbert, *Anal. Chem.* **31**, 1914 (1959).
9. M. S. Egorow, *Z. Untersuch Lebensm.* **56**, 355 (1928).
10. See on this point S. C. Lind, *Radiation Chemistry of Gases* (Reinhold, New York, 1961).
11. Z. I. Kertesz *et al.*, *A Study of the Radiation Induced Softening of Plant Tissues, Final Rept., Contract DA-19-129-QM-1584* (Office of Technical Services, U.S. Dept. of Commerce, Washington, D.C., 1962).
12. N. I. Sax, *Dangerous Properties of Industrial Materials* (Reinhold, New York, 1957).
13. A. W. Ewell, *Ice and Refrig.* **120**, 55 (1951); W. Witheridge and C. Yaglon, *J. Am. Soc. Heating Ventilating Engrs.* **45**, 509 (1939).
14. Approved by the director of the New York State Agricultural Experiment Station, Geneva, as Journal Paper 1277, 28 August 1961. This investigation was supported in part by U.S. Public Health Service grant A2367 from the National Institute of Arthritis and Metabolic Diseases.
* Present address: Nutrition Division, Food and Agriculture Organization of the United Nations, Rome, Italy.

19 August 1963

Miocene-Pliocene Boundary in the Philippines as Related to Late Tertiary Stratigraphy of Deep-Sea Sediments

Abstract. *Planktonic foraminiferal trends across the Miocene-Pliocene boundary in the Philippines suggest that sections of eight deep-sea cores reported to be Pliocene are actually latest Miocene, and that a marked extinction of discoasters in the deep-sea cores is due to an unconformity, separating Miocene and Pleistocene sediments, representing a time gap of some 10 million years of Pliocene time.*

Recently, a "Pliocene-Pleistocene" boundary was defined by various paleontological criteria in seven deep-sea cores from the Atlantic Ocean and one in the Indian Ocean, all apparently from submarine rises, by Ericson, Ewing, and Wollin (*1*). Riedel, Bramlette, and Parker (*2*) have questioned the position of the boundary as representing the Pliocene-Pleistocene boundary. The eight cores were selected specifically because the Pleistocene sediment blanket was thin, probably owing to loss of sediments by slumping or submarine erosion, or to the nondeposition of sediments; thus, it was possible for the core barrel to penetrate through the Pleistocene into older sediments beneath. I have found planktonic foraminiferal trends in sections (*3*), deep water in origin, of the Philippines (Fig. 1) that indicate the "Pliocene-Pleistocene" boundary in the eight deep-sea cores is a Miocene-Pleistocene boundary, and suggesting that some 10 million years of sediment deposition is absent at the boundary in the deep-sea cores of Ericson *et al.* The deep-water origin of the Philippine section is based upon deep-water benthic foraminifera such as *Bulimina rostrata, Nonion pompilioides, Pyrgo serrata,* and *Uvigerina hispida,* all of which have modern representatives in deep bathyal areas of modern oceans.

Ericson, Ewing, and Wollin gave six criteria for defining the boundary in their cores. First, a prominent extinction of discoasters occurs at the boundary. It has been pointed out by Riedel *et al.* (*2*) that there has been a gradual decline of discoasters since the Middle Miocene; thus, an unconformity representing a gap of many millions of years would result in abundant discoasters below such a boundary and few if any above the boundary. Second, a change occurs in the coiling direction of *Globorotalia menardii* from 95 percent dextral, or right-coiling, below the boundary to 95 percent sinistral, or left-coiling, above the boundary in the Pleistocene. Such a change occurs in the Philippine sections (Fig. 1) from dominantly dextral specimens of *G. menardii* in the uppermost Miocene to mostly sinistral specimens in the lower part of the Pliocene, as defined in that area; hence, dextral Miocene populations below sinistral Pleistocene populations would be expected. Third, *Globorotalia truncatulinoides* appears in abundance above the boundary in the deep-sea cores in the Pleistocene sediments and they report it as absent in the "Pliocene" sections of deep-sea