Variations in the Isotopic Composition of Carbon in Urban Atmospheric Carbon Dioxide

Abstract. *Measurement of the abundance of atmospheric carbon dioxide as an indicator of air pollution has been of very limited value because of variations in urban areas in the substantial concentration of natural carbon dioxide produced from combustion and noncombustion (natural) sources. A solution to this problem is the use of precise isotopic assay of ratios of carbon-13 to carbon-12 in atmospheric carbon dioxide. There is very little variation of carbon isotopic composition in samples taken over rural or urban areas where rapid mixing and diffusion of gaseous combustion products is possible. Significant differences in this composition in samples taken at centrally located points at street level in the lower Manhattan business district show an increase in concentration of atmospheric carbon dioxide of roughly 20 percent produced primarily by automobile exhaust.*

The isotopic composition of carbon in carbon dioxide (CO_2) produced from the combustion of fossil fuels has been shown to differ from carbon in atmospheric CO_2 by 1 to 2 percent (*1*). This difference provides a basis for an isotope dilution analysis of CO_2 in areas of intense industrial emission. The problem of industrially produced CO_2 and its effect on the atmosphere has long been a subject of interest (*2*). Clarke and Faoro (*3*) showed that a major problem in the use of CO_2 as an indicator of air pollution is the difficulty in predicting the contribution of natural sources to urban CO_2 concentrations. Significant variations in urban atmospheric CO_2 have been observed and attributed to changes in both natural and combustion CO_2. The measurement of isotopic composition of atmospheric CO_2 provides a means of estimating the relative concentrations of natural and combustion CO_2 and thus permits the use of the major component of combustion products as an air pollution indicator. We now report results of a study on the abundance of carbon isotopes in samples of atmospheric CO_2 taken in New York City, its suburbs on Long Island, and the eastern tip of Long Island over 100 miles away (*4*).

The CO_2 was obtained from air samples (3-liter) which were pumped through three glass radiator traps connected in series and cooled, respectively, with dry ice, liquid nitrogen, and dry ice. The last trap was inserted to prevent diffusion of oil back from the mechanical pump used in the preliminary separation of CO_2 from air. The first trap was used primarily as a means of drying the air prior to condensation of CO_2. This separation technique required a carefully controlled flow rate and was tested with synthetic mixtures of O_2 and N_2 and CO_2 to establish the quality of separation and recovery. The trapped CO_2 was then subject to final purification by gas chromatography. A column 5.5 m in length packed with coated firebrick (30- to 70-mesh) was used (*5*). This column was operated at $-20°C$. Here again, samples of reference CO_2 were processed to insure the quality of separation and establish the technique as one that did not perturb the isotopic composition of the CO_2 as measured mass spectrometrically.

Samples of CO_2 were collected from the gas chromatograph and analyzed with an Atlas-Werke M86 mass spectrometer which has (i) dual ion collectors that permit a direct determination of ratios of C^{13} to C^{12} and (ii) a dual heated sample inlet system which facilitates rapid comparison of samples with a reference (*r*) standard. The data are presented (Table 1) as δ values with δ defined by the relation

$$\delta = \frac{(C^{13}/C^{12}{}_s) - (C^{13}/C^{12}{}_r)}{C^{13}/C^{12}{}_r} \times 1000$$

Samples were analyzed for O^{18} as well as C^{13}, but no significant variation in O^{18} content of atmospheric CO_2 samples was detected. The ratios determined were corrected for the small contribution from natural O^{17} to the mass-45 peak used to measure $C^{13}O^{16}O^{16}$.

At least three air samples were taken at each location; in most cases six to twelve samples were analyzed to give the data in Table 1. The precision of analysis attainable with the Atlas M86 mass spectrometer is 0.01 percent or a δ value of 0.1. Errors reported are probable errors obtained from the scatter in data from the analysis of separate samples of CO_2. The major potential source of error is in the possible introduction of impurities in the mass-45 region in the mass spectrometer. Because the natural abundance of CO_2 in the atmosphere is approximately 300 ppm and the ratio of C^{13} to C^{12} is approximately 1 percent, an impurity in the air in a concentration of 3×10^{-8} which contributes selectively to mass 45 could double values of δ observed in this work. Quantitative removal of impurities at this level taxes chromatographic techniques. It was found that a sample of CO_2 from automobile exhaust deposited sufficient impurities on the chromatograph to require a cleanup period of constant flushing with helium for more than 1 week. Memory in the chromatograph and mass spectrometer was checked with standard reference samples between each analysis of an atmospheric CO_2 sample.

Table 1. Variation in the isotopic composition of atmospheric CO_2.

Locality	δ C^{13}/C^{12} (per mil)
Hither Hills	17.6 ± 0.2
Brookhaven National Laboratory	17.9 ± .1
Plainview	17.9 ± .4
Queens Blvd.	17.9 ± .3
Queens Midtown Tunnel	9.9 ± .3
Manhattan	
2nd Ave. and 37th St.	15.1*
6th Ave. and 25th St.	15.1 ± 0.1
10th Ave. and 15th St.	16.5 ± .5
115th St. and Broadway	18.1 ± .8
Battery Park	18.9 ± .5
Empire State Building, top	17.5 ± .3†
	17.5 ± .6
Empire State Building, bottom	14.9 ± .2
	15.9 ± .5
CO_2 from auto exhaust	1.7 ± .3

* Result of one sample. † Results from two sets of six samples taken at top and bottom of Empire State Building, respectively, on 2 different days. Values show constancy of isotopic composition of natural CO_2 at the top of the building and variations at the bottom.

The isotopic composition of carbon in atmospheric CO_2 (Table 1) is, within limits of experimental error, the same in air samples taken at three sites: the eastern tip of Long Island; midway between New York City and the eastern tip at Brookhaven National Laboratory; and Plainview, Long Island, approximately 48 km east of New York City. The sample taken at Hither Hills State Park near Montauk Point is considered representative of air above the ocean approximately 193 km from the metropolitan area. The remarkable observation was that air samples taken in the Borough of Queens on Queens Boulevard and in upper Manhattan at 115th Street were found to have a ratio of C^{13} to C^{12} identical within limits of experimental error to that of samples taken outside New York City.

Samples from the Queens Midtown Tunnel during moderate traffic drop significantly to a δ of 9.9 ± 0.3. This is consistent with the observation that air in the tunnel contained approximately twice as much CO_2 as the ordinary atmospheric samples. The ventilation system in the tunnel circulates air at a rate of 6600 metric tons per hour, but this is insufficient to reduce emission of CO_2 in bumper-to-bumper rush-hour traffic to a level well below that of atmospheric CO_2. A δ of 7.0 is obtained from a calculation based on estimates of emission of CO_2 under these circumstances. The samples reported in Table 1 were taken under moderate traffic conditions. The isotopic abundance of carbon in CO_2 from the tunnel provides an independent check on the technique.

Differences in δ's were observed in Manhattan near the tunnel exit on 37th Street and in the skyscraper canyons at 25th Street and near the Empire State Building. The evidence suggests that mixing of air in streets surrounded by closely spaced high-rise buildings is poor and that CO_2 from automobile exhausts contributes significantly to the inventory of atmospheric CO_2 in these areas. Normal higher values of δ's were found at Battery Park, at 115th Street and Broadway, and at the observation tower of the Empire State Building.

Sources of CO_2 other than automobile exhaust are not expected to contribute to the variation observed between ratios of samples taken at street level and at the Empire State Building observation tower. Samples taken in the center of the business district in lower Manhattan indicate that approximately 20 percent of the CO_2 in the atmosphere at street level is produced by automobile exhaust; this points up the need for ventilation of streets in areas of where there are high-rise buildings and a large concentration of motor vehicles.

L. FRIEDMAN
A. P. IRSA
Department of Chemistry, Brookhaven National Laboratory, Upton, New York

References and Notes

1. H. Craig, *Geochim. Cosmochim. Acta* **3**, 53 (1953); S. R. Silverman, *Isotopic and Cosmic Chemistry* (North-Holland, Amsterdam, 1964), chap. 8.
2. F. A. Rohrman, B. J. Steigerwald, J. H. Ludwig, *Science* **156**, 931 (1967).
3. J. F. Clarke and R. B. Faoro, *J. Air Pollut. Contr. Ass.* **16**, 212 (1966).
4. H. Craig (*1*) reported a variation in the isotopic composition of carbon in CO_2 obtained from air in Chicago. He tabulated values that differ by approximately 2.0 per mil in air sampled during the week and on Sundays. His technique did not include gas chromatographic purification prior to analysis by mass spectrometer; variations nearly as large as those observed between weekdays and Sundays were observed in samples taken during the week. Craig left open the question of the role of industrially emitted CO_2 when he remarked that there was a need for data which would establish the isotopic composition of atmospheric CO_2 in uncontaminated air over the oceans. His work clearly suggests the possibility of a perturbation of the isotopic composition of atmospheric CO_2 by industrially emitted CO_2.
5. The firebrick was coated with Dow-Corning 710 silicone pump fluid.
6. Research performed under the auspices of the AEC. We thank Dr. Y. Y. Chu for assistance, and W. R. Suchanek and the management of the Empire State Building for their cooperation.

25 August 1967

Biohazards Symbol: Development of a Biological Hazards Warning Signal

Abstract. *The need for a symbol to warn of potential infection hazards became apparent during Public Health Service contract work on the development of containment facilities for virus-leukemia research. A program of direct inquiry and a search of the literature revealed that there was no universally used signal and that scientific and safety organizations concurred in the need for one. Criteria for symbol design were established, and final selection was based on "uniqueness" and "memorability." The National Institutes of Health is recommending use of the symbol as a warning of biological hazard.*

The scientific community, engaged in infectious disease research, has accepted as unfortunate, but unavoidable, the occasional accidental infection of microbiology laboratory personnel and associated nonlaboratory personnel. Since the mid-1940's, the seeming inevitability of such accidents has received an increasing amount of study. The eventual consensus was that perhaps most of these accidents need not happen, providing proper precautionary measures are taken and enforced. The last decade, in particular, saw great strides in the development of containment systems and in the design of safety equipment to protect the laboratory worker, his work, and the exterior environment from contamination by infectious agents. A new science of containment, founded on the concept of continuous agent control through the creation of intelligently designed barrier systems, has emerged. Design of these barriers is based on a rational assessment of risk; the barriers may be created in the form of solid walls, pressure differentials to control movement of air, controlled movement of personnel and materials, or inactivation of the infectious agents themselves. In the maintenance of the barrier systems, one essential factor is that, at all times, the locations of the infectious agents must be known. In order not to inadvertently violate the barrier systems, each person in the vicinity must know what equipment, glassware, rooms, corridors, and ducts are contaminated by the infectious agents, and that thereby, they constitute a biological hazard.

Unfortunately, such biological hazards, like radiation hazards, are usually impossible to detect by cursory examination only. Being invisible, odorless, and tasteless, they require special procedures for detection. It seems logical, then, to mark the location of "biohazards," as they are commonly called, with a suitable warning sign that is readily noticed and easily recognized.

During investigations of biological control and containment conducted under contract for the National Cancer Institute, the need for such a symbol became apparent to the Dow biohazards research and development team. A search of the literature revealed that, while certain biological warning signs are used by various agencies, a *universal* symbol to warn of danger from infectious or potentially infectious agents—a symbol whose immediate significance is known to all—does not exist. Colleagues in the field of biological research concurred, in reply to direct query, that such a warning symbol is needed.

Universally accepted symbols for hazards that are not readily detectable have already been established, such as those used in denoting radioactive areas. Similar warning notices are being sought to point out danger due to laser emission. In biology laboratories, however, a number of different symbols are in use; none of these has been universally accepted, and none imply or encompass all possible biohazards. For example, an inverted blue triangle bearing the term "BIO" is used by the Army to warn of biological contamination; a rectangular "hot-pink" label, with radiating yellow bands, is used by the U.S. Navy laboratories in areas containing infectious organisms; a red and black sign is used by the National Institutes of Health to mark restricted areas; and the white snake-and-staff imprint on a violet field is sponsored by the Universal Postal Convention to mark infectious materials during transit.

In formulating the design for the proposed biohazards symbol, six criteria were established, mainly dealing