# Water Pollution: Organic Compounds in the Charles River, Boston

Abstract. *The major lipophilic organic compounds present in water collected during November and December 1971 from the Charles River Basin (Boston) are as follows: normal alkanes ($C_{15}$ to $C_{31}$), alkyl naphthalenes, alkyl anthracenes or phenanthrenes, pyrene, fluoranthene, dibutyl phthalate, and di(2-ethylhexyl) phthalate. The concentration of the naphthalenes (determined by liquid chromatography) correlates with the effective storm-water runoff content of the river. These data suggest a multiplicity of sources ranging from indigenous biological materials to automobile exhaust condensate.*

Any program for water pollution abatement requires a detailed knowledge of the identity and concentration of the specific pollutants and their sources. Although the major inorganic components can be well characterized, the specific organic compounds in polluted water are usually not known (*1*). This is unfortunate since certain organic compounds may be highly toxic and those that are nonbiodegradable may accumulate in living systems, particularly if they are lipophilic [for example, DDT, 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane] (*2*). The dearth of knowledge concerning the specific organic compounds in polluted (or even unpolluted) water is due, in large part, to the lack of suitable analytical methods (*1*). This problem can now be overcome by the application of modern analytical instrumentation, particularly computerized gas chromatography–mass spectrometry (GC/MS) and high-pressure liquid chromatography (LC). The determination by these techniques of the lipophilic organic compounds in the Charles River Basin has given data which indicate that automobile exhaust condensate contributes to the pollution of this river.

The Charles River Basin is located completely within Greater Boston and is presently quite polluted, having a $BOD_5$ (biochemical oxygen demand) of 3 to 6 mg/liter (*3*). The river is impounded between two dams and thus has little net flow or vertical mixing. The inputs to the river consist of urban storm-water runoff and occasionally untreated sewage from combined sewer systems.

Samples were collected from the river at weekly intervals during November and December 1971. All of these 3.5-liter samples were taken from the center of the Harvard Bridge at a depth of 0.9 to 1.5 m. The river at this point is about 0.7 km wide and about 5 m deep. In order that both neutral and acidic components might be extracted, the samples were immediately acidified with 5 ml of concentrated HCl and then thoroughly mixed with 200 ml of methylene chloride (Mallinckrodt, Nanograde) in a closed brown glass jug on a magnetic stirrer for 2 days (*4*). The methylene chloride layer was separated and the solvent removed at 30°C under reduced pressure in a rotary evaporator. The residue was dissolved in 200 $\mu l$ of methylene chloride and analyzed by GC/MS. A procedural blank consisting of 3.5 liters of doubly distilled water showed only traces of material and was judged acceptable.

A gas chromatogram resulting from an extract of water from the Charles River Basin is shown in Fig. 1A. Although it is quite complex, the major components of this mixture can be identified by the use of various computer-assisted interpretation techniques (*5–7*). Mass chromatograms (*6*) (plots of the absolute intensity of one mass versus time) are particularly useful as a means of detecting a specific compound or a specific class of compounds. For example, the mass chromatograms corresponding to various alkyl ions ($C_nH_{2n+1}^+$) will accentuate those GC peaks due to alkanes and display a pattern similar to a gas chromatogram conventionally obtained after more tedious chemical and physical preliminary separations. Such a mass chromatogram for a mass-to-change ratio *m/e* of 99 ($C_7H_{15}^+$) corresponding to the gas chromatogram shown in Fig. 1A is shown in Fig. 1B. That it displays peaks only for the alkanes present in the mixture has been confirmed by an inspection of the individual mass spectra recorded at the peak tops and the mass chromatograms of other alkyl ions. The compounds corresponding to the maxima of this bimodal distribution have been identified from their mass spectra as well as their GC retention times as heptadecane and pentacosane. Inspection of other mass chromatograms and mass spectra has revealed several aromatic compounds (see Fig. 1A), the most prominent being a series of polymethyl-substituted naphthalenes. We confirmed the identifications in Fig. 1A by comparing the mass spectra and the GC, and, where applicable, the LC, retention times with those of authentic materials. The approximate concentrations of these compounds range from about 0.05 part per billion (ppb) for pyrene to about 1 ppb for di(2-ethylhexyl) phthalate.

Table 1. Naphthalene concentration as a function of rainfall.

| Date (1971) | Rainfall in preceding week (inches) | Effective runoff (inches) | Total naphthalene concentration (ppb) |
|---|---|---|---|
| 11 October | 1.54 | | |
| 18 October | 0.13 | | |
| 25 October | .21 | | |
| 1 November | .33 | | |
| 8 November | .95 | | |
| 15 November | .27 | 0.91 | 0.1 |
| 22 November | .90 | 1.33 | 1.0 |
| 29 November | 3.53 | 4.19 | 3.4 |
| 6 December | 0.59 | 2.68 | 2.1 |
| 13 December | .52 | 1.86 | 2.6 |
| 20 December | .54 | 1.45 | |
| 27 December | .45 | 1.17 | 1.0 |

Since phthalate esters are frequently encountered in the laboratory as artifacts, it should be pointed out that they were *not* found in the procedural blank; therefore, these widely used plasticizers do seem to be present in the river.

The individual extracts of the various river samples taken on different days were all qualitatively similar to the sample discussed above (Fig. 1). There were considerable quantitative differences, however. In general, the abundance of the larger alkanes ($C_{22}$ to $C_{31}$) remained constant, whereas the amount of the smaller alkanes ($C_{15}$ to $C_{21}$), aromatic hydrocarbons, and phthalate esters showed considerable variation. In one case (sample taken on 15 November 1971), these latter compounds were almost completely absent.

The aromatic hydrocarbons were quantified by LC. The experimental conditions (*8*) were selected such that these compounds would separate according to the number of aromatic rings, with the various alkyl substituents having almost no effect on the retention times. This mode of separation facilitates group quantification because, for example, all naphthalenes elute together. Furthermore, an ultraviolet absorption detector provides high, selective sensitivity for aromatic compounds. The total naphthalene concentration as measured from the liquid chromatograms of the individual samples is summarized in the last column of Table 1 (*9*).

Since the largest value for naphthalene concentration (3.4 ppb) was observed after a week of heavy rainfall [3.53 inches (9.0 cm), see the second column of Table 1], it was thought that the storm-water sewer system may be bringing these compounds into the river. Because it is unlikely that material brought into the river by runoff would completely disappear within 1 week, it was necessary to calculate an effective runoff content in order to test the above hypothesis. Effective runoff is defined here as the precipitation (in inches) of the current week plus some fraction of the precipitation occurring in each of the previous weeks. If one assumes that the runoff in the river has a half-life of about 1 week, the effective runoff for week $n$, $E_n$, can be expressed as

$$E_n = \sum_{i=0}^{5} 2^{-i} R_{n-i}$$

where $R_{n-i}$ is the precipitation for the $n$-minus-$i$th week. The effective runoff values for the period under consideration are shown in the third column of Table 1. The correlation coefficient between effective runoff and naphthalene concentration is 0.888, which is significant at the 2 percent level. This is quite good agreement in view of the simplicity of the above model and the uncertainty of the assumed half-life. Since the concentrations of the other aromatic hydrocarbons are roughly proportional to the naphthalene concentration, it therefore seems likely that all of these compounds enter the river through the storm-water runoff sewer system.

The above qualitative (Fig. 1) and quantitative (Table 1) information allows one to assign probable sources to the individual compounds. Aromatic hydrocarbons (such as alkyl naphthalenes) are usually derived from petroleum-related sources (*10*). In this case, automobile exhaust condensate which is washed from the streets directly into the river by rainfall is the most likely immediate source. Indeed, a GC/MS analysis of automobile exhaust (collected by methylene chloride scrubbing) has demonstrated the presence of the various aromatic hydrocarbons in about the same relative abundance as that found in the river. The absence of alkyl-substituted pyrenes or fluoranthenes is also indicative of petroleum pyrolysis products rather than petroleum itself (*11*).

Of the smaller alkanes, heptadecane and, probably, nonadecane are derived from biological sources such as algae (*12, 13*) whereas the underlying smooth envelope ($C_{15}$ to $C_{21}$) may be due to fuel oil. The larger alkanes ($C_{22}$ to $C_{31}$) probably have a different biological source. Although it is impossible to assign these alkanes to a specific species, the distribution found here is similar to that resulting from *Chlorobrium*, a sulfur bacterium (*12*). Terrestrial plants may be responsible for the odd over even predominance of nonacosane and hentriacontane versus octacosane and triacontane (*12*).

The source of the phthalate esters is not yet known. The concentration of these esters is quite variable and does not seem to correlate with effective runoff. Locating their source is of particular interest because of their unusual ubiquity (*14*) and their possible teratogenicity (*15*).

Although the study reported here has been quite limited in scope (one site sampled over only 2 months and major components only identified) and therefore must be considered preliminary, it has demonstrated that the application of sophisticated organic analytical techniques such as GC/MS and LC can

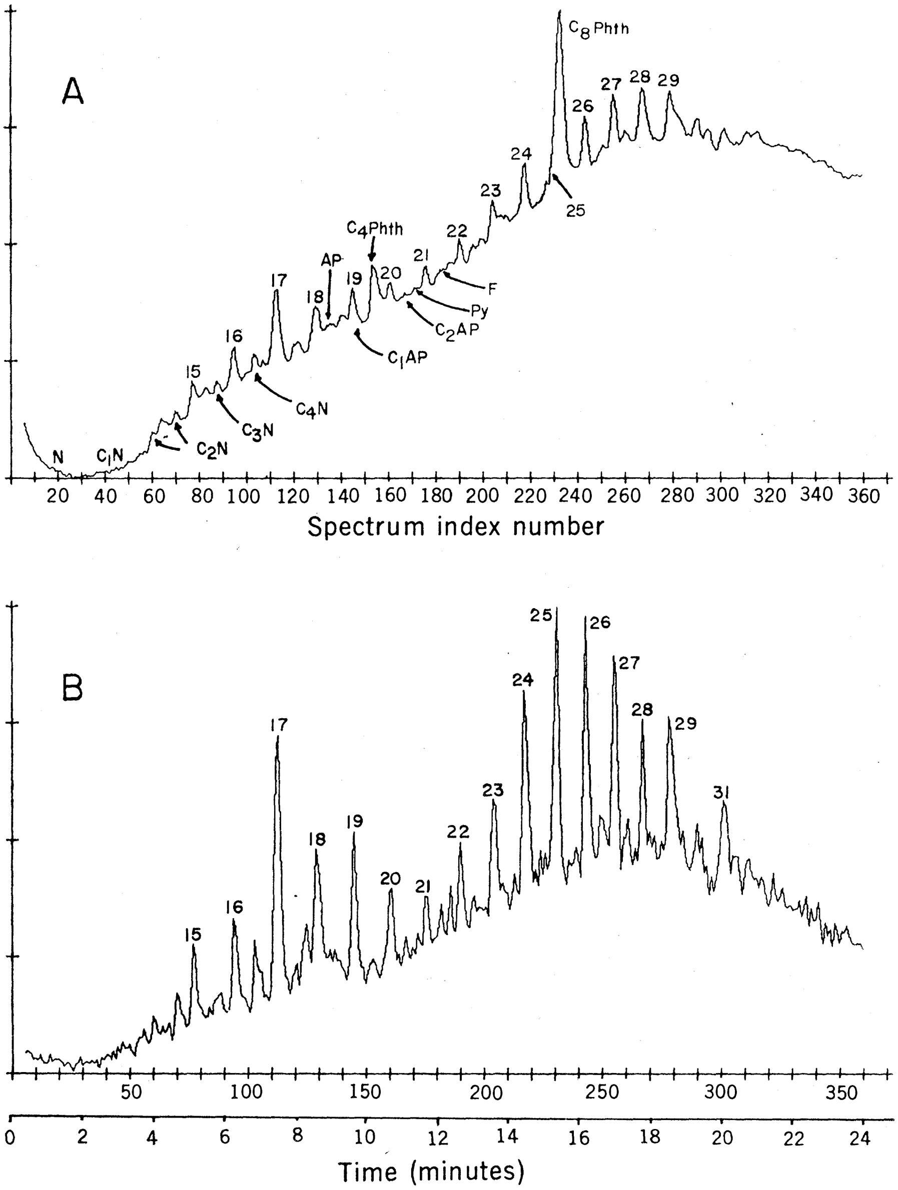

Fig. 1. (A) Gas chromatogram of a methylene chloride extract of Charles River Basin (Boston) water as reconstructed from a continuously scanning GC/MS (*5*). Conditions: temperature 70° to 260°C at 8° per minute; column (150 by 0.32 cm) containing 0.1 percent OV-1 on glass beads. Abbreviations: numbers refer to the chain length of normal alkanes; *N*, naphthalene; *AP*, anthracene or phenanthrene; *Py*, pyrene; *F*, fluoranthene; $C_4$*Phth*, dibutyl phthalate; $C_8$*Phth*, di(2-ethylhexyl) phthalate; $C_x$, total alkyl substitution of $x$ carbon atoms. (B) Mass chromatogram (*6*) of $m/e$ 99 corresponding to the gas chromatogram in (A).

give quite useful results. Specifically, it has shown that GC/MS is a powerful survey technique by which it is possible to identify the general nature of the organic pollutants and that LC is a rapid and sensitive technique for monitoring, in this case, aromatic compounds.

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### References and Notes

1. L. M. Cook, Ed., *Cleaning Our Environment, the Chemical Basis for Action* (American Chemical Society, Washington, D.C., 1969), pp. 95–99.
2. P. H. Abelson, *Science* **170**, 495 (1970).
3. W. H. Walker, Jr., thesis, Massachusetts Institute of Technology (1971).
4. Subsequent investigations revealed that stirring times as short as 6 hours are effective for extraction.
5. R. A. Hites and K. Biemann, *Anal. Chem.* **40**, 1217 (1968).
6. ———, *ibid.* **42**, 855 (1970).
7. H. S. Hertz, R. A. Hites, K. Biemann, *ibid.* **43**, 681 (1971).
8. The LC conditions were as follows: liquid-solid chromatography on a Porasil T column (120 by 0.32 cm) with heptane as the eluent; pressure, 27.0 atm; temperature, 23°C; ultraviolet detector at 254 nm.
9. The LC peak areas were calibrated on the basis of a known concentration of 1-methylnaphthalene. The concentrations (given in parts per billion) have an estimated accuracy of 10 to 15 percent.
10. M. Blumer, G. Souza, J. Sass, *Mar. Biol.* **5**, 195 (1970); M. Blumer, in *Man's Impact on Environment*, T. R. Detwyler, Ed. (McGraw-Hill, New York, 1971), p. 295; M. Blumer and J. Sass, *Science* **176**, 1120 (1972).
11. M. Blumer, personal communication.
12. J. Han and M. Calvin, *Proc. Nat. Acad. Sci. U.S.A.* **64**, 436 (1969).
13. W. W. Youngblood, M. Blumer, R. L. Guillard, F. Fiore, *Mar. Biol.* **8**, 190 (1971).
14. R. J. Jaeger and R. J. Rubin, *Science* **170**, 460 (1970); *Lancet* **1971-II**, 151 (1971); G. Ogner and M. Schnitzer, *Science* **170**, 317 (1970); D. J. Nazir, A. P. Alcaraz, B. A. Bierl, M. Beroza, P. P. Nair, *Biochemistry* **10**, 4228 (1971); for a review, see K. P. Shea, *Environment* **13** (No. 8), 2 (1971).
15. R. K. Bower, S. Haberman, P. D. Minton, *J. Pharmacol. Exp. Ther.* **171**, 314 (1970); A. R. Singh, W. H. Lawrence, J. Autian, *J. Pharm. Sci.* **61**, 51 (1972); F. L. Mayer Jr., paper presented at the 27th midwest regional meeting of the American Chemical Society, St. Louis, October 1971.
16. We thank B. D. Andresen, R. Bopp, and L. S. Ramos for assistance and Dr. M. Blumer for comments regarding possible sources. This work was supported by a National Institutes of Health grant (RR00317) from the Biotechnology Resources Branch, Division of Research Resources, and by a research grant (22-009-005) from the National Aeronautics and Space Administration.

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# Visual Sensations Induced by Relativistic Nitrogen Nuclei

Abstract. *The ability of the human eye to detect nitrogen nuclei that enter the retina at speeds just above the Cerenkov threshold has been confirmed in an experiment at the Princeton Particle Accelerator. A system for beam transport and subject alignment delivered individual nitrogen nuclei onto a spot 3 millimeters in diameter on the retina at a visual angle of 7 degrees on the temporal side of the fovea. The beam particles entered the retina within 25 degrees of normal and induced visual sensations that had the appearance of streaks for three out of four subjects.*

The light flash phenomena (*1*) described by astronauts on Apollo missions 11 through 16 have stimulated research on visual sensations induced by radiation. Theoretical models suggested for these phenomena include Cerenkov radiation (*2*), isomerization of the photochemical rhodopsin molecules in collisions (*3*), and scintillations produced in the lens (*4*). Stars and streaks have been reported by subjects exposed to neutrons with kinetic energies above a threshold of 3 to 4 Mev (*5*). Both stars and streaks have been observed when helium (*6*) and nitrogen (*7*) nuclei near the end of their range (linear energy transfer 10 Kev/$\mu$m or more) intersect the posterior portion of the retina at angles close to grazing. At near normal incidence to the peripheral retina 1 cm anterior to the posterior portion of the eyeball, no visual sensations were observed with either helium or nitrogen. A small but distinct correlation between star-type phosphenes and individual relativistic cosmic ray muons that pass through the eye was first reported by D'Arcy and Porter (*8*) and confirmed by Charman and Rowlands (*9*), who attributed it to non-Cerenkov effects at the retina. The passage through the eye of thousands of muons in large 0.44-second bursts has been shown (*10*) to result in bright extended flashes that come and go with each burst and are similar in appearance to the "lightning behind the cloud" phenomena described by some Apollo astronauts (*1*). The visible Cerenkov radiation generated by the burst during each 0.1-second interval (in which the retina is known to integrate signals) was calculated to be above the threshold for peripheral vision, whereas the ionization produced at the retina was much less than that required with other forms of radiation to produce haze. We report here on visual sensations of stars and streaks experienced by four subjects when exposed to individual relativistic nitrogen nuclei that are incident within 25° of the normal to the retina at a visual angle of 7° on the temporal side of the fovea.

A schematic outline of the facility for these investigations at the Princeton Particle Accelerator (PPA) is shown in Fig. 1. The brass collimator, which is 9.4 cm thick, was positioned upstream, mounted on a motor-driven mechanism that allowed quick and accurate insertion in the beam. The electronics of the motor drive were removed after insertion to avoid accidental removal of the collimator. The insertion of the collimator, which has a channel 0.25 by 0.25 mm in cross section, resulted in a reduction of the beam intensity by a factor of $10^5$. Thus, the synchrotron could be operated near its maximum intensity while the subjects were exposed to beam rates as low as 1 particle per minute. Failures of the equipment or changes in the timing of extraction would only result in a further reduction of the beam intensity. The beam particles that emerged from the collimator were separated from any secondary particles by a dipole magnet before they arrived at the subject alignment table. This table consisted of a steel frame 180 cm long, which supported a collimator (diameter 0.32 cm) and a shield at its downstream end (Fig. 1). A pivot at the upstream end and leveling screws were used to align the collimator with the nitrogen ion beam.

Each subject maintained the align-

Table 1. Summary of the first round of exposures.

| Subject | Counter triggers | Subject marks | | Description of coincidence phenomena |
|---|---|---|---|---|
| | | Coincidences | Misses | |
| L.P. | 51 | 5 | 18 | Diffuse streaks with slight curvature; one point flash |
| V.B. | 33 | 2 | 0 | Streaks |
| V.P. | 108 | 11 | 4 | Thin, sharply defined streaks with slight curvature |
| P.M. | 85 | 9 | 20 | Diffuse flashes |