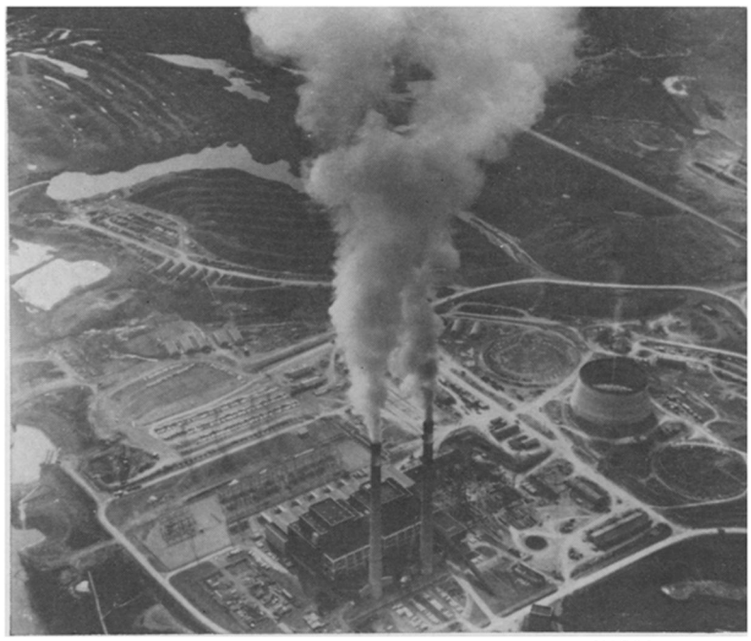
Trace elements in air and water

Closer looks being taken at sources, distribution and effects

by Richard H. Gilluly



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Out of the power plant stacks: More than meets the eye.

Concern over air and water pollution is widespread. There exists a respectable body of information about the grosser pollutants. Knowledge of the sources, the ecological effects and abatement techniques for sulfur oxides, carbon monoxide and photochemical smog in the air and phosphates and raw sewage in the water, for example, is at least within the reach of science and technology.

But today's knowledge of the more subtle aspects of environmental pollution, by elements and compounds in minuscule quantities, is less advanced.

It will not always remain so; standard techniques for sampling the air and water are getting wider use; exotic techniques are being applied, and chemists now know of the existence of trace amounts—in micrograms per cubic meter in the atmosphere, for example—of a growing number of elements in the environment. Often these have been identified only as elements, and the compounds in which they occur have not all been isolated. Knowledge of the sources of the elements is often limited to intelligent guessing. Although there may be well-established knowledge of toxic effects of some of the elements in grosser amounts, work on the toxicology of trace elements is just beginning.

The very definition of trace elements is unclear; the Bureau of Standards uses a rule of thumb which says the existence of 100 parts per million or less of any substance constitutes a trace amount. But the real definition of a trace element is that it exists in amount heretofore undetected. And much of the work to date has been involved with developing tools for simply identifying, measuring and cataloguing trace elements.

Drs. W. H. Zoller and Glen E. Gordon of the University of Maryland, for instance, find that the application of instrumental neutron activation analysis (INAA) to urban air sampling reveals the presence of a number of elements that were heretofore unidentified (SN: 2/28, p. 223). The initial work was in the Boston area, but it is now being extended to a number of cities in the United States, as well as to the atmosphere over the open ocean.

The two Maryland researchers found trace amounts of 24 elements in the Boston atmosphere. INAA is not a new technique, having been used for analysis of geological, biological and metallurgic samples in the past. But Drs. Zoller and Gordon used a new gamma-ray detector which provided far better resolution and also greatly reduced the need for chemical separation of elements or groups of elements before readings were made.

The technique, which involves irradiating a sample with neutrons and measuring the intensity of the gamma rays emitted from the isotopes thus formed, is considerably more sensitive in most cases than the emission spectography used by the National Air Sampling Network (NASN) or atomic absorption analysis, which has also been used in air analyses.

A particular advantage is that the samples—obtained by pumping air through 0.5 micron filters—can be irradiated before any chemical reagents are added, thus eliminating the possibility of introducing impurities.

Drs. Zoller and Gordon identified eight elements in amounts from 0.01 microgram up to several micrograms per cubic meter after short irradiations. They were sodium, aluminum, chlorine, calcium, vanadium, manganese, copper and bromine. Elements found generally in far smaller quantities after longer irradiation were scandium, iron, cobalt, nickel, zinc, selenium, antimony, barium, lanthanum, cesium, samarium, europium, ytterbium, lutetium, hafnium and thorium. Only eight of these 24 elements had been detected in the Boston NASN station. On the other hand, Dr. Gordon points out, NASN has reported values for elements not identified by INAA: beryllium, bismuth, cadmium, chromium, lead, molybdenum, tin and titanium.

Each geographic area apparently has its peculiar trace element fingerprint. Boston, for example, has far higher readings for vanadium than San Diego, Los Angeles or Honolulu, and mid-ocean areas, predictably enough, have far higher readings for sodium and chlorine than do the cities.

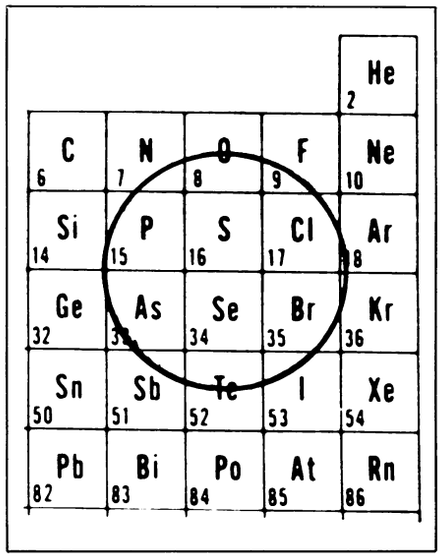
The varying amounts and proportions of the elements also provide a key to the sources. Boston's relatively high level of vanadium—up to 2.5 micrograms per cubic meter—probably comes from power plant burning of a heavy fuel oil that has high vanadium levels—originally part of the porphyrin structures that were in the prehistoric animals from which petroleum came. Analysis of airborne lead in San Diego by Dr. Tsaihwa J. Chow of the Scripps Institution of Oceanography, reveals the lead contains proportions of stable isotopes characteristic of lead which is used by manufacturers of tetraethyl lead gasoline additives (SN: 3/21, p. 284).

Bromine levels seem to correlate with lead levels. Because the lead comes from gasoline additives, Dr. Gordon and other researchers think the bromine, a component of certain additives, does also.

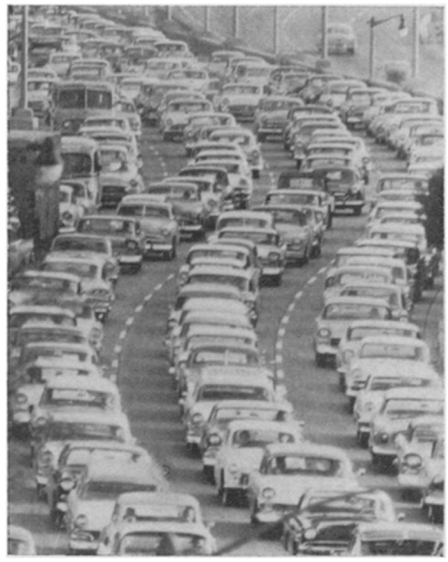
Aluminum and selenium are probably a product of coal burning, selenium being associated with sulfur in the same group in the periodic table and

Bureau of Standards

Spectography: One way of sampling.



Togetherness: Sulfur and selenium.



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Auto exhausts: Lead and bromine.

sulfur being a common component of coal.

It appears, in fact, that many of the elements discovered are probably connected with fuel burning of one kind or another. But because of the existence of a number of metal-processing industries in Boston, it is not certain that this is always the case there. Plans are now under way for INAA sampling in a number of cities, and fractionation of samples by particle size is expected to yield more clues as to sources, since various industrial processes create various-sized particles.

The earth, air and water are a continuum, and fallout in precipitation carries the trace elements into water and onto the earth. Or, in some cases, the elements are part of effluents that go directly into waterways.

Using neutron activation analysis, researchers at Argonne National Laboratory have discovered many of the same elements in Great Lakes fish that have been found in the air at various locations (SN: 3/21, p. 284). The researchers plan now to analyze Great Lakes water itself, and Interior Secretary Walter Hickel recently announced that Interior's Fish and Wildlife Service plans monitoring of Great Lakes fish, as a result of mercury found in fish in Lake St. Clair, Lake Erie and connecting waterways (SN: 4/18, p. 388).

Individual researchers have discovered hitherto undetected waterborne elements; Dr. E. E. Angino of the Kansas Geologic Survey, for example, discovered two to eight parts per billion of arsenic in the Kansas River—approaching the Public Health Service limit of 10 parts per billion—and he believes the arsenic has its source in detergents—in which he also found arsenic (SN: 3/28, p. 321) at levels as high as 72 parts per million. Although treatment processes in Lawrence, Kan., reduced the arsenic levels in drinking water there, Dr. Angino says other processes used elsewhere—such as in the Ohio River, where water is heavily reused—might fail to do this. □

(Next: The toxicology of traces)

Limit of Detectability (micrograms/cubic meter)

Element	INAA	Emission spectrography	Atomic absorption
Short Runs			
Sodium	0.001	0.003	0.001
Aluminum	0.001	0.003	0.2
Chlorine	0.2	....	....
Calcium	1.0	0.003	0.002
Vanadium	5×10^{-4}	0.003	0.2
Manganese	0.001	0.011	0.002
Copper	0.02	0.01	0.002
Bromine	0.002	....	....
Long Runs			
Scandium	2×10^{-5}	2×10^{-4}	....
Iron	0.001	0.084	0.01
Cobalt	10^{-6}	0.0064	0.01
Nickel	0.01	0.0064	0.006
Zinc	2×10^{-5}	0.24	0.001
Selenium	2×10^{-5}	....	0.2
Antimony	10^{-5}	0.04	0.04
Barium	10^{-4}	0.003	0.2
Lanthanum	5×10^{-5}	0.002	4.
Cerium	10^{-5}	0.02	....
Samarium	5×10^{-5}	0.01	1.
Europium	10^{-5}	0.001	....
Ytterbium	10^{-5}	0.003	0.01
Lutetium	10^{-5}	0.1	....
Hafnium	10^{-5}	0.02	....
Thorium	10^{-6}	0.01	....

Three techniques: INAA shows greatest sensitivity.

Concentration (micrograms/cubic meter)

Element	Average	Approximate Average	Range
Short Runs			
Sodium	0.8		0.40—3.0
Aluminum	0.7		0.15—2.5
Chlorine	0.5		0.2—4.0
Calcium		2.	
Vanadium	0.6		0.4—2.0
Manganese	0.02		0.01—0.05
Copper		0.05	
Bromine	0.15		0.02—0.8
Long Runs			
Scandium		8×10^{-4}	
Iron		1.0	
Cobalt		2×10^{-4}	
Nickel		....	
Zinc		0.1	
Selenium		6×10^{-5}	
Antimony		5×10^{-4}	
Barium		2×10^{-4}	
Lanthanum		8×10^{-4}	
Cerium		2×10^{-3}	
Samarium		2×10^{-4}	
Europium		3×10^{-5}	
Ytterbium		2×10^{-3}	
Lutetium		1×10^{-5}	
Hafnium		3×10^{-5}	
Thorium		5×10^{-5}	

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Air in Boston: Trace amounts of 24 subtle pollutants.