Elemental Tracers of Distant Regional Pollution Aerosols

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The routine transport of pollution aerosol through long distances is increasingly recognized as an important aspect of atmospheric science. Atmospheric transport on the scale of 1000 to 10,000 km is now invoked regularly to explain the results of aerosol studies in rural and remote areas (*1*).

Summary. A seven-element tracer system shows that regional pollution aerosols of both North America and Europe have characteristic signatures that can be followed into remote areas up to several thousand kilometers downwind. In aerosols of mixed origin, regional contributions to the tracer elements can be resolved by least-squares procedures. After transport of several hundred kilometers, secondary sulfate can also be apportioned satisfactorily. Regional elemental tracers thus offer a way to determine the sources of pollution aerosol in important areas such as the northeastern United States, Scandinavia, and the Arctic.

But long-range transport has created a new set of interpretive problems. While it is relatively easy to identify pulses of transported pollution aerosols in remote areas which are otherwise clean, it is often difficult or impossible to pinpoint the source areas of these aerosols. (At distances of a few hundred kilometers or more, source areas are normally much more important than point sources.)

Sheer distance can cause problems. For example, it has been extremely difficult to decide whether the important sources of pollution aerosol observed at Barrow, Alaska, are located in North America, Europe, or Asia. With air-mass trajectories from these sources being 5000 to 10,000 km or more in length and representing travel times of 5 to 10 days or more, pure meteorological techniques have not led to a consensus about even the continents of origin, much less particular regions within the continents (*2*).

The configuration of sources can also make identification difficult. In the northeastern United States, for example, where the source areas of acid aerosol and precipitation are currently in dispute, distances of transport are much shorter (1000 km or less) but the spatial pattern of sources is complex. As a result, trajectories to areas of concern such as the Adirondacks or New England often pass over several strong source areas in their last few hundred kilometers. No available transport model can reliably apportion the contributions of these sources to the final sulfate, acid, or other ubiquitous constituents of the pollution aerosol.

There is thus a need for a more direct way to identify distant sources of pollution aerosol. Such a capability would be of practical as well as scientific importance, because it could be extended ultimately to determining source areas of acid precipitation. It may cost as much as $20 billion to $100 billion to reduce emissions of sulfur dioxide in the eastern United States over the next decade; controlling the wrong sources would be a very costly error.

We feel that the use of chemical tracers in the aerosol itself holds considerable promise. This article deals with our efforts to develop regional elemental tracers of pollution aerosol; eventually, organic and stable isotopic tracers can probably be developed and used analogously.

Prospects for Regional Elemental Tracers of Pollution Aerosol

Pollution aerosol contains all elements; no true tracers, or elements unique to specific source areas, exist. But it is reasonable to expect the proportions of at least some elements to vary with source area because different areas have different mixes of the major aerosol sources (combustion, industry, transportation, and so on), different mixes of fuels, fuels from different origins, different industrial bases, and different degrees of pollution control. However, the number of regional elemental signatures, the magnitude of their differences, and the elements involved cannot be predicted; they must be determined empirically.

In general, regional tracers are constructed and used quite differently from urban tracers. Elemental signatures used to deduce sources of urban aerosol by receptor-oriented techniques (*3*) are usually derived for either point sources or specific types of sources (automotive exhaust, for example). Regional aerosols, by contrast, are mixes of many sources and should thus resemble one another much more than signatures within an urban region should. Similarities among pollution aerosols have been recognized for years (*4*), and many have doubted whether useful regional differences could be found. We have determined that characteristic regional signatures do exist, many of which are very different from one another.

The two keys to deriving regional signatures are finding the right elements and handling the data with the appropriate statistical techniques. The "marker-element" approach sometimes used in urban studies (where the contribution of a source is evaluated by a single element) cannot be used with regional signatures because of their great similarities. The opposite approach, constructing signatures from all available elements, is practiced in some urban studies but adds too much noise to regional pollution signatures. The best approach seems to be a compromise—limit regional signatures to those few elements with the greatest tracer power.

Several requirements should be met by elements and signatures before they can be used in a regional tracer system: the elements should be pollution-derived, sampled and measured accurately, emitted stably and homogeneously in each region, and present on particles small enough to be transported long distances; each signature should remain recognizable during transport. Our preliminary assessment indicates that all these requirements are met adequately; we illustrate several of them in the discussion that follows. Nevertheless, some of these requirements, such as conservation of proportions during transport, are sufficiently critical that we have built routine checks into our operating system.

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A Seven-Element Tracer System for Pollution Aerosol

The first regional tracer was the noncrustal Mn/V ratio (*5*), which was designed to determine whether Arctic aerosol originated mainly from Europe or eastern North America. The noncrustal Mn/V ratio demonstrated the general feasibility of regional elemental tracers and stimulated the development of more sophisticated tracing systems. At present, we are using a seven-element tracer system involving As, Sb, Se, Zn, In, noncrustal Mn, and noncrustal V. The design of this system and several of its applications are discussed below.

These seven elements were chosen from the 40 to 45 that we have measured by neutron activation as best meeting the criteria of being pollution-derived, fine-particle (*6*), and accurately analyzable (*7*). Potential tracers rejected because of larger analytical uncertainties included Cu, Ni, Ga, Mo, Ag, Cd, Sn, W, Au, and Hg. With better analysis, any or all of these might be included in the system. Lead and elemental carbon are strong candidates which should also be investigated. Indium, whose analysis is poorer than those of the other six elements, was retained because of its great utility in tracing nonferrous smelters (*8*).

Our regional signatures consist of six elemental ratios to Se. Ratios are used to normalize for variable meteorological effects such as dispersion and removal; Se is used in the denominator because it is a general pollutant found at similar concentrations in diverse source areas and hence will not bias the ratios toward any particular region. In spite of Se's ubiquitous but modest vapor phase of 15 to 30 percent near the surface (*9*) and its natural sources such as volcanoes, it works well as a normalizing element in regions as remote as the Arctic in winter. We tested Zn as an alternative denominator (because of its similarly low coefficient of variation) and obtained the same results as with Se. Other general pollution

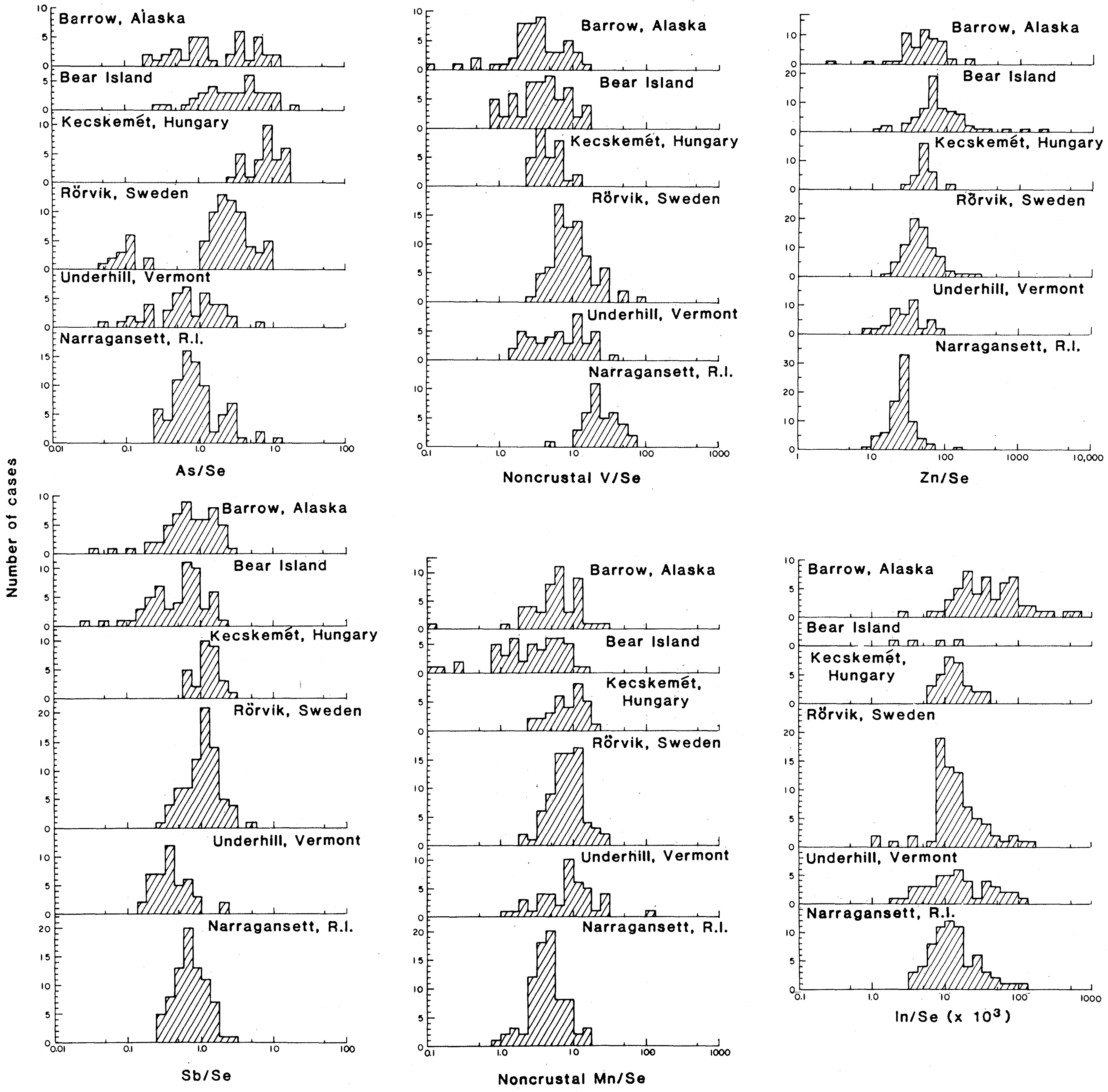

Fig. 1. Frequency distributions of six elemental ratios at six sites in eastern North America, Europe, and the Arctic.

elements such as Pb or C might also be considered for the denominator.

The signature of a source region cannot be derived in a completely straightforward fashion because most regions can be affected by pollution aerosols transported from other regions. To eliminate such interference, we are developing a protocol which involves multiple samples at multiple sites inside and outside the region. At each site, at least 100 (ideally) daily samples are taken and analyzed for the tracer elements. Logarithmic frequency distributions of the various X/Se ratios are then constructed and examined for the presence of modes, or maxima, which represent characteristic aerosols for the sites. The meteorological and chemical characteristics of the samples in a mode usually give a good idea of its source. By combining the modal information from several sites in a region, its aerosol may usually be distinguished from those transported from neighboring regions. As a final check, regional signatures are verified by sampling downwind of the region. This also shows whether any elemental ratios change significantly during transport.

To date, we have used filter samples of total aerosol for our tracer system. In effect, this provides size-segregated data because the tracer elements chosen are mostly submicrometer. True fine-particle samples would probably improve the tracer system by reducing the variability of elemental ratios and allowing mixed-mode elements such as Fe, Co, and Cr to be considered. But how much the improvement would be is not yet known, and size-segregated samples are much smaller and not readily available from many regions of interest. When elemental tracer techniques are eventually applied to precipitation, total aerosol will be a more appropriate reference than fine-particle aerosol, for coarse particles are scavenged more efficiently by precipitation than are fine particles.

Factor analysis, while useful for understanding broad elemental relations and the general sources of pollution aerosol of a site, has not been particularly successful in selecting elements as tracers or defining regional signatures. The reason for this seems to be that any technique which is based solely on single measures of similarity between elements (such as correlations) in a collection of samples does not adequately reveal the complex relations implicit in mixed frequency distributions.

Modes in Pollution Aerosols from North America, Europe, and the Arctic

Figure 1 shows the six X/Se distributions for six sites at which we have reasonable amounts of data: Narragansett, Rhode Island, and Underhill, Vermont, in eastern North America; Kecskemét, Hungary, and Rörvik, Sweden, in Europe; and Barrow, Alaska, and Bear Island, Norway, in the Arctic (*10*). Depending on element and location, one or more modes are seen in each distribution. The modes are reasonably symmetric (that is, log-normal), with geometric standard deviations of 1.4 to 1.6 (68 percent of the points found within a total factor of 2 to 3). Some modes have geometric standard deviations as low as 1.2. The presence of these modes shows that a few major types of pollution aerosol are found at each site.

More types of pollution aerosol may be present at a site than are revealed directly by the major modes, however. Broader-than-normal modes may be composed of two or more unresolved modes, as seems often to be the case for Zn/Se and Sb/Se, for example. Small features may represent infrequent appearances of aerosols which are more important elsewhere. An example of this is the small upper mode of As/Se at Rörvik (ratios of 8 to 10), which coincides with the principal mode (6 to 12) at Kecskemét (we show below that the upper mode at Rörvik was created by a pulse of aerosol from eastern Europe). Another example is the low shoulder of Zn/Se at Narragansett (ratios of 10 to 20), which has been resolved into a discrete mode by subsequent shorter period samples. The real number of modes in most distributions is not known and may be considerably larger than the number apparent from Fig. 1.

Membership in most modes is organized; that is, samples in a certain mode of one distribution are usually found together in other distributions. For example, the samples from eastern Europe which comprise the upper As/Se mode of Rörvik also comprise the low shoulder of noncrustal V/Se there (ratios of 3 to 6). This illustrates that well-defined pol-

Table 1. Geometric mean elemental signatures for source aerosols in North America and Europe (geometric standard deviations in parentheses).

Source	*N*	As/Se	Sb/Se	Noncrustal V/Se	Zn/Se	Noncrustal Mn/Se	In/Se (×1000)
Individual sources							
SCANS	5	2.8 (1.3)	0.94 (2.0)	24 (1.3)	43 (1.5)	5.2 (1.8)	9.5 (1.7)
WEURS	5	1.88 (1.2)	1.01 (1.4)	5.8 (1.3)	37 (1.1)	6.5 (1.2)	13.1 (1.6)
WEURH	5	3.5 (1.1)	0.75 (1.3)	7.2 (1.8)	56 (1.4)	6.8 (1.7)	11.1 (2.2)
EEURF	5	7.2 (1.2)	1.33 (1.3)	7.8 (1.2)	54 (1.1)	10.0 (1.2)	13.1 (1.3)
EEURS	3	7.3 (1.1)	1.73 (1.1)	4.8 (1.2)	66 (1.1)	13.7 (1.2)	15.1 (1.2)
EEURH	4	8.9 (1.0)	1.18 (1.1)	5.2 (1.3)	48 (1.1)	8.9 (1.8)	9.8 (1.4)
NE	4	0.130 (1.4)	0.45 (1.3)	11.3 (1.2)	32 (1.2)	9.2 (1.3)	9.8 (1.9)
BOS	3	0.68 (1.5)	0.82 (1.8)	35 (1.2)	37 (1.1)	4.1 (1.2)	5.3 (1.1)
NYC	3	1.10 (1.1)	1.63 (1.7)	11.1 (1.3)	40 (1.1)	6.5 (1.3)	9.6 (1.6)
WASH	4	1.46 (1.2)	0.82 (1.2)	9.9 (1.2)	22 (1.2)	4.0 (1.8)	7.1 (1.2)
INT	4	0.92 (1.2)	0.28 (1.4)	1.96 (1.4)	10.8 (1.3)	2.6 (1.5)	3.9 (1.7)
SONT	3	8.0 (1.2)	0.75 (1.2)	1.77 (1.9)	57 (1.1)	13.9 (1.1)	46 (1.7)
Regional means							
SCANS	5	2.8 (1.3)	0.94 (2.0)	24 (1.3)	43 (1.5)	5.2 (1.8)	9.5 (1.7)
WEUR	10	2.6 (1.4)	0.87 (1.4)	6.4 (1.6)	45 (1.4)	6.6 (1.5)	12.1 (1.9)
EEUR	12	7.8 (1.2)	1.37 (1.2)	6.0 (1.4)	54 (1.1)	10.4 (1.5)	12.3 (1.3)
ECOAST	14	0.58 (2.9)	0.80 (1.8)	13.8 (1.7)	31 (1.3)	5.7 (1.6)	7.8 (1.6)
INT	4	0.92 (1.2)	0.28 (1.4)	1.96 (1.4)	10.8 (1.3)	2.6 (1.5)	3.9 (1.7)
SONT	3	8.0 (1.2)	0.75 (1.2)	1.77 (1.9)	57 (1.1)	13.9 (1.1)	46 (1.7)
Continental means							
EUR	27	4.2 (1.8)	1.08 (1.5)	8.0 (1.9)	49 (1.3)	7.6 (1.6)	11.6 (1.6)
NAMER	21	0.93 (3.5)	0.65 (1.9)	7.1 (3.0)	28 (1.8)	5.6 (1.9)	8.8 (2.4)

lution aerosols with recognizable signatures do exist. As shown below, they can usually be identified with specific geographic source areas.

Regional Signatures of Pollution Aerosols in North America and Europe

At present, we use the modes of Fig. 1 only qualitatively. To derive signatures of pollution aerosol for specific regions, we use subsets of the modes composed of samples deemed most representative. With experience, it should be possible to increase the numbers of samples used to define signatures.

We are currently working with 12 regional signatures, six from North America and six from Europe, as shown in Table 1. The signature of regional New England (NE) was derived from four daily samples at Underhill (4 to 7 August 1982), in aged Canadian air masses which had not been affected by the large nonferrous smelters of the Sudbury Basin. The outstanding feature of this signature is its low As/Se ratio, which we interpret as indicating minimal coal influence. We have also detected this signature in Narragansett and South Portland, Maine (the small low-As mode at Narragansett in Fig. 1 is associated with this kind of aerosol). The "Boston" (BOS) aerosol was derived from three daily samples at Narragansett when the winds came from the direction of Boston and Providence and SO_2 concentrations were high (20 July and 3 and 6 August 1982). The New York City (NYC) signature came from six semiweekly samples taken in midtown Manhattan during the 1977–1978 winter. In order to better apply this signature to summer samples elsewhere, we reduced its noncrustal V by 50 percent (*11*). To better simulate the regional signature near New York, we reduced the Zn, which is abnormally enriched in urban aerosol, by 30 percent (because roughly 30 percent of the Zn is from coarse particles and presumably local, not regional, there). The Washington, D.C. (WASH), signature came from grand averages of individual average concentrations from ten sites in the Washington area during August and September 1976 (*12*). As in New York, Zn was reduced by 30 percent in an attempt to represent aerosol from the central mid-Atlantic states. The interior (INT) signature was derived from four daily samples in Underhill, Vermont, in July 1982, when an unusually strong signal of coal was present and associated with winds from the south-southwest. This signature does not represent pure coal emissions but rather an area where coal emissions are unusually strong. The Canadian smelter (SONT) signal was derived from three samples in southern Ontario roughly 300 km east-southeast of Sudbury (*13*). It is enriched in As and In. (The small groups of samples defining the signatures were representative distillations of larger sets of data; numbers of samples in each group were kept comparable for statistical purposes.)

The samples from Kecskemét and Rörvik allowed us to construct six regional signatures for Europe, three from the East and three from the West. Signature EEURH came from four samples associated with the most prominent mode of As/Se in Kecskemét. Signature EEURS came from three samples at Rörvik during the most intense "black episode" (*14*) of the past decade. As shown in Table 2, this aerosol was very different from that before and after the episode and had eastern European rather than western European characteristics. These samples made up most of the small upper mode of As/Se at Rörvik shown in Fig. 1. Signature EEURF came from four samples at Ähtäri, southern Finland, during the same black episode. Table 2 also shows these samples and how they closely resembled aerosol at Rörvik during the same period. The two signatures of western Europe, WEURS and WEURH, were derived from five samples at Rörvik when the winds were from the southwest and five samples at Kecskemét when the winds were from the west, respectively. For at least As/Se and noncrustal V/Se, these samples appeared in well-defined modes at the two sites. The last European signature is for Scandinavia (SCANS), as determined from periods of unusually high noncrustal V/Se at Rörvik, which usually coincided with weak circulation or winds from the north.

The western and eastern European signatures confirm the existence of general regional aerosols which appear at

Table 2. Episode of east European aerosol at Sweden and Finland.

Dates of sample (1982)	Sulfate ($\mu g\ m^{-3}$)	As/Se	Sb/Se	Non-crustal V/Se	Zn/Se	Non-crustal Mn/Se	In/Se ($\times 10^3$)
				Rörvik, Sweden			
11–13 January	2.4	3.0	0.67	15.4	69	13.1	17.4
13–15 January	5.4	9.6	2.4	50	52	26.5	31
15–18 January	12.9	4.0	0.8	5.2	49	6.0	< 3
18–20 January*	11.1	7.4	1.85	6.0	70	13.0	16.1
20–21 January*	19.5	8.2	1.68	3.8	65	11.7	12.8
21–22 January*	35.5	6.3	1.68	4.8	63	16.8	16.7
22–25 January	8.3	3.3	1.83	4.2	33	4.5	7.6
25–27 January	3.6	1.8	0.98	14.6	31	3.5	13.1
				Ähtäri, Finland			
17–18 January	6.5	3.4	0.60	9.4	54	3.8	7.2
18–19 January	5.3	2.6	0.64	8.0	66	5.7	11
19–20 January*	3.7	5.5	1.3	8.9	58	9.5	15
20–21 January*	19.4	6.6	1.6	5.7	52	13	13
21–22 January*	9.0	6.8	1.5	7.0	56	11	11
22–23 January*	17.8	5.9	1.6	8.3	52	10	10
23–24 January	0.95	4.6	0.86	10	52	7.6	18

*East European aerosol present.

Table 3. Two estimates of the relative discriminatory power of various elemental ratios on the 48 signature samples of Table 1.

Elemental ratio omitted	Number of samples misclassified (out of 48)		
	With 12 individual signatures	With 6 regional signatures	With 2 continental signatures
	1	2	7
As/Se	6	13	13
Sb/Se	1	2	6
Noncrustal V/Se	3	6	7
Zn/Se	2	3	9
Noncrustal Mn/Se	1	4	7
In/Se	2	2	7
As/Se, noncrustal V/Se	13	19	10
Noncrustal Mn/Se, In/Se*	2		
Sb/Se, Zn/Se*		5	
Sb/Se, Zn/Se, noncrustal Mn/Se, In/Se*			8

*Ratios indicated by stepwise discriminant analysis to be lacking in discriminatory power.

Table 4. Classification of nonsignature aerosol samples in North America and Europe.

Site	Classification					
	With 12 individual signatures		With 6 regional signatures		With 2 continental signatures	
	North America	Europe	North America	Europe	North America	Europe
Narragansett, R.I.	98	3	92	9	94	7
Underhill, Vermont	25	10	22	13	29	6
Rörvik, Sweden	21	45	19	47	28	38
Kecskemét, Hungary	0	22	0	22	0	22
	With five regional signatures					
Bear Island, Norway (without In/Se)			1	31		
Barrow, Alaska (without In/Se)			5	28		
	SONT	NE	BOS	NYC	WASH	INT
Narragansett, R.I.	0	17	17	8	37	22
Underhill, Vermont	1	14	1	7	3	9

various sites in and around large source regions. Because the three eastern signatures are so similar, they can be combined into a general eastern European signature (EEUR), as shown in Table 1. Similarly, the two western European signatures can be combined into the general WEUR. As more data become available from eastern North America, it should be possible to construct general signatures there as well. For illustrative purposes, we have combined the four coastal signatures NE, BOS, NYC, and WASH into ECOAST, which is also shown in Table 1. (All samples from North America and Europe were combined to form the continental signatures NAMER and EUR.) Note that the principal modes of As/Se, noncrustal V/Se, and Zn/Se at Barrow and Bear Island agree quite well with the WEUR and EEUR modes at Rörvik and Kecskemét.

Some of the most significant features emerging for elemental tracers are that the tracing power varies widely from element to element, that most of the tracing power is vested in a very few elements, and that the discriminatory power of an element, as measured by the range of its X/Se ratio and its degree of modality, is similar at widely diverse sites. For example, As/Se and Zn/Se have, respectively, large ranges with well-defined multiple modes and small ranges with single modes at most sites. Thus some elements are inherently much better tracers than others. The reasons for this are probably geochemical. They may be related to large-scale elemental variations in the earth's crust.

Table 3 illustrates two ways to measure the relative discriminatory power of tracer elements. In the first, linear discriminant analysis (*15*) on log-transformed data was used to classify the 48 signature samples of Table 1 into the 12, 6, and 2 groups shown in Table 3. Initially, all six of our X/Se ratios were used. Then the samples were reclassified with each of the ratios removed in turn. The greater the discriminatory power of a ratio, the more samples will be misclassified when it is removed. The results showed that As/Se and noncrustal V/Se had the greatest discriminatory power, Zn/Se had somewhat less power, and the other three ratios contributed little or nothing on the average. When both As/Se and noncrustal V/Se were removed, the extent of misclassification became greater than their summed individual effects. As a more sophisticated test of discriminatory power, stepwise discriminant analysis (*16*) was applied to the six ratios (log-transformed) as they were used to segregate the 48 samples into groups of 12, 6, and 2 signatures. The results are shown at the bottom of Table 3. The only two ratios having good tracer power in all three cases were As/Se and noncrustal V/Se.

It may be possible to improve the discriminatory power of our ratios by using discriminant analysis in which elemental ratios are replaced by higher order terms as generated and selected by the group method of data handling (*17*). The discriminatory power of optimized functions of ratios seems to be at least 20 to 40 percent greater than that of linear functions. Products involving As/Se and noncrustal V/Se are the most useful.

Empirical confirmation that certain elements are crucial to a successful regional tracer system was obtained by comparing our experience in southern Sweden with results of Lannefors *et al.* (*18*), who took daily aerosol samples for 1 year at Sjöängen, 200 km northeast of Rörvik. Their data, which included S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, and Pb but lacked As, Se, Sb, and In, were unable to differentiate between aerosols from eastern and western Europe.

To test whether the criteria on which our seven-element tracer system was based—that the components be pollution-derived, fine-particle, and determined well by neutron activation—are unduly restrictive, we investigated the tracer power of nine other elements (Al, Sc, Cr, Co, Fe, La, Ce, Sm, Th) by means of stepwise discriminant analysis on the same 48 signature samples. These elements are as well determined as the seven basic tracers but are mostly coarse-particle in the aerosol (Cr, Co, and Fe usually have a fine-particle component and La and Ce occasionally do). In general, the tracer power of La, Ce, and Sc was comparable to or better than that of Sb, In, and noncrustal Mn but less than that of As, noncrustal V, and Zn. The Al, Sm, and Th appeared to have little promise as tracers, and Fe, Co, and Cr behaved in an intermediate fashion. We do not know how the apparent tracer power of La, Ce, and Sc is partitioned between their coarse- and

Table 5. Elemental concentrations in five source-area aerosols.

Element	Concentration (ng m^{-3})				
	NE	BOS	NYC	WASH	INT
As	0.060 ± 0.033	0.49 ± 0.15	2.0 ± 0.2	3.2 ± 0.9	1.54 ± 0.40
Sb	0.143 ± 0.048	0.83 ± 0.41	3.1 ± 0.6	2.1 ± 0.7	0.55 ± 0.20
Se	0.37 ± 0.20	1.00 ± 0.60	1.88 ± 0.42	2.4 ± 0.7	1.78 ± 0.79
Noncrustal V	4.0 ± 1.7	35 ± 6	20 ± 4	23 ± 8	3.4 ± 1.0
Zn	11.1 ± 4.3	37 ± 3	70 ± 17	60 ± 12	18.2 ± 8.0
Noncrustal Mn	2.2 ± 0.3	4.2 ± 0.8	13.0 ± 1.1	9.2 ± 3.4	4.3 ± 2.4
In	0.0028 ± 0.0001	0.0050 ± 0.0040	0.0160 ± 0.0032	0.020 ± 0.006	0.0064 ± 0.0006

fine-particle components. The fraction associated with coarse aerosol may be less useful than suggested by these signature samples, because coarse aerosol is not transported as efficiently as fine aerosol. Overall, it is probably prudent to measure as many elements as possible (both natural and pollution-derived) in the aerosol, with an eye toward occasions when they could be useful as tracers. Dust storms, volcanic eruptions, or bursts of aerosol from unexpected point sources of pollution may all provide transient aerosols with unusual signatures which could be understood by use of additional tracer elements.

Use of Regional Pollution Signatures to Classify Unknown Aerosol Samples

Once discriminant analysis has been used to determine classification criteria from samples with distinctive signatures, one may classify nonsignature samples into those groups. In principle, the origin of an aerosol sample could be determined from its chemical composition alone.

Table 4 shows the present status of geographic classification of unknown samples by our seven-element tracer system. In the upper part of the table, nonsignature samples from Narragansett, Underhill, Rörvik, and Kecskemét have been classifed as North American or European based first on 12 individual signatures, then on six regional signatures, and finally on the two continental signatures of Table 1. In general, the posterior probability for membership in one of the source groups was greater than 90 percent. All samples from Kecskemét were classified correctly (as European). At Narragansett, 90 to 95 percent were classified correctly (as North American). At Underhill and Rörvik, however, only 60 to 80 percent were classifed correctly. Similar results were obtained when the noncrustal Mn/Se and In/Se ratios were eliminated. Classifying samples by continent is a severe test, however, because it is much more difficult for entire continents than for regions to have distinct signatures.

The center of Table 4 shows how samples at Bear Island and Barrow were classified relative to the five most appropriate regional signatures (SCANS, WEUR, EEUR, ECOAST, INT). Only 1 of 32 (3 percent) and 5 of 33 (15 percent), respectively, were called North American. This confirms our earlier conclusions, reached independently, that Arctic pollution aerosol is strongly Eurasian in origin (*19*).

Table 6. Contributions of various source regions to elements in Narragansett aerosol sample GSO 176, 3 to 8 August 1979.

Element	Weighting factor	Concentration (ng m^{-3}) NE	BOS	WASH	INT	Total predicted	Observed
As	300	0.03	0.06	0.20	0.36	0.65	0.67
Sb	30	0.08	0.10	0.13	0.13	0.44	0.55
Se	100	0.20	0.13	0.15	0.42	0.90	0.90
Noncrustal V	20	2.20	4.42	1.44	0.80	8.9	9.0
Zn	4	6.11	4.68	3.76	4.31	18.9	18.4
Noncrustal Mn	0.4	1.21	0.53	0.58	1.02	3.34	2.00
In	100	0.0015	0.0006	0.00	0.0015	0.0036	0.0040

The bottom of Table 4 illustrates how the nonsignature samples at Narragansett and Underhill were classified relative to the six North American signatures. At Narragansett, the four coastal signatures accounted for three-quarters of the cases, with the other quarter coming from the interior signature. This result confirms with multielemental data the conclusions about dominance of coastal aerosol reached earlier from noncrustal Mn and V alone (*11*). At Underhill, on the other hand, the most common signature is New England (40 percent), followed by other East Coast (30 percent) and the interior (25 percent). Considering Underhill's location in northern New England, this distribution of sources is reasonable.

Apportionment of Tracer Elements Among Regional Pollution Sources

Discriminant analysis is used to determine which of several signatures is most likely to account for an aerosol sample. In actuality, however, most aerosol samples come from more than one source, either because of the history of the air mass or because of changes in it during sampling. By using least-squares techniques similar to those employed in previous chemical element balance analyses (*3*), a sample can be apportioned among the various regional aerosols which may have contributed to it (*20*). For the elemental concentrations of five regional aerosols listed in Table 5 (*21*), Table 6 shows such an apportionment for an August 1979 aerosol sample from Narragansett. In this sample, the abundances of six of the seven tracer elements were accounted for to better than 20 percent by four of the signatures (NYC gave a negative coefficient, so it was eliminated and the regression was rerun with four sources). The weighting factor in Table 6 is really two factors, one to scale the numerical values of the different elements and another, based on Table 3, to weight As, Se, noncrustal V, and Zn relative to Sb, In, and noncrustal Mn. (The final apportionment is insensitive to weighting factor, however.) Note that about half of the As and Se were associated with the interior signal, whereas 60 to 80 percent of the Sb, Zn, In, and noncrustal Mn and more than 90 percent of the noncrustal V came from the coastal sources. This type of result is common for Narragansett during summer.

Table 7 summarizes the apportionments of 14 consecutive semiweekly

Table 7. Least-squares regional coefficients for 14 Narragansett aerosol samples from summer 1979.

Sample dates	SO_4^{2-} (μg m^{-3})	Regression coefficient NE	BOS	NYC	WASH	INT
13–17 July	8.63	0.66	0.11	0.11	0.02	0.07
17–24 July	12.32	0.37	0.26	0.12	0.01	0.20
24–27 July	11.24	0.00	0.36	0.00	0.00	0.56
27–31 July	19.12	0.00	0.19	0.16	0.00	0.47
31 July–3 August	16.49	0.76	0.00	0.04	0.00	0.34
3–8 August	10.28	0.55	0.13	0.00	0.06	0.24
8–10 August	5.47	0.56	0.08	0.22	0.00	0.23
10–14 August	10.49	0.30	0.37	0.00	0.00	0.19
14–17 August	8.31	1.17	0.07	0.19	0.00	0.00
17–21 August	12.14	0.47	0.35	0.00	0.02	0.00
21–24 August	22.48	0.38	0.47	0.09	0.00	0.00
24–28 August	12.90	0.78	0.17	0.00	0.00	0.16
28–31 August	11.00	0.80	0.05	0.02	0.00	0.14
31 August–4 September	8.71	0.55	0.16	0.00	0.00	0.27

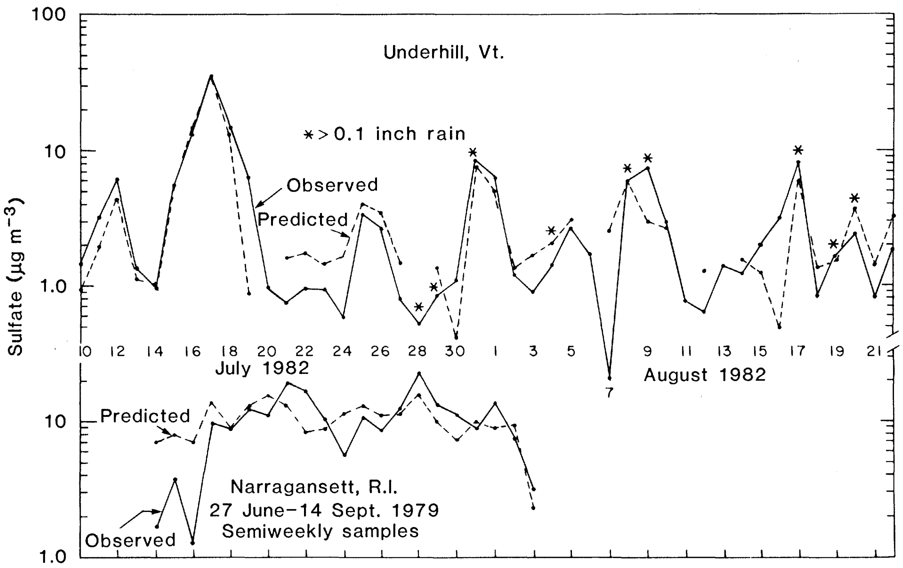

Fig. 2. Observed sulfate at Underhill, Vermont, and Narragansett, Rhode Island, compared to that predicted from least-squares regression of regional signatures.

samples from Narragansett during summer 1979, and shows that the mix of sources can vary strongly in response to large-scale meteorology. During summer 1979, Narragansett had two major sulfate episodes, one in July and one in August. The first was a "typical" summer episode, with winds from the south to west. The second episode was different, however. It had the highest summer sulfate seen to that time in Narragansett but the lowest (most northeastern) noncrustal Mn/V ratios and the lowest As. Meteorological maps showed that this episode was the result of large-scale stagnation in the Northeast of air which had originated largely in the upper Great Lakes and Canada. Thus, the first episode appeared to be mid-Atlantic or interior in origin, whereas the second appeared to be more from New England and Canada.

The apportionments bore out these observations. The first episode had high regression coefficients from the interior, normal coefficients from Boston, and low coefficients from New England. The second episode, by contrast, had zero coefficients from the interior and normal to high coefficients from Boston and New England. Washington aerosol was negligible throughout the period; contributions from the New York area were low to moderate and irregular.

Regional Apportionment of Sulfate Aerosol

Although our tracer system is based on primary pollution elements, that is, those emitted directly as aerosol, an important use of the system will be to understand the regional origins of secondary species, such as sulfate and acidity, which are formed in the atmosphere from primary precursors. Sulfate is the most abundant constituent of many remote aerosols, and both sulfate and acidity are of great concern in acid deposition.

Strictly speaking, primary constituents cannot trace secondary constituents. Near strong sources of (primary) aerosol, such as large urban or industrial areas, our tracer system should work poorly for sulfate. Outside such areas, where regional aerosols dominate, a primary tracer system should work better, although there may still be difficulties. In remote areas, primary tracers should work still better because most of the primary precursors, such as SO_2, will have been converted or otherwise removed; that is, the secondary species will have reached quasi-stable proportions. Under these conditions, the aged regional aerosols would effectively contain a sulfate component linked to the primary signature elements.

This appears to be the situation at Underhill, Vermont, for example. In a series of 39 daily samples from July and August 1982, we determined the "effective" sulfate in the various regional signatures by first apportioning the seven tracer elements, then regressing the sulfate of each sample against the regional coefficients derived for that sample. The results gave the following approximate concentrations of sulfate: 21 ± 1 $\mu g\ m^{-3}$ for the interior signature (INT), 7 ± 3 $\mu g\ m^{-3}$ for the mid-Atlantic region (WASH), and 3 ± 1 $\mu g\ m^{-3}$ for the local aerosol (NE). Based on these values, the predicted sulfate concentrations generally reproduced the observed values to within ~ 25 percent (Fig. 2). This accuracy is comparable to that obtained for the primary tracer elements. In particular, each of the peaks and valleys of sulfate was predicted.

At Narragansett, Rhode Island, however, the same approach gave poorer results. Figure 2 shows the observed and predicted sulfate for 21 semiweekly samples during June to September 1979. The fractional errors were twice as large as at Underhill, neither peaks nor valleys were predicted correctly, and a period of low sulfate at the beginning was missed entirely. This behavior is consistent with Narragansett's less remote location and with the abundant SO_2 observed there even during summer (2 to 20 $\mu g\ m^{-3}$) (*22*). The "noise" in sulfate at Narragansett most likely results from variable and unpredictable oxidation of this subregional SO_2, on a scale too small to be seen at Underhill. Time traces of the elements at Narragansett are considerably more irregular relative to each other and to sulfate than at Underhill. Thus, it appears that both primary and secondary aerosol of the coastal Northeast are more local in origin than those in interior New England and that control of this aerosol and its deposition will require different strategies for different parts of the Northeast.

Future of the Method

The outlook for regional tracers of pollution aerosol is bright. In the 3 years since the first regional tracer was developed, the system has been expanded from two elements to seven and used to demonstrate that characteristic regional signatures are the rule rather than the exception. But the use of regional tracers of pollution aerosol is still new, and nearly every aspect of the procedure is sure to be improved. Particular benefits may come from attention to a few key areas: systematically searching for additional elements with higher tracer power, increasing the statistical validity of regional signatures (including the effects of seasonal and longer period variations in signatures), evaluating the gains from size-segregated sampling, and refining techniques of tracing secondary species such as sulfate and acidity. Incorporation of organic compounds and stable isotopes into signatures should also be beneficial.

Eventually, the ability to follow pollution aerosol over great distances should prove useful in broader areas of the atmospheric sciences. Applications might include verifying air-mass trajectories on scales at which they cannot be otherwise verified and evaluating large-scale diffusion. A particularly valuable application of elemental tracers should be in determining the source areas of contaminants in precipitation, which is important in the field of acid deposition.

References and Notes

1. P. J. Samson, *J. Appl. Meteorol.* **19**, 1382 (1980); K. A. Rahn and R. J. McCaffrey, *Ann. N.Y. Acad. Sci.* **338**, 486 (1980); R. D. Borys and K. A. Rahn, *Atmos. Environ.* **15**, 1491 (1981); L. A. Barrie, R. M. Hoff, S. M. Daggupaty, *ibid.*, p. 1407; C. Brosset, *Ambio* **5**, 157 (1976).
2. J. M. Miller, *Atmos. Environ.* **15**, 1401 (1981); E. R. Reiter, *ibid.*, p. 1465; D. E. Patterson and R. B. Husar, *ibid.*, p. 1479.
3. G. E. Gordon, *Environ. Sci. Technol.* **14**, 792 (1980).
4. K. A. Rahn, "The chemical composition of the atmospheric aerosol," Technical Report, Graduate School of Oceanography, Unversity of Rhode Island (1976).
5. ——, *Atmos. Environ.* **15**, 1457 (1981). The noncrustal component of an element is used here to mean the mass present in excess of that calculated from a crustal reference element like Al, Si, Fe, or Ti, assumed to be totally crustal in the aerosol (a), and a crustal reference material such as bulk rock or soil (r). The formula typically used to calculate the noncrustal component of element X is

$$\text{Noncrustal } X_a = \text{total } X_a - Al_a \left(\frac{X}{Al}\right)_r$$

In most cases, global mean crustal rock or soil is satisfactory; occasionally, local rock or soil must be used as reference material.
6. The dividing line between fine and coarse aerosol is usually taken to be radius ~ 1 μm. This corresponds to the approximate breakpoint between (i) particles which penetrate to the lung and those which do not, (ii) coarser particles formed by mechanical subdivision (of soil and seawater, for example) and finer particles formed by coagulation or nucleation, and (iii) the original German "large' and "giant" ranges of particles.
7. Instrumental neutron activation normally allows As, Sb, Se, Zn, and noncrustal V to be determined in replicate aerosol samples to uncertainties of 5 to 15 percent, and In and noncrustal Mn to 10 to 40 percent. Differences between elements in simultaneous samples are usually less than 10 percent; for ratios, most of this difference disappears.
8. K. A. Rahn, N. F. Lewis, D. H. Lowenthal, in *Identification and Quantification of the Sources of Ambient Particulate Matter by Receptor-oriented Techniques*, S. Dattner, Ed. (Air Pollution Control Association, Pittsburgh, Pa., in press).
9. B. W. Mosher and R. A. Duce, *J. Geophys. Res.* **88**, 6761 (1983).
10. Seventy-nine Narragansett samples taken semiweekly during February–April and June–August 1978 and January–March and June–September 1979; 43 Underhill samples taken daily during July–August 1982; 76 Rörvik samples taken for 1 to 3 days each during fall and winter 1981–1982; 31 Kecskemét samples taken daily during fall and winter 1981–1982; 66 Bear Island samples taken for 2 to 3 days each during winter 1977–1978; 54 Barrow samples taken semiweekly from October 1977 to May 1978.
11. K. A. Rahn, D. H. Lowenthal, and N. F. Lewis ["Elemental tracers and source areas of pollution aerosol in Narragansett, Rhode Island," Technical Report, Graduate School of Oceanography, University of Rhode Island (1982)] show that noncrustal V in both New York City and Narragansett decreases from winter to summer by 50 percent relative to other pollution-derived elements.
12. G. S. Kowalczyk, G. E. Gordon, S. W. Rheingrover, *Environ. Sci. Technol.* **16**, 79 (1982).
13. K. A. Rahn, thesis, University of Michigan (1971).
14. C. Brosset, in (*1*).
15. Linear discriminant analysis is used to define groups from observations with known attributes and then classify other observations into one of these groups [D. F. Morrison, *Multivariate Statistical Methods* (McGraw-Hill, New York, 1976), pp. 230–246]. For linear discriminant analysis, we used a program in SAS-79 (SAS Institute Inc., Cary, N.C., 1979).
16. In stepwise discriminant analysis, variables are added to the discriminant function in the order that they enhance the separation between groups. For stepwise discriminant analysis, we used a program in BMDP, "Biomedical Computer Programs, P-Series" (Univ. of California Press, Berkeley, 1979).
17. A. G. Ivakhnenko *et al.*, in *Theoretical Systems Ecology*, E. Halfon, Ed. (Academic Press, New York, 1979), p. 325.
18. H. Lannefors, H.-C. Hansson, L. Granat, *Atmos. Environ.* **17**, 87 (1983).
19. K. A. Rahn, *ibid.* **15**, 1447 (1981); *Idöjárás* **86**, 1 (1982).
20. For least-squares apportionments of aerosol we used the program PETMIX, originally developed for petrologic studies [T. L. Wright and P. C. Doherty, *Geol. Soc. Am. Bull.* **81**, 1995 (1970)], and a program in SAS-79.
21. Tables 5 to 7 are from K. A. Rahn and D. H. Lowenthal, paper presented at the 17th Annual Conference on Trace Substances in Environmental Health, Columbia, Mo., 13 to 16 June 1983.
22. T. R. Fogg, personal communication.
23. We thank N. F. Lewis, K. A. Schweitzer, M. A. Voytek, T. R. Fogg, D. L. Smith, and T. J. Conway for technical assistance. Samples were provided by R. Poirot of the Vermont Agency of Environmental Conservation, C. Brosset of the Swedish Water and Air Pollution Research Laboratory, E. Mészáros and A. Mészáros of the Institute for Atmospheric Physics (Budapest), B. Ottar of the Norweigian Institute for Air Research, R. Kartastenpää and K. Markkanen of the Finnish Meteorological Institute, and various observers at the GMCC Baseline Observatory in Barrow, Alaska. Samples were analyzed at the Rhode Island Nuclear Science Center. M. Prager performed the calculations involving higher order discriminant analysis. This work was supported in part by ONR contract N00014-76-C-0435, NSF grant DPP 8020928, NOAA grant NA-80-RA-C-0207, a grant from the Ohio Electric Utilities Institute, and the Edison Electric Institute.

Childhood Leukemia and Fallout from the Nevada Nuclear Tests

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In 1979 Lyon *et al.* (*1*) reported an association between increased risk of mortality from childhood leukemia and residence in the southern 17 counties of Utah between 1951 and 1958, the major period of aboveground nuclear weapons testing at the Nevada Test Site. They observed different patterns of risk with respect to age and calendar time between children from 17 rural counties in southern Utah, which they designated as the "high-fallout" area on the basis of maps of estimated fallout distribution, and those from the remaining 12 northern counties of Utah, which they called the "low-fallout" area (Fig. 1). Within each of these two geographic areas, the number of leukemia deaths that occurred after 1950 among children born before 1959, the "high-exposure cohort" of Lyon *et al.* (*1*), were compared with those in their so-called "low-exposure cohort"—that is, childhood deaths between 1944 and 1950, before nuclear testing began, and deaths among children born after 1958, when aboveground testing had practically ceased (Fig. 2). The association between fallout and leukemia mortality was indicated by a difference between the standard mortality ratios used to compare the high-exposure and low-exposure cohorts within each area. That is, the ratio of observed deaths in the high-exposure cohort to the number expected on the basis of the observed number in the low-exposure cohort was higher in southern Utah than in northern Utah.

The mortality rate for the high-exposure cohort in southern Utah was not extraordinarily high but was comparable to the corresponding rate in northern Utah. But the rate for the low-exposure cohort, for the period 1944 through 1950 and for children born after 1958, was lower in southern Utah than in northern Utah (Table 1). Presumably, leukemia mortality among children (ages 0 to 14 years) in an area of normally low risk was increased, after their exposure to fallout, to a level comparable to that in the northern part of the state. In contrast, for children born after the testing period, the level of risk was substantially lower, as it had been before testing be-

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