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Bromine* Accumulation in Soil and Vegetation Surrounding a Liquid Bromine Spill

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In a previous study (WOODS et al. 1979) we reported the results of an investigation of some factors affecting the concentration of naturally-occurring bromine in freshwater and freshwater organisms. A report (WILKINS 1978) on the distribution of bromine in soils and herbage suggests no clear relation between soil bromine and the amount of the element taken up by the herbage at the same site. Rarely is there an occasion where an isolated area is impacted by large accidental spills of toxic elements. Such an incident occurred on the afternoon of July 12, 1977 when a truck tanker, east-bound on Interstate 40, overturned on a mountain overlooking Rockwood, Tennessee. The accident dumped some 40,000 pounds of liquid bromine beside the interstate. The spill resulted in the evacuation of over five thousand people, blocked the interstate for twenty-four (24) hours, and sent dozens of people to the hospital. The bromine was neutralized with soda-ash and lime to minimize the danger due to the free bromine. The bromine concentration still present is expected to depend upon the extent of leaching and runoff through the soil and uptake by the vegetation in the area. The purpose of the present study was to determine the bromine concentration remaining at the spill and the degree of trans-location of the bromide to various parts of the surrounding soil and vegetation.

MATERIALS AND METHODS

Representative soil and vegetation samples were collected during October, 1978 and February, 1979 both at the spill site and in the immediate vicinity. Samples used as controls were collected at a sufficient distance from the spill to not have been affected by it, but close enough to be representative of the general area. All samples were lyophilized at -50°C and 50μm Hg and then crushed, ground, and mixed to pass a U.S. Standard 70-mesh sieve, before analysis. Samples, in dry powder form, were placed in polyethylene sample cups covered with 4 micron Mylar film. Analysis was accomplished through the use of source excited x-ray fluorescence and an energy dispersive spectrometer. The fluorescing source consisted of 9mCi of Cadmium-109 in ring geometry and presented approximately 10^8 photons/cm^2/sec in 2π steradians.

*We have used "bromine" to describe both organic and inorganic forms of the element since the method of detection is insensitive to the form in which it exists.

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Determination of the bromine concentration was accomplished by the method of standard additions, in which known amounts of pure potassium bromide (KBr) were ground to 70-mesh, mixed with the original samples and re-seived. The increase in fluorescence intensity and the added concentrations form a linear relationship which, when extrapolated to zero addition, gives the initial concentration. The correlation coefficient from the linear regression analysis was 0.9998. Concentrations are reported on a dry-weight basis. The x-ray fluorescence spectrum for sample number 1 is shown in Figure 1. This spectrum is typical of many of the soil samples.

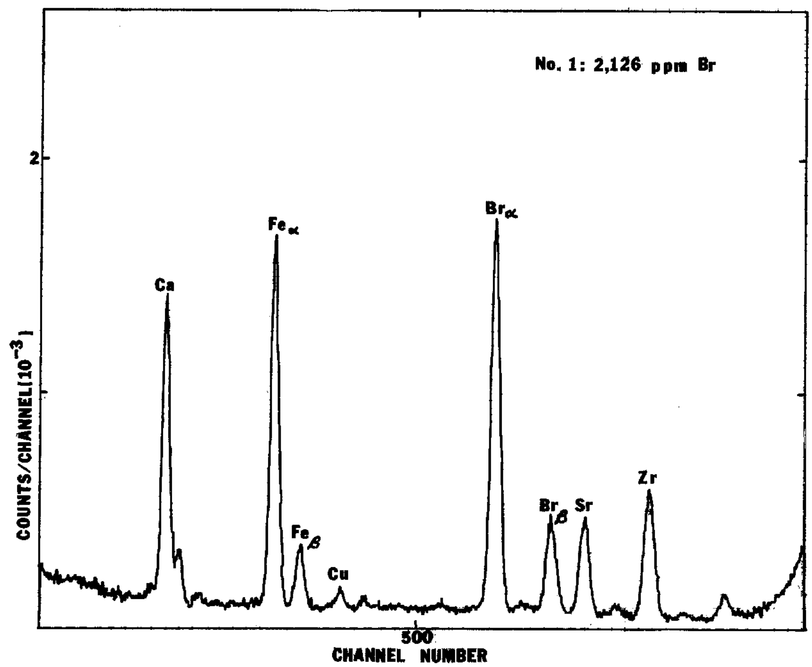

Figure 1. X-Ray Flourescence Spectrum of Soil at Spill Site.

An effort was made to minimize errors peculiar to the fluorescence techniques through standardization of sample preparation and through "same day" analysis of a sample and its addition. As a result, reproducibility of determined concentrations were within 5% for a given sample type. However, due to matrix effects, the relative concentrations among different sample types will likely be greater than 5% and could not be ascertained using the present sample preparation techniques.

RESULTS AND DISCUSSION

The results for all samples collected are presented in Table 1. (A schematic view of the area surrounding the spill is presented in Figure 2.) Samples 3,16,17 were only of cursory interest because they were near the area and showed surface coloration characteristic of bromine stain. The results indicate, however, that bromine levels were near the detection limit for the control sample (17) as well as the samples (3,16) at the spill site.

TABLE 1
Summary: Results of Bromine Survey

Sample-Type No.	Location	Br conc. ppm=µg/g.dry weight
1 - Soil	5" depth @ spill	2126†
2 - Soil	5" depth 40' E of #1	233
3 - Rock	@ spill	<0.5
4A - *Pinus virginiana*-Needles	N edge of spill	195
4B - *Pinus virginiana*-Cones	N edge of spill	145
5 - *Lonicera japonica*-Leaves	@ spill	84
6 - Soil	Road Level N of spill	19
7 - Soil	8' N* of #6	<0.5
8 - Soil	15' N* of #7	14
9 - *Pinus virginiana*-Needles	@8	276
10 - *Phytolaca americana*-Berries -	@ spill	1549
11 - *Phytolaca americana*-Leaves	@ spill	5005
12 - *Paulownia tomentosa*-Leaves	@ spill	4592
13 - Soil	Drain E of spill	94
14 - Soil	Drain 75' W of #13	208
15 - Coal	@ spill	247
16 - Pavement	I-40 @ spill	<0.5
17 - Pavement	I-40 W of spill	<0.5
18 - Soil Control	600' W of spill	<0.5
19 - *Pinus virginiana*-Needles	I-40 near spill	8
20A - *Phytolaca americana*-Berries	1 mile E of spill	59
20B - *Phytolaca americana*-Leaves	1 mile E of spill	25
21A - *Phytolaca americana*-Berries	1-40W near spill	28
21B - *Phytolaca americana*-Leaves	1-40W near spill	152
22 - *Paulownia tomentosa*-Leaves	1-40 W near spill	103
23 - Soil	@ #1	1826
24 - *Pinus virginiana*-Needles	@ #4 (same Plant)	503
25 - *Pinus virginiana*-Needles	30' N* of spill	115
26 - Soil	@ #24	<0.5
27 - *Lespedeza cuneata* (Plant)	@ @ spill	461
28 - *Lespedeza cuneata* (Plant)	N end of drain	364
29 - Soil	S end of drain	171
30 - *Lespedeza cuneata* (Plant)	@ #29	158
31 - Soil	3 miE of spill	<0.5
32 - *Lespedeza cuneata* (Plant)	@ #31	399
33 - *Paulownia tomentosa*-Leaves	Rutherford Co. Hosp.	584

*Distances given also correspond approximately to elevations, due to steep grade.

NOTE: Sample numbers 23 through 32 collected in February.

†Concentrations shown are calculated numbers only and are not intended to convey accuracy. See discussion of errors under MATERIALS AND METHODS.

Sketch of Bromine Spill and Surrounding Area*

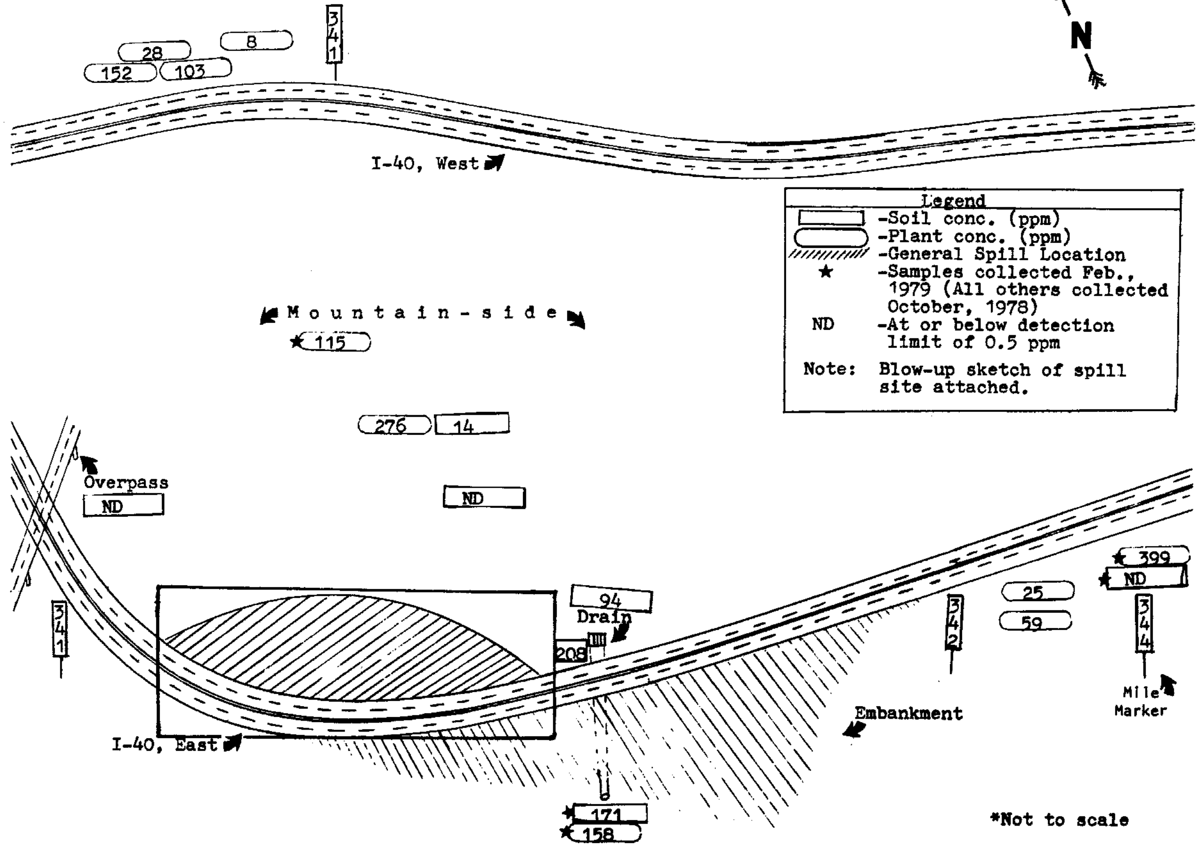

Figure 2a. Schematic View of Area Surrounding Bromine Spill

Detailed Sketch of Spill Site

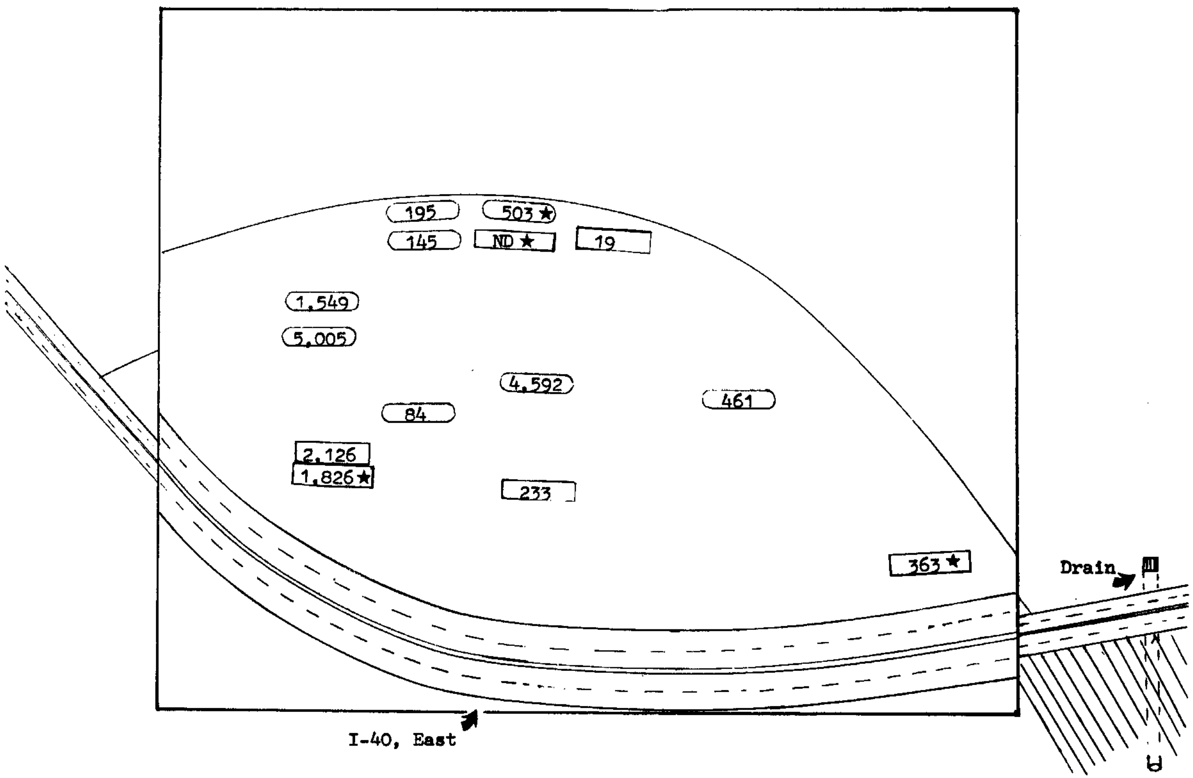

Figure 2b. Detailed sketch of Immediate Area Surrounding Bromine Spill

The soil and vegetative samples each revealed an expected general decrease in bromine concentration with increasing distance from the spill site (see Table 2). Exceptions noted are due, in the case of soils, to the location of such sampling sites along the drainage pathway where concentrations might, under silting conditions, be expected to vary differently. Other exceptions can be attributed to elevation differences and sample collecting times as indicated in Table 1. Similar comparisons, in the case of vegetation, can only be made for a given vegetation type, since this factor seems dominant in determining bromine concentration.

TABLE 2
Bromine Concentrations
(in order of nearness to center of spill)

Soil No.	Soil Conc.(ppm)	Vegetation No.	Vegetation Conc.(ppm)
1	2126	5	84
23	1826	11	5005
2	233	10	1549
26	<0.5	12	4592
6	19	27	461
7	<0.5	24	503
8	14	4-A	195
14	208	4-B	145
13	94	9	276
29	171	25	115
18	<0.5	28	364
31	<0.5	30	158
		20-A	59
		20-B	25
		32	399
		19	8
		21-A	28
		21-B	152
		22	103
		33	584

Vegetation shows higher bromine concentration than soil taken from around the vegetation (see Table 1, samples 8,9; 24,26) in marked contrast to results reported (WILKINS 1978) for naturally-occurring bromine. Samples (24,26) taken 4 months subsequent to the original samples (4,6) from the same plant indicate that plant concentrations are increasing and soil concentrations are decreasing. This suggests that the soil is being leached of its bromine and is losing it in part to the vegetation.

Comparison of the bromine concentration with that of other elements common to samples 24 (near spill site) and 25 (30 ft. North of spill site) suggests that most of the increase in bromine concentration is due to the spill site proximity (see Figure 3).

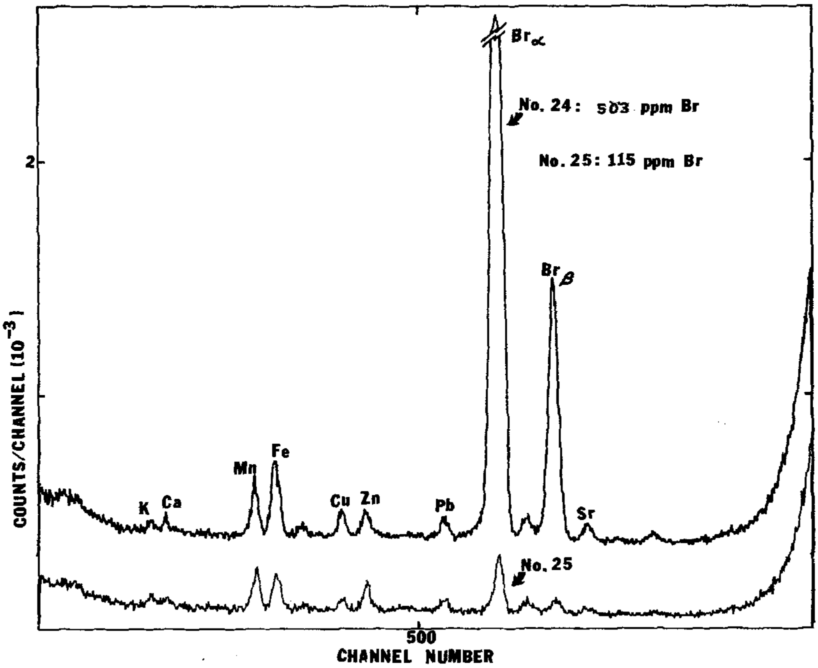

Figure 3. X-ray Fluorescence Spectrum of Vegetation Samples

Available data also indicate large variations among plant types in their affinity for bromine. Foliage from samples 11,12 and 4 in the immediate vicinity of the spill, for example, contained 5005,4592 and 195 ppm of bromine, respectively, while the same type plants collected at sites unrelated to the spill show respective concentrations of 152,103, and 8 ppm of bromine. Different portions of a given vegetative sample also show markedly different concentrations. Leaves from sample 11, for example, contained 5005 ppm of bromine while berries from the same plant contained 1549 ppm of bromine. In the case of the pine cone and foliage the variation was not so pronounced, showing respective concentrations of 145 and 175 ppm of bromine.

ACKNOWLEDGEMENT

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REFERENCES

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