Bull. Environ. Contam. Toxicol. (1991) 47:368–373

Bulletin of Environmental Contamination and Toxicology

Temporal Variation of Ethylene Dibromide (EDB) in an Unconfined Aquifer, Whatcom County, Washington, USA: A Twenty-Seven Month Study

J. Richard Mayer,[1] Thomas E. Lacher, Jr.,[2] Nancy R. Elkins,[1] and Chris J. Thorn[1]

[1]Water Research Laboratory, Huxley College of Environmental Studies, Western Washington University, Bellingham, Washington 98225-9079, USA and [2]Archbold Tropical Research Center, Clemson University, Clemson, South Carolina 29634-1019, USA

Many organic chemicals are known to infiltrate soils and enter aquifers; among these are 1,1,1-trichloro-ethane; trichloroethylene; 2,3,4,6-tetrachlorophenol; toluene; and 1,2-dibromoethane (ethylene dibromide or EDB) (Mackay 1985). The Office of Technology Assessment (1984) reported that chemical contaminants are found in groundwaters of every state and are being detected with increasing frequency.

The fact that EDB can infiltrate agricultural soils and enter groundwaters is well known in the United States. Many drinking-water aquifers have been contaminated in agricultural regions where EDB was used as a soil fumigant to control nematodes (root worms) which can attack raspberry, strawberry and other row crops (Brown, Jr. 1984). This chemical has been used intensively in Whatcom County, Washington on raspberry and strawberry fields until banned in the U.S. by USEPA in 1983.

Organic chemical contaminants in groundwaters can pose potentially adverse human health effects since about half of all Americans obtain their drinking water from subsurface waters (USEPA 1984). EDB is of particular concern since it is a potent human mutagen and carcinogen (*USEPA 1981. Ethylene dibromide: position document 2/3. Office of Pesticide Programs*). It has been estimated that at a concentration of 0.02 μg/L (ppb) in drinking water, EDB creates a lifetime risk of 3 x 10^{-5} excess cancers (three per 100,000) of exposed population (Simpson 1984). The USEPA has therefore established a health advisory and a proposed MCL (maximum contaminant level) of 0.02 μg EDB/L in drinking water.

The transport and fate of subsurface contaminants is of increasing concern. It is not known, for example, how levels of a groundwater contaminant might change month by month over a long period of time, and whether these changes would correlate with soil temperature or precipitation. We initiated a long-term study of EDB in an unconfined aquifer in Whatcom County, Washington with these questions in mind.

Send reprint requests to R.Mayer at the above address.

MATERIALS AND METHODS

Studies of EDB in groundwater were carried out at several sites in northern Whatcom County, Washington State. Our principal study site is shown in Figure 1.

Duplicate well-water samples were collected at each study site in 100 ml Class "A" volumetric flasks shown by GC analysis to be free of traces of EDB. Analyses for EDB (Method 504, modified, USEPA, 1988) utilized an HP 5890A gas chromatograph (Hewlett Packard, North Hollywood, California) fitted with a ^{63}Ni electron capture detector; 0.53 mm id, 30 m SPB-5 GC column (Supelco Inc., Bellefonte PA) and on-column injector. 2.0 μL hexane extracts were chromatographed isothermally at $50^{\circ}C$ and 30 kPa nitrogen head pressure.

Confirmation chromatography (10% of samples) was conducted isothermally using a 0.53 mm id, 30 m Supelcowax-10 GC column (Supelco Inc.) at $70^{\circ}C$ and 30 kPa nitrogen head pressure. The EDB standard was obtained from Supelco Inc. EDB results are expressed as μg EDB/L (s.d. $\pm$ 0.05 μg/L).

Average precipitation and air temperatures were based on daily observations at the Intalco Aluminum Corporation in Ferndale, WA 15 km southwest of our primary experimental site (Figure 1). The local topography and prevailing winds suggest that air temperatures and precipitation at our experimental site were substantially the same as at the Intalco site.

Twenty-seven months of Well 1 (Figure 1) EDB data, air temperatures and precipitation were obtained. These data were analyzed using time series correlation techniques. Initially all three variables (EDB, air temperature, and precipitation) were subjected to autocorrelation in time-series analysis to look for repeated trends over time. Cross correlations in time series were run for EDB and temperature, and for EDB and precipitation. In both cases we allowed EDB levels to lag behind the environmental variables from 0 to 12 months.

Our statistical approach was exploratory looking for possible effects of temperature and precipitation on EDB levels.

RESULTS AND DISCUSSION

We found that groundwater in Whatcom County is contaminated with EDB at several sites. Over a four-year period 107 wells were tested at several locations; EDB levels exceeding the USEPA health advisory (0.02 μg EDB/L) were found in 18 wells. At one of our study sites (Well 2, Figure 1) levels as high as 6.17 μg EDB/L were observed; this is 308 times the USEPA health advisory level.

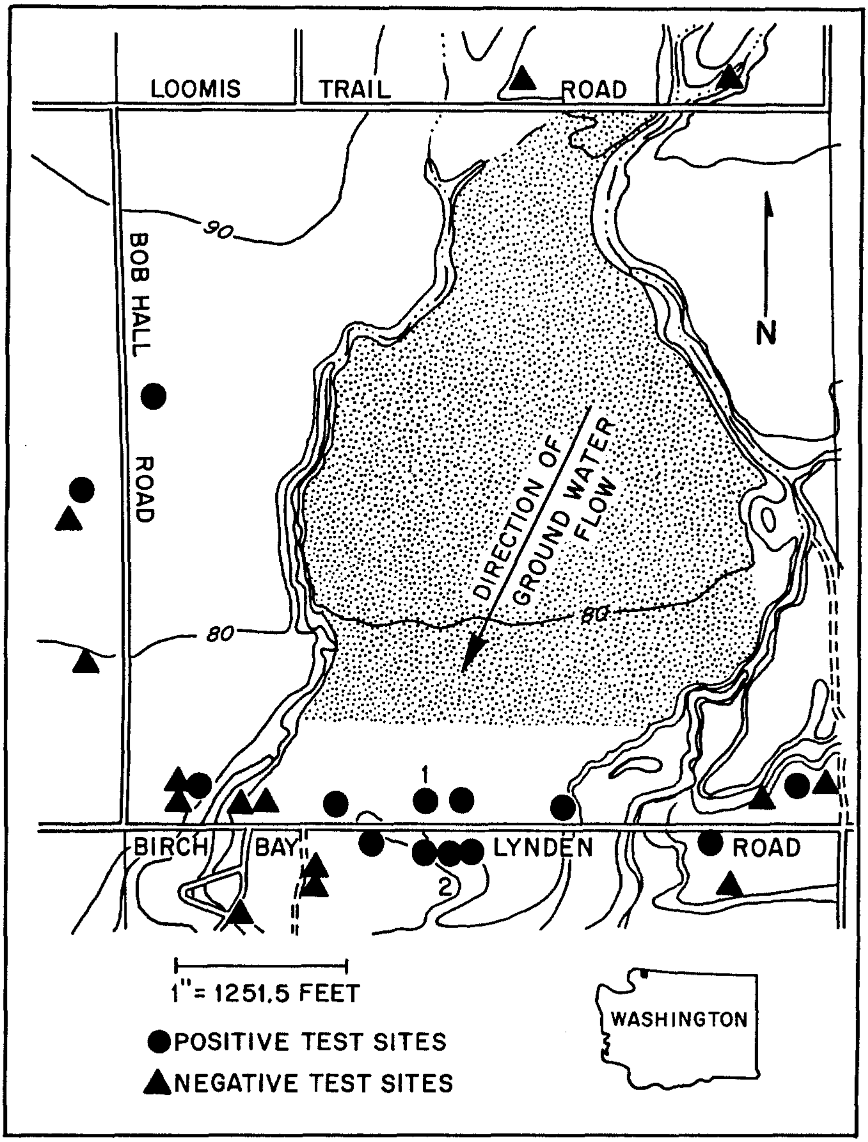

Figure 1. Whatcom County, WA study area; EDB monitoring sites; Wells 1 and 2; direction of groundwater flow in study area.

In March 1988 we began monthly monitoring for EDB in a 36-foot domestic well (Well 1, Figure 1) 15 m south of a large commercial raspberry farm. The direction of groundwater flow in the unconfined aquifer (Figure 1) was established by Creahan (1988). Average daily air temperature and precipitation were recorded for the time interval prior to each EDB sampling (see Materials and Methods). These data are reported in Table 1 and plotted in Figure 2.

While the initial EDB level in Well 1 was 1.69 μg/L, EDB concentrations varied significantly during the 27-month study including a high of 2.29 μg EDB/L and a low of 0.94 μg EDB/L. Curve fitting these data best supports an exponential decay curve:

$$[EDB] = 1.99e^{-0.00364t}$$

where [EDB] is reported as μg EDB/L and "t" is elapsed time in weeks. The correlation coefficient "r" = 0.67. Using this model we predict that the EDB level in Well 1 will decline to the USEPA health advisory level (0.02 μg EDB/L) by 2012.

Autocorrelation analyses (Table 2) showed several significant correlations with respect to EDB levels, all within the first six-months of lags. This reflects the tendency of EDB levels to change slowly over time (Figure 2). There was little suggestion of autocorrelation in precipitation due to its high variability from year to year (Figure 2 and Table 2). Temperature exhibited the expected pattern of positive and negative correlations (Table 2).

Cross correlation analyses (Table 3) revealed no correlation between the EDB time series and air temperatures. There was a strong pattern, however, in the cross correlation between the EDB time series and precipitation: EDB levels exhibited significant negative correlations with precipitation during the preceding three months.

These statistics suggest that a precipitation event can create a pulse of aquifer infiltration (a rapid process) diluting groundwater EDB. This is followed by a slow process: EDB infiltration from overlying soils which tends to reestablish prior EDB levels, a process which appears to require one to three months following the precipitation event. This model is supported by the work of Pignatello (1987) who observed that EDB can diffuse to soil matrix sites inaccessible to microbial degraders; residual EDB, strongly bound to soil particulates, can persist at these sites for 20 years.

Our work shows that long-term aquifer contamination can result from continuing infiltration of soil-matrix-derived contaminant residuals, such as EDB, long after its surface application has ceased.

We have also demonstrated that precipitation can affect groundwater monitoring data for contaminants such as EDB. Groundwater sampling that closely follows a significant precipitation event may reflect unrealistically low levels of a contaminant. A lag time of one to three months following precipitation was required in this study in order to observe ecologically prevailing levels of EDB in groundwater.

Table 1. Week of study, Well 1 EDB levels (ug/L), average air temperatures (oC), and total precipitation (cm) for the period preceding each EDB sampling period.

Week	EDB	Temp	Precip	Week	EDB	Temp	Precip
0.00	1.69	11.0	1.95	64.43	1.46	12.4	0.07
3.14	1.99	7.1	2.19	68.00	1.69	14.5	2.02
7.14	1.45	9.8	1.37	73.43	1.62	15.2	6.41
12.14	1.83	16.8	1.62	78.29	1.51	15.0	3.94
16.14	2.16	19.0	0.96	82.43	1.48	12.8	4.48
20.14	1.92	17.0	1.19	87.14	1.58	8.4	15.85
21.29	1.92	14.8	0.00	88.14	1.18	5.8	0.92
25.14	1.92	13.6	0.00	91.29	1.48	6.1	6.89
29.57	1.59	11.0	1.95	95.15	1.26	5.8	4.59
33.14	1.72	8.7	3.06	100.29	1.33	2.5	16.44
37.14	1.64	6.5	1.71	104.43	1.23	6.9	3.26
42.14	2.29	4.5	1.37	108.14	0.94	9.6	4.40
46.14	2.02	1.4	0.64	112.14	1.38	10.4	4.98
50.14	2.13	2.6	0.56	118.14	1.68	13.2	9.15
55.57	1.60	7.5	0.64				

Table 2. Autocorrelation analyses of EDB levels, air temperatures, and precipitation data.

Lag	DF	EDB			Precipitation			Temperature		
		Corr	t	P	Corr	t	P	Corr	t	P
1	26	0.5731	3.5657	0.00000	0.1764	0.9138	0.62753	0.7968	6.7237	0.00000
2	25	0.4729	2.6832	0.00000	0.3730	2.0102	0.05275	0.4250	2.3478	0.00000
3	24	0.3895	2.0718	0.04689	0.2065	1.0340	0.31255	0.0570	0.2795	0.77857
4	23	0.3325	1.6905	0.10086	0.5836	3.4465	0.00000	-0.2944	1.4773	0.14969
5	22	0.4060	2.0837	0.04675	0.1235	0.5839	0.57178	-0.6137	3.6456	0.00000
6	21	0.4493	2.3047	0.00000	0.1676	0.7791	0.54979	-0.7813	5.7372	0.00000
7	20	0.4012	1.9590	0.06146	0.1827	0.8311	0.57949	-0.7098	4.5066	0.00000
8	19	0.3061	1.4015	0.17419	0.2418	1.0863	0.29127	-0.4490	2.1901	0.03931
9	18	0.1129	0.4822	0.63992	0.0470	0.1997	0.83823	-0.0566	0.2403	0.80767
10	17	-0.0370	0.1528	0.87509	0.0460	0.1899	0.84587	0.3704	1.6443	0.11507
11	16	-0.0268	0.1071	0.91252	0.2188	0.8969	0.61332	0.7067	3.9953	0.00000
12	15	0.0061	0.0238	0.97926	-0.1179	0.4599	0.65575	0.7914	5.0143	0.00000

Table 3. Cross correlations of time series.

Lag	DF	EDB Lagging Temperature			EDB Lagging Precipitation		
		Corr	t	P	Corr	t	P
0	27	0.1339	0.7022	0.50481	-0.3568	1.9847	0.05475
1	26	0.0328	0.1673	0.86288	-0.5428	3.2959	0.00000
2	25	0.0677	0.3394	0.73619	-0.5004	2.8902	0.00000
3	24	0.2193	1.1010	0.28181	-0.5595	3.3067	0.00000
4	23	0.2249	1.1069	0.27970	-0.2671	1.3293	0.19410
5	22	0.1808	0.8624	0.59796	-0.3792	1.9219	0.06477
6	21	0.1402	0.6487	0.53030	-0.2318	1.0919	0.28744
7	20	-0.0693	0.3105	0.75695	-0.1138	0.5124	0.61932
8	19	-0.1798	0.7965	0.55911	-0.1318	0.5796	0.57541
9	18	-0.1870	0.8074	0.56489	-0.1094	0.4670	0.65014
10	17	-0.0570	0.2355	0.81137	-0.3464	1.5225	0.14293
11	16	-0.0272	0.1090	0.91096	0.1626	0.6591	0.52568
12	15	0.0177	0.0685	0.94463	-0.0479	0.1859	0.84921

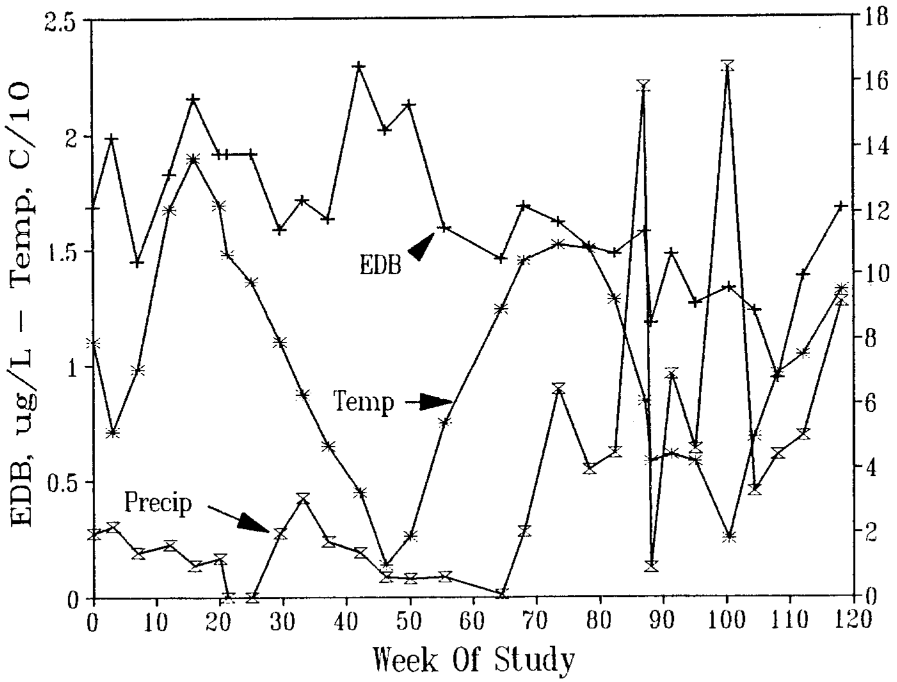

Figure 2. Well 1 EDB levels, temperature and precipitation data.

REFERENCES

Brown Jr AF (1984) Ethylene dibromide: its use, hazards, recent regulatory action. J of Environ Health 46(5): 220-225

Creahan K (1988) Water table elevations and groundwater flow in an unconfined aquifer in northern Whatcom County, Washington. MS Thesis, Wilson Library, Western Washington University, Bellingham WA

Mackay DM, Roberts PV, Cherry JA (1985) Transport of organic contaminants in groundwater. Environ Sci Technol 19: (5) 384-392

Office of Technology Assessment (1984) Protecting the Nation's groundwater from contamination. US Congress, Washington DC. US Government Printing Office Document: 052-003-00966-8

Pignatello JJ, Sawhney BL, Frink CR (1987) EDB: Persistence in soil. Science 236: 898

Simpson MM (1984) Ethylene Dibromide. Science Policy Research Division, Congressional Research Service Report IP280, Feb 15. Library of Congress. Washington, DC

United States Department of Commerce (1988) Methods for the determination of organic compounds in drinking water. National Technical Information Service: EPA-600/4-88/039

United States Environmental Protection Agency (1984) National primary drinking water regulations: volatile synthetic organic chemicals. 40 CFR Part 141 [OW-FRL-2514-3]

Received December 13, 1991 Accepted May 1, 1991