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A National Survey of Tri(haloalkyl)-, Trialkyl-, and Triarylphosphates in Canadian Drinking Water

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Tri(haloalkyl)-, trialkyl- and triarylphosphates (TAP) have a variety of uses as flame retardant plasticisers, fire-retardant hydraulic fluids, lubricants, air filter media, adhesives, and coatings (MIDWEST RESEARCH INSTITUTE 1979). Although significant quantities may be released inadvertently to the environment, laboratory studies (SAEGER et al. 1979, HOWARD & DEO 1979) have indicated that TAP should readily hydrolyse or undergo biodegradation in the aquatic environment. However, there have been reports on trace levels of TAP in fish (MURRAY 1975, LOMBARDO & EGRY 1979, MAYER et al.), river water (SHELDON & HITES 1978, FREUDENTHAL 1978) and drinking water (SUFFET et al. 1980, THURSTON 1978, LEBEL et al. 1981).

In 1979, Canada designated triaryl phosphates and related substances as Category III substances for review under the Environmental Contaminants Act. Category III substances are defined as those which may pose a significant danger to human health or the environment and about which further information is required. To gather relevant information, a method was developed for the analysis of $ng.L^{-1}$ levels of these phosphates in drinking water (LEBEL et al. 1981) using XAD-2 resin cartridges previously developed for the field sampling of large volumes of potable water (LEBEL et al. 1979). Using this method recoveries of TAP were 25% triethyl (TEP), 70% tributyl (TBP) and 80% tricresyl (TCP), triphenyl (TPP), tributoxyethyl (TBEP) and trichloroethylphosphate (TCEP). Analysis of treated water samples from six eastern Ontario potable water treatment plants showed $ng.L^{-1}$ concentrations of these TAP (LEBEL et al. 1981) and, therefore, an extended survey of drinking water from 29 municipalities located across Canada was conducted.

SAMPLING AND ANALYSIS

Twenty-nine municipalities were chosen across Canada for this survey so as to represent the major population centres in the country. The sampling procedure involved passing 50 to 200 L of treated potable water through XAD-2 resin cartridges during a 24 h sampling period (LEBEL et al. 1979, 1981). The samples of potable water were obtained at the treatment plant of each municipality. Samples were collected at two times of the year,

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August-September and November-December and, where possible the sampling interval was 3 mo. After sampling, the resin cartridges were sent by air or courier to the central laboratory where they were eluted with solvent within 24-48 h of sampling. Procedures for solvent elution and the preparation of the eluate for gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) analysis have been previously described (LEBEL et al. 1979, 1981). The GC analyses were conducted on a 3% OV-17 column and on a 3% OV-101 column using a nitrogen-phosphorus specific detector for both columns. GC-MS confirmation was conducted on selected samples with TAP concentrations greater than 10 $ng.L^{-1}$.

RESULTS AND DISCUSSION

The municipalities from which the field samples of potable water were obtained in the national survey are listed alphabetically in Table 1, together with the province and raw water source. The sampling locations were distributed geographically in relation to population density to cover a statistically significant representation of the total population of Canada and a variety of raw water sources. Table 1 lists the levels of seven TAP detected in the potable water collected at the treatment plant of each municipality. The results have not been corrected for percentage recovery; tri(1,3-dichloropropyl) phosphate by analogy with the other TAP would be expected to have a 80% recovery. TEP and TCP were only occasionally detected in the water samples but considering the poor percentage recovery for TEP the levels would be relatively high when TEP was detected. Comparison of the data in Table 1 indicates that the individual TAP levels for the two sampling periods are of similar magnitude although the November-December values are usually lower. However, some municipalities show the reverse relationship for one or more TAP. One might predict that environmental degradative processes (SAEGER et al. 1979, HOWARD & DEO 1979) would lead to lower TAP levels during the summer months. However, MAYER et al. (1981) have reported that TAP are adsorbed preferentially to the sediment layer and partitioning between the sediment and water layers would then favour higher TAP levels in the summer months.

Comparison of TAP levels with raw water source (Table 2) indicated that higher TAP levels were found in potable water obtained from river sources compared to lake sources. Ground water sources, in general gave very low TAP levels in the treated water. This is well illustrated by the results for Selkirk (Table 1) which changed from a river source to a well source between the two sampling periods. To arrive at an estimate of TAP levels present in waters in the major drainage basins, the mean TAP values for each drainage basin are consolidated in Table 3. It can be seen that the three central drainage basins, St. Lawrence, Great Lakes and Lake Winnipeg, have higher levels of TAP compared to other basins.

TABLE 1. Levels of Trialky-aryl Phosphates Found in Potable Water of Municipalities Across Canada (1979)

city and water source[a]	province[b]	month sampled[c]	TAP concentration ($ng.L^{-1}$) ethyl	n-butyl	2-chloro ethyl	1,3 dichloro propyl	phenyl	butoxy-ethyl	cresyl
Barrie (W)	ON	S	--[d]	0.2	0.3	--	--	1.7	--
		N	--	0.3	0.3	--	--	61	--
Brantford (R)	ON	A	9.5	24	26	23	2.5	560	0.8
		D	1.1	5.4	4.1	2.5	0.7	52	--
Calgary (L,R)	AL	A	--	2.9	1.0	0.3	1.0	110	--
		N	--	1.0	0.5	--	0.4	33	--
Dartmouth (L)	NS	S	--	0.6	--	--	--	2.1	--
		N	--	0.6	0.7	0.3	0.3	1.1	--
Drummondville (R)	QU	S	--	3.4	30	6.7	3.7	140	--
		N	--	31	52	1.2	6.5	97	--
Edmonton (R)	AL	A	--	3.1	0.9	0.6	1.3	240	2.3
		N	--	0.3	--	--	--	6.9	--
Fredericton (W)	NB	S	--	0.7	--	--	--	97	--
		D	--	1.1	--	--	--	150	--
Granby (R)	QU	S	--	4.5	11	10	1.2	560	--
		N	--	2.4	6.4	8.9	1.0	45	--
Guelph (W)	ON	A	--	2.4	--	--	--	28	--
		D	--	2.4	--	--	--	45	--
Halifax (L)	NS	S	--	0.6	0.2	--	0.2	100	--
		N	--	0.3	0.3	--	0.3	51	--
Kelowna (L)	BC	S	--	0.5	0.7	--	--	100	--
		D	--	0.6	1.0	--	--	7.0	--
La Salle (R)	QU	S	16	9.1	7.1	2.5	0.3	240	--
		N	23	3.9	7.5	2.0	0.9	94	--
Laval (R)	QU	A	--	2.3	1.1	0.8	--	140	--
		N	--	0.8	0.8	1.5	0.3	44	--

TABLE 1 (Continued)

city and water source[a]	province[b]	month sampled[c]	TAP concentration ($ng.L^{-1}$)						
			ethyl	n-butyl	2-chloro ethyl	1,3 dichloro propyl	phenyl	butoxy-ethyl	cresyl
Longueuil (R)	QU	A	21	12	8.5	1.9	1.7	150	2.3
		N	14	9.0	7.5	7.4	5.0	53	--
Medicine Hat (R)	AL	S	--	4.8	7.9	3.3	2.4	170	--
		D	--	19	16	12	4.3	340	--
Ottawa (R) (1)	ON	S	--	0.9	0.6	--	0.6	19.4	--
		D	--	0.4	0.6	--	0.3	4.9	--
Ottawa (R) (2)	ON	S	--	0.6	0.3	--	0.4	6.0	--
		D	--	0.6	0.4	--	0.4	9.5	--
Penticton (R)	BC	S	--	--	--	--	--	2.0	--
		D	--	--	--	--	--	15	--
Quebec (L,R)	QU	S	--	1.4	1.2	--	--	200	--
		D	--	0.3	0.8	--	0.5	9.4	--
Regina (L)	SK	S	--	0.9	1.8	--	--	120	--
		N	--	0.3	1.4	--	--	15	--
Saint John (L)	NB	S	--	1.2	0.3	--	1.2	18	1.6
		D	--	1.2	0.3	0.9	0.2	42	0.8
St. John's (L)	NF	S	--	--	--	--	2.0	13	--
		D	--	1.3	--	--	--	9.8	--
Saskatoon (R)	SK	A	--	6.7	4.3	1.8	0.3	26	--
		N	--	6.7	12	2.2	0.8	28	--
Selkirk (R)	MN	O	--	62	12	4.5	8.6	390	4.3
(W)		D	--	0.4	--	--	--	38	--
Sudbury (R)	ON	A	--	1.2	--	--	--	200	--
		N	--	0.6	--	--	0.3	19	--

TABLE 1 (Continued)

city and water source[a]	province[b]	month sampled[c]	TAP concentration ($ng.L^{-1}$)						
			ethyl	n-butyl	2-chloro ethyl	1,3 dichloro propyl	phenyl	butoxy-ethyl	cresyl
Thunder Bay (L)	ON	A	--	4.6	7.7	--	--	190	--
		N	--	1.0	--	0.3	0.7	64	--
Toronto (L)	ON	A	22	17	11	1.6	1.8	180	--
		N	11	42	8.3	1.9	3.9	92	--
Truro (B)	NS	S	--	0.3	--	--	--	48	--
		D	--	0.3	--	--	--	18	--
Vancouver (L)	BC	S	--	0.5	0.3	--	--	140	--
		N	--	0.4	--	--	--	25	--
Winnipeg (L)	MN	O	--	0.8	--	--	0.8	9.6	0.7
		D	--	0.8	--	--	--	140	--

[a] W, Well; R, River; L, Lake; B, Brook.

[b] NF, Newfoundland; NS, Nova Scotia; NB, New Brunswick; QU, Quebec; ON, Ontario; MN, Manitoba; SK, Saskatchewan; AL, Alberta; BC, British Columbia.

[c] A, August; S, September; O, October; N, November; D, December.

[d] --; Not detectable, < 0.05 $ng.L^{-1}$.

TABLE 2. TAP Levels ($ng.L^{-1}$) as a Function of Raw Water Source

water source	no. of cities[a]	mean butyl	2-chloro ethyl	1,3 dichloro propyl	phenyl	butoxy-ethyl
River	13(12)[b]	8.5	8.7	3.7	1.7	150
Lake	10	3.8	1.7	0.3	0.6	66
Well	3(4)[b]	1.2	0.1	0	0	64
Brook	1	0.3	0	0	0	33

[a] Two cities with both lake and river sources not included.

[b] One city changed from river to well source between sampling periods.

TABLE 3. Mean TAP Concentration ($ng.L^{-1}$) for Major Drainage Basins

drainage basins	no. of cities sampled	mean butyl	2-chloro ethyl	1,3 dichloro propyl	phenyl	butoxy-ethyl
Atlantic Sea Board	6	0.7	0.2	0.1	0.4	46
St. Lawrence	7	5.8	11	3.1	1.6	130
Great Lakes	6	8.4	4.8	2.4	0.8	130
Lake Winnipeg	7	7.8	4.1	1.7	1.4	120
Columbia	2	0.3	0.4	0	0	32
Pacific Sea Board	1	0.5	0.2	0	0	84

Apart from TBEP, the fraction of TAP values greater than 10 $ng.L^{-1}$ is very small (10%). However, for TBEP most values (75%) are higher than 10 $ng.L^{-1}$. This compound is used in rubber gaskets etc. and has been reported as a contaminant in blood (BORGA et al. 1977) and distilled water samples (WILLIAMS et al. 1981) Rubber gaskets, used in plumbing, can cause high TBEP levels if water is left standing in water pipes (LEBEL et al. 1981). Even though the survey samples were collected at the treatment plants it is not possible to exclude the possibility that the water was in contact with rubber gaskets etc. during the water treatment processes. Studies at the two Ottawa treatment plants (LEBEL et al. 1981) indicated that raw water TBEP values were as high as treated water TBEP values but it was not possible to verify this for the other treatment plants in the survey.

In those samples with general TAP levels greater than 10 $ng.L^{-1}$, other compounds were detected as peaks on the GC chromatogram using the nitrogen-phosphorus selective detector but their concentrations were not sufficient to permit identification by GC-MS.

The results of this study indicate that trace levels of TAP are present in Canadian potable water supplies sampled at the water treatment plants. Further studies of changes in TAP levels from raw water to potable water collected at the consumer's tap would be of interest. Studies should also be carried out to locate sources of TAP contamination.

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