COMPARATIVE ANALYSIS OF TOXAPHENE (CHLOROCAMPHENES) IN GROUNDWATER FROM THE HERCULES 009 LANDFILL

Maruya K[*1], Noltemeyer T[2], Wang H[3], Lynch C[3]

[1]Southern California Coastal Water Research Project, 7171 Fenwick Ln, Westminster, CA 92683 USA; [2]PACE Analytical Services Inc., 25 Kessel Ct, Suite 10, Madison, WI 53711 USA; [3]Hercules Research Center, 500 Hercules Rd, Wilmington, DE 19808 USA

Introduction

The 2.83 hectare Hercules 009 Landfill site, located near the city of Brunswick, Georgia (USA), received wastewater sludge and miscellaneous industrial waste from the nearby Hercules Brunswick plant for a period (1975-80) during which the biocide toxaphene was produced. Residues of toxaphene (chlorocamphenes) have been detected at levels exceeding 15,000 parts per million in landfilled sludges. After toxaphene was detected in an adjacent ditch, the landfill was closed and later added to USEPA's National Priorities List (NPL) as a Superfund site. Cement stabilization and solidification of the soils/sludges within the landfill was completed in 1999 to isolate and reduce mobility of the toxaphene contamination. A series of groundwater monitoring wells were also installed for periodic monitoring of toxaphene in order to characterize the effectiveness of the remedial activity[1].

The analysis of toxaphene residues in groundwater, as well as in other environmental matrices of concern (e.g. estuarine sediments, fish tissue)[2-4] has evolved over the past two decades. Because analytical methods approved for regulatory issues -- e.g. USEPA SW-846 Method 8081 for organochlorines[5] -- are not necessarily optimized for environmental toxaphene, concerns over their applicability and relevance have surfaced, in part, because very few, if any, detectable levels of toxaphene have been reported post-remediation.[1] The purpose of this study was to compare chlorocamphene concentrations in Hercules 009 Landfill groundwater samples using (non-selective) GC-ECD to those determined by GC-negative chemical ionization (NCI)-MS, typically a much more selective instrumental method for semivolatile halogenated organic compounds.

Materials and Methods

Eighteen (18) groundwater samples from the Hercules 009 Landfill were collected using slow purge (low flow) techniques from existing monitoring wells in March 2005 (Table 1). Five hundred ml of each sample was liquid-liquid extracted with dichloromethane (EPA Method 3510C), concentrated and exchanged to hexane by gentle evaporation with high purity nitrogen, and labile organics removed by shaking with sulfuric acid (EPA Method 3665)[5].

One μL of each extract was analyzed by GC-ECD (Varian 3400CX) and GC-NCI-MS (Agilent 6890 Plus GC/5973 quadrupole MSD/8486 autosampler) using 30 m x 0.25 mm i.d. fused silica columns coated with 0.25 μm DB-XLB (J&W Scientific, Folsom, CA, USA). The GC-ECD injector (splitless mode) and detector temperatures were held constant at 250 and 300°C, respectively. The oven was programmed at 120°C (1 min hold); and ramped to 280°C @ 2°C/min (11 min hold). The GC-MSD oven was programmed at 60°C (1 min hold); ramped to 200°C @ 10°C/min; and ramped again to 280°C @ 2°C/min (15 min hold). The cool-on-column injector was programmed to track oven temperature. Source and MSD temperatures were 106 and 150°C, respectively. The MSD was operated in the selected ion monitoring (SIM) mode with a dwell time of

75-100 ms for characteristic chlorobornane homolog NCI fragment ions (e.g. 307/309; 343/345; 377/379; 411/413). Total chlorocamphene concentrations (ΣCC) were estimated by ECD using a "total area under the curve" (TAUC) method[2-4]. The retention time window (RTW; 24-49 min) for TAUC computations was defined by the early eluting 2-endo,3-exo,5-endo,6-exo,8,8,10-heptachlorobornane (B7-1000) and the late eluting 2,2,5,5,6-exo,8,9,9,10,10-nonachlorobornane (Parlar 69). ΣCC was independently estimated by NCI-MS by summing peak areas for Cl_5-Cl_9 bornane homologs and applying the appropriate average homolog response factor. Initial GC-ECD analyses indicated a prominent tailing peak @ 25.8 min in several extracts (Table 1), identified as sulfur using NCI-MS, eluting within the RTW defined for the TAUC method. Because this peak was clearly not toxaphene related, it was subtracted from initial ECD-based estimates of ΣCC. Affected extracts were subsequently treated with acid-activated, solvent-rinsed copper granules and re-analyzed by GC-ECD.

High purity solutions of B6-923, B7-1001 and a 22-component chlorocamphene mixture were obtained from Ehrenstorfer (Augsburg, Germany). An aliquot of B7-1000 was provided by Dr. W. Vetter (Univ. of Hohenheim, Germany). Technical toxaphene product standard ("TTX") was supplied by Hercules Inc (Wilmington, DE, USA). Organic solvents used in this study were of pesticide grade or better. Instrument external calibration curves for TTX were highly linear for both instruments (R^2 of 0.998 and 0.999 for NCI-MS and ECD, respectively). The response of the NCI-MS at the end of the sample run, based on injection of the mid-level TTX solution, deviated from the initial calibration response by 5.2%. TTX recoveries for spiked lab water duplicates (~40 ug/L) were 102 and 100%. Mean ($\pm$ sd) percent recoveries for tetrachloro-*m*-xylene and decachlorobiphenyl spiked prior to extraction were 97 ± 6.3 and 76 ± 13, respectively. Final ΣCC values were not corrected for surrogate recovery. For a limit of quantitation equaling the lowest calibration standard (0.111 µg/mL) and a 500 mL sample volume, the reporting limit (RL) for both techniques was 0.222 µg/L.

Results and Discussion

Estimated ΣCC using GC-NCI-MS-SIM ranged from nondetect (<0.222 µg/L) for 4 samples (N-03, -07, -13, and –15D) to 1.55 µg/L for N-6SR (Table 1). The only other sample clearly above the RL was N-11 (0.740 µg/L). Monitoring wells N-6SR and N-11 were downgradient, in closest proximity, and were among the shortest depth to groundwater (1.45 and 1.63 m, respectively, Table 1) of all 18 stations, indicating the greatest potential for landfill soil/groundwater interaction. The next highest ΣCC (<=0.0463 ug/L for N-9S) was 16-fold less than that for N-11.

Two estimates of ΣCC reflecting slightly different retention time windows for NCI-MS-SIM analyses were also reported (Table 1). Estimated ΣCC for the wider RTW (i.e. 30-62 min) includes lower chlorinated homologs eluting before B7-1000 (e.g. Cl_5-camphenes)[3], and therefore represent the more conservative of the two measurements. The difference between these two estimates was < 15% for the four most contaminated samples (6SR, 11, 9S and 14S) indicating that chlorocamphene homologs eluting prior to B7-1000 were in low relative abundance, perhaps due to their absence in the extracts and/or the inherently lower response of lesser halogenated analytes using this technique. To demonstrate the potential effect of sulfur interferences on GC-ECD analysis of these samples, pre- and post-copper treatment ΣCCs were also compared (Table 1). A small, yet positive increase in post-Cu ΣCC for N-6SR and N-11 was noted; however, no apparent positive or negative trend was apparent for the remaining samples.

Because of the greater selectivity of NCI-MS for organohalogens such as the chlorocamphenes that make up environmental toxaphene residues, one might expect quantitation by ECD to result in greater concentrations due to the presence of (non-chlorocamphene) electron withdrawing constituents in environmental samples. The presence of elemental sulfur in these extracts, if not properly identified (e.g. by full scan NCI-MS),

would represent a potential positive bias to estimates of ΣCC using the non-specific ECD and TAUC quantitation method. When present in > ppb concentrations, elemental sulfur can easily mask target chlorocamphenes such as 2-exo,3-endo,6-exo,8,9,10-hexachlorobornane (B6-923 or Hx-Sed) and 2-endo,3-exo,5-endo,6-exo,8,9,10-heptachlorobornane (B7-1001 or Hp-Sed), two major toxaphene metabolites that are prominent in environmental media impacted by toxaphene contamination.[3,4,8] For example, treatment to remove sulfur interferences resulted in a 41 and 9.4% increase in estimated ΣCC for the two highest samples (N-6SR and –11), attributable to the detection of early eluting (and previously masked) chlorocamphenes like Hx- and Hp-Sed. When applied to samples with levels at or below the reporting limit, the differences between pre- and post Cu ΣCC estimates appeared to be random (Table 1), indicating little to no bias resulting from this additional treatment step. The highly selective NCI-MS technique using the SIM mode, on the other hand, was immune to sulfur interferences, eliminating the need for additional extract manipulation.

The average ratio of MS- to ECD-based ΣCC estimates was 1.15 ± 0.268, including only those samples that were greater than the MDL (n=5). The ratio for the fifth sample (not shown in Table 1) -- a lab control aqueous sample spiked with TTX @ ~ 40 ug/L (88 and 67% recovery by NCI-MS and ECD, respectively)-- was 1.30. These ratios suggest good overall agreement between the two GC techniques. For samples with ppb or higher levels, ECD/TAUC provides a relatively accurate estimate in the absence of non-chlorocamphene interferences such as sulfur. Although NCI-MS-SIM offers an advantage in selectivity, the instrumental response of lower chlorinated (i.e. $\leq$ 5 Cl atoms) camphenes decreases much more rapidly for NCI-MS compared with ECD. Thus, one must consider both matrix/procedural interferences and expected congener homolog abundances in order to select an appropriate quantitation technique.

All concentrations reported herein were less than 0.003 mg/L, the current maximum contaminant level (MCL) for toxaphene in drinking water[1]. Independent GC-ECD analysis per EPA Method 8081 of the Cu-treated groundwater extracts resulted in a single reported detection -- 1.6 ug/L for N-6SR – a value that corresponds well with the NCI-MS values (1.38, 1.55 ug/L). The general agreement between ECD/TAUC (after removal of S) and NCI-MS suggests the two methods are interchangeable for quantifying low level environmental toxaphene residues in groundwater matrices. With careful development, however, NCI-MS may prove to be a more accurate and efficient analytical alternative to ECD for other matrices (e.g. contaminated sediment, fish tissue) as well.

References
1. Barnes B, Miesfeldt MA. *Annual Groundwater Sampling Results and Inspection Report for the Hercules 009 Landfill in Brunswick, Georgia*, Report no. L007010261-001, RMT, Inc., Greenville, SC, USA.
2. Maruya KA, Lee RF. *Environ Sci Technol* 1998;32:1069.
3. Maruya KA, Wakeham SG, Vetter W, Francendese L. *Environ Toxicol Chem* 2000;19:2198.
4. Maruya KA, Manning RO, Francendese L. *Estuaries* 2005;28:786.
5. USEPA. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846, U.S. Environmental Protection Agency, Washington, DC, USA.
6. Stern GA, Loewen MD, Miskimmin BM, Muir DCG, Westmore JB. *Environ Sci Technol* 1996;30:2251.

Table 1. Estimated total chlorocamphene concentration (ΣCC) in 009 Landfill (Brunswick, GA) groundwater samples.

Sample ID	Depth to Water (m)	MS Conc (ug/L) 35-62 min	MS Conc (ug/L) 30-62 min	%DIF NCI-MS	ECD Conc (ug/L) pre-Cu	ECD Conc (ug/L) post-Cu	%DIF ECD	NCI-MS/ ECD
N-01	2.10	<=0.00584	<=0.00584	n/d	<=0.0326			
N-02	2.24	<=0.0213	<=0.0248	15	<=0.0616	<=0.0345	-44	
N-03	2.44	<0.222	<0.222	n/a	<=0.0222	<=0.0608	174	
N-05	2.10	<=0.0114	<=0.0114	n/d	<=0.0154	<=0.0442	188	
N-6DR	3.51	<=0.00258	<=0.00258	n/d	<=0.00513			
N-6SR	1.45	1.38	1.55	12	0.722	1.02	41	1.52
N-07	3.44	<0.222	<0.222	n/a	<=0.0164	<=0.0328	100	
N-08	3.35	<=0.00547	<=0.00547	n/d	<=0.0357			
N-9D	1.67	<=0.0144	<=0.0144	n/d	<=0.0209	<=0.0340	63	
N-9S	3.21	<=0.0430	<=0.0463	7.4	<=0.0219	<=0.0202	-7.5	
N-10	3.28	<=0.00687	<=0.00687	n/d	<=0.0739			
N-11	1.63	0.671	0.740	9.8	0.547	0.599	9.4	1.23
N-12	2.41	<=0.0169	<=0.0262	43	<=0.141			
N-13	2.10	<0.222	<0.222	n/a	<=0.0293			
N-14D	0.72	<=0.000914	<=0.000914	n/d	<=0.0370			
N-14S	2.59	<=0.0263	<=0.0263	n/d	<=0.0347	<=0.0290	-17	
N-15D	0.76	<0.222	<0.222	n/a	<=0.0171			
N-15S	2.09	<=0.00413	<=0.00413	n/d	<=0.0443	<=0.0376	-15	
BLANK		<0.222	<0.222	n/a	<=0.0546			
N-14S (MS)		25.5	n/a	n/a	30.8			0.83
N-14S (MSD)		24.5	n/a	n/a	28.7			0.85

<0.222 -- chlorocamphenes not detected (value is the reporting limit); n/d - no difference; n/a - data not available

<= signifies a detectable concentration but value is less than MDL (0.222 ug/L); MS – matrix spike; MSD – matrix spike duplicate